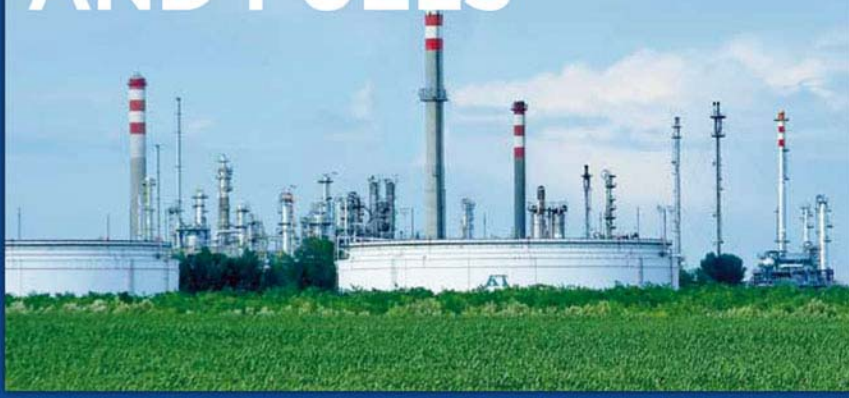
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Michele Aresta, Angela Dibenedetto, Franck Dumeignil (Eds.)

BIOREFINERY: FROM BIOMASS TO CHEMICALS AND FUELS



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Biorefinery: From Biomass to Chemicals and Fuels

Edited by Aresta, Dibenedetto and Dumeignil

Biorefinery

From Biomass to Chemicals and Fuels

Edited by Michele Aresta,
Angela Dibenedetto and Franck Dumeignil

DE GRUYTER

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Preface

A biorefinery is a multidisciplinary and complex concept addressing, at the same time, the production of *value-added bioproducts* (chemical building blocks, materials), and *bioenergy* (biofuels, power, and heat) from biomass, within a sustainability assessment carried out along the entire value chain and life cycle. Development of sustainable biorefineries calls for research, development, and integration of innovative technologies to prove the technical and economical viability related to the entire value chain (biomass production, biomass conversion, safe recycling and/or disposal of waste, and conformity of end-products to end-user requirements) of advanced biorefineries. This concept attempts to integrate the different scientific and industrial communities with the expectation to achieve a breakthrough beyond the "business as usual" scenario.

DG Research has been frequently requested to work in closer coordination between its different Themes in order to better answer the emerging challenges in several research domains. The Commission launched a joint call by joining for the first time the forces of four different Themes of the 7th Framework Program (FP7) (*food, agriculture, and fisheries; biotechnology; nanosciences; nanotechnologies; materials and new production technologies; energy; and environment, including climate change*) and of two different DGs (*RTD and ENER*). Directorates E, G, K, and I of DG RTD and Directorate C of DG ENER agreed to establish a joint call within the Work Programme 2009 on the development of biorefineries. Even if biorefineries were intended here not only for the production of a new generation of biofuels, the political importance and urgency of this research activity was boosted by the recent Commission's political initiative on renewable energies and biofuels, within the energy/climate change package. The joint call on biorefineries represents the first attempt to fully address the need for more integration and multidisciplinarity in the Commission's Research Work Programme, making also use of new management solutions. Moreover, for the first time, several different scientific/industrial communities were requested to work together, creating synergies and exploiting the potential richness of their different scientific knowledge and research approaches. As a result, three collaborative projects are funded in order to implement the topic *sustainable biorefineries,* aiming at integrated multifeedstock and multiproduct biorefineries, while one coordinating action project is additionally funded in order to exchange information and enhance synergies and cross-fertilization between projects in the field of biorefineries. The Commission contributes €52 million for four years. Eighty-one partners from universities, research institutes, and industry in 20 countries will invest an additional €28 million.

The EUROBIOREF project (European Multilevel Integrated Biorefinery Design for Sustainable Biomass Processing: FPA/2007–2013 no. 241718) is the largest of the three collaborative projects. It is supported by €23 million in funding from the European Commission's 7th Framework Program and an additional €14.4 million from partners. The project will run for four years and will deal in a sustainable manner with the entire process of production and transformation of biomass, from fields to final commercial products, including chemicals, polymers, materials, and specific biojet fuels. It will

adopt a flexible and a modular process design adapted to not only large- but also small-scale production units easier to install in various European areas. The overall efficiency of this approach aims to exceed existing pathways with specific targets of improving cost-efficiency by 30%, reducing energy consumption by 30%, and producing *zero waste*. The impact of the project in terms of environment, social, and economic benefits is important and could give a serious advantage to the European bioindustry. The project includes the technoeconomic evaluation of the whole integrated biorefinery, the environmental life-cycle assessment in line with the requirements of the International Reference Data System (ILCD) Handbook, and the social sustainability approach on the basis of the recently developed UNEP guidelines for social life-cycle assessment of products. A commercialization plan of the project results in comprising a list of actions with the associated costs and timeframe, and a report of all the product types and their applications obtained through the project will be developed. The project involves 28 partners from 14 different countries under the coordination of the Centre National de la Recherche Scientifique, France. Fifty-seven percent of the consortium partners are enterprises, while the four SME partners of the project receive 21% from the total contribution of the European Commission.

In conclusion, the aim of the joint call on biorefineries was achieved beyond expectations. Several other joint calls have been launched since, following its practices and pathway. The Commission's response to the member states need for cross-thematic research has undertaken the challenge to bring together different scientific and industrial communities under a joint call on biorefineries and to overcome internal administrative burdens for the horizontal operation of its services. As a result, a limited number of large multidisciplinary and integrated projects in the field of biorefineries were funded, exactly as depicted in the Work Programmes. Now is the time for implementation in prospecting for the breakthrough and beyond the "business as usual" results from the side of both the scientific and industrial beneficiaries of the grant agreements.

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1 A new concept of biorefinery comes into operation: the EuroBioRef concept

Franck Dumeignil

The development and implementation of biorefinery processes is of the upmost importance and constitutes the keystone for the establishment of an economy based on bioresources. Nevertheless, contrary to petro-resources, of which the nature and composition variations are relatively limited, under the terms *bioresource* or *biomass* are gathered compounds of very different natures, namely cellulose, hemicellulose, oils, lignin, and so on. Thus, a complete set of specific technologies must be developed in order to convert as smartly as possible each fraction. This implies, among others, the elaboration of a lot of processes based on catalysis. These latter constitute core technologies that will be implemented in the so-called biorefineries of the future. Within this frame, we are elaborating and developing the EuroBioRef concept "EUROpean multilevel integrated BIOREFinery design for sustainable biomass processing" (eurobioref.org) as a large-scale European project. EuroBioRef is a new highly integrated, diversified, and sustainable concept that involves all of the biomass sector stakeholders. The potential of all of the fractions issued from the various types of biomass is used to yield as high a value-added as possible in a sustainable and economical way. Further, the project has the specific aim of overcoming fragmentation in the biomass industry. This means that decisive actions are taken to facilitate better networking, coordination, and cooperation among a wide variety of stakeholders involved at all levels comprising large and small chemical and biochemical industries, as well as academics and researchers from the whole biomass value chain and also relevant European organizations. Specifically, the new concept adopts a flexible and modular process design adapted to not only large-scale but also small-scale production units that will be easier to install in the various European areas. The overall efficiency of this approach will be a vast improvement to the existing situation, considering sustainable options, such as the production and the use of a high diversity of sustainable biomass adapted for European regions, the production of multiple products in a flexible and optimized way that takes advantage of the differences in biomass components and intermediates, or zero-waste production associated with the smart and parsimonious consumption of feedstock.

1.1 General context

1.1.1 Toward a bio-based economy

Within a future sustainable society, biomass is expected to become one of the major renewable resources for the production of food, cattle feed, materials, chemicals, fuels, power, and heat. To realize this vision, a combined coherent package of measures is necessary; that is, an increase in the overall energy efficiency, a reduced consumption of raw materials, and a decrease in the costs of goods, while offering the framework for enabling the large-scale transition toward a bio-based sustainable economy.

The transition to a bio-based economy with the implementation of sustainable bioresourced raw materials as a source with increased value requires completely new approaches

in research and development (R&D). On the one hand, biological (the so-called biotechs) and chemical sciences will play a leading role in the construction of the future industries of the 21st century. On the other hand, new synergies between agronomical, biological, physical, chemical, and technical sciences must be elaborated and established. This will be combined with new transportation technologies, logistics, media and information technology, economy, policy, and social sciences. Specific requirements will be placed on both the industry and R&D sides with regard to raw materials and product line efficiency and sustainability. The development of substances-converting basic product systems, namely biorefineries, is the key to initiating this new approach in R&D and will enable access to an integrated production of chemicals, materials, goods, and fuels of the future.

1.1.2 Biorefineries and the level of integration

The development and implementation of biorefinery processes – that is, the sustainable processing of biomass to a spectrum of marketable products and energy (IEA Bioenergy 2009) – is an absolute necessity and the key to meet this vision of a bio-based economy; that is, the use of the available biomass as efficiently as possible and with the lowest environmental impact, energy consumption, manufacturing costs, and CO_2 footprint; the redefinition of the transformation routes; and the change in products specifications according to the new processes performances and limitations.

Biorefineries can use various combinations of feedstock and conversion technologies to produce a variety of products. However, most of the existing biorefinery concepts use limited feedstocks and technologies, and solely produce ethanol or biodiesel. Thus, they generally focus on producing biofuels with the consequence of substantially reducing the value-added of the biomass chain. Only a relatively small fraction of materials is used for chemistry and chemical products that have a higher value-added. Economical and production advantages increase with the overall level of integration in the biorefinery. The benefits of an integrated biorefinery are mostly based on the diversification in feedstocks and marketable final products. As mentioned previously, this is what is missing from the majority of the current biorefinery concepts that are limited in using one feedstock and producing one product. Continuous developments in the areas of feedstock, conversion processes (biochemical, chemical, and thermochemical), and their integration with powerful downstream separations will enable more economical and environmentally sustainable options for integrated biorefineries. Such an approach will also enable a spreading of biorefinery implementation within a wider geographical area in all of Europe with adaptation to local conditions and resources. Moreover, according to different studies (Kamm, Gruber, and Kamm 2006), bio-based industrial products can only compete through biorefinery systems where new value chains are developed and implemented. This means that new marketable products like high value-added chemical or biochemical products together with high value-added specific biofuels like high energy biofuels for aviation could enhance the viability and interest of biomass.

This is why the EuroBioRef project is focused on developing and deploying a highly integrated and diversified concept with feedstocks, technologies, and processes that can be bundled to enable and define a new interweaved value chain with integrated flexible biorefinery facilities (▶Fig. 1.1).

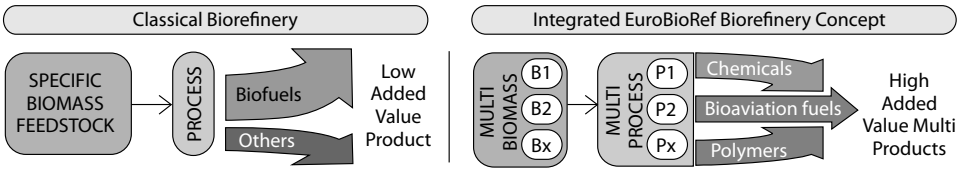


Fig. 1.1: The EuroBioRef integrated biorefinery approach.

These facilities will enable the development of the optimized production of high value-added products that also could be adapted in large and/or dedicated small production units for application in wider regions throughout Europe.

1.2 The EuroBioRef biorefinery concept, objectives, and methodology

1.2.1 Flexibility, adaptability, and multidimensional integration of the EuroBioRef project

The ambitions of the EuroBioRef project are high, but as its basic concept uses a new flexible approach to combine "virtual integration" with proximity to both feedstock sources and product markets, the project will be able to fully address:

- The variety of available biomass feedstocks matched with a variety of preprocessing options to pretreat feedstocks into viable preproducts, which are subject to logistical optimization;
- The variety of markets for bio-based products matched with a variety of integration options to combine several conversion modules with pretreated feedstock availability, thus avoiding excessive transport needs for both inputs and outputs;
- The flexibility of conversion routes, which enables integration of key modules with existing facilities to reduce investment risks; and
- The proximity to both adapted feedstock and expected markets, which can be combined with the integration into existing or specifically adapted facilities, selecting adequate sites through system analysis.

The standard biorefinery concepts use massive economies of scale at one dedicated site to achieve higher performance and optimization along only a few product lines (e.g., liquid biofuels and electricity or basic biochemicals plus ethanol or biodiesel). They are subjected to respective risks for investors, as logistical requirements drastically increase with the size of a single plant and market dynamics may cause simplistic product output optimization to be a dead end. To avoid these risks, the on-purpose nonselective nature of the EuroBioRef approach achieves integration along the whole system; that is, from feedstock through conversion to product markets, thus taking into account overall logistics, feedstock, and product diversification to reduce risks, and internal integration of multiple conversion routes, which are subject to the regionally available (preprocessed) feedstocks, and the prospective (regional) markets of the possible bioproduct outputs. The EuroBioRef concept thus adapts to the regional conditions, integrating with

existing infrastructure, and minimizes risks both for the investors/operators and for the feedstock suppliers as well as for downstream market partners. This chain integration is fundamental to the concept and can be extended through "virtual integration" along logistical chains to cover larger regions. The process integration starts with the feedstock options; their potential pretreatment; the biochemical, chemical, and thermochemical conversion; as well as their combination(s), the use of conversion residues as inputs for other internal or external value chains (e.g., renewable electricity and syngas production), and the output optimization with regard to downstream markets. This concept enables widening biorefinery implementation to the full geographical range of Europe, adapting to local conditions and resources. It also offers better opportunities to export the biorefinery technology "packages" to more local markets and feedstock hot spots in developing countries and economies in transition. The overall logic of the EuroBioRef concept can be visualized by a radar plot covering the three key dimensions of integration described by a certain combination of feedstocks, conversion routes, and product markets, with the inclusion of pretreatment options and logistics (▶Fig. 1.2).

This approach enables full flexibility and adaptability in the biorefinery concept design that can be applied for identifying among the variety of EuroBioRef options the most adapted and optimized one for a specific regional context. According to this context, an optimized, economically viable and sustainable solution can be proposed that is more adapted than the conventional solutions of biorefinery.

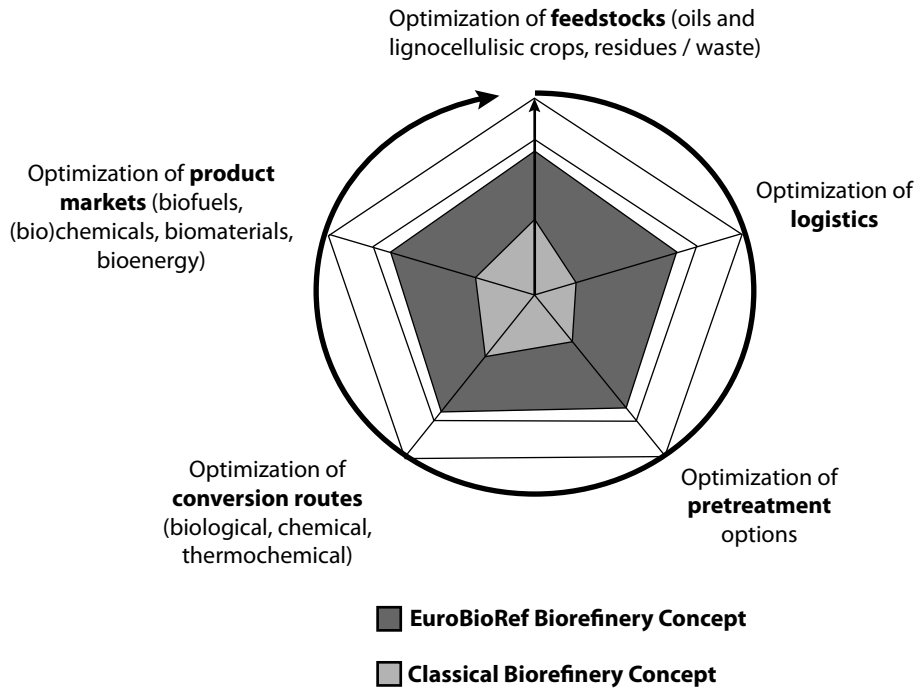


Fig. 1.2: Radar plot of the EuroBioRef concept.

This approach allows the EuroBioRef project to supply not only original technological solutions for an original biorefinery but also flexible concept design for the various European regional needs, especially in both north and south conditions.

1.2.2 The concept principles of EuroBioRef

The novel proposed concept is based on several principles that must be included in the new integrated and flexible biorefinery that bridges the gap between agriculture and chemical industries by providing a stream for a variety of biomass feedstocks and producing a menu of finished green chemical products adapted to the future sustainable bioeconomy-based European society. More specifically:

- Biomass raw materials can be issued from a large variety of sources coming from not only various regions in Europe (north and south) but also other parts of the world. They can be sourced from agricultural and forest residues and dedicated nonfood crops, which do not compete with food crops in terms of agricultural land use because they can grow on less fertile fields with low water and fertilizer requirements.
- Such production in integrated biorefinery should be flexible enough to match a variety of sustainable biomass sources specific to the various regional (e.g., within Europe) contexts by proposing adapted logistics, flexible processes, and socioeconomic viability.
- The diverse biomass sources should be efficiently pretreated and produce a variety of fractions (cellulose; hemicellulose; lignin; and refined nonedible oils, seed-meal, glycerine, fatty acids/esters, and solid residues) for which separation has to be optimized and used in the most value-added, eco-efficient, and optimized way for the production of marketable products.
- Development of an original variety of eco-efficient chemical, biochemical, and thermochemical routes is key for the production of marketable high value-added chemicals, high-energy biofuels like aviation fuels, polymers, and high value-add materials in a competitive way. An intelligent crossroad design can combine these routes in a way that optimizes them and uses their byproducts.
- The byproducts of the different routes have to be reintroduced in the integrated process as reactants, or energy, or to be transformed in products in order to obtain a zero-waste biorefinery.
- Lifecycle, economic, and socioeconomic analyses are performed to ensure that the whole production chain is optimized in a sustainable way.

The EuroBioRef integrated concept (▶ Fig. 1.3) is based on a diversified, flexible, and zero-waste biorefinery concept including an integrated cluster of bio and chemical industries, which use a variety of different technologies to produce a wide range of valuable commodities and end products (chemicals and biofuels) from diverse sources of biomass-pretreated raw materials in an eco-efficient way. In the new concept, integration aspects will be simultaneously treated, which enables:

- Integration of different feedstocks to produce the targeted molecules
- Integration of different transformation pathways to efficiently convert biofeedstocks

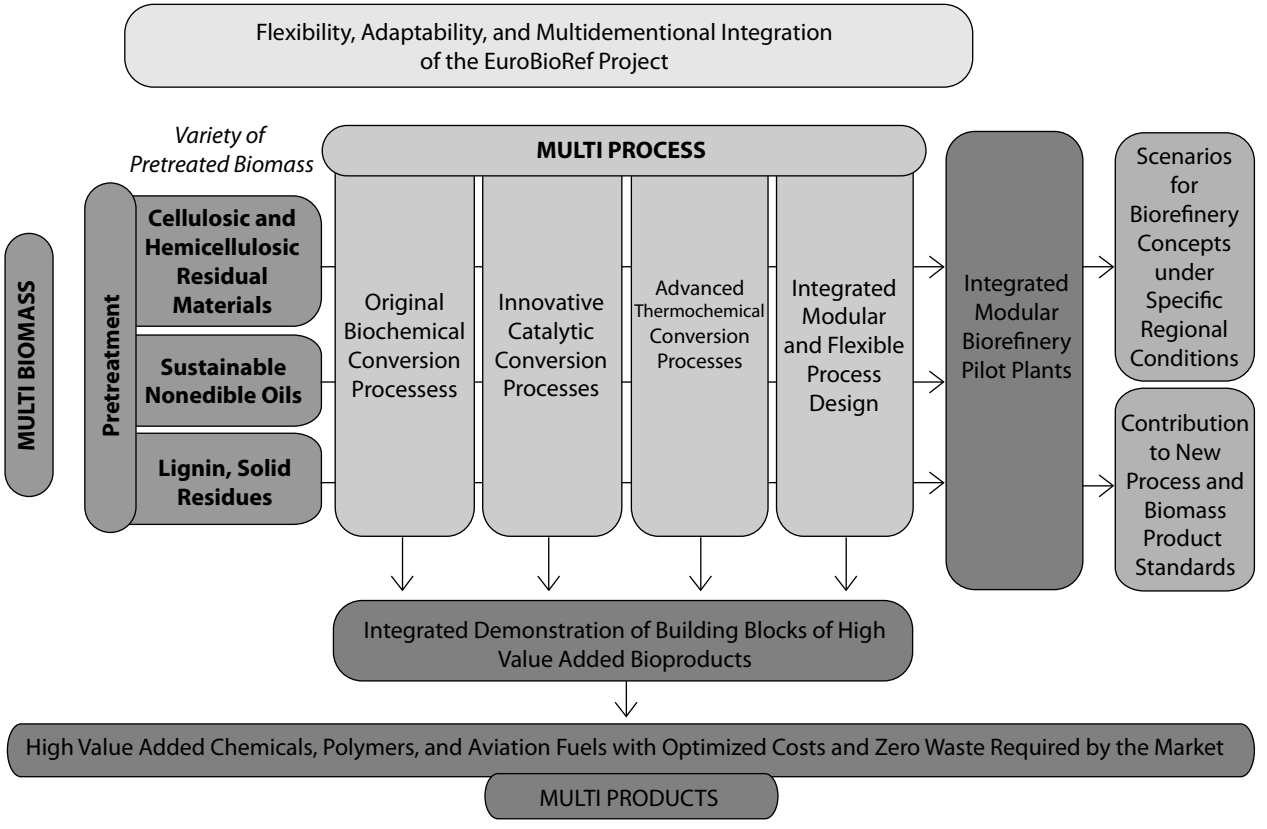


Fig. 1.3: The EuroBioRef concept for demonstration of an integrated, sustainable, diversified, and economically feasible biorefinery.

- Integration of (bio)reactions and separations in order to generate new efficient processing technologies
- Integration of various sustainable and flexible process designs that take under consideration the various socioeconomic and regional contexts

The project is developing to then demonstrate at the industrial scale the closer to the market, socioeconomic viable processes of the EuroBioRef biorefinery concept.

1.2.3 The objectives of the EuroBioRef project

The EuroBioRef concept is an integrated, sustainable, and diversified biorefinery involving all the biomass value chain stakeholders (i.e., biomass production, logistics, biomass conversion, biochemical and chemical industry, market needs, economics, policy, and environment assessment analysts) that will enable large-scale research, testing, optimization, and demonstration of processes for the production of a wide range of products with the dual aim of using all the fractions of various biomasses and to exploit their potential to produce as high a value as possible in an eco-efficient and sustainable way. Moreover, the project attempts to overcome the fragmentation of efforts of the whole biomass value chain (land use, agriculture, second-generation biomass treatment, [thermo][bio]chemical conversion, new green marketable products, bioaviation fuels, and socioeconomic sustainable development) requiring enhanced networking, coordination, and cooperation among a large variety of actors from agriculture, biochemical, and chemical industries, including small- and medium-sized enterprises (SMEs) and the scientific biomass knowledge chain, as well as actors from sustainable development and policy rules advisors.

The new EuroBioRef design will adopt a flexible and modular process design adaptable in not only large but also small-scale production units that are elaborated and tuned to be installed in the various European regions according to the site-specific biomass resources and needs. The overall efficiency of this approach will clearly exceed existing pathways and will consider sustainable options in order to:

- Produce and use a large diversity of sustainable biomass adapted for various European regions (north and south) and also for sustainable development in developing countries (▶Fig. 1.4).
- Produce high-energy bioaviation fuels (42 MJ/kg) that could replace traditional aviation fuels.
- Produce multiple products (chemicals, polymers, materials) in a flexible and optimized way that takes advantage of the differences in biomass components and intermediates and maximizes the value derived from the biomass feedstock (▶Fig 1.5).
- Improve cost efficiency of 30% through improved reaction and separation effectiveness (e.g., reduced separation and waste disposal costs), reduced capital investments (e.g., novel integrated processes and reactor concepts), improved plant and feedstock flexibility, and reduction of production time and logistics.
- Produce zero waste and rationalize the use of raw materials with reduction of the feedstock consumption by at least 10%.

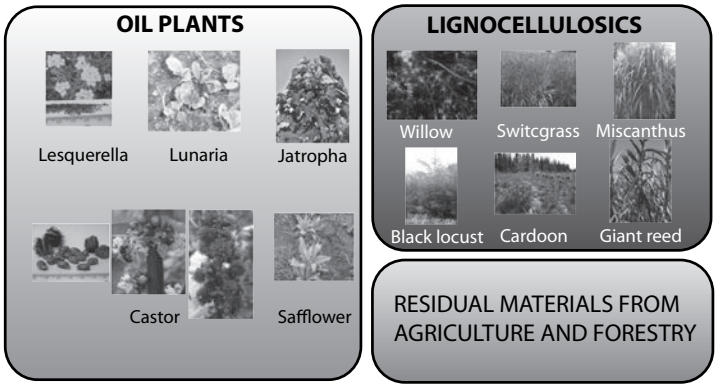


Fig. 1.4: Several examples of raw materials considered in EuroBioRef.

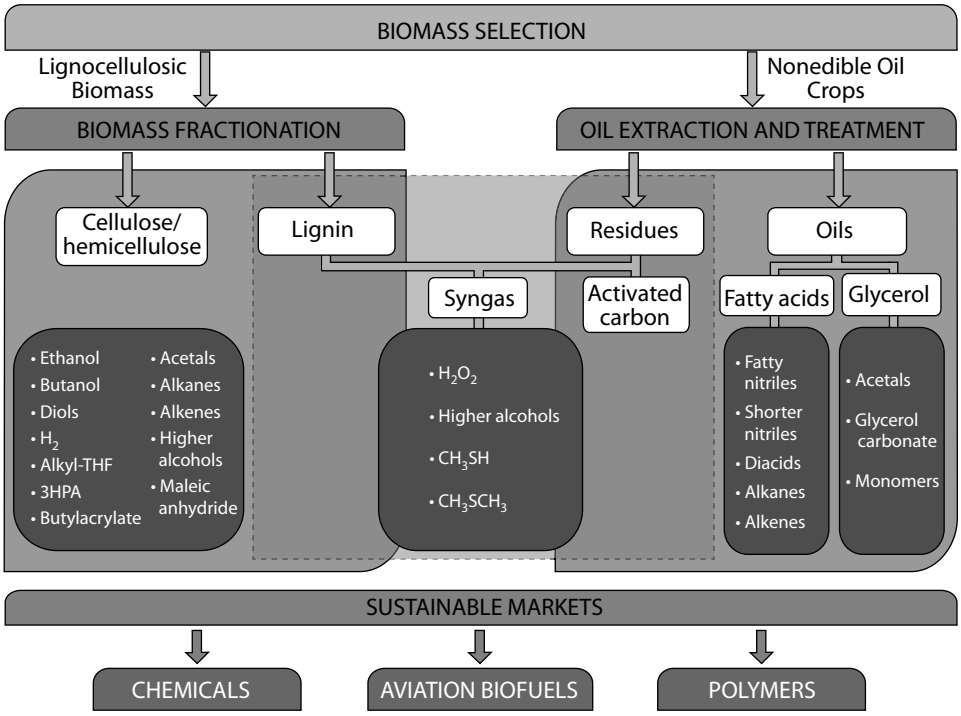


Fig. 1.5: Target products.

- Reduce by 30% the energy needed to manufacture the desired products and operate specific processes using more efficient land use and less energy-consuming reactions and producing the needed heat/power from the biorefinery.
- Reduce the time-to-market by 30% by the development of new biorefinery manufacturing processes adapted in particular regional contexts through intelligent conceptual process design methods.

1.2.4 The EuroBioRef approach to reach the objectives

The key challenge for the new biorefinery process design is to apply its potential to significant improvement of the whole biomass efficiency, which will benefit the biomass producers, the environment, the European industry, and the product end users. This will be obtained through the proposed multilevel integrated approach, involving:

- Efficient and adapted biomass production for Europe and integration of sustainable development in third-world countries. This can be achieved by several transition paths: (1) improving the efficiency of using existing residual forms of biomass and (2) sustainable improvement of the yield and quality of biomass crops and, particularly, nonedible crops.
- A transversal activity for the rationalization of the whole process through a combination of assessments on optimization of crop-culture rotation logistics aspects of the whole biomass value chain, flexible process design, and consideration of lifecycle analysis and socioeconomic and policy aspects.
- Second-generation biomass advanced pretreatment for sustainable production of lignocellulosic materials. Cross-integration of a bio-oil route with a lignocellulosic route, which offers original perspectives for cross-valorization of derived primary products (cellulose, oils) including byproducts (glycerine, lignin) while in parallel developing original applications inherent to each route.
- Interweaving of enzymatic and catalytic (homogeneous and heterogeneous) transformations including, when necessary, their integration with new separation techniques and/or reactor technologies.
- Proposing a large variety of products with niche applications (high value-added) and large-volume applications, including bioaviation fuels, chemicals, and solvents, that have either very fast access to the market because of substituting homologous petrochemical-derived products or are very innovative with high potential, thus implying larger downstream developments.
- Some targeted markets are as follows: bioaviation fuel blends (€30 billion/year), butanol markets (4.9 million tons/year; €2.6 billion), maleic anhydride (1.5 million tons/year, and several million €/year), acetals (several million €/year), short fatty nitriles (a few million €/year), 3-hydroxypropionic acid (several million €/year), hydrogen peroxide (€50 million/year), glycerol carbonate (30 million tons/year, more than €50 million/year), 1,3-propanediol (more than €2.7 billion/year), and butylacrylate (more than €400 million/year).
- Demonstration of technical and economic feasibility and efficiency in pilot plants of the different steps and building blocks as well as of the majority of applications. The realized units will work either in a centralized or a decentralized mode. This ensures remarkable design flexibility to propose the most rational assembly adapted to each local/global economical constraint. Selected subprocesses will be demonstrated in industrial pilot plants.
- Generation of zero wastes by:
  - Implementation of applications for each type of byproduct with reutilization in the global loop;
  - Optimization of the catalytic processes for atom/energy economies;
  - Application of green solvents in purification processes;

- Conversion with new technologies of the most refractory byproducts; and
- Conversion of wastes into energy.

- Setting up new definitions for product quality, taking into account the biomass-issued products specificity that are thus specifically suitable for biorefinery-dictated applications ("Quality by design").

Actors within the entire biomass value chain are involved, including biomass producers, culture developers, and logistics (SOABE, CRES, DTI, UWM), advanced biomass (lignocellulosic and oil crops) pretreatment industries (BORREGAARD, NOVANCE), catalytic and enzymatic reactions developers (CNRS, TUDO, FEUP, CIRCC, RWTH, TUHH, BKW, NOVOZYMES), thermochemical reactions developers (ISFTH/CERTH, NYKOMB), catalyst and enzyme producers (HTAS, NOVOZYMES, UMICORE), process designers and engineers (PDC, ISFTA/CERTH, SINTEF), and final chemical and biochemical producers and end users (ARKEMA, BKW, ORGACHIM, MERCK, NYKOMB, OBRPR). The consortium also includes an aviation refinery (OBRPR) and a jet-engine maker (WSKRZ) for bioaviation fuel testing. The sustainability of the whole project is analyzed and optimized by socioeconomics and lifecycle analysts (IMPERIAL COLLEGE, QUANTIS), civil organization analysts (EUBIA), as well as specialists for project management (ALMA). The 28 project partners from 14 countries comprise large and small chemical and biochemical industries, as well as academics and researchers for the whole biomass value chain (▶Fig. 1.6).

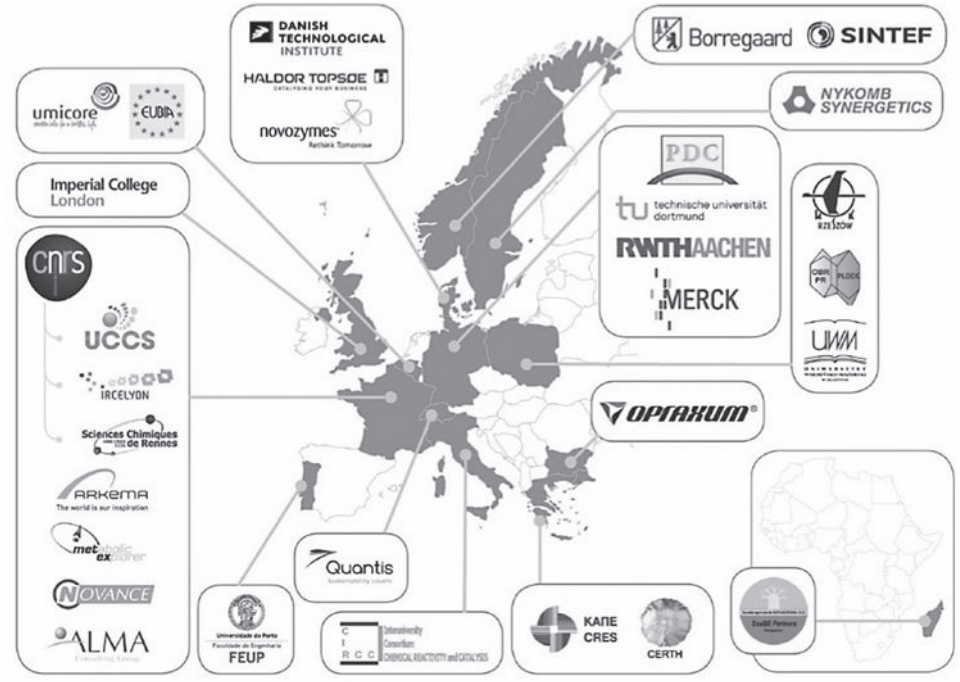


Fig. 1.6: The EuroBioRef consortium. Note that from March 1st, 2012 some changes have occurred in the Consortium: METEX is not partner anymore, TUHH and BKW (Germany) are new partners and PDC is located in The Netherlands.

1.2.5 EuroBioRef innovation and expected results (▶Fig. 1.7)

Business results are expected on:

- Demonstration of the economic and technical overperformance of bio-based products including bioaviation fuels and chemical commodities markets;
- Demonstration of the increase in economical performance due to use of second-generation feedstocks;
- Demonstration of the sustainable value chain of nonfood crops cultivated in synergy with food crops; and
- Definition of final product specifications and tests of new products (blend of several components into bioaviation fuel).

Scientific innovations are focused on:

- Methods for conceptual process design widely applied in the chemical sector toward bio/chemical applications;
- Heterogeneous, homogeneous, and enzymatic catalytic systems including fermentation and optimization of the formulations, taking into account the purity of the feedstocks. New catalytic reactions;
- New low-energy separation techniques and adaptation to biomass-derived products (microdistillation, reactive separations, bioextraction, etc.);
- New reactor technologies for minimizing production of byproducts while enabling substantial energy savings (continuous displacement of equilibrium reactor, reactive separation using ionic liquids, etc.);
- Co-product reutilization technologies (thermochemical transformation to, e.g., activated carbon, efficient use of byproducts in the process loop, and energy integration using wastes to produce heat and electricity);
- Integrated reaction/separation technologies (reactive distillation, simulated mobile bed reactors, membrane-assisted separations and reactors, and in situ extraction); and

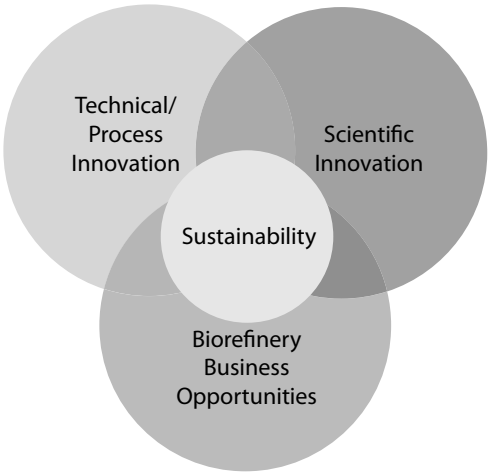


Fig. 1.7: EuroBioRef innovation and value-added.

- Development of new purification technologies of fermentation broth using green solvents (e.g., ionic liquids).

Technical advancements are expected on:

- Crop rotation optimization for northern/southern Europe and Africa, selection of appropriate sustainable biomass feedstocks for diverse EU environments;
- Rationalization of the elaborated chain to yield each product and global integration/optimization of the whole process, including logistics and up-front lifecycle analysis for selection of economically sustainable products and process routes;
- Quality control of a variety of feedstock for a variety of end products;
- Elaboration of multidisciplinary processes combining heterogeneous/homogeneous catalysis with enzymatic catalysis;
- Demonstration at the lab/bench scale of the subunits described in the project and demonstration at the pilot scale of integrated production chains for significant products. Some demonstration will also be carried out at the industrial level; and
- Integration of several reaction and separation steps for high selectivity and conversion, energy and investment costs savings.

Sustainability assessment and performances include:

- Specific logistic methodology for cultures in northern and southern Europe;
- Life-cycle assessment (LCA) methodology for evaluation of environmental performances;
- Economic modeling for assessment of economic process viability; and
- Sustainable assessment of the whole chain for macroeconomic viability.

1.2.6 S/T methodology and associated subprojects

1.2.6.1 Overall strategy and general description

The EuroBioRef project is an ambitious biorefinery approach aimed at demonstrating the technical and economic viability of a synergy between the biomass agro industry and biochemical chemical and thermochemical conversion processes and technologies that will be combined in a way to optimize production routes of high value-added aviation fuels, chemicals, and polymers. The final objective is to show in pilot or industrial plants the feasibility of the biorefinery and produce some of the subprocesses in industrial pilot plants. The integration of all of the elements will be designed for large- or small-scale production in order to adapt production in various European Union regions and will take in consideration lifecycle management, socioeconomic constraints, and policy rule issues. The project is divided into 11 subprojects (SPs):

- **SP0** is related to the management of the project.
- **SP1** is dedicated to the strategy definition of the project as well as the requirements and the common methodology definitions. Possible scenarios for fine studies are also considered.
- **SP2** aims at reviewing, evaluating, configuring, and analyzing sustainable biomass chains (nonedible oils, residual lignocellulosic materials in priority) for a biorefinery. The analysis is outlining feedstock production and supply chain logistics,

including storage, and refers to different regional scales (southern, central, and northern Europe), as well as sustainable possibilities offered by African feedstocks.

- **SP3** is dedicated to the development of optimized biomass pretreatment processes to yield primary raw materials as suitable as possible for further biochemical/thermochemical transformations from lignocellulosics and nonfood crops.
- **SP4** is designing an integrated process combining new fermentation methods and innovative separation technologies to produce 3HPA as well as to develop continuous production of *n*-butanol and 1,3-propanediol from respective carbohydrates (C6 and C5 from lignocellulose) and glycerol. Biogas production is also considered.
- **SP5** involves developing catalytic processes to yield a variety of products with tailored properties. The catalytic formulations will be optimized in terms of tolerance toward the specific impurities in biomass-derived raw materials, including water. This will enable utilization of lower input qualities and thus reduction of pretreatment costs.
- **SP6** is dedicated to the development of the thermochemical process units. The EuroBioRef concept is a zero-waste biorefinery that includes the lignin/black liquor and solid residue conversion to syngas as an intermediate for the production of power and value-added chemicals; for example, higher alcohols (C_2^+ alcohols from syngas), hydrogenation of sugars to alcohols, methylmercaptan (CH_3SH), and hydrogen peroxide (H_2O_2).
- **SP7**'s objective is to integrate all the process steps from biomass as a raw material to bio-based products for end use in such a way that the resulting overall biorefinery will operate at optimal performance with regard to the criteria (economics and sustainability) specified in SP1 and the application of a systematic methodology for conceptual design to integrate all (sub-)processes/units involved in the whole process chain in the most suitable way. Available or new lab/bench scale units for specific processes and/or process steps will be operated for a preliminary pilot test.
- **SP8** is the place for decisions for demo tests, which will be based on the economic viability of the process and on the strongest integration with other processes. This SP comprises the construction and/or adaptation of existing pilot/industrial units of the various SPs according to the process design (SP7). These pilot scale tests and, in some cases, also industrial pilot tests will be realized in various sites, enabling integration of the different modules of the process. EuroBioRef will demonstrate the technical and economic feasibility of the phases of production, logistics, biomass pretreatment, first conversion, and bioproducts production. The aim is also to produce a sufficient quantity of bioproducts (15 m^3) necessary to produce an elaborated bioaviation fuel. Its efficiency will be demonstrated in air engine tests for 50 hours and will be validated under flying conditions. Examples of application of the biorefinery concept will be described and a biorefinery business platform will be created.
- **SP9** is dedicated to the development of an adapted LCA methodology, economic models related to the EuroBioRef concept, socioeconomic and policy analysis for an easier introduction, and acceptance of the project and recommendations for a higher and rapid integration of the results into the market.
- **SP10** is, finally, related to exploitation, dissemination, training, and standardization.

This methodology enables achieving integration along the whole system, starting with the feedstock options; their potential pretreatment; the biochemical, chemical, and thermochemical conversion; as well as their combination(s), the use of conversion residues

as inputs for other internal or external value chains (e.g., renewable electricity and syngas production), and the output optimization with regard to downstream markets.

This chain integration is fundamental to the concept and can be extended through "virtual integration" along logistical chains to cover larger regions, enabling widening biorefinery implementation to the full geographical range of Europe and adapting to local conditions and resources. It also offers better opportunities to export the biorefinery technology "packages" to more local markets and feedstock hot spots in developing countries and economies in transition.

1.2.6.2 Scientific/technological methodology to reduce risks

EuroBioRef is an ambitious initiative aiming at linking in a sustainable way agriculture, chemical industry, and green bioproducts by integrating the whole chain in a common project with various competencies from all over Europe (13 European countries and 1 African country). The proposed flexible, adaptable, and multidimensional biorefinery concept will enable the development of various biomass feedstocks, advanced and original biochemical chemical and thermochemical routes, and a high variety of bioproducts and their integration at the demo scale.

In order to improve the scientific/technical methodology to reach successful demo objectives of the biorefinery concept and limit the risks without reducing ambitious objectives, the project has adopted a progressive commitment process. EuroBioRef has implemented an R&D strategy that aims at identifying the best concepts and joining them into an integrated innovative solution. The entire challenge is to rapidly converge to the most promising and sustainable routes and solutions in order to obtain project results without rejecting relevant alternatives. A step-by-step approach is adopted in order to avoid research directions that are likely to fail or provide nonsustainable solutions. This approach perfectly complies with the EuroBioRef objectives to provide a flexible and adaptable concept design for the biorefineries of the future and is shown in ▶Fig. 1.8 indicates the four main steps of the EuroBioRef development/implementation:

- First, the feedstock selection and pretreatment;
- Second, the conversion routes selection and characterization;
- Third, the sustainable process design and pretesting validation; and
- Fourth, the integration and market products demonstration.

Each step is punctuated by decision-making points (milestones), where results are validated and the choice of whether to continue, change direction, or abort the step is made. This progressive strategy enables the evaluation and optimization of the new processes at all of the stages of the development cycle, avoiding risks when selecting the most promising technologies for the targeted ambitious applications.

1.3 Main achievements of the first year of the project

As of March 2012, the EuroBioRef project had just entered in its third year out of a four-year duration. Some important results have been obtained during the first two years, an outline of which is given here.

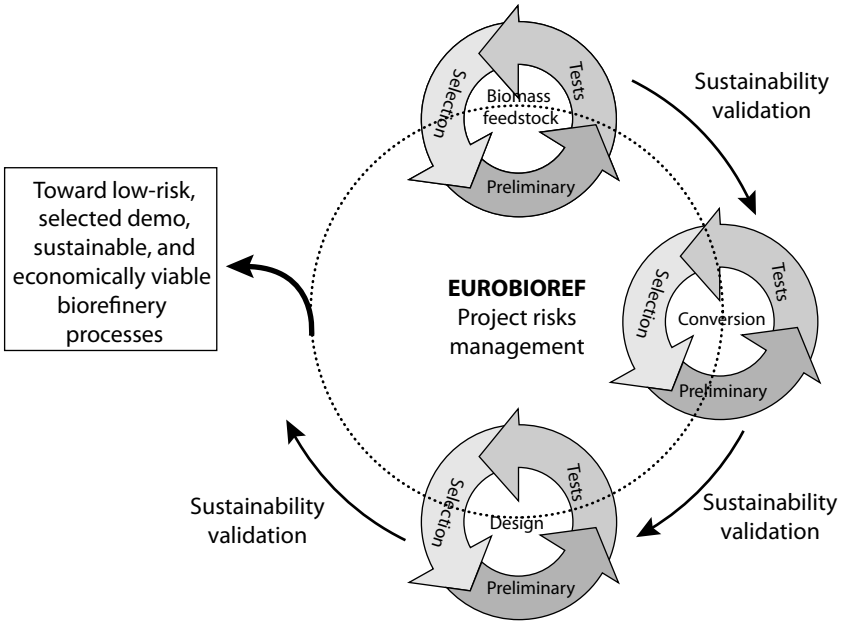


Fig. 1.8: The step-by-step approach for reduction of risks toward the demo phase.

As a very strategic point, it has been decided after extensive analysis that EuroBioRef biorefineries should definitely be chemicals/materials-driven, meaning that the best part of the crops are being used to make high-value chemicals and products and that the residues are being used to produce energy, either consumed on-site or being exported under various forms. This is a rethinking of commonly admitted biorefineries concepts that are strongly biofuels-driven.

In the various test fields in Poland, Greece, and Madagascar, lignocellulosic plants (willow, giant reed, miscanthus, switchgrass, cardoon) and oil crops (castor, crambe, safflower, lunaria, jatropha, as well as sunflower and rapeseed for comparison) were grown according to smart rotation strategies, and all of them have already been harvested for feasibility evaluations and, when relevant, for further downstream applications in the biorefinery. Among all the considered plants, additional large test fields for demonstrations are being set with willow and crambe in Poland, giant reed and safflower in Greece, and castor in Madagascar, while work is still being done on other plants of interest for developing further potential applications. An international workshop on harvest, pretreatment, and storage of biomass for biorefineries was also organized in Herning, Denmark, on January 11–12, 2012, in order to evaluate the state-of-the-art of harvesting equipment for both lignocellulosic and oil crops and underline requirements for further technological advances in order to ensure raw material that is of good quality and at low prices. In addition, the skeleton for the logistics model has been developed, and a first version of this model has been tested with data from Salix. Now, the model is populated with data for four crops; namely, willow, castor, safflower, and giant reed.

Three different kinds of lignocellulosic materials (miscanthus, giant reed, and switchgrass) were successfully tested in a new pretreatment process, showing its remarkable

versatility. This motivated the construction of a brand new pilot plant in Norway that will be able to operate 50 kg of dry lignocellulosic materials per hour from mid 2012. Concerning oil plants, economic issues were identified with jatropha, of which the cultivation by farmers seems not sufficiently attractive. Its interest, however, relies in its possible use as a fence for crop protection against stray cattle and wind, for limiting erosion, and then as biofuel for local consumption. Cardoon exhibited the interesting property of being grown in the Mediterranean area without the necessity of being irrigated; however, its ashes are limiting its possible applications. In addition to the extraction and characterization of various oils, fatty acids were produced by saponification of Lunaria oil, and a study on enzymatic splitting of triglycerides was initiated in order to obtain fatty compounds suitable for downstream processing. In the reporting period, eight new patents were filled mostly related to vegetable-oil conversions. Further, we highlighted that bifunctional molecules can be efficiently obtained, which opens the interesting perspective for our products to reach the high-value monomers market. Thus, the lab work for the next reporting period moved to metathesis pilot test and polymer applications.

Upgrading of the solid coproducts issued from the primary transformation of biomass was also evaluated, for example, by gasification, in specifically designed/constructed units. We found that, while cardoon is not adaptated for such a thermochemical process because it would need a specific technology that can handle high ashes, some other plants addressed by the project can be efficiently processed. As another way of upgrading the solid coproducts of the biorefinery, carbonization to charcoal has been attempted on a wide range of different materials issued from the project. Some samples exhibit excellent properties with a high specific surface area. The possible applications of such upgraded solids are investigated in the biorefinery concept. Indeed, they can be used as, for example, absorbents or catalysts supports.

Further, a short list of the most relevant jet-fuel properties has been prepared and the testing schedule has been fixed. Viscosity and density properties of firstly received samples were evaluated. Various options for the modification of the test stand fuel supply system were analyzed and the most suitable version was chosen. The test combustion chamber was prepared for the investigation of bioaviation blending/combustion performances, and is now ready.

All the results obtained so far by the partners dealing with (bio)chemical transformations are continuously and methodically gathered, sorted, and analyzed through conceptual process design, which enables selecting a priori the most viable options. This enables time-saving in technology development by discarding nonoptimal options and retaining the most promising ones at their very early stage of development.

For evaluating the sustainability of the envisioned solutions, we started the development of some specific tools for life-cycle assessment, taking into account harmonization efforts with major sister projects in the European Union. As another strong point, this assessment is not restricted to the carbon footprint, but also integrates the socioenvironmental and economic impact assessments. Internally, an interactive LCA database, which combines a user-friendly interface (for nonspecialists) with a rigorous LCA approach, has been partially developed and tested. In parallel, and as a complementary assessment tool, a basic framework for biorefinery costs modeling has been developed, which will enable economical viability classification of the various possible biorefinery configurations. The socioeconomic assessment has included a detailed selected case

study, designed to provide insights about best practices that can be transferred to the assessment of socioeconomic impacts more broadly.

EuroBioRef is also developing a strong network of dissemination and education. The first EuroBioRef Summer School "The Concept of Biorefinery Comes into Operation," aiming at the effective training of young researchers from academia and staff from the industry on the most up-to-date scientific and technological aspects of biorefineries, took place on September 18–24, 2011, in Castro-Apulia in Italy, followed by the edition of the present book. Finally, a 20-minute video on the project has been realized and will soon be available on the EuroBioRef Web site.

These multilevel, multidisciplinary achievements are keystones for the further developments of the concept that will be translated to a full set of demonstrations in the upcoming months. For doing this, six value chains corresponding to six different scenarios of biorefineries integrating results and concepts developed in EuroBioRef have been designed and are being now multidimensionaly assessed.

Acknowledgements

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2 Refinery of the future: feedstock, processes, products

Jean-Luc Dubois

2.1 Introduction

Petroleum refineries, as we know them today, have experienced several revolutions since the initial development of the industry. Initial refineries were very simple, trying to recover what today we call kerosene, which was used in petroleum lamps. At that time, gasoline was considered a waste, for which new applications were looked. Later, with the demand for gasoline increasing, the refineries were modified with new units such as catalytic crackers, them selves improved into the current Fluid Catalytic Cracker (FCC) with which most of the modern refineries are equipped.

Biorefinery is a new word, built on the analogy with petroleum refineries to specify plants using all kinds of biomass to make chemicals, material, and fuels. Some of these plants have a long history, such as sugar fermentation to ethanol or oleochemical plants. Many projects to produce chemicals and fuels from biomass have already been launched in the 1970s and 1980s after the huge increase of petroleum prices. Very few of these projects survived the mid-1980s, when the petroleum price decreased to just a few US dollars per barrel. The winning technologies have in common that they either bring a unique technical solution or they offer a local supply solution in remote areas.

Operating cost is, of course, of primary importance. The operating cost includes fixed cost, variable cost, and business overhead cost. These include salaries, raw materials, licence or equivalent fees (such as those imposed by a government), real estate expenses, utilities (water, fuel, electricity, etc.), maintenance, insurance and taxes, and, last but not least, capital depreciation. In many industrial projects, the amount of capital required to build a plant is the limiting factor, especially when the biomass and the petroleum future value and the legal environment are uncertain due to changing local legislation on biofuels, for example.

2.2 Competition

In the history of crude oil (we'll use the word *petroleum* to avoid confusion with vegetable oil, which might be crude also), high prices are linked with a shortage of supply. This was the case with the early production in the 18th century, and again in the 1970s with the embargo from some oil producers and the Iranian revolution, and more recently with the booming Asian economies increasing global demand. Finding alternative sources of carbon for fuels and chemicals is also stressed by the perspective of a peak oil (meaning the time at which the oil production will start to decline), and taking into account impacts on global warming. ►Fig. 2.1 illustrates the variation of petroleum production over the past 45 years.

The peak oil for OECD (Organisation for Economic Co-operation and Development) and non-OPEC (Organization of the Petroleum Exporting Countries) countries was already reached in 2000, and worldwide, production has been leveling off since

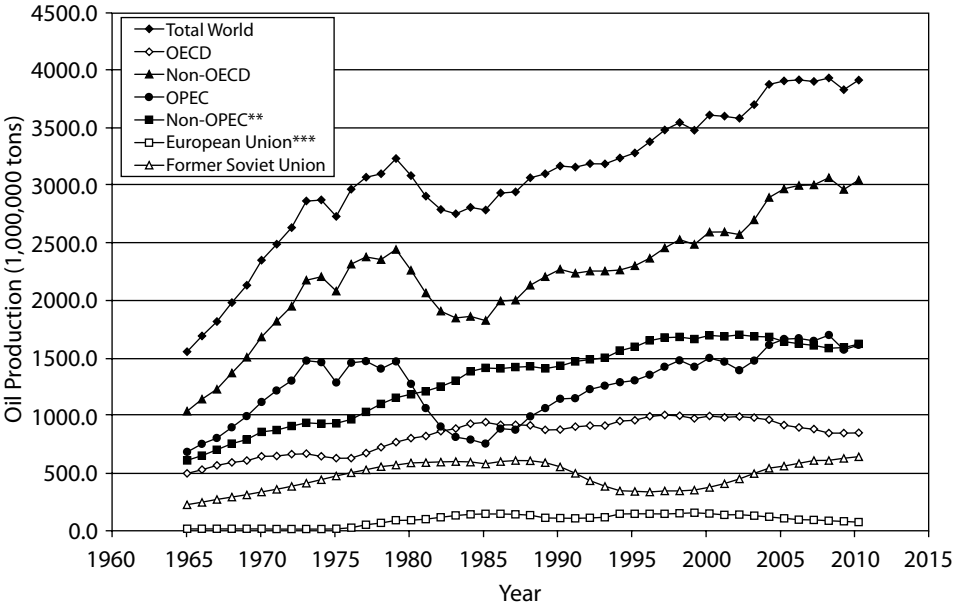


Fig. 2.1: Evolution of petroleum production worldwide. (**Excludes the former Soviet Union; ***Excludes Estonia, Latvia, and Lithuania prior to 1985 and Slovenia prior to 1991). Figure adapted from the data in the BP Statistical Review of World Energy June 2011, available at http://www.bp.com/statisticalreview.

2005. Historically we have already encountered peaks due to the shortage of supply in the 1970s, but this was not related to the decrease in oil reserves. ▶Fig. 2.2 plots the number of years of oil reserves at annual consumption rate. It shows that over the past 25 years, oil reserves have been neither increasing nor decreasing, and have remained stable at 40 years of consumption. New oil fields are being discovered, and as the crude oil price is increasing, new fields become economically accessible. This figure would suggest that we do not face an immediate shortage of petroleum so long as the demand does not rapidly increase.

New technologies are being developed that use biomass to make not only low-value products such as fuels but also high-value materials such as polymers. It is also important to look back at what happened in the past when crude oil prices surged.

There is a common feeling that when crude oil price is high, then any bio-based (hereafter called *renewable* or *biosourced*) product will be able to make its route to the market. Interestingly, in this too simple analysis the key role of the farmer is forgotten. The farmer will be in a position to increase his or her prices if there is a large demand, and if most of the industrial crops (in opposition to food crops) are used to make fuels, then there is no doubt that the cost for the industrial crops will follow the trend of petroleum. Over the 2005–2010 period, the petroleum price increased from US$50 to $140/barrel, and in the same period the return over variable costs and all costs for an Iowa dry-mill ethanol plant decreased (see ▶Fig. 2.3).

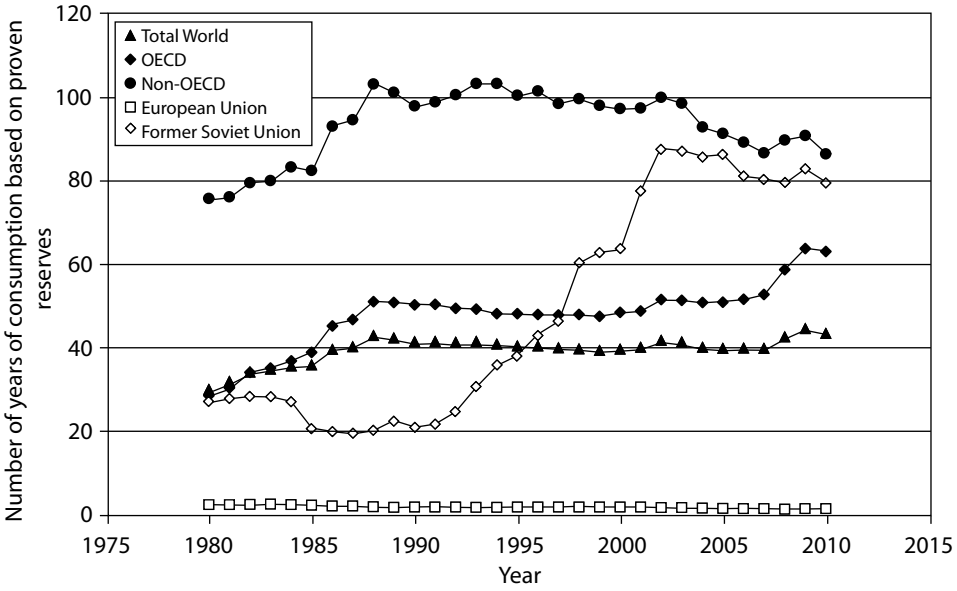


Fig. 2.2: Petroleum reserves expressed as years of consumption. Figure adapted from data in the BP Statistical Review of World Energy June 2011, available at http://www.bp.com/statisticalreview.

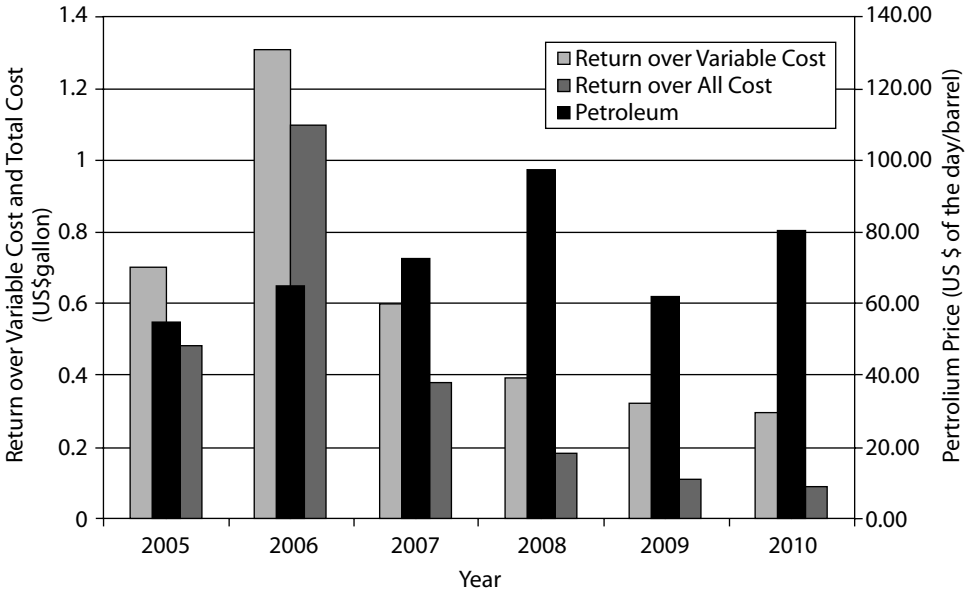


Fig. 2.3: Profitability of an Iowa dry-mill ethanol plant versus petroleum price. Data show that profitability is not increasing at high petroleum prices.

In the past 6–10 years, most of the major crops have been correlated with the price of crude oil, although in this case it is not possible to claim that there is a direct massive use of biomass in fuel applications. A limited amount of about 5% of the vegetable oils are being directed to biodiesel, and if some countries – like Brazil with sugar cane and the United States with corn – are major producers of bioethanol, it takes only a limited share of the market. Nevertheless, in 2010, 37% of the corn production in the United States ended as bioethanol for gasoline engines. Vegetable oil used to make biodiesel has long been seen as a co-product of the production of the protein-rich seed meal (animal food) in Europe. In this case, biodiesel was seen as being an outlet for excessive production of vegetable oil.

In recent years, biomass prices seem to be correlated to the crude oil prices as mentioned earlier (Anonymous 2008, 2011). One could see in this the impact of the competition between food and fuels. However, the recent economic development of China, India, and Brazil, for example, implies a higher demand for energy and higher revenues for workers. Obviously people there expect a better living standard and expect higher quality food, thereby increasing the demand for edible oil and sugar.

2.3 Impact of legislation

Current legislations, all over the world, to favor biofuels are creating huge market distortions, especially versus long-lasting bio-based chemicals. The amount of public money poured into biofuels has reached in some cases €1/liter of equivalent petroleum-based biofuels (Dubois 2011). Nevertheless, we can recognize that in many cases this public funding benefits also the development of new chemicals and materials starting from either ethanol or vegetable oils. But the ever-changing rules, or stop-and-go policy, do not contribute to a clear picture of the future for the market players. Recent examples of that are the changes in public support of biodiesel in Germany, which led many new plants to shut down. Another example is a new regulation in Europe that allows a double count of biofuels when it is made from wastes – animal fats being listed as wastes although they have a long history of being used in oleochemistry. The negative impact of this regulation is that the demand for vegetable oil decreased. Another example is the so-called blender credit in the Untied States, which distorted the market three years ago and still generates a lot of debate (De Guzman 2011a). Initially this regulation was passed to promote the use of biodiesel in the United States and gave a credit to those blending diesel fuel into Fatty Acid Methyl Ester (FAME, or biodiesel B100 when it is pure). Some individuals and companies then started to import cheap biodiesel B100 from South East Asia or Argentina, for example, and blended 1% of diesel into it to receive the benefit of the blender credit while producing a B99. Of course, the U.S. farmer in this case does not see any benefit. In addition, since the market for biodiesel in the United States is rather limited (the United States is more of a gasoline consumer while Europe is a diesel consumer), the B99 was exported to Europe where it took time to adjust the regulations, especially since the U.S. tax payer was subsidizing the European biofuels! But during this period, the price of glycerine in Europe surged to high levels. Because glycerine is a co-product of the biodiesel and oleochemical industry, it is directly affected by any variations in these markets. With cheap imports coming from the United States, biodiesel production did not increase as initially expected in Europe, and neither did glycerine.

These limited examples illustrate how a decision to favor a type of bio-based product can adversely affect several other products. Unfortunately, many of these political decisions, although with good motivations, are not made on a long-term basis and do not contribute to clarify the future for the companies that have to make decisions on major investments. In section 2.7, the amount of capital needed to build plants for biofuels, chemicals, and materials will be illustrated. The development of biorefineries will need appropriate economic conditions.

2.4 Regional impacts

Biomass might seem to be ubiquitous, or available everywhere, but in fact the type of biomass that is grown depends of many factors, especially the climate. For example, for ethanol production, sugar cane (a tropical crop) is used in Brazil, corn is used in the United States, and sugar beets and wheat are mostly used in Europe. For biodiesel production, rapeseed oil is used in Europe, soybean oil is used in the United States, and palm oil is used in South East Asia. Biorefineries use available biomass, and at the corresponding cost. These climatic and soil factors are the key reason why the local cost of sugar production in Europe is higher than in Brazil, and why palm oil is only produced in equatorial regions. In addition to climate and soil conditions, other parameters, such as the harvesting mode, will affect the localization of major plantations. For example, castor is an oil-seed crop that is mainly cultivated in India, China, and Brazil. It is a tropical crop, but it also has been cultivated in the United States and Ukraine, for example. It can be cultivated as an annual or a perennial crop. Most of the harvesting is done manually, as long as all the fruits are not mature at the same time. This means that the cultivation is possible only in countries with rather cheap labor cost. There are a lot of efforts to mechanize this crop, but this means not only building harvesters but also selecting the appropriate seeds/hybrids that will produce a plant that is not too tall, that has a stem that does not require a saw to cut (many of the perennial species look like trees), and where all the fruits are mature at the same time. In addition, to be able to cultivate these types of crops, which are not frost resistant, in European climates it is also necessary to select them for the duration of the growth cycle. This cycle should be short enough so that the farmers can grow them in 5–6 months maximum.

2.5 Biorefineries – definitions and examples

Biorefinery defines an assembly of processing units that convert one or several biomass sources into several commercial products (chemicals, materials, and energy). Two main types of biorefineries are: the energy-driven and the product/chemical-driven biorefineries. The energy-driven biorefinery aims to produce fuels, power, and/or heat, and residues are upgraded as bio-based products to optimize profitability. The chemical/material-driven biorefinery aims to produce bio-based products, and residues are used to optimize the profitability of the value chain. Current ethanol plants belong to the energy-driven biorefinery, in which the residues are commercialized as animal feed. Biodiesel units in France could correspond to both categories since the initial target was to produce a protein-rich animal feed, the oil then being used to produce energy rather than oversupplying an edible oil market.

There are efforts (see, for example, the classification developed within the International Energy Agency, Bioenergy Task 42, [Cherubini et al. 2009]) to classify biorefineries in to standard types, based either on the *platform-type* designing the main or several intermediates; for example:

- C6 sugar or C5 sugar
- Oil
- Syngas
- Lignin
- Bio oil
- Biogas
- Hydrogen

Based on *products* made, either as *energy-* or *material*-related

- Bioethanol
- Animal feed
- Biodiesel
- Glycerine
- Synthetic biofuels (for example, Fischer-Tropsch fuels) and chemicals (alcohols)
- Biomethane
- Bio-based chemicals such as lactic acid, amino acids, and biomaterials

Based on *feedstocks* used

- Starch crops (corn, wheat, etc.)
- Oil crops (rapeseed, soybean, etc.)
- Lignocellulosic residues (straw) and crops (switchgrass, cardoon, miscanthus, etc.)
- Grasses
- Algaes

Based on the type of technology used (*processes*) and their combinations

- Hydrolysis
- Fermentation
- Seed crushing
- Transesterification
- Pretreatment
- Gasification
- Fischer-Tropsch synthesis
- Alcohol synthesis
- Fiber separation
- Anaerobic digestion, upgrading, and so forth

And, finally, including the source of *auxiliary energy* (heat and power)

- Natural gas
- Electricity

Integrated biorefineries combine several types of raw materials, technologies, and products to generate the best value from the whole crop.

Among the different types of existing biorefineries, the most common ones are:

- Paper mills, producing paper and energy (many export energy as electricity)
- Oleochemical plants
- Ethanol production units
- Biodiesel production units
- Sugar-based complexes, such as the Cargill (U.S.) plant or the Pomacle (F) "Les Sohettes"
- Vegetable oil–based plants

2.5.1 Arkema's castor oil-based biorefinery

Arkema's biorefinery in Marseille (France) belongs to the last family. It uses castor oil to produce the monomer of Polyamide-11 (sold as RILSAN-11), a highly technical polymer. This plant co-produces glycerine, heptanaldehyde-heptanol and heptanoic acid, and "Esterol" (see the following paragraph). This plant corresponds to a type of biorefinery in which a single type of raw material can be used. Here, castor oil is unique in the vegetable oil arena since it is the only oil with a high content (85–90%) of ricinoleic acid (12-Hydroxy 9-octadecenoic acid). Castor oil is nonedible, and the castor meal too. It is a tropical crop, and currently most of the production (about 80%) occurs in India. When the Arkema plant was built in 1955, there were oilseed mills in the Marseille harbour, which is why the plant is located there. So it was an integrated biorefinery, long before the term was invented.

The process in the Arkema plant starts with a transesterification of castor oil with methanol and production of Castor Oil Methyl Ester (COME) and glycerine. The second step is a high temperature thermal cracking, in which only the methylricinoleate will react, leading to methylundecylenate (a C11 unsaturated ester) and heptanaldehyde. After hydrolysis of the ester, the acid (undecenoic acid) will be converted to 11-Bromoundecanoic acid, through an anti-Markovnikov mechanism with hydrogen bromide. Finally, the Bromoacid is converted into the aminoundecanoic acid by reaction with ammonia, and is further purified to become a monomer of high value. In this process, the mixture of the esters, which cannot be converted during the thermal cleavage (oleic, stearic, palmitic, linoleic, etc.), will be recovered and sold as a solvent named "Esterol." This solvent has numerous applications, including as a demolding agent for concrete. Heptanaldehyde can be sold as such and has applications in fragrances and is hydrogenated to heptanol where it also has a small market. Most of the heptanaldehyde is oxidized as heptanoic acid, and has several applications, such as aviation lubricant. Details on the process can be found in a book on chemical and petrochemical processes (Chauvel et al. 1986).

In this type of plant, with a single type of raw material, all the co-products are made with a constant ratio, and it is particularly important to find the best possible value for each of them. This also means that when the price of refined glycerine decreased from €1,500/ton down to €400–500/ton, the production cost of the other co-products mechanically increased. In this type of biorefinery, it is important to identify the key product. The average product value is well above €2/kg, since the key product ends up as a high value polymer. There are two ways to calculate the production cost for all the products:

1. The production cost at each step is split between the products, and each of them are then sold with a margin/profit.
2. The co-products are assumed to be sold without any profit (meaning that as much production costs as possible are charged to the co-products), and the remaining production costs are allocated to the key product. This is a way to minimize the cost of the key product, but it will fluctuate with the value made on the co-product.

Both ways are acceptable since it is impossible to make the product without the co-product. A major difficulty with this type of biorefinery is that it relies on a single crop, the production of which is located mostly in the same geographical area, such as India for 80% of the world production of castor oil, for example, and the price of castor oil fluctuates with the Indian climate and monsoon season.

By analogy to petroleum-based refineries, this type of plant would be similar to a refinery built on a petroleum well. The raw material is always the same, with only minor variations. If there is a shortage of supply, the whole refinery has to be shut down. All the products made from this remote refinery have to be transported to the final customer, and all of them have to find the best possible market.

2.5.2 Elevance Renewable Sciences oil-based biorefinery

An other type of oil-based biorefinery is the complex Elevance Renewable Sciences is building with Wilmar in Indonesia based on ethenolysis of vegetable oils (metathesis with ethylene). In this case, since the plant is being built in South East Asia, palm oil is an interesting raw material, but the technology itself will allow the complex to use other vegetable oils, such as soybean oil. This type of biorefinery has a greater degree of flexibility, since by choosing the raw material mix, it is possible to tune the product slate. For example, if palm oil becomes expensive and the demand for alpha-olefins increases, it is possible to switch to soybean oil, to some extent.

To illustrate this type of plant, let's assume that palm oil is made only of three fatty acids: oleic acid (a C18 unsaturated fatty acid with the double bond between the 9th and 10th carbons), stearic acid (a saturated C18 fatty acid), and palmitic acid (a saturated C16 fatty acid). Ethenolysis is a reaction of ethylene with other C=C double bounds, and obviously here it can only react with oleic acid. In the Elevance plant, the ethenolysis is carried out on the vegetable oil, previously purified to remove any impurity that could affect the reaction. The first step generates an alpha olefin – 1-decene – and a new triglyceride, which contains short chains and long chains. The long chains are those of the saturated fatty acid that could not react here and the short chains are those of the 9-decenoic acid, an omega-unsaturated fatty acid (meaning acid at one end and a C=C double bond at the other end of a 10-carbon-atom linear chain). Since the alpha-olefin is lighter compared to the triglyceride, it easily separates. The triglyceride is then processed to a transesterification unit "biodiesel-like" where glycerine is formed together with the methyl ester of the saturated fatty acids and the methyl ester of 9-decenoic acid. Methyl ester of saturated fatty acids have a high cetane number, which would make them attractive as biodiesel. However they also have low cold-flow properties (a high melting point), which restricts their application as biodiesel. Even palm oil has a limited potential as biodiesel in Europe, although it is much cheaper than many other

vegetable oils because of its high content of saturated fatty acids. Another possible market for these saturated fatty acids is the classical oleochemistry, including conversion to fatty alcohols, which offers a good added value (De Guzman 2011a, 2011b). Methyl ester of 9-decenoic acid is basically a new product, which has to find new applications. It could be used as a fuel, since the chain length and the unsaturation makes it more compatible in cold flow properties. It can also be hydrogenated to produce capric acid (decanoic acid)/methyl ester. This is an attractive value proposition (Mirasol 2009b) since this acid has long been the most expensive natural fatty acid together with the C8 caprylic acid (see ►Fig. 2.4).

Decanoic acid is much less present in palm kernel and coconut oils than dodecanoic acid (lauric acid, the C12 saturated fatty acid). The price of lauric acid has been increasing lately, so there might also be interest to produce it through cross-metathesis with 1-butylene, followed by hydrogenation, instead of ethenolysis. If all the products have to be sold as fuels, there is no real benefit to add the complexity (capital and operating costs) of an ethenolysis to the palm oil biodiesel that would anyway address the same market (Mirasol 2009a). Ethenolysis should also focus on high-value products and use wastes to produce fuels.

So this type of biorefinery also needs to find customers for each of the products made. But it has the flexibility to switch to other raw materials, if needed. For example, it could switch easily to beef tallow, since the major components are not much different from palm oil. But this raw material might be difficult to find in the same location than palm oil plantations. If the demand for bio-based alpha-olefin (1-decene) is increasing, it would be wise to turn to an oil containing more oleic acid such as rapeseed oil

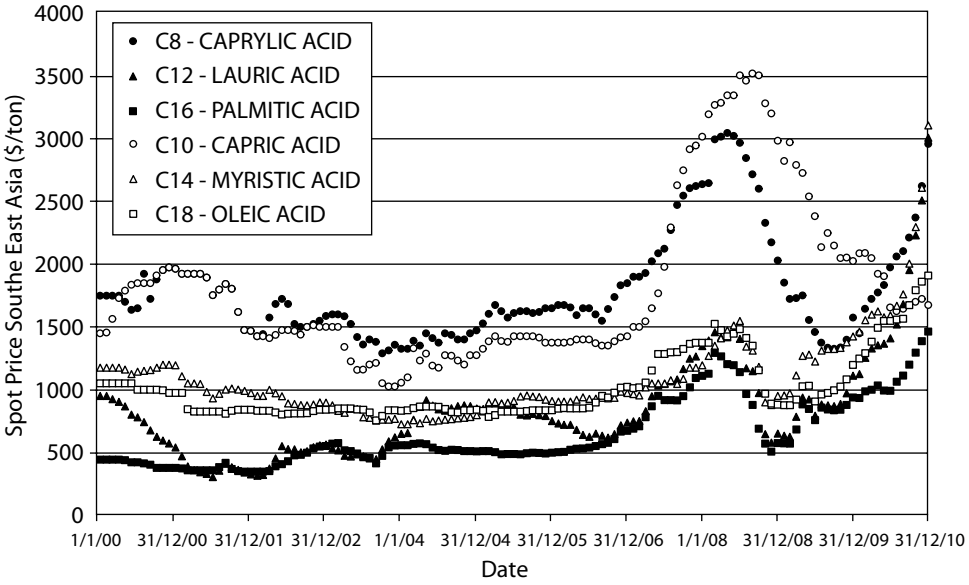


Fig. 2.4: Spot prices for fatty acids in South East Asia from January 2000 to December 2010.

(also called canola oil in the Untied States) or sunflower oil. But then the production of methyl ester of 9-decenoic acid is also increasing. If other alpha-olefins are being looked for like 1-heptene, then an oil rich in linoleic acid such as soybean oil is more interesting.

This type of biorefinery now needs to tune the raw material supply to the market demand in products. By analogy to petroleum-based refineries, this type of plant would be similar to a refinery built, for example, in Europe, which can purchase petroleum from the North Sea or from the Middle East or even Russia. Each of these feedstocks have different compositions, some are more appropriate to produce gasoline and others for bitumen, for example. Depending on the season, the refinery does not make the same product slate. From July and even earlier, petroleum refineries will start to produce more domestic fuel oil used as heating fuel in winter. But from January on, the refineries will start to produce more transportation fuels since summer (vacation period) corresponds also to the so-called driving season. The refineries produce all kinds of products, including diesel and gasoline, in ratios that are not only defined by the petroleum source that they use but also by the type of processing units that they have. An FCC unit is designed to make more gasoline, while a hydrocracking unit is designed to make more diesel fuel. As mentioned earlier, Europe is now more a diesel-consuming area, so the excess production of gasoline made in Europe needs to be exported. Refineries on the Atlantic Ocean used to export gasoline to the United States and import diesel from Russia.

To optimize their revenues/profits, these types of refineries have to use a mathematical model, which is being used on a daily basis. On the basis of the petroleum available and on the type of product that the refinery has to and can make (requirements from the market) the model is used to determine the daily production generating the highest revenue. On a predictive basis, it determines the type of petroleum to be purchased. This type of model integrates all the expertise from the refinery and is specific to each refinery.

2.5.3 Vandeputte oil-based biorefinery

Vandeputte is a Belgian company based in Mouscron. It has a long history, since 1887, of using linseed oil for the production of various products such as Linoleum, soaps, standoils (heat polymerised oils), blown oils (oxypolymerised oils), and alkyd resins. Linseed oil is also an industrial oil and, like castor oil, is rather unique since it has an unusually high (50% to 62%) linolenic acid content (C18 fatty acid with three C=C double bonds at 9th, 12th, and 15th carbon). Currently, linseed is mainly produced in Canada.

The plant based in Mouscron includes a seed-crushing capacity, an oil refining unit, and downstream processing units. According to communications from the company, the plant corresponds to an investment of €30 million, produced 35 kt/year of linseed oil for a 120 kt/year seed-crushing capacity, and generates €100 million/year of sales (Baudouin 2011).

Here again the biorefinery relies on the climatic conditions of the localized production of linseeds. The linseed meal has as significant an interest as animal food, and it probably generated 25% of the revenues (exact data not available). So about €75 million of the revenues are linked to 35 kt annual oil production. This means that the oil-based products need to find an average value above €2/kg.

2.5.4 The "Les Sohettes" biorefinery

Located in Pomacle, France, this is a typical sugar- and starch-based biorefinery complex. On a single location several productions are being made, using both sugar beets and wheat starch.

There is a sugar beet processing unit, a wheat refinery and a sugar plant, an ethanol distillery (Cristanol), a cosmetic ingredients producer (Soliance), a succinic acid pilot plant (BioAmber), a research center (ARD), a demo-plant for second-generation ethanol (Futurol), and a straw-based paper production pilot unit (CIMV). There is a strong integration for water supply and water treatment, a steam network, waste treatments, and an energy supply. Of course there is also a strong integration in the product networks.

In this type of biorefinery two major crops are being used: sugar beets and wheat. The sugar beet harvesting period is rather short and the beets have to be processed rapidly. The combination of both crops offers a synergy for ethanol and other downstream applications. A sugar beet–only production would never be economical if it had to run only a few months per year. This is an important concept for the idea of biorefineries on multiple crops.

The shareholders of this complex are also unusual for industrial plants and include farmer cooperatives, banks, and companies. The promotion of this type of biorefinery was done by cooperatives to find an outlet for their crop productions. This was also done in the context of the European farming policy, which was providing subsidies to farmers but was also trying to limit the overproduction of food products. Because the location of this complex is far from usual crop transportation networks, it was necessary to build processing units in the farmers' backyards.

2.5.5 The starch-based Cargill biorefinery

Cargill's Blair (Nebraska, USA) biorefinery is an other example of an integrated biorefinery with multiple products: corn is processed and there is corn oil production, a sugar unit, an ethanol plant, a lactic acid unit, and a polylactic acid plant (Natureworks). The biorefinery is managed by a single company the policy of which includes contract farming to supply the raw material. The objective is then slightly different than in the previous case. In addition, other companies also have a facility near the industrial complex.

In both cases, the optimum of the global biorefinery is not the optimum of each individual plant, as was the case for the ethenolysis-based biorefinery discussed previously. Market prices of all the products are changing as the raw materials do, but not exactly in the same correlation. So to optimize the profit, it is important to decide on a daily basis which product slate should be made. In this case, the average product value (sugar, lactic acid, PLA, ethanol, corn oil) is certainly below €2/kg but above €0.5/kg.

2.5.6 Other biorefineries

There are many other biorefinery types, such as the lignocellulosic biorefineries. The oldest types are paper mills, now looking to also produce chemicals. A paper mill produces paper pulp, and the energy needed is supplied by the combustion of lignin and other wood residues. In some cases, some chemicals, including specialty cellulose and

cellulose derivatives, can be made. The Borregaard biorefinery is an example of a plant where high-value products such as vanillin are made. Because of the decrease in paper consumption, it is also important for paper mills to find other markets. Paper mills have been able to manage their logistics in order to guaranty a permanent supply to their plants. Paper is by nature bio-based, but its production is made in remote locations. So the carbon footprint of paper is mainly the result of the transportation required to deliver the paper to the final customer. Paper mills are now turning to energy production in order reduce their own carbon footprint.

Many projects to use wood as a sugar source in a biorefinery. ▶Fig. 2.5 compares the historical market value of sugar and the market value of bleached paper pulp. Paper pulp then corresponds to a first step of lignocellulosic biomass pretreatment, in which the lignin has been separated, but in which cellulose and hemicellulose are not yet hydrolysed. Of course, for paper production it is important to have a process that preserves the fibers, but the production cost also includes all the logistical issues for supplying a large amount of biomass to the paper mill, the distribution cost of the product, the energy consumption, and capital cost depreciation, among others. The straight comparison shows that paper pulp is about two times the price of sugar. However, newsprint paper quality (which is not bleached) is about 35% cheaper than Northern Bleached Softwood Kraft paper pulp. Because of the fierce competition in the paper industry, the paper pulp market value can be considered very close to the cost of production, on a depreciated plant. This means that it will require an efficient process to be able to use cellulose to substitute sugar where it is being used today.

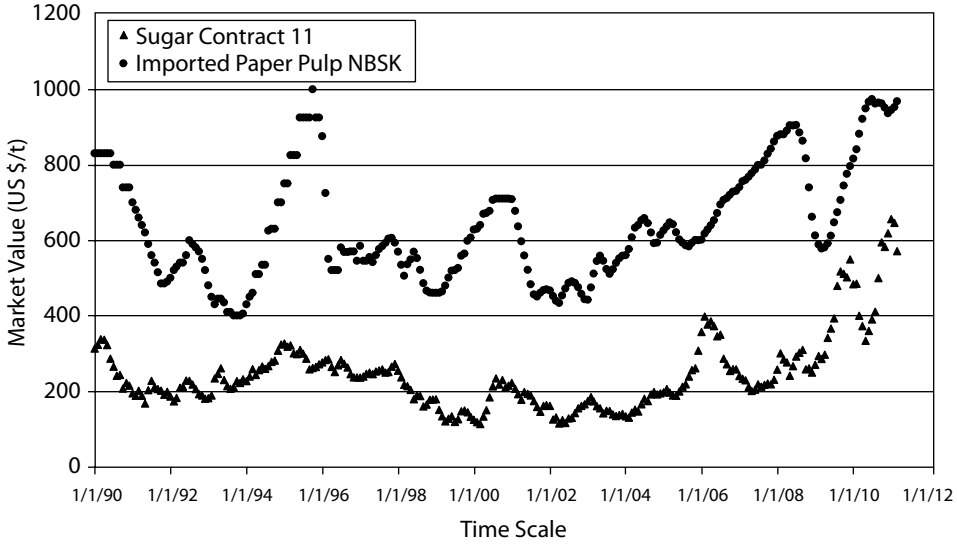


Fig. 2.5: Historical prices for sugar (contract 11 nearest future position, listed on Index Mundi) and or imported paper pulp (Northern Bleached Softwood Kraft [NBSK]), available on http://www.indices.insee.fr.

2.6 Processing units

Processing units in biorefineries include chemical, biochemical (fermentation), and thermochemical processes. In the examples listed previously the vegetable oil–based biorefineries are using chemical and/or thermochemical processes (thermal cracking in the Arkema plant).

Industrial fermentation also has a long history. Many products are made by fermentation processes, as illustrated in ▶Tabs. 2.1–2.4.

Tab. 2.1: Fermentation products.

Product	Application	Market Value 2011 (€/kg)	Market 2010 (kt/y @ €/kg)	Market 2009 (€/kg)	Market 2007 (kt/y) (% in China)
Antibiotics	Penicillin		Bulk: 35 @ 12.5 €/kg		
	Others		Spec. 5kt @ 1,500 €/t		
Aminoacids					
Lysine	Animal food		350 @ €2	1.2	
Glutamic/ Glutamate	Food additive, Pharma		1,000 @ €1.5	€1	255 kt
Phenylalanine	Aspartame synthesis		10 @ €10		
Threonine	Animal food				
Tryptophane	Nutrition				
Arginine					
Organic acids					
Citric	Food, preservative, chelating agent		1,000 @ €0.8	0.6	1,700 kt (50)
Lactic	Food, preservative, chemical synthesis, polymer	1.5/2.0	250 @ €2		400 kt (33)
Itaconic	Resins, synthetic fiber			1.3	50 kt (18)
Gluconic	Pharma, food, paint stripper, cement		50 @ €1.5		
Ascorbic					
Acetic	Food, industrial	0.6–0.7 (contract)			

(*Continued*)

Tab. 2.1: Fermentation products. (*Continued*)

Product	Application	Market Value 2011 (€/kg)	Market 2010 (kt/y @ €/kg)	Market 2009 (€/kg)	Market 2007 (kt/y) (% in China)
Enzymes (amylase, Glucose isomerase, Protease, etc.)	Starch industry, glucose industry, soaps, detergents				
Polysaccharides	Xanthan gum		20 @ €8		100 kt
Vitamins (C, B2, B12)	Vitamin C (comb. ferm and chem)		80 @ €8	10	
	Others		B12 0.015 @€20,000		
Butanol				235 kt @ €1/ kg (5% higher than regular butanol)	
Ethanol	Drinks, Perfumes, Pharma, Biofuels	>61,000 @ €0.6	49,000 @ €0.4		
Reference			Krijgsman, 2010	Anonymous, 2009	Huang et al., 2010

Tab. 2.2: Fermentation products.

Product	Application	Market Value <2006 (kt/yr @ €/kg)	Market Value (year unknown) (kt/yr @ €/kg)	Market 2006 (kt/yr)	Market Value <2007 (kt/yr [% Fermentation/ Chemical])
Antibiotics	Penicillin	Bulk 30 @ 1.5		60	
	Others	Specialty 5 kt @ €150/t			
Aminoacids					
Lysine	Animal food	350 @ 2		800	
Glutamic/ Glutamate	Food additive, pharma	1,500 @ 1.50	1,500 @ 1.2	1,000	

(*Continued*)

Tab. 2.2: Fermentation products. (*Continued*)

Product	Application	Market Value <2006 (kt/yr @ €/kg)	Market Value (year unknown) (kt/yr @ €/kg)	Market 2006 (kt/yr)	Market Value <2007 (kt/yr [% Fermentation/ Chemical])
Phenylalanine	Aspartame synthesis	10 @ 10			
Threonine	Animal food				
Tryptophane	Nutrition				
Arginine					
Organic acids					
Citric	Food, preservative, chelating agent	1,500 @ 0.8		1,200	1,600 (100%)
Lactic	Food, preservative, chemical synthesis, polymer	250 @ 2	150 @ 1.8	400	150 (100%)
Itaconic	Resins, synthetic fiber			($4/kg)	15 (100%)
Gluconic	Pharma, food, paint stripper, cement	50 @ 1.5	100 @ 1.5		87 (100%)
Ascorbic					
Acetic	Food, industrial				190 (2.7%)
Enzymes (amylase, Glucose isomerase, Protease, etc.)	Starch industry, glucose industry, soaps, detergents			$3,800 M	
Polysaccharides	Xanthan gum	20 @ 8		100	
Vitamins (C, B2, B12)	Vitamin C (comb. ferm and chem)	80 @ 8	80 @ 8		
	Others	B12: 0.003 @ 25,000			
Butanol					
Ethanol	Drinks, perfumes, pharma, biofuels	>38,000	30,000 @ €0.6/kg	26,000	@ €0.4
Reference		Soetaert and Vandamme, 2006	Penttilä, 2010	Yang, 2007	Sauer et al. 2007

Tab. 2.3: Fermentation products.

Product	Application	Market 2005 (kt/yr [in China])	Market value 2004 (kt/y @ €/kg)	Market Value 2004 (kt/yr @ €/kg)	Market 2003 (kt/yr)	Market Value 2002 (kt/yr @ €/kg)
Antibiotics	Penicillin		45 @ 300			
	Others		#40 @ 8-5200			
Aminoacids						
Lysine	Animal food		700 @ 2			
Glutamic/Glutamate	Food additive, pharma	1,200	1,500 @ 1.2	1,500		
Phenylalanine	Aspartame synthesis		10 @ 10			
Threonine	Animal food		30 @ 6			
Tryptophane	Nutrition		1.2 @ 20			
Arginine			1 @ 20			
Organic acids						
Citric	Food, preservative, chelating agent	800	1,000 @ 0.8	1,000		
Lactic	Food, preservative, chemical synthesis, polymer	150	290 @ 1.80/2.25	140	100	70 @ €2.2–3.4/kg
Itaconic	Resins, synthetic fiber		4 kt/yr			
Gluconic	Pharma, food, paint stripper, cement		100 @ 1.5			

Ascorbic				
Acetic	Food, industrial		190 @ 0.5	190
Enzymes (amylase, Glucose isomerase, Protease, etc.)	Starch industry, glucose industry, soaps, detergents	400		
Polysaccharides	Xanthan gum	20	40 @ 8.4	
Vitamins (C, B2, B12)	Vitamin C (comb. ferm and chem)	60	80 @ 8	
	Others		80+	
Butanol				
Ethanol	Drinks, perfumes, pharma, biofuels	2,000	>18,500 @ 0.4	
References		Chervenak, 2006	Anonymuos, 2004	Dubal et al., 2008

Tab. 2.4: Fermentation products.

Product	Application	Market Value <2006 (kt/yr @ €/kg)	Market Value 1998–2000 (kt/yr)	Market Value 1999 (kt/y @ €/kg)
Antibiotics	Penicillin	25 @ $20/kg	20	
	Others		30–40	
Aminoacids			1,000	
Lysine	Animal food	450 @ $2.2/kg	600	300 @ €1.9/kg
Glutamic/Glutamate	Food additive, pharma	1,000 @ $1.9/kg	350	800 @ €1.1/kg
Phenylalanine	Aspartame synthesis	15 @ $40/kg for Aspartame	18	13 @ €14/kg
Threonine	Animal food		5	13 @ €8.3/kg
Tryptophane	Nutrition		1	13 @ €19/kg
Arginine				
Organic acids			1,000	
Citric	Food, preservative, chelating agent	900 @ $1.7/kg	750	400
Lactic	Food, preservative, chemical synthesis, polymer	70 @ $2.1/kg	50	100 @ €2.2/kg
Itaconic	Resins, synthetic fiber		25	

Gluconic	Pharma, food, paint stripper, cement	40 @ $1.7/kg		40 @ €1.8/kg
Ascorbic		60 @ $1/kg		
Acetic	Food, industrial			
Enzymes (amylase, Glucose isomerase, Protease, etc.)	Starch industry, glucose industry, soaps, detergents		<10	
Polysaccharides	Xanthan gum	30 @ $8/kg	30	30 kt
Vitamins (C, B2, B12)	Vitamin C (comb. ferm and chem)		60	60 @ €0.95/kg
	Others		<5	B12: 0.003 @ 22000 €/kg
Butanol				
Ethanol	Drinks, perfumes, pharma, biofuels	13,000 @ $1.7/kg		
Reference		Demain, 2006	Baduel, unknown	Demain, 2000

However only ethanol has seen a significant growth over the past 10 years. Antibiotic, amino acid, organic acid, and vitamin growth is rather limited except for lactic acid, which is developing as polylactic acid. But even this polymer, which has more than 20 years history, cumulates only a volume of about 200 kt/year.

From those data, it should be noticed that the highest volumes also correspond to product values of less than €2/kg.

Many of the products that can be made from biomass have a higher applicative value than their corresponding fuel value (see ▶Fig. 2.6).

In ▶Fig. 2.6 the lower heating value (LHV) for many chemicals that could be made from biomass have been calculated, and the market value is expressed in terms of energy content. Most of them have a marketable value well above the petroleum value (€12/GJ). Data are plotted for two reference periods – August 2006 and April–May 2011. From these data, it appears that there could be a significant interest in focusing on products having an O/C ratio between 0.4 and 0.8. Another way to look at the data is to determine the carbon value in all these chemical compounds (see ▶Fig. 2.7).

The market value is calculated based on the carbon content, and shows that the value is increasing with the O/C ratio. Therefore, trying to produce a paraffin (or hydrogenated fuel) from a sugar molecule does not seem to be the most attractive value.

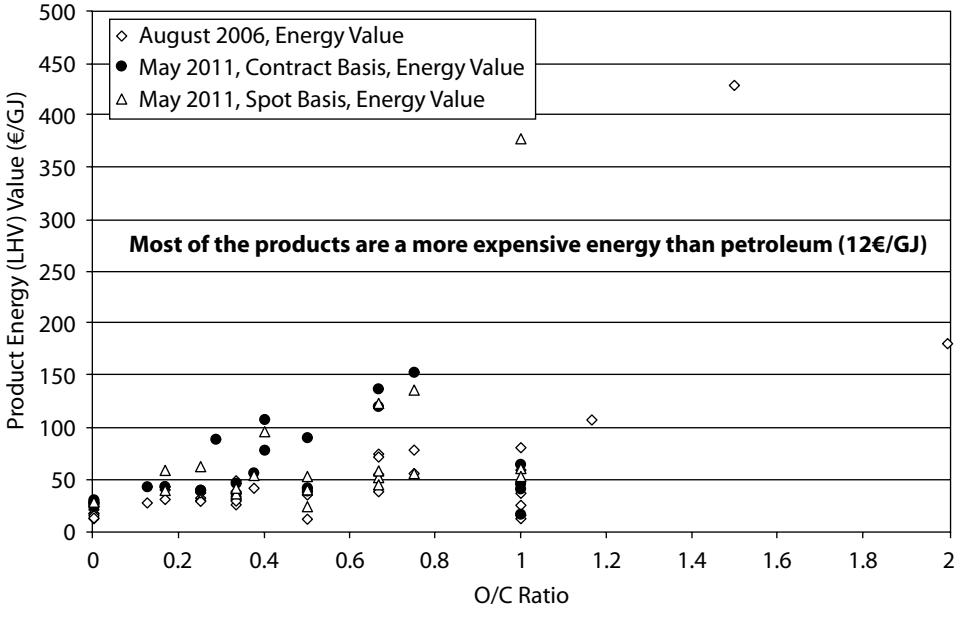


Fig. 2.6: Product value based on energy content (lower heating value). Market value can be on a contract basis or a spot-market basis.

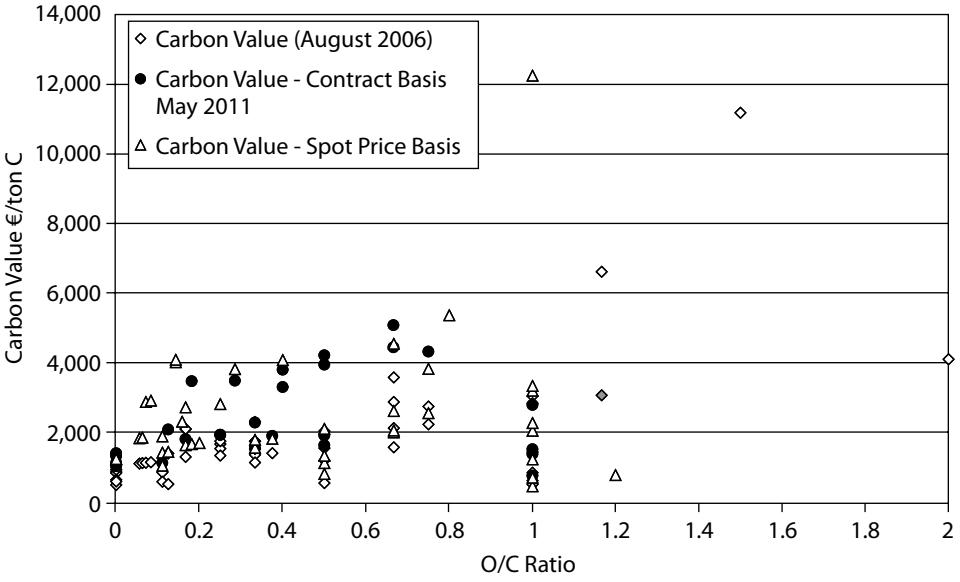


Fig. 2.7: Product carbon value. Market value calculated as a value of the carbon content.

2.7 Capital cost

The high capital cost of biorefineries is one of the main reasons why they are not more common today. A recent study listed 34 biorefineries in Europe, mainly located in Western Europe (Steinmetz 2009). On top of the capital cost, labor cost and raw material cost are, of course, of primary importance.

In ▶Tabs. 2.5 and 2.6 the capital costs of some biosourced products are listed.

For comparison, the capital cost was recalculated as if the plant was built in France in April–May 2011. Capital expenditure (CAPEX) is a significant contribution to the final product production cost, mainly through depreciation. Assuming a 10-year amortization of the capital cost, and an additional 2% capital for maintenance and 2% for taxes and insurance, the impact of capital cost on the production cost is as high as 14%. (*Note*: Plants might have been announced but never constructed because of the economic crisis. Regardless, the announced estimated construction cost is a useful figure).

Data were collected over the past 3–5 years from press releases and from the economic press. These data sources are important in order to have a general view of the required capital for biomass processing units. However, in press releases it is never clear what the capital expenses cover exactly, especially if the cost announced is inside or outside battery limits. Although the data have been screened to select the most appropriate ones, a confidence of +/- 30% should be taken into account. The data cover a short time period, but nevertheless during this time the construction cost changed. So all the data were also corrected using a Chemical Engineering Plant Cost Index to recalculate a capital cost in April 2011. Similarly all costs were converted to a single currency: Euros. And finally all the plants were relocated in the same country: France, to

Tab. 2.5: Bioproducts – nonexhaustive listing taking into account plants for which capital cost has been communicated.

Bioproduct	Company	Capacity (kt/y)	Location	Status	Date (announced)	Capital cost (local currency in millions)	Capital cost corrected for April 2011 and a location in France (M€)
1,3 Propanediol	DuPont	50	U.S.	Running	2004	$100	116
	Metex	8 to be debottlenecked to 50	Malaysia	Planned	2011	€36	40
PHA, Polyhydroxyalkanoate	Metabolix/ADM Telles	50	U.S. (Iowa)	Running	2008	$400	301
Polyethylene from ethanol	Braskem	200	Brazil	Running	2008	$278	217
Propylene	Braskem	30	Brazil	Under construction	2010	$100	83
Epichlorohydrine	Solvay	100	Thailand	Under construction	2010	$184	157
	Huanyang	30	China	Planned	2011	$28.8	23
Lactic Acid	Purac	100	Thailand	Running	2006	$144.8	161
	Purac	100	Thailand	Planned	2010	$155	131
Lactic Acid to Lactide	Purac	75	Thailand	Under construction	2010	€45	51

Succinic Acid	BioAmber	3	France	Running demo unit	2010	€21	21
	Myriant	13.6	U.S. (Louisiana)	Under construction	2010	$80	64
Ethanol by syngas fermentation	Ineos	24	U.S. (Florida)	Under construction	2011	$130	98
	Ineos	24	UK	Planned	2011	£52	60
Glucaric acid	Rivertop	0.045	U.S.	Under construction	2011	$6	4.5
Isobutylene	Global Bioenergies	100	Unknown	Lab	2011	$70	50
L-Methionine and Thiochemicals	CJ and Arkema	80 kt Methionine + thiochemicals	Malaysia or Thailand	Planned	2011	$400	312
Cellulosic Ethanol	Dupont/Danisco	74	U.S.	Planned	2011	$235	176
	MG Gruppo Mossi	45	Italy	Under construction	2011	€110	119
	BP/Verenium	106	U.S.	Planned	2011	$275	225

Tab. 2.6: Bioethanol and Biodiesel plants – nonexhaustive listing.

Bioproduct	Company	Capacity (kt/yr)	Location	Status	Date (announced)	Capital cost (local currency in millions)	Capital cost corrected for April 2011 and a location in France (M€)
Ethanol 1G	Cristanol	80	France		2005	€90	115
	Cristanol	273	France	Running	2006	€271	327
	Roquette	80	France	P 2008	2007	€75	86
	Terreos	200	France	P 2008	2007	€130	149
	Abengoa	180	France	P 2008	2007	€150	172
	Abengoa	200	France	Running	2005	€130	167
	Dupont/BP (Vivergo)	336	UK	Planned	2011	$400	252
Renewable Diesel	Neste	800	Singapore	Running	2010	$753	596 (hydrogenation of vegetable oil)
Biodiesel	Diester Industries	200	France (Sete)	Running	2008	€30	32 (heterogeneous catalyst)
	Diester Industries	250	France		2006	€35	42
	Diester Industries	200	France	Running	2006	€25–25	36
	Diester Industries	250	France	Running	2007	€40	46

	Diester Industries	100 (debottleneck)	Austria	Running	2009	€20	23
	Daudruy-Nord Ester	100	France	Running	2007	€25	29
	Serani Biofuels	120	Malaysia	Completed	2010	$23.3	18
Seed Crushing and Biodiesel Plant	Diester Industries	200 kt BD, 650 kt oil, 1.5 Mt Seeds	France)		2007	€150	172
	Diester Industries	250 kt BD, 450 kt oil, 1 Mt Seeds	France	Running	2009	158 M€	184 M€
Seed Crushing	Diester Industries	440 kt SM, 350 kt oil	France	Running	2006	70 M€	84 M€
	Cargill	250 kt S, 100 kt oil	France		2005	50 M€	64 M€
	Louis Dreyfus-Mitsui	500 kt SM, 350 kt Oil, 850 kt seeds	Canada	Running	2007	120 M$	106 M€
	Glencore	100 kt oil, 250 kt S	Ukraine	Planned	2011	66 M$	52 M€

take into account different construction costs in different countries, but always assuming the same construction quality standards. A plant could be much cheaper to build in China or India using local construction standards that are far lower than European or U.S. standards, but this cannot be taken into account. So in the list of plants taken into account, the amount of Chinese plants has been restricted.

From the available information, the impact of CAPEX on the product production cost is illustrated in ▶Fig. 2.8.

Of course, in this simplified analysis we have to assume that the target product is taking all the load of the depreciation, since in most cases the co-products have not been communicated. ▶Fig. 2.8 illustrates that, without subsidies, second-generation ethanol and syngas conversion to ethanol will need more than 10 years for depreciation, since the CAPEX impact is high. However since the calculations do not take into account tax breaks and other benefits on biofuels, these advantages could help to facilitate market penetration. Succinic acid either by the BioAmber process or the Myriant process has a huge CAPEX contribution to date. To become economically viable, without subsidies, these technologies will need either a much higher plant size or a significant technology improvement. For the other products, the CAPEX contribution remains roughly lower than 18% of the product market price. These general trends should be used to design new processes for biorefineries. Generally, most of the new technologies will rely on heavy public participation to the capital and/or various kinds of subsidies, until the

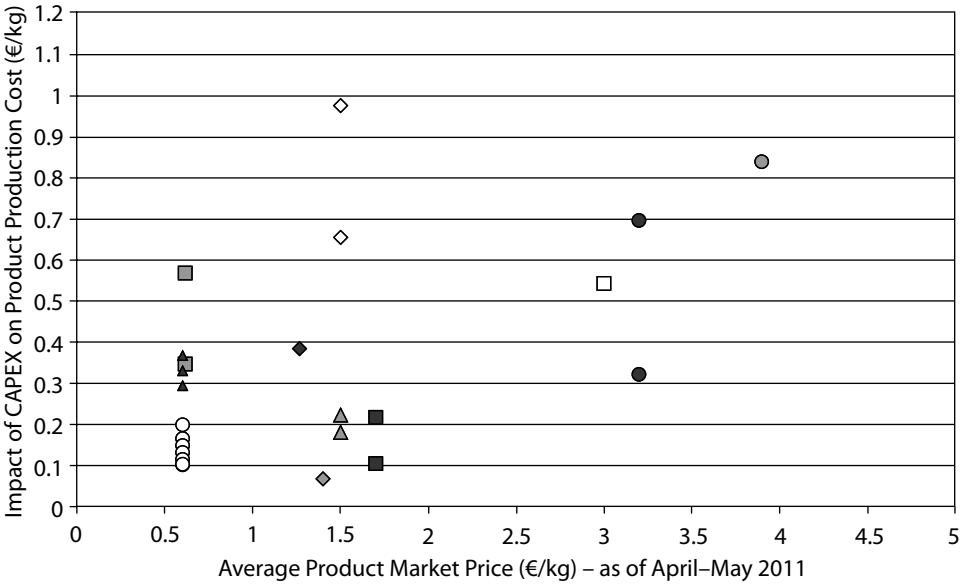


Fig. 2.8: Impact of the capital expenditure (CAPEX) on the product production cost. (F: fermentation, C: chemical, T: thermochemical) ○ Open circle: first-generation ethanol (F), ▲ Black triangle: second-generation ethanol (F), ■ Grey square: syngas fermentation to ethanol (F); ♦ Black diamond: propylene from ethanol (C); ♦ Grey diamond: bioisobutylene (F); ▲ Grey triangle: lactic acid (F); ◊ Open diamond: succinic acid (F); ■ Black square: epichlorohydrine from glycerine (C); □ Open square: methionine (F/C); ● Black circle: 1,3-propanediol (F): ● Grey circle: Polyhydroxybutyrate (F).

technology is proven. Syngas conversion to ethanol, or 2G-Ethanol (second-generation ethanol plants) might find a more interesting target in butanol, as long as the same CAPEX can lead to similar plant capacity since the market value for this chemical compound is higher.

Recently, a Biofuels Council on Economics, Science, and Technology introduced the concept of "Victory Plants" (Lane 2011). A Victory Plant would produce American Society for Testing and Materials (ASTM)-qualified advanced biofuels for an operating cost of $1.50 per U.S. gallon equivalent (eq) ethanol (at the refinery gate) on an unsubsidized basis (or €0.35/kg), can be constructed for no more than $4 per installed gallon of capacity (or €0.19/kg with a depreciation on 10 years) in 24 months or less, and must meet the low-carbon targets of the Renewable Fuel Standard. The Council will also seek to find cooperative ways for industry to reduce costs and improve carbon performance. Victory Plants have a target to reduce the investment, timelines, and risk for building advanced bioenergy projects. Compared to existing technologies, the challenge is high especially for the operating cost since it includes depreciation.

Usually, economy of scale is possible by building larger plants. ▶Figs. 2.9 and 2.10 illustrate the impact of plant size on the CAPEX for ethanol and biodiesel plants.

Three different technologies for ethanol production are illustrated in ▶Fig. 2.9: the first-generation (1G) ethanol plants using sugar and starch crops, second-generation (2G) ethanol based on cellulosic ethanol, and the newest syngas fermentation to ethanol projects. In the case of 1G ethanol, the plant also co-produces animal feed since it starts from the whole grain. In the case of lignocellulosic plants, other sugars and lignin are also coproduced. Syngas technology could use the whole biomass available,

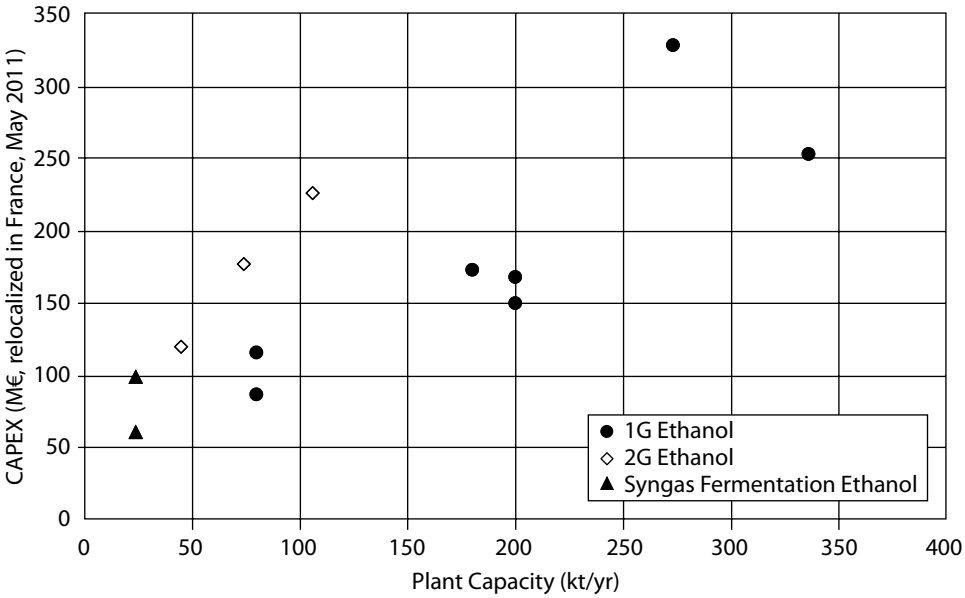


Fig. 2.9: Capital expenditure (CAPEX) for different ethanol plants and technologies. Capital cost includes grain processing and coproduction of animal food.

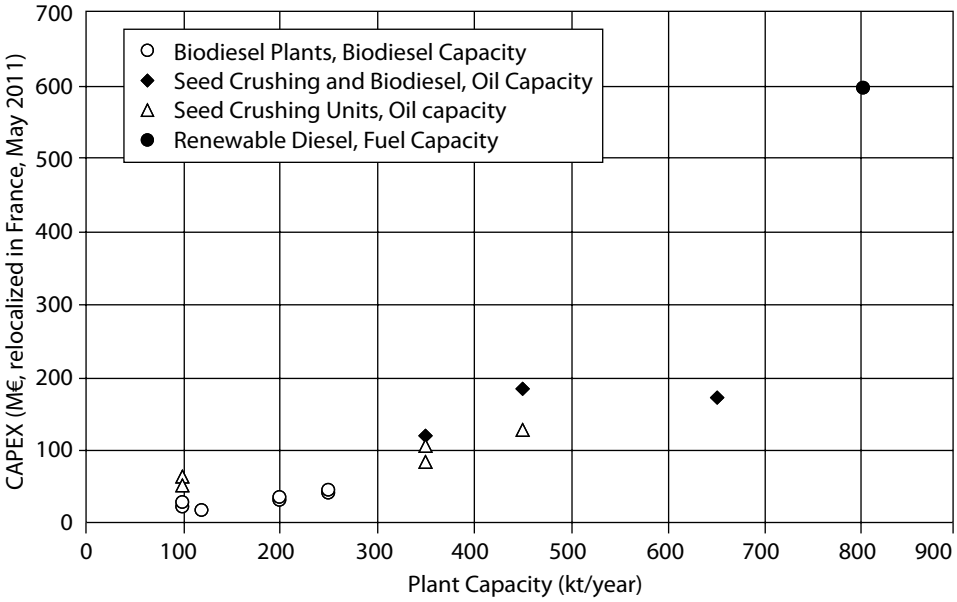


Fig. 2.10: Capital expenditure (CAPEX) on the processing of oilseeds. Open circle: Biodiesel plants using vegetable oils; closed circles: Renewable diesel using palm oil; open triangle: seed-crushing plants (data given for the oil production capacity); closed diamond: combined oilseed crushing and biodiesel plant (data given for the oil production) – note that biodiesel production is lower than oil production (200 kt for 350 kt oil, 250 kt for 450 kt oil, 200 kt for 650 kt oil).

thereby allowing larger plants, but the capital cost required is high since a gasification unit is needed on top of the fermentation process. In the case of lignocellulosic plants, the capital cost is about twice the amount needed for a 1G ethanol facility, so the challenge in this case is to find the best value for the co-products in order to split the impact of the capital cost on several products.

For oilseed crops, the full capital cost includes a seed-crushing unit, oil-refining unit, and a transesterification unit. However, in this case the capital cost should be split between the seed meal (animal feed), the oil, and the biodiesel. When the oil is the co-product of the animal feed (protein) production, the biodiesel process is a way to upgrade a co-product as an energy source. When oil can be purchased on the market, only the capital cost for the transesterification is necessary. This is probably one of the lowest CAPEX for a bio-based product, and explains the recent development of biodiesel. More recently, the renewable diesel where vegetable oil is fully hydrogenated and isomerized to isoparaffins has received a lot of attention. The Neste process required a very large plant in Singapore (De Guzman 2011c) in order to keep the capital depreciation low enough. Although, in this case, the impact of the CAPEX on the product cost is 4 to 5 times higher than in a conventional biodiesel plant of a much smaller scale. A strategy to reduce the impact of CAPEX, which is also true for many other biofuels, is to integrate this hydrotreating technology into an existing refinery. Several projects are ongoing this way. This type of fuel has a higher cetane number than biodiesel, but is not really

necessary for the diesel pool, which is mainly looking for volumes. However, it has a higher technical value as an aviation fuel, where the energy content (energy density) is critical, but where the certification process is long and difficult. Nevertheless, it raises again the important issue of the impact of regulations, which force the introduction of a dose of biofuels in all type of fuels, including aviation fuels, rather than where they bring additional technical values. On a global perspective, in terms of carbon footprint, it would probably be wiser to use vegetable oil into biodiesel rather than to force it into a hydrogenated stream for aviation fuel. The EuroBioRef project, although also targeting aviation fuels, is looking at technical value and also aiming at high value-added chemicals and materials. It is also important to note that recently the U.S. Air Force said that it would be ready to take as much biofuels as it can, as soon as the industry brings down the price of renewable jet fuel from it current US$35/gallon (€7–8/kg) by one order of magnitude.

A way to reach the targets of the so-called Victory Plant is certainly to combine the production of high-value chemicals and materials and to use the residues of the biorefinery to produce fuels. In this case, the fuel does not need to support most of the capital cost and can have access to lower-value feedstock. Usually chemicals/materials-oriented biorefinery, or ethanol plants, consume their own residues to supply the plant with the required energy.

2.8 Conclusions

Several practical examples of biorefineries based on vegetable oils, wood, and sugars have been highlighted. Capital cost for several recent plants of conversion of biomass have been analyzed and the results indicate that to increase the chance for success, biorefinery should have as a primary target high-value chemicals/materials and use the residual waste to produce energy and fuels. Projects based on vegetable oil should preferably target products with commercial value above €2/kg. For sugars/starch/lignocellulosic-based projects the main limitation is the high capital cost and the limited market value of the products (below €2/kg) that can be made from them.

There is currently a tremendous interest in bio-based products, but at the same time all the conditions are met to build a bio-economy bubble, with projects without enough economic background.

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3 The terrestrial biomass: formation and properties (crops and residual biomass)

Myrsini Christou and Efthimia Alexopoulou

3.1 Residual biomass

A number of studies (Siemons et al. 2004; Kim and Dale 2004; Edwards et al. 2005; Hoogwijk et al. 2005; Ericsson and Nilsson 2006; European Environment Agency 2006; Smeets et al. 2007; Alakangas et al. 2007; Ganko et al. 2008; De Wit and Faaij 2008; Wii et al. 2008) and European-funded projects (LOT5; REFUEL; RENEW Project, http://www.renew-fuel.com/home.php; BIOSYNERGY Project, http://www.biosynergy.eu; EUBIONET Project, http://eubionet2.ohoi.net/; BEE Project, www.eu-bee.com; and Biomass Futures Project, www.biomassfutures.eu) have reported biomass potentials with a wide range of feedstock types in a EU27, regional, or country level during several time frames (now, 2010, 2020, 2050). Because the main target of each article or research project differs, the applied methodologies and the elaborated assumptions also differ, making it difficult to compare technical potentials under sustainable development policies.

3.1.1 Straw

Cereal straw is the main field byproduct of small grain cereals, and it is considered to be one of the most widespread resources among the field of agricultural residues in Europe. The main crops producing straw in the region are wheat, barley, oats, rye, and rice, with wheat having the highest share among them.

Fifty-nine million hectares were cultivated with cereals in EU27 in 2009, which is almost 38% of the arable and permanent crop land in the region (FAOSTAT 2009). France, Poland, Germany, and Spain cover half of the cultivated lands (▶Fig. 3.1).

Straw production in the European Union (EU) varies among the regions and the same applies to yields and residue ratios. Literature reports average straw estimates of 0.5 grain-to-straw ratio for central and northern EU countries and a 0.9 grain-to-straw ratio for southern EU countries.

Biomass potential is subject to a number of availability constraints relevant to the agricultural biomass feedstocks. The main constraints can be categorized as:

- Land-use issues: Quality and suitability of land
- Yields: Diversified yields/species (3 t ha^{-1} – 5.5 t ha^{-1})
- Crop management patterns: Field and pressing losses amount for approximately 20% of the available biomass potential. Straw collection is performed within a few weeks to a year with high storage requirements. Transport and storage losses of approximately 10% are reported.
- Alternative markets: There is high demand from well-developed competitive markets (≤ 50%).

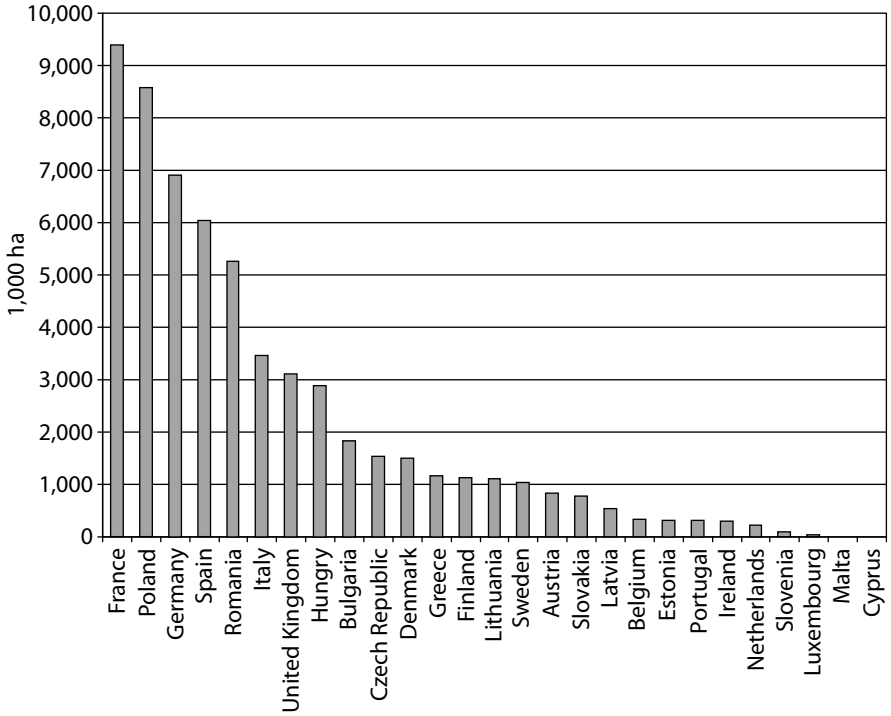


Fig. 3.1: Cereals land use in EU27 (FAOSTAT 2009).

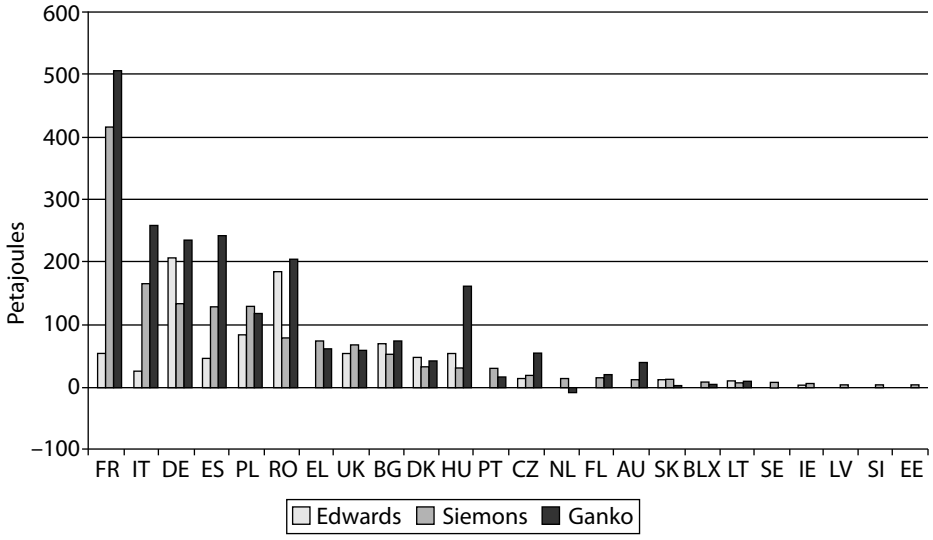


Fig. 3.2: Total cereal straw potential in selected Member States (based on productivity) from three different studies (Edwards et al. 2005; Siemons et al. 2004; Ganko et al. 2008).

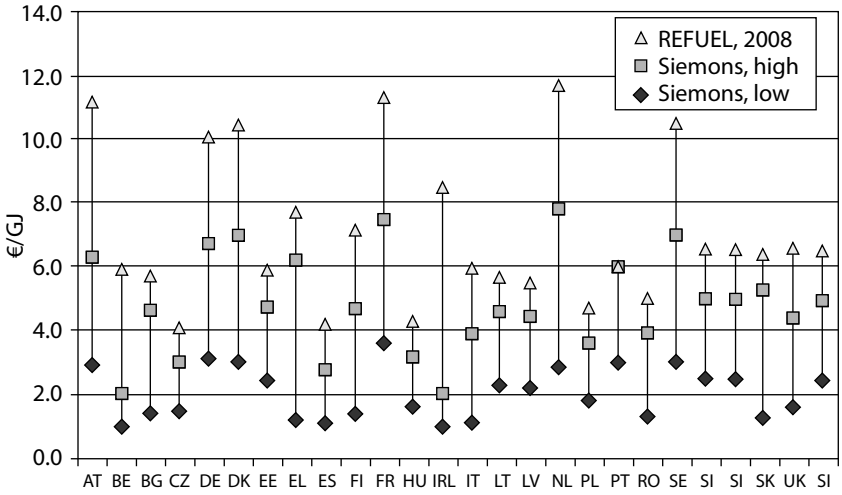


Fig. 3.3: Costs for solid agricultural residues (mainly straw) in EU Member States (€/GJ).

The total straw amounts calculated by Ganko (▶Fig. 3.2) resulted from data on cereal cultivation and relevant straw-to-grain mass ratios. The ratios refer to the amount of crop residue that could be technically harvested. The straw potential available for biomass-to-liquid (BtL) fuels do not include straw used for animals, soil-related needs, and other purposes; that is, gardening. In each scenario the results show the surplus straw that could be used without affecting fiber-related needs.

The total cost for straw (at plant gate) is reported to range from 2.09 to 3.29 €/GJ (Allen et al. 1996; Edwards et al. 2005) (▶Fig. 3.3). From the total cost, transport contributes 31%; harvesting, chipping, and baling for another 24% (together accounting for more than half the cost). Handling of the biomass is still significant (13%) while storage only contributes 4%. ▶Fig. 3.3 presents the cost ranges per EU Member State for solid agricultural residues based on two of the reviewed studies (Siemons et al. 2004; REFUEL 2008).

3.1.2 Wood

Woody biomass from forestry includes all biomass from forests (or other wooded land), tree plantations, and trees that grow in orchards, gardens, parks, and so on. Woody forestry residues include both primary residues (i.e. leftovers from cultivation and harvesting/logging activities) and secondary residues (i.e. those resulting from all further industrial processing, such as sawdust, black liquor, bark, etc.).

Several methods were used to estimate and project the woody biomass potentials (▶Fig. 3.4). Most of the studies used an inventory method to assess current potentials. Differences in forest inventories concerning spatial levels and statistical data restrict the comparability of the results (European Environment Agency 2006; Obersteiner et al. 2006). The same restriction is also caused from the fact that different multipliers have been used to estimate the amounts of different woody biomass types (e.g. logging residues, sawdust, etc.) in case this information was not available from statistics.

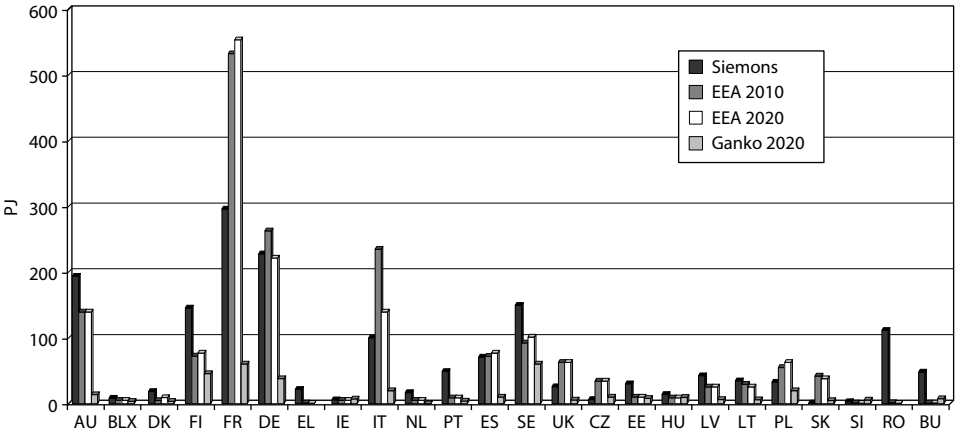


Fig. 3.4: Forestry biomass potentials per Member State from three different studies (Siemons et al. 2004; Ganko et al. 2008).

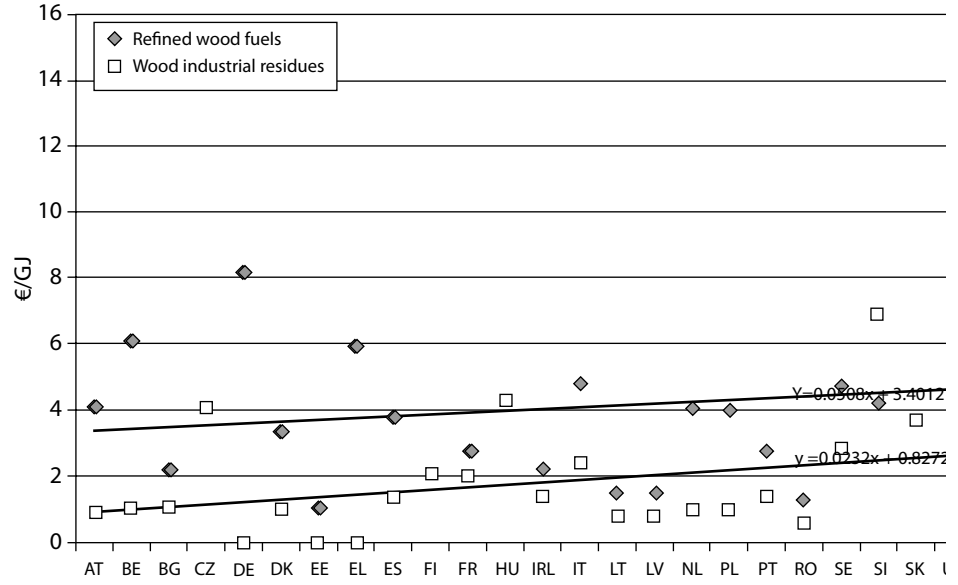


Fig. 3.5: Costs for woody biomass types in EU Member States (€/GJ).

The assessment of forestry residues and wood industry byproducts potential was based on areas covered by forests available for wood supply, net annual increment, and current national felling (harvesting) rates (Ganko et al. 2008). Based on the total amount of residues and byproducts (theoretical potential) that can be produced in the forestry and wood industry sectors, the technical potential was estimated. This refers to the biomass material that is available after fulfilling the forest environmental requirements and subtracting the proper amount of biomass used in competitive branches in

the wood industry. The wood industry byproduct use for energy purposes in the wood industry sector was not included in the potential available for BtL fuels. The costs for forest biomass are depicted in ▶Fig. 3.5. They are dominated by the transport distance from the forest collection site to the plant (or intermediate-use site).

3.2 The oil crops

Approximately 120 million tons of vegetable oils were produced worldwide in 2009, according to Food and Agriculture Organisation (FAO) statistics. In the recent years, the produced amounts have continuously increased by around 3% per year. It is predicted that this trend will continue in the medium and long terms. Four main vegetable oils dominate the industry, accounting for around 82% of the worldwide vegetative oil production in 2009: soya oil (31%), palm oil (20%), rapeseed oil (18%), and sunflower oil (11%). In addition, a number of other oil crops are produced around the world, including peanut, cottonseed, palm kernel, coconut, linseed, groundnut, and corn oil. While European oilseed production is dominated by rapeseed (*Brassica napus*) and sunflower (*Helianthus annus*), accounting for 59% and 20% of the total vegetable oil production, respectively, a number of other oilseed crops are produced, and this range has increased with the accession of new European Member States. Rapeseed dominates in most northern countries and sunflower in most central and southern countries. Although the largest proportion of the produced oil was used for food purposes, a significant proportion was used for nonfood purposes. Soya bean (*Glycine max*) cultivation was shown to be increasing in southern Europe, accounting for 16% of the total vegetable oil production in 2009; the cultivation of linseed (*Linum usitatissimum*) was shown to fluctuate and was largely subsidy driven; considerable quantities of, primarily tropical, oilseeds were imported to supplement European production. From the selected crops, only safflower (*Carthamus tinctorius*) production is commercialized. Safflower oils correspond to 0.10% of total vegetable oil production. The main producers of safflower are India (54,000 tons), the United States (39,256 tons), and Argentina (27,460 tons).

With the recent food versus fuel debate, more oil crops are being considered worldwide. For several oil crops, cultivation at the European level is not at a commercial scale, thus their yields are reported from primarily from the United States. For certain crops like castor seed and safflower there is considerable research going on in the Mediterranean area, thus it is highly likely that these crops could be candidates for larger-scale development. In the cold climate of central Europe, crambe seems to have a potential to grow as it shows similar performances as rapeseed.

The oil crops considered in this chapter are castor seed, crambe, cuphea, lesquerella, lunaria, safflower, and jatropha. These nonfood crops do not compete with food crops in terms of agricultural lands, because they can grow on less fertile lands with low inputs (water, nitrogen, pesticides, etc.). Their selection was also based on their favorable oil properties for the various green chemical products dealt with in this project.

3.2.1 Castor seed (*Ricinus communis L*, Euphorbiaceae)

Castor seed is a tropical plant that is cultivated around the world for its nonedible oilseed. Castor seed (▶Fig. 3.6) is indigenous to the Mediterranean Basin and originates



Fig. 3.6: Castor seed.

in East Africa, especially Tanzania, Kenya, Uganda, and India (see Wikipedia, http://en.wikipedia.org/wiki/Castor_oil_plant; and IENICA 2002a). It can be found as decorative plants in parks and in wastelands.

The plant has been subjected to substantial breeding, and a number of varieties and genotypes have been produced, either for ornamental use or for oil production (Brickell 1996; Koutroubas, Papakosta, and Doitsinis 1999). In contrast to unimproved varieties yielding between 400 and 900 kg ha^{-1} (Bonjean 1991), the new genotypes have higher reported yields, varying from 1,600 to 2,620 kg ha^{-1} (Laureti and Marras 1995; Laureti et al. 1998; Soratto et al. 2012), whereas yields reaching 5,140 kg of seeds per hectare were also reported in field experiments (Laureti and Marras 1995; Soratto et al. 2012; Koutroubas et al. 1999). Seed yields and oil properties are presented in ▶Tab. 3.1.

Castor seed is the source of castor oil, which has a wide variety of uses. The seeds contain between 40% and 60% oil that is rich in triglycerides, mainly ricinolein. The seed contains ricin, a toxic protein, which is also present in lower concentrations throughout the plant.

The world production of castor seed is around 1,200,000 ton. The main producers are India, China, and Brazil, but it is also produced in Africa. There is significant variation in the price of oil, ranging from US$800 to US$1,800 per ton.

Castor seed as a tropical-season crop cannot tolerate temperatures lower than 15°C. The crop requires 120–140 days from planting to maturity. It can survive in arid conditions and on various types of soils but requires an appropriate and consistent rainfall

or irrigation. While castor requires adequate soil moisture during pod set and filling, a subsequent dry period as the plant matures promotes high yields. Agronomic practices are summarized in ▶Tab. 3.2.

Castor is sown in March–April (as spring crop) and harvested in October. Recommended seed densities vary from 20,000 to 30,000 plants ha^{-1}, sown in rows 100 cm × 90 cm, or 100 cm × 50 cm.

Castor seed can be grown in crop rotation schemes. Best maize yields are obtained after castor in crop rotation (Arkema).

3.2.2 Crambe (*Crambe abysinica* Hochst ex R.E. Fries, Brassicaceae/Crucifera)

Crambe (▶Fig. 3.7) is an annual oilseed crop with a high content of erucic acid (55%–60%) in the seed oil, which is inedible and used in the plastics industry (Adamsen and Coffelt 2005; Laghetti, Piergiovanni, and Perrino 1995; Masterbroek, Wallenburg, and van Soest 1994). Crambe is believed to be native to the Mediterranean area and Ethiopia, and is well adapted to the cool and wet climate conditions of northwest Europe. It has been grown in tropical and subtropical Africa, the Near East, Central and West Asia, Europe, the United States, and South America.

Crambe, which is closely related to rapeseed and mustard, is an erect annual herb with numerous branches that grows to a height of 60–100 cm. The seed remains in the pod or hull at harvest. It achieves seed yields of 2,300–3,200 kg ha^{-1} in Italy at 32%–37% oil content and oil yields of 730–1,100 kg ha^{-1} (Laghetti, Piergiovanni, and Perrino 1995) (▶Tab. 3.1). In the United States it gives yields of 1,500–2,250 t ha^{-1} at 27%–35% oil content (Oplinger at al. 1991).

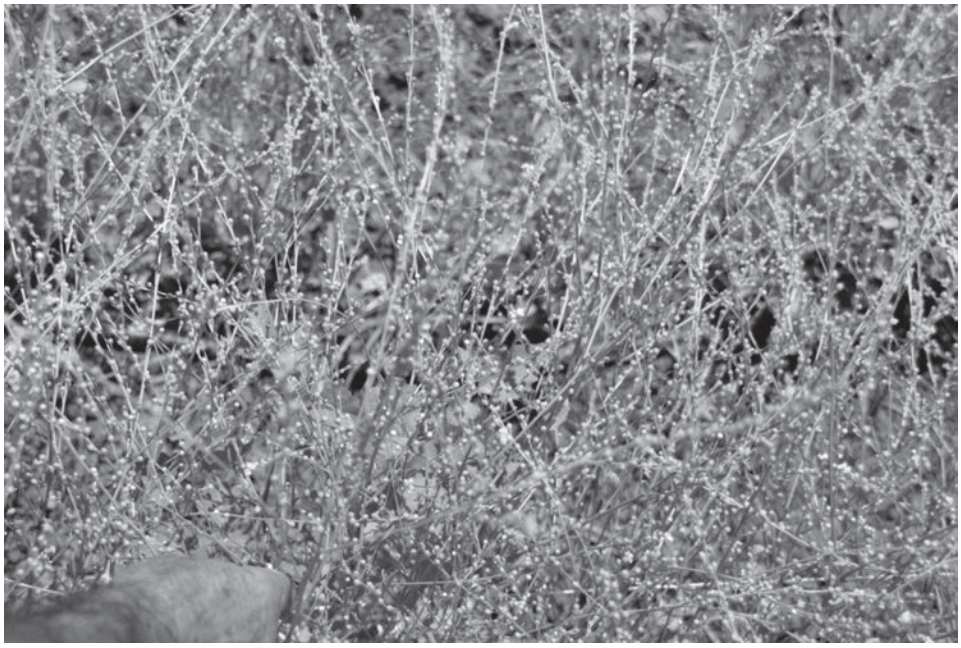


Fig. 3.7: Crambe.

Tab. 3.1: Seed and oil yields and oil properties.

	Ricinus communis	*Crambe abyssinica*	*Cuphea viscosissima*	*Cuphea painteri*	*Jatropha curcas*	*Lesquerella fendleri*
Seed yields (kg/ha)	1500–3500	2300–3200	350–1500	350–1500	1250–5000	800–2300
Oil yields (kg/ha)	600–2000	730–1100	240–300	240–300	450–2250	220–380
Oil content (%)	40–55	32–37	27–32	27–32	35–45	22.5–25
Fatty acid (%)						
C8:0 Caprylic			9.1	73		
C10:0 Capric			75.5	20.4		
C12:0 Lauric			3.0	0.2		
C14:0 Myristic			1.3	0.3		
C16:0 Palmitic	0.5–1.0	1.8			12.0–16.0	0.8–1.1
C18:0 Stearic	0.5–1.0	0.7			5.0–7.0	1.4–1.8
C18:1 Oleic	2.0–6.0	17.2			40–45	14.0–17.9
C18:2 Linoleic	1.0–5.0	8.7			30–35	5.2–6.5
C18:3 Linolenic	0.5–1.0	5.2			0.5	9.7–11.2
C20:1 Eicosanoic	0.5–1.1	3.4			0.5	0.6–0.8
C22:1 Erucic		56.2 (58–66)				
C22:1 Brassidic trans		0.7				
C24:0 Tetracosanoic		0.7				
C24:1 Nervonic		1.6				
C18:2 Epoxylinoleic						0.5–1.1
C16:1 Hydroxypalmitol						0–0.1
C18:1-OH Ricinoleic	85–95					0.3–0.4
C18:2 Densipolic						0–0.1
C20:1-OH Lesquerolic	0.0–1.0					54.7–59.7
C20:2 Auricolic						3.0–4.7

L. gordonii	*Lunaria annua*	*Carthamus tinctorius* (commercial)	*Carthamus tinctorius* (high linoleic)	*Carthamus tinctorius* (high oleic)	*Carthamus tinctorius* (high ste aric)
800–2300	2000–2500	2600–4000	2600–4001	2600–4003	2600–4005
220–380	600–1000	560–1000	560–1001	560–1003	560–1005
22.5–25	30–40	21–22	21–23	21–25	21–27
1.1–2.0	1.0–3.0	6.4–7.0	6.0–6.8	4.0–8.0	6.2
0.9–2.5	1.0–2.0	2.4–2.8	2.1–2.9	4.0–8.0	9.5
11.0–20.0	16.0–20.0	9.7–13.1	9.8–12.7	74.0–79.0	11.9
5.0–14	8.0–10.0	76.9–80.5	77.5	11.0–19.0	71
3.8–9.2	2.0–4.0				
	38.0–48.0				
	22.0–25.0				
0.0–0.7					
0.0–0.2					
55–68					
0.8–3.0					

Tab. 3.2: Comparison among the oil crops, in terms of their agronomic characteristics and yields.

	Castor	Cuphea	Crambe	Lesquerella	Lunaria	Safflower
Planting date	March–April (spring crop)	Early May–June	October–December (winter crop); March–April (spring crop)	October	June–August (UK)	October–December (winter crop); March–April (spring crop)
Seed quantities	12–15 kg/ha	21 kg/ha	21 kg/ha	5–11 kg/ha (9 kg/ha)	15–20 kg/ha	20 kg/ha
Planting densities	In rows 100 cm × 90 cm, or 100 cm × 50 cm, 20,000–30,000 plants/ha	in rows 31 cm apart, 500,000 plants/ha,	in rows 35 cm apart, 1,000,000 plants/ha	in rows 33 cm apart, 750,000–1,000,000 plants/ha	in rows 50 cm apart, 250,000–500,000 plants/ha	in rows 50 cm apart, 400,000–1,500,000
Basic fertilization	30–60 kg P/ha	90 kg N/ha	90 kg N/ha	60–80 kg N/ha and 40–70 kg P/ha	75 kg N/ha, 50 Kg P/ha 50 kg K/ha	60–80 kg N/ha and 40–70 kg P/ha
Nitrogen fertilization	30–60 kg N/ha	90 kg N/ha	75 kg N/ha	0–120 kgN/ha	75 kg N/ha	0–200 kg N/ha
Irrigation	600 mm	300–400 mm		300–400 mm	300–400 mm	600–700 mm
Harvesting date	October	July–August	June–July	June–July	October–February or July of the next year	September

The crambe planting date is a crucial factor that affects seed yields and oil content but not the content of erucic acid and glucosinolates (Adamsen and Coffelt 2005; Laghetti, Piergiovanni, and Perrino 1995; Masterbroek, Wallenburg, and van Soest 1994; Johnson et al. 1995; Morrison and Stewart 2002). Sowing time depends on location and climatic conditions, but as a general rule, advanced sowing favors higher yields (Laghetti, Piergiovanni, and Perrino 1995). In temperate climates crambe could be sown from September to November, like rape, whereas in colder climates it is advised to be sown as a spring crop sown in late April or May.

Although it is relatively drought-tolerant, the best yields have been obtained in moist areas. Crambe's response to soil fertility is similar to that of small grains, mustard, and rape (Enders and Schatz 1993). Agronomic practices are summarized in ▶Table 3.2.

Crambe crops are managed in the same way as spring rapeseed crops. Machinery used for tillage, planting, spaying, and harvesting crambe is similar to that used for small grains. Successful harvests have been obtained when crambe is planted in rows of 12–50 cm.

Crambe is advised to be grown in four-year crop rotation schemes to keep insects, disease, and weeds to a minimum, following small grains, corn, grain legumes, or fallow, while it can be sown as companion crop for alfalfa and other biennial or perennial forage-type legume establishment (Laghetti, Piergiovanni, and Perrino 1995; Enders and Schatz 1993). It should never follow crambe or other akin crops, such as colza, rape, or wild mustard (Laghetti, Piergiovanni, and Perrino 1995).

Constraints in crambe cultivation are mainly the low genetic variability in *C. abyssinica* (WEISS 1983) and also the low germinative capacity of seeds. Crambe has a higher erucic acid content than erucic rapeseed, but this is attenuated by its lower oil yield. Crambe, unlike rapeseed and most other crucifers, has each seed encapsulated in its own hull. Such a bulky commodity increases the cost of transportation from the farm gate to the processing facility (Carlson et al. 1996).

3.2.3 Cuphea (*Cuphea sp.*, Lythraceae)

Cuphea sp (▶Fig. 3.8) is an industrial oilseed crop that belongs to the Lythraceae family. It contains about 260 wild species, mostly native to Mexico and to Central and South America and many third-world countries (Phippen 2009; Guesh et al. 2006). Cuphea species are annual and perennial flowering plants or evergreen shrubs native to tropical and subtropical areas, but only a few species are used commercially.

Due to its lack of frost tolerance it may not be suitable to grow in many European countries, however, several species have been identified for cultivation in central Europe, like *Cuphea paucpetala, C. leptopoda, C. wrightii, C. tolucana, C. lanceolata, C. procumbens, C. micropetala,* and *C. ignea*. In Europe it is highly likely that best performances may be achieved only in the Mediterranean countries.

Cuphea has attracted interest as a source for C8, C10, C12, and C14 oils (medium-chain fatty acids) in the seeds recorder in temperate regions (Guesh et al. 2003, 2006; Guesh and Forcella 2007; Moscheni, Angelini, and Macchia 1994; Berti, Johnson, and Henson 2008). It thus has the potential to replace coconut and palm kernel oil and satisfy the growing demand (e.g. for biodiesel production) with decreasing needs for imports from tropical countries.



Fig. 3.8: Cuphea.

Cuphea is produced as a summer annual in the Untied States using existing row-crop machinery. In Europe, only in the Netherlands and Italy has scientific interest/development in the growth of *Cuphea spp* been expressed, but germination is slow (12–14 days) even in late May. Germination is slowed down due to the thick seed hull. The first seed is produced six weeks after sowing in the greenhouse (IENICA 2002b).

Cuphea gives a seed yield range of 350–1500 kg ha^{-1} (mean 900 kg ha^{-1}) (Phippen 2009; Walsh 2007; Guesh et al. 2003, 2006; Guesh and Forcella 2007) with an oil content of 27%–35% and oil yields of 240–300 kg ha^{-1} (▶Tab. 3.1). The seed contains 32% (dry basis, db) oil and 21% (db) crude protein. Glutelins and albumins account for 83.5% and 15.4%, respectively, of the total protein extracted (Phippen 2009).

Cuphea is sown in early May–June at seed densities of 500,000 plants ha^{-1} (in rows 31 cm apart). Agronomic practices are summarized in ▶Tab. 3.2. Seed germination is typically low (40%–60%) and low germination is often associated with low seed vigor (Berti, Johnson, and Henson 2008). Cuphea has also been shown to improve agricultural crops in the United States when used in crop rotation with corn, wheat, and soybean every three years using the same farm equipment.

The major constraints to the development of this crop for industrial uses are its frost sensitivity, sequential maturation due to the intermediate growth habit of the crop, release of seeds from seed pots, and seed shattering. Thus the highest priority to assure maximum seed yields is genetic and plant breeding research to obtain determinate flowering and nonshattering cultivars. If seed shattering, indeterminate flowering nature, and stickiness can be overcome, cuphea's chemistry, coupled with the annual and, therefore, renewable nature of the plant, certainly can make it a new promising crop.

3.2.4 Lesquerella (*Lesquerella fendlheri L, Communis L,* Cruciferae/Brassicaceae)

Lesquerella (▶Fig. 3.9) is a crop originating from the southwest United States (Texas, Arizona, and California), where over 70 lesquerella species are grown as annual (winter or summer), biennial, or perennial herbs (IENICA 2002c; Dierig, Thompson, and Nakayama 1993). There are three varieties of lesquerella that have been tested for domestication: *Lesquerella fendleri*, *L. gordonii*, and *L. mendocina* (South America). *L. padilla* and *L. lindheimeri* have led to lesquerolic acid contents higher than 80% (Jenderek, Dierigb, and Isbell 2009), which opens large opportunities for breeding programs.

Lesquerella seed yields range from 1,100 to 2,300 kg ha^{-1}, as reported in experimental trials and breeding tests (Agricultural Commodities as Industrial Raw Materials 1991). Yields above 2,200 kg ha^{-1} were expected for commercial production (USDA 1991) and have been recently announced (Isbel 2009). In European trials the reported seed yields are 440 kg ha^{-1} (in UK), 1,390 kg ha^{-1} (NL), and 950–1120 kg ha^{-1} (USA), but only 800–900 kg ha^{-1} in large scale. Oil yields ranged from 220 to 380 kg ha^{-1} (22.5%–25% oil content) and oil content ranged from 22% (UK), 36% (NL), to 21% (USA) (versus 50% for castor).

Approximately the 55% of that is lesquerollic hydroxyl fatty acid (C20:1-OH) homologue of ricinoleic acid (C18:1-OH) found in castor seed (85% for castor) (Puppala and Fowler 2002). There are, however, lesquerella species, mainly hybrids, containing up to 39% oil and 79% lesquerolic acid, which gives huge possible opportunities for improvement through breeding. The seed meal is rich in proteins (29.8%), very close to rapeseed meal, and has a good balance in amino acids, which can then be used as animal feed (Carlson, Chaudhry, and Bagby 1990). However, the lesquerella meal contains glucosinolates (as many other crops of the family of *Brassicaceae*) and the enzyme thioglucosidase, which converts them into antinutritional compounds. Lesquerolic oil is a lubricant that is commercialized at higher prices than castor oil and is used in industrial products, like resins, waxes, plastics, lubricants, cosmetics, and coatings (Carlson, Chaudhry, and Bagby 1990; Dierig, Thompson, and Nakayama 1993). If developed as



Fig. 3.9: Lesquerella.

a commercial crop, lesquerella could reduce imports of castor oil. Seed yields and oil properties are depicted in ▶Tab. 3.1.

Lesquerella grows in altitudes of 600–1,800 m above sea level with annual precipitation of 250–400 mm (Dierig, Thompson, and Nakayama 1993). The plants geminate in late summer–early autumn, exhibiting little vegetative growth during winter but then increased growth, flowering, and seed set by late spring (IENICA 2002c). One of the major problems of growing lesquerella is the establishment of the stand, which is mostly associated with seed dormancy. Lesquerella has varying degrees of seed dormancy depending on the species and age of the seed, but the major dormancy problem is the light requirement during germination that led to further research on presowing treatments (Puppala and Fowler 2002). Agronomic practices are summarized in ▶Tab. 3.2.

Like castor, lesquerella is not demanding in soil quality and irrigation, and even though it is initially a desertic crop, literature indicates that the oil yield is higher with higher rains or irrigation. It was reported (Hunsaker et al. 1998) that to achieve maximum yields, more than 600 mm of water application was required. The same study suggested that lesquerella should not be water-stressed during flowering (late February through late March) and during the formation and ripening of the seed (late April) to avoid reduction in the seed yield, although it appears that it can tolerate reduction in water availability after the crop has reached full bloom (mid-April). According to U.S. Department of Agriculture (USDA) studies, with an equivalent amount of water of 650 mm, yields of 390 kg oil ha^{-1} have been obtained, with a higher lesquerolic acid content during trials in Arizona in 1988. These results were confirmed by those of Angelini et al. (1997) obtained in Italy. Similarly, lesquerella cultivated in California in the frame of the study by Jenderek et al. led to higher lesquerolic acid content than when planted in Washington State.

Trials have been done in several European and Mediterranean countries, including Italy, the Netherlands, and Turkey (IENICA 2002c). From these trials it has been established that *L. fendleri* is not well adapted to the temperate western European climate – the crop showed very poor establishment and germination. In the UK a modest plant stand was established.

Major constraint are the very poor establishment and germination that the crop showed in the European trials.

3.2.5 Lunaria (*Lunaria annua L*, Brassicaciae/Crusiferae)

Lunaria (▶Fig. 3.10) is commonly known as the honesty or money plant because of the shape of its seed pods. *Lunaria annua* is a plant native to southern Europe and western Asia, is well adapted to many temperate countries of Europe and North America, was introduced in northern Europe several centuries ago, and is widely grown as an ornamental flowering plant or as a wildflower in gardens and in wastelands (Smith et al. 1997; Walker, Walker, and Booth 2003; Cromack 1998; Masterbroek and Marvin 2000).

Interest in the commercial exploitation of the plant was peaked because its seeds contain 30%–40% oils with high proportions of long-chain fatty acids, like erucic (C22:1) and nervonic (C24:1) acids (Cromack 1998) (▶Tab. 3.1), and thus they can be used by the oleochemical industry for the production of high-temperature lubricants, erucamides,



Fig. 3.10: Lunaria.

additives, and pharmaceutical products (Smith et al. 1997; Walker, Walker, and Booth 2003; Cromack 1998; Masterbroek and Marvin 2000; IENICA 2002d).
Lunaria is still at the developmental stage. Agronomic trials have started in the Netherlands, Germany, the UK, and the United States (Smith et al. 1997; IENICA 2002d). Reported seed yields are 1,000–2,500 kg ha^{-1} (mean 900 kg ha^{-1}) at 30%–40% oil content and oil yields are 600–1000 kg ha^{-1} (Walker, Walker, and Booth 2003) (▶Tab. 3.1). In the United States the yields reported are 900–1,500 kg ha^{-1} (able to reach 1,900–2,900 kg ha^{-1}) and the oil content is 24%–34%. Early results from clinical trials suggest that preparations derived from honesty seed oil may be helpful in treating some disabling conditions such as multiple sclerosis (Smith et al. 1997).

Biennial honesty plants have an absolute (and considerable) vernalization requirement; they will not flower in spring unless they have been overwintered as well-established plants (Smith et al. 1997; IENICA 2002d). Sowing dates must, therefore, be early enough to allow the plants to grow sufficiently before winter. Winter vernalization conditions are adequate for June and July sowings; the optimum sowing dates reported in Scotland and southern England is likely to be late-May to mid-July, with harvest in late-August to September of the following year (Walker, Walker, and Booth 2003;

Cromack 1998; Masterbroek and Marvin 2000). Late sowing is unlikely to achieve harvestable crops. Walker, Walker, and Booth (2003) reported an optimum row spacing of 50 cm and a seed rate of 15 kg ha^{-1}, which corresponds to a population of 20–25 plants per m^{-2}. However, more research is required on lunaria's agronomic requirements, field performance, and harvesting methods. Yield data is limited, but lunaria's shatter resistance should make harvesting straightforward, although field experiments indicate that mechanical harvesting and cleaning of the seeds is a problem. Late sowing allows the crop to be sown in rotation after a summer-harvested crop. Agronomic practices are summarized in ▶Tab. 3.2.

The major constraints involved with lunaria cultivation are that the production potential, agronomy, and logistics of the crop require investigation. At present, commercial production of honesty is limited to seed multiplication for ornamentals.

3.2.6 Safflower (*Carthamus tinctorius L*, Compositae)

Safflower (▶Fig. 3.11) is an oilseed crop grown throughout the semiarid region of the temperate climates in many areas of the world and is used as vegetable and industrial oils, spices, and birdfeed (Oelke et al. 1992).

Safflower was known as carthamine in the 19th century. About 600,000 tons of safflower is produced commercially in more than 60 countries worldwide. India, the United States, and Mexico are the leading producers, with Ethiopia, Kazakhstan, China, Argentina, and Australia accounting for most of the remainder (see Wikipedia, en.wikipedia.org/wiki/Safflower). Safflower has been known since ancient times as a source of orange



Fig. 3.11: Safflower.

and yellow dyes and food colorings, and more recently it has been grown for oil, meal, birdseed, and for the food and industrial product markets (Oelke et al. 1992). Present interest focuses on types of safflower with different fatty acid profiles in the seed oil, which are suitable for industrial use in products such as paints and varnishes (Smith et al. 1997) as well as for the oil food market (Oelke et al. 1992).

There are two types of safflower varieties: the high oleic varieties that produce oil rich in monounsaturate fatty acids (oleic acids and higher than in olive oil) and the high linoleic varieties that produce oil rich in polyunsaturated fatty acids (linoleic acid) (Oelke et al. 1992) (►Tab. 3.1). Safflower also makes an acceptable livestock forage if cut at or just after bloom stage. The meal, which is about 24% protein and high in fiber, is used as a protein supplement for livestock and poultry feed. The seeds, which resemble small, slightly rectangular sunflower seeds, contain 35%–45% oil (IENICA 2002e).

Seed yields of 785 kg ha^{-1} (wind pollinated) and 1,700 kg ha^{-1} (bee pollinated) have been reported (IENICA 2002e). In the United States yields of 500–2,000 kg ha^{-1} are reported, and they could be as high as 3,000 kg ha^{-1} in irrigated regimes (Oelke et al. 1992). In Greece seed yield varied greatly among genotypes and ranged from 923 to 3,391 kg ha^{-1}, whereas hybrids showed a mean seed yield superiority of 12.5% against varieties (Koutroubas, Papakosta, and Doitsinis 2008). Seed yields can vary from 5 to 1,400 kg ha^{-1} according to varieties, and oil contents range from 8%–34%. This great variation may be due to cool temperatures during the flowering period, which can result in poor seed set and grain filling (Oelke et al. 1992). Safflower yields under irrigation for winter sowing are within a range of 2.10–4.05 t ha^{-1} and 1.31–3.74 t ha^{-1} for summer sowing. FAO presents that good rain-fed yields are in the range of 1.0–2.5 t ha^{-1} and 2.0–4.0 t ha^{-1} under irrigation (Istanbulluoglu et al. 2009). Hull proportion can be a handicap to commercial production, as it reduces seed-oil percentage. Varieties with fewer hulls may have higher oil content (above 40%–45%) (IENICA 2002e). Seeds yields and oil properties are presented in ►Tab. 3.1.

Safflower does best in areas with warm temperatures and sunny, dry conditions during the flowering and seed-filling periods (Oelke et al. 1992). In the temperate regions of the Mediterranean basin (Greece, Turkey, Lebanon) safflower can be sown either in October–December as a winter crop, or in March–April as a spring crop (Koutroubas, Papakosta, and Doitsinis 2008; Dordas and Sioulas 2008, 2009; Istanbulluoglu 2009; Istanbulluoglu et al. 2009). Early planting allows the crop to take full advantage of the entire growing season (Yau 2007). However, in water-scarce regions such as the Mediterranean area, winter sowing is more preferably than summer sowing in order to meet vegetable oil requirements (Istanbulluoglu et al. 2009). In addition, in low-input farming, the crop is capable of using residual soil nitrogen efficiently to increase seed yields and compensate for the losses in seed yields caused by low plant densities (Elfadl et al. 2009). Agronomic practices are summarized in ►Tab. 3.2.

Yields are low under humid or rainy conditions because seed set is reduced and the occurrence of leaf spot and head rot diseases increases. Safflower is significantly affected by water stress during the sensitive late vegetative stage (Istanbulluoglu 2009).

Safflower most often is grown on fallow or in rotation with small grains and annual legumes. It should not follow safflower in rotation or be grown in close rotation with other crops susceptible to the disease *sclerotinia* (white mold). These crops include dry bean, field peas, sunflower, mustard, crambe, and canola/rapeseed (Oelke et al. 1992). A crop-following safflower should be grown only if there has been a significant recharge

of soil moisture. Very little crop residue remains after harvesting safflower. Therefore, reduced tillage or chemical fallow after safflower may help reduce wind and water erosion of the soil. The production practices and equipment needed for safflower are similar to those used for small grains (Oelke et al. 1992).

3.3 The lignocellulosic crops

The lignocellulosic crops include perennial crops and short-rotation forestry. Such crops have low input requirements over 10–25 years of productive life coupled with high yielding potential. They offer not only an important energy resource but can also positively contribute to biodiversity, soil protection, landscape improvement, and so on. In the past decade, the EU has provided funds to research and develop perennial crops in a wide range of European environments. There have been several sizeable pan-Europe initiatives for perennial rhizomatous grass species.

The lignocellulosic crops described in this chapter are cardoon, giant reed, miscanthus, and switchgrass. Cardoon can show a wide variation in yielding potential, from 3 to 15 t ha^{-1} dry matter, but has the advantage of being a winter crop and thus it is not water demanding and can be grown in marginal lands. Miscanthus has gained interest in the energy market because of its high biomass potential, perennial nature, low inputs, and good biofuel characteristics (i.e. low moisture content at harvest time in spring). Annual yields of 10–12 and 20–25 odt ha^{-1} are expected under commercial conditions in central-north and south Europe, respectively. Likewise, the recorded yields of giant reed from a large number of experiments indicate that under real conditions and supply of sufficient water a yearly production of 10–15 odt ha^{-1} could be feasible. The yielding potential of switchgrass is achieved from the third year onward, and the best varieties can yield from 16 to 22 odt ha^{-1}, depending on the irrigation and fertilization provided.

3.3.1 Cardoon (*Cynara cardunculus L*, Compositae)

Cardoon (▶Fig. 3.12) is a perennial herb often richly branched with a tap root. Its stems have a height of 20–180 cm and are 17 mm wide.

The cultivated cardoon and artichoke originated from the Mediterranean westerly distributed *C. cardunculus* subsp. *flavescens*. Outside the Mediterranean region, there are also some naturalized cultivars – similar to *C. cardunculus* subsp. *flavescens* – in America (California, Mexico, and Argentina) and Australia (Bioenergy Chains Project 2006). Despite its old origin and its good flavor, the cardoon has never become a widespread crop. Existing cultivars have been selected for the horticultural application of the crop.

The potential of cardoon as an energy crop mainly lies in its application as solid biofuel. The main characteristics of the crop that suggest this application are: (a) relatively low crop inputs (Gominho et al. 2000); (b) large biomass productivity – about 14–20 t odm ha^{-1} $year^{1}$ if the crop is well established and rainfall is about 500 mm $year^{-1}$ (Fernandez 1993, 1998); (c) low moisture content (14%) of the biomass at harvest – 14%–50%, it varies with the particular conditions of harvesting; (d) biomass composition mainly lignocellulosic – values depend on the biomass partitioning into the different plant organs; the ranges of variation are approximately 16%–27% hemicellulose, 24%–60%



Fig. 3.12: Cardoon.

cellulose, and 3%–13% lignin (Gominho et al. 2000); and (e) higher heating value – about 15 MJ kg^{-1} at equilibrium moisture. However, the irregular distribution of the rainfall that characterizes the Mediterranean climates is a limiting factor.

Cardoon, when cultivated in Spain (agricultural land with low inputs at annual yields of 14.2 t ha^{-1}), had an estimated profit of 93.86 euro per ha^{-1} (▶Fig. 3.13).

The potential of cardoon as solid biofuel has been studied for several years (Bioenergy Chains Project 2006). The oil of cardoon is similar to the oils from sunflower

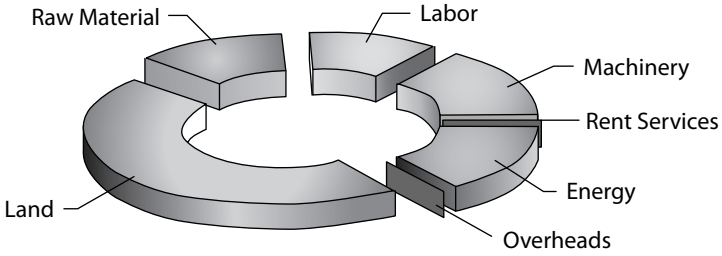


Fig. 3.13: Economic viability of cardoon when it is cultivated in Spain in agricultural land with low inputs. (*Source*: 4Fcrops Project, University of Catania, http://www.4fcrops.eu)

and safflower in its composition. The main characteristics of the crop that suggest this application are: (a) seed productivity of cynara – about 1,360 kg ha^{-1} $year^{1}$ as average (Fernández and Curt 2004); (b) seed oil content – 25% as average, 33% oil was the maximum figure reported by Curt, Sánchez, and Fernández (2002); (c) oil composition similar to sunflower – 11% palmitic, 4% stearic, 25% oleic, 60% linoleic, as main fatty acids of the cardoon oil; and (d) higher heating value – 22 MJ kg^{-1} at equilibrium moisture.

Cardoon germinates whenever the soil moisture and temperature are favorable. Hence, the sowing time can be autumn or spring in the Mediterranean climates. During autumn sowing the plant develops in autumn a leaf rosette large and strong enough to survive wintertime. At the end of this first cycle of growth the biomass production is usually low, but in the following cycles the crop yield usually increases, depending mainly on the climate conditions. In case of a cold autumn (early frosts), spring sowing is recommended. In this case, plants reach the rosette stage during summertime and complete the development cycle in the following summer, when the first harvest can be carried out.

Cardoon is harvested in August–September every year, when above-ground plant parts dry off naturally in the field but the underground plant part remains alive. When the climate conditions become more favorable, the buds on the underground parts of the plant sprout and a new development cycle begins. For energy purposes, mechanical harvest is similar to cereals. However, to harvest separately the seeds and the remaining above-ground biomass, several trails of mechanical harvest with conventional machinery gave poor results showing the need for specific machinery. In new trials carried out in the frame of the BIOCARD Project, cardoon was harvested by prototype machinery in two steps: harvesting of tops by a specially designed pickup for harvesting the heads of cardoon and separation of seeds (step 1) and harvesting of stems and baling (step 2). Agronomic practices are summarized in ▶Tab. 3.3.

Cardoon has been investigated at a European level in the following projects: AIR CT92 1089 (*Cynara carduculus L.* as a new crop for marginal and set-aside lands), ENK CT2001 00524 (Bioenergy Chains Project 2006), and recently in the BIOCARD Project. Being a perennial rain-fed crop that can be grown in marginal lands, its biomass productivity is highly variable, depending on the climate and soil conditions as well as on the growing period. Thus, cardoon cultivation still needs investigation over a longer period of time before commercial yields are defined. Harvesting of the crop in order to separate the seeds from the whole plant is still under investigation.

3.3.2 Giant reed

Arundo donax (▶Fig. 3.14) is a tall, perennial C3 grass that belongs to the subfamily *Arundinoideae* of the Gramineae family (Perdue 1958; Tucker 1990). It grows in dense clumps; the stems can reach a height of up to 8–9 m, exhibiting growth rates of 0.3–0.7 m per week over a period of several months during the vegetative stage when conditions are favorable (Perdue 1958). Stems arise during the whole growing period from the large knotty rhizomes. They do not all emerge at the same time, and later-emerging shoots fail to grow well and often die off. The rhizomes usually lie close to the soil surface (5–15 cm deep, maximum 50 cm), while the roots are more than 100 cm long (Sharma, Kushwaha, and Gopal 1998). The root system has two functions: to hold the plant in a stationary position and to absorb the water and nutrients from the soil.

Tab. 3.3: Comparison among the perennial lignocellulosic crops in terms of their agronomic characteristics and yields. (*Source*: 4FCROPS Project, University of Catania, http://www.4fcrops.eu)

	Reed canary grass	Switchgrass	Miscanthus	Giant reed	Cardoon
Area of origin	Europe	North America	South East Asia	Asia and Mediterranean	Mediterranean
Available genetic resource	Many variables available	Many variables available	Many variables available	Wild genetic base	Wild genetic base
Photosynthesis system	C3	C4	C4	C3	C3
Yield (t ha^{-1})	4–15	10–25	10–30	15–35	10–22
Raw material characteristic	Lignocellulosic biomass	Lignocellulosic biomass	Lignocellulosic biomass	Lignocellulosic biomass	Lignocellulosic biomass/Oil seed
Adaption range in EU	Cold and wet regions of EU	Cold and warm regions of EU	Cold and warm regions of EU	Warm region of southernEU	Mediterranean regions
Rotation time	10–15yrs	15 yrs	15–20 yrs	15–20 yrs	4–5 yrs
Establishment	seed	seed	Rhizomes	Rhizomes or stem cuttings	seed
Harvest time	Autumn/early spring	Autumn/early spring	Autumn/early spring	Autumn/early spring	Summer
Required machinery	Normal farm equipments	Normal farm equipments	Special farm equipments	Special farm equipments	Special farm equipments
Fertilizers input (kgha^{-1} N):	50–140	0–70	0–100	50–100	50–100
Pesticide and herbicides	First year and post-harvest	First year and post-harvest	First year and post-harvest	First year and post-harvest	First year and post-harvest



Fig. 3.14: *Arundo donax.*

A. donax is thought to have originated in Asia (Boose and Holt 1999; Rossa et al. 1998), but it is also considered a native species to the countries surrounding the Mediterranean Sea. It is currently found growing in India, Burma, China, southern Africa, Australia, America, and regions adjoining the Nile River and in the Mediterranean area (Veselack and Nisbet 1981).

The production potential of *A. donax* can reach up to 100 tons of fresh matter per year-1 ha^{-1} in the second or third growing period under optimal conditions in a warm climate and by supplying it with sufficient water (Shatalov and Pereira 2001). According to Morgana and Sardo (1995), in Sicily a mature plantation of giant reed yielded over 40 t DM ha^{-1}, indicating that this high potential for dry matter production brings promise of even higher production if cultivation's limitations are overcome. Yields reported in Spain showed 45.9 t odm ha^{-1} on average, ranging from 29.6 to 63.1 t odm ha^{-1} (Hidalgo and Fernandez 2000). Yields higher than 40 t odm ha^{-1} were recorded in Greece,

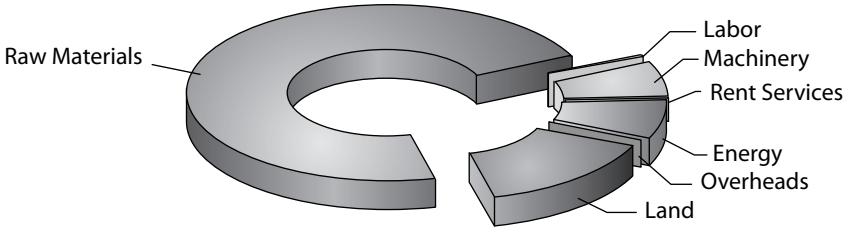


Fig. 3.15: Economic viability of giant reed when it is cultivated in Portugal in agricultural land with low inputs.

Italy, France, and Spain, and up to 30 t odm ha^{-1} in Germany and the United Kingdom (Christou et al. 2002). In Greece the recorded average dry matter yields, estimated from 40 giant reed populations, for the first, second, third, and fourth growing periods were 15, 20, 30, and 39 t odm ha^{-1}, respectively, on irrigated small plots (Mardikis, Christou, and Alexopoulou 2000; Mardikis et al, 2002). Stems constituted the largest part of the harvested material and amounted, on average, to 67%, 87%, 83%, and 86% of the odm, for the first, second, third, and fourth growing periods, respectively. The results show increasing yields from the first to the third year. Since from the third year on, stable, increasing, and decreasing yields were measured, no clear conclusion can be drawn on when the maximum yields of giant reed are achieved. Giant reed, when cultivated in Portugal (agricultural land with low inputs) at annual yields of 46 t ha^{-1}, had an estimated profit of 399.67 euro per ha^{-1} (Alexopoulou et al. 2011) (▶Fig. 3.15).

Giant reed can be used as a fiber and energy crop. The calorific value of different aerial parts, for a number of *A. donax* populations grown in Greece, ranged from 17.3 to 18.8 MJ (stem) and from 14.8 to 18.2 kg^{-1} odm (leaves), depending on the population and the growing periods. The contents of ash and fixed carbon contents ranged, in dependence of the population and the growing period, from 4.8% to 7.4% and from 17.7% to 19.4% of odm, respectively. Apart from the physical attributes of the stems, the high measured values for ash should be attributed to the contribution of sheath as well as of impurities such as sand, which raise the ash content. Nitrogen (0.2%–0.4% on odm), volatiles (75%–77% on odm), ash (4.8%–7.4% on odm), and fixed carbon (17.7%–19.4% on odm) can be considered satisfactory for energy production.

A. donax tolerates a wide variety of ecological conditions. It prefers well-drained soils with abundant soil moisture. It can withstand a wide variety of climatic conditions and soils from heavy clays to loose sands and gravelly soils (Perdue 1958), and it tolerates soils of low quality such as saline (Singh, Kumar, and Pacholi 1997). *A. donax* is a warm-temperate or subtropical species, but it is able to survive frost. When frosts occur after the initiation of spring growth it is subject to serious damage. It has a broad photosynthetic temperature optimum between 24°C and 30°C.

Establishment is the most critical point of *A. donax* cultivation and it has strong influences on productivity and economical viability. The two main factors determining establishment success and costs are the propagation material and the planting density. Because of seed sterility, only vegetative propagation is foreseen for the commercial production of *A. donax*. Planting of rhizomes, whole stems, and stem cuttings have been

tested but appropriate machinery for these operations is not yet available (Pari 1996; Vecchiet et al. 1996). In the tests done so far, the rhizome establishment turned out most promising. The planting of large rhizome pieces with well-developed buds directly into the field early in spring in southern European areas had nearly 100% success (Mardikis et al. 2002). However, this is a very costly labor-intensive method as this includes digging the rhizomes, transporting them to the site, keeping them wet for a certain period of time, cutting them into smaller pieces, and then planting them in the new field. Agronomic practices are summarized in ▶Tab. 3.3.

Because high yields were obtained from unimproved wild populations and by using conventional cultivation methods, future breeding efforts and optimized production methods will probably lead to an increase in biomass yields from *A. donax*.

Giant reed has been investigated in two EU projects: (1) FAIR CT86 2028 "Giant reed" and (2) ENK CT 2001 00524 "Bioenergy chains from perennial crops in South Europe."

3.3.3 Miscanthus (*Miscanthus x giganteus*, Poaceae)

Miscanthus (▶Fig. 3.16) is a woody rhizomatous C4 grass species that looks like bamboo or a reed. Stems are constituted of several strong lignocellulosic units (such as sugar cane). They are characterized by a rapid growth of up to three meters during the third or fourth year of production (Walsh and McCarthy 1998). *Miscanthus x giganteus* is a



Fig. 3.16: Miscanthus.

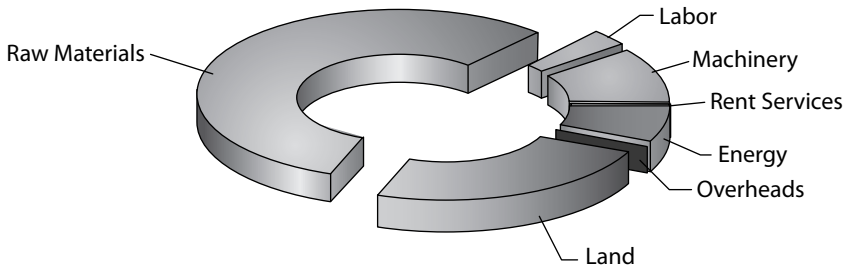


Fig. 3.17: Economic viability of miscanthus when it is cultivated in the UK in agricultural land with low inputs. (*Source*: 4Fcrops project, University of Catania, http://www.4fcrops.eu)

sterile (3n) naturally occurring interspecific hybrid that remains an unimproved plant like all Miscanthus species (Scurlock 1998).

Originating in Asiatic countries and first introduced to Europe in the 1930s as an ornamental plant, it has been spread out mainly throughout Europe due to some species bring better adapted to cooler conditions (Scurlock 1998). Miscanthus is frequently cultivated in the United States and southern Canada, and is now established in some parts of the United States. Approximately 40 forms and cultivars are available.

Miscanthus's estimated productive life span is about 10–15 years. The results of the main European trials have shown ceiling yields ranging from 15 to 25 t ha^{-1} at the end of the growing season in northern Europe. In central and southern Europe a higher productivity has been recorded (from 25 to 40 t ha^{-1}) but irrigation was required (Jones and Walsh 2001; Lewandowski et al. 2003). Nevertheless, according to Scurlock (1998), large-scale semicommercial trials suggest that a yield above 7–9 t ha^{-1} odt is a more reasonable estimate over large areas. Their first results suggest that yields of up to 25 t ha^{-1} $year^{-1}$ odt may be obtained at the time of harvest (February) under climate conditions ranging from central Germany (lat. 50 N) to southern Italy (lat. 37 N). Miscanthus, when cultivated in the UK (agricultural land with low inputs) at annual yields of 24 t ha^{-1}, had an estimated profit of 251.92 euro per ha^{-1} (Alexopoulou et al. 2011) (▶Fig. 3.17).

One of the potential end uses is as a fuel energy product by combustion in farm heating plants or co–combustion with coal, for example. In this last case, miscanthus is comparable to straw (18.2MJ kg^{-1}) (McCarthy and Walsh 1996). This energy can then be transformed into electricity, heat, and so on (Walsh and McCarthy 1998).

Miscanthus has a low impact on soil erosion, as well as on soil and water quality, due to its low requirements for pesticides and fertilizers. It may have a beneficial impact on wildlife and biodiversity compared to other high-input arable crops (Walsh and McCarthy 1998).

Despite the fact that C4 species are best suited to tropical and subtropical climates, some miscanthus species naturally occur in temperate climates. The results of the Miscanthus Productivity Network showed that their yields were nevertheless limited by low temperatures in northern countries and water deficits in southern EU countries (Jones and Walsh 2001).

The plant is established by rhizomes or rhizome cuttings with better results obtained with large pieces of rhizomes. Miscanthus rhizomes act as storage organs for nutrients

that allow a rapid growth in spring by a retranslocation processes; the nutrients that are built during the vegetative period and filled in at the beginning of autumn (September–October) are depleted during spring for the production of the above-ground biomass. The remaining nutrients are retranslocated to the rhizomes at the end of the growing period (McCarthy and Walsh 1996).

Miscanthus is harvested from autumn to spring, depending on local conditions. Winter and early spring (before shoot regrowth) offer good harvest conditions, especially during a frost period. For economic reasons, a late harvest with moisture content lower than 30% is recommended because harvesting and drying costs increase with water content (Huisman 1998). Agronomic practices are summarized in ▶Tab. 3.3.

Miscanthus has been investigated in several EU projects such as: FAIR CT97 1707, FAIR 1392, AIR1 CT92 0294, and so forth.

3.3.4 Switchgrass (*Panicum virgatum L*, Poaceae)

Switchgrass (*Panicum virgatum L.*) (▶Fig. 3.18) is a high-producing warm-season perennial C4 grass native to North America, where it is thoroughly investigated. It has erect stems that range from 50 to 270 cm tall.

It was firstly introduced to Europe in 1998 when some small fields were established in the frame of an EU-funded switchgrass productivity network (Lewandowski et al. 2003). The results of this project as well as of other relative projects performed afterward indicate that switchgrass is a highly productive grass and its introduction into European agricultural systems is recommended. Switchgrass has a wide range of climatic adaptability,



Fig. 3.18: Switchgrass.

but it is more suitable for central and southern Europe because it is characterized by the following advantages: easy establishment by seeds, high biomass potential, high competitiveness to weeds once it is well established, high nutrient and water-use efficiency, it can be harvested easily by existing equipment, long harvest window expanded from late autumn to early spring, low moisture content at late harvest, good combustion qualities of the biomass, and high genetic variability. It is a crop that can be cultivated in all of Europe because there are available varieties for most climatic regions found in Europe.

According to the morphological characteristics, "lowland" and "upland" ecotypes exist. Lowland ecotypes are generally taller, faster growing, and thus more suited as biomass crops than upland ecotypes. Alamo and Kanlow (lowland varieties) usually gave higher dry-matter yields than upland varieties (Alexopoulou et al. 2008).

Usually switchgrass is cultivated for forage production (Stritzlet et al. 1996), but since the late 1980s it has been studied as a biomass crop for energy through gasification and combustion (Turnhollow 1991). Other recent uses are for paper pulp and fiber-reinforced composite materials (Girouard and Samson 1998).

The yielding potential of switchgrass is achieved from the third year onward, while in the establishment year yields are quite low and in the second year a two-thirds fraction is reached. The annual recorded yields ranged from 5–23 odt ha^{-1} but the best varieties yielded about 16 odt ha^{-1} averaged over all plots, with yields in excess of 22 odt ha^{-1} occurring at the best plots (Lewandowski et al. 2003). Switchgrass when cultivated in the UK (agricultural land with low inputs) at annual yields of 11.8 t ha^{-1} had an estimated profit of 189.15 euro per ha^{-1} (Alexopoulou et al. 2011) (▶Fig. 3.19).

Switchgrass has high tolerance to severe water stress conditions (Monti, Di Virgilio, and Venturi 2008) and thus it is more drought tolerant than miscanthus (Van der Hilst et al. 2010). Its establishment is quite easy and cheap because it is made by seed. Temperatures at sowing time have to be higher than 15.5°C to allow seed germination. Plant density varies from 100 to 200 plants per square meter. Compared to the other perennial grasses, switchgrass was found to be the one with the least nitrogen needs (0–70 kg N ha^{-1}). At the same time, compared to miscanthus, it needs less irrigation and this makes switchgrass a valuable perennial grass for southern Europe. It can be cultivated in most

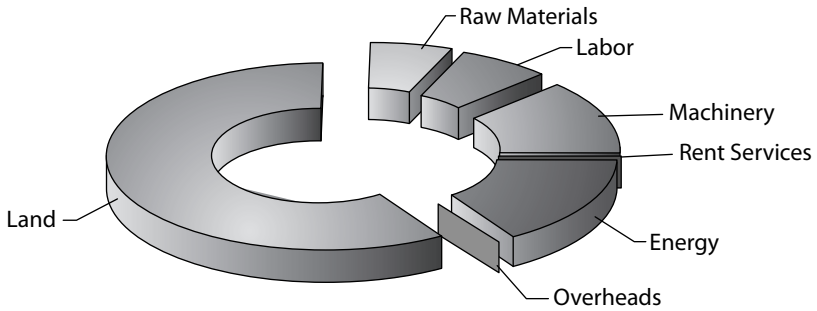


Fig. 3.19: Economic viability of switchgrass when it is cultivated in the UK in agricultural land with low inputs.

climatic zones of Europe because there are many varieties available for most climatic zones.

Switchgrass should be harvested late in the season because lower levels of nutrients are removed. Yields may be reduced by 20% (approximately) at late harvest, but this can result in improved yields the following years and improved quality of the harvested material due to low mineral content (Monti, Di Virgilio, and Venturi 2008). The harvest is executed using normal grass-baling methods and equipment. At late harvest moisture content ranged from 20% to 30% and if is to be stored for a long period of time, the moisture content should decrease down to 15%–20%. Agronomic practices are summarized in ▶Tab. 3.3.

In a European context, the crop has been investigated in the projects FAIR-CT97–3701 (www.switchgrass.nl) and ENK6-CT2001–00524 (www.cres.gr/bioenergy_chains).

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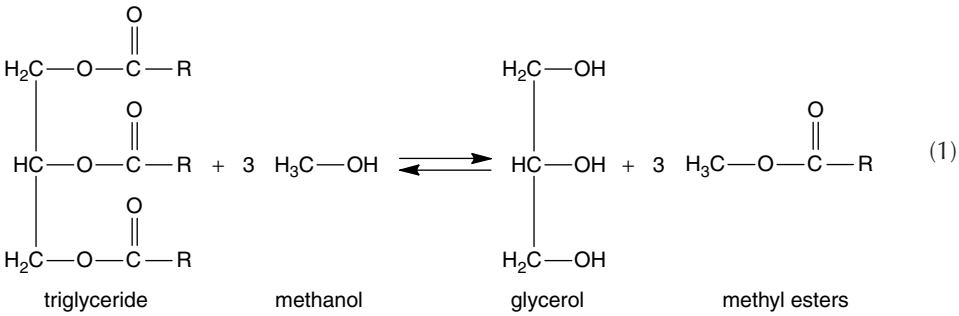
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4 Production of aquatic biomass and extraction of bio-oil

Angela Dibenedetto

4.1 Introduction

The increase of the world energy consumption implies an increase in fossil-fuel demand and highlights two important aspects to consider: the limited reserve of fossil carbon and the emission of greenhouse gases generated in the combustion of fossil fuels. For these reasons, biofuels, produced with *quasi*-zero CO_2 emission, are considered an alternative to fossil fuels at least in the transport sector. Particular attention is paid to bioethanol or to fatty acid methyl esters (FAMEs). The latter can have properties similar to diesel and are often named "biodiesel." FAMEs are produced by transesterification of lipids (Eq. 1) with an alcohol, such as methanol, ethanol, or buthanol, in presence of a catalyst (Meher, Vidya Sagar, and Naik 2006).



(1)

First-generation biofuels, which have now attained economic levels of production, have been mainly extracted from food crops, including cereals and rapeseeds, sugarcane, sugar beets, as well as from vegetable oils and animal fats using conventional technologies (FAO 2007, 2008). The use of first-generation biofuels has generated a lot of controversy, mainly due to their impact on global food markets and on food security, especially with regards to the most vulnerable regions of the world economy. This has raised pertinent questions on their potential to replace fossil fuels and the sustainability of their production (Moore 2008). Currently, about 1% (14 million hectares) of the world's available arable land is used for the production of biofuels, providing 1% of global transport fuels. Clearly, increasing such a share to anywhere near 100% is impractical owing to the severe impact on the world's food supply and the large areas of production land required (IEA 2006).

The advent of second-generation biofuels is intended to produce fuels from the whole plant matter of dedicated energy crops or agricultural residues, forest harvesting residues, or wood processing waste, rather than from food crops.

Aquatic biomass is currently considered an ideal second- or third-generation biodiesel (or biofuel in general) feedstock. It do not compete with food and feed crops, does not require arable land for cultivation, and can grow under enhanced CO_2 concentration.

Biodiesel can be obtained from vegetable oils and animal fats (Marchetti, Miguel, and Errazu 2007), and it can be used in diesel engines blended with standard gas oil or

alone. From an environmental point of view, biodiesel includes several benefits, such as the reduction of carbon monoxide (50%) and carbon dioxide (78%) emissions (Sheehan et al. 1998), it is nontoxic and biodegradable, and its use reduces fossil-fuel consumption. The interest in the production and use of liquid biofuels from biomass is not limited to FAMEs. However, based on current knowledge and technology projections, third-generation biofuels specifically derived from aquatic biomass are considered to be a technically viable alternative energy source that is devoid of the major drawbacks associated with first- and second-generation biofuels.

Macro- and micro-algae are photosynthetic organisms with simple growing requirements (light, sugars, CO_2, N, P, and K) that can produce lipids, proteins, and carbohydrates in large amounts over short periods of time. These products can be processed into both biofuels and valuable coproducts.

4.2 Characterization of aquatic biomass and its cultivation

4.2.1 Macro-algae

Macro-algae are classified as *Phaeophyta* (or brown algae), *Rhodophyta* (or red algae), and *Chlorophyta* (or green algae), based on the composition of photosynthetic pigments. The green macro-algae have evolutionary and biochemical affinity with higher plants. The life cycles of macro-algae are complex and diverse, with different species displaying variations of annual and perennial life histories, combinations of sexual and asexual reproductive strategies, and alternation of generations.

The distribution of macro-algae is worldwide. They are abundant in coastal environments, primarily in near-shore coastal waters with suitable substrate for attachment. Macro-algae also occur as floating forms in the open ocean, and floating seaweeds are considered one of the most important components of natural materials on the sea surface (Vandendriessche, Vincx, and Degraer 2006). The use of macro-algae for energy production has received attention only very recently (Aresta et al. 2002). The great advantage of macro-algae with respect to terrestrial biomass is its high biomass productivity (faster growth in dry weight ha^{-1} y^{-1} than for most terrestrial crops). The productivity of natural basins is in the range of 1–20 kg m^{-2} y^{-1} dry weight (10–150 t_{dw} ha^{-1} y^{-1}) for a 7–8 month culture. Interestingly, macro-algae are very effective in nutrients (N, P) uptake from sewage and industrial waste water. The estimated recovery capacity is 16 kg ha^{-1} d^{-1} (Ryther, DeBoer, and Lapointe 1979). To this end, macro-algae have been used for cleaning municipal wastewater (Schramm 1991) (essentially in Europe), for recycling nutrients and for the treatment of fishery effluents (Cohen and Neori 1991; Hirata and Xu 1990) (either in Europe or in Japan). The latter use has an economic value because macro-algae can reduce the concentration of nitrogen derivatives like urea, amines, ammonia, nitrite, or nitrate to a level that is not toxic for fishes, allowing the reuse of water, reducing, thus, the cost of their growth and the water use. The capacity of macro-algae as biofilters or nutrient uptake has been tested in the northwestern Mediterranean Sea, along French coasts (Sauze 1983) using *Ulva lactuca* or *Enteromorpha intestinalis* that adapted to non-natural basins.

In Europe macro-algae are grown in experimental fields and natural basins. They can be grown on nets or lines and can be seeded onto thin lightweight lines suspended over a larger horizontal rope (Adams, Gallagher, and Donnison 2009). Also, in a colder climate, macro-algae grow at an interesting rate. For example, in Denmark the Odjense Fiord produces about 10 kt per day of dry-weight-biomass equivalent to about 10 t per year per hectare.

Although macro-algae can grow in both hemispheres, the climatic factors may affect the productivity by reducing either the rate of growth or the growing season. The Mediterranean Sea has ideal climatic conditions for a long growing season, with good solar irradiation intensity and duration and with a correct temperature. Moreover, along the coasts of several European Union (EU) countries (Italy, Spain, France, Greece) fish ponds exist that may be the ideal localization for algae ponds.

Very interesting is the fact that the photosynthesis of macro-algae is saturated at different levels of carbon dioxide, ranging from 500 to 2000 ppm (Brown and Tregunna 1967; Smith and Bidwell 1987), which means that with carbon dioxide concentration up to five times the atmospheric concentration, under the correct light conditions and nutrient supply, macro-algae may grow with the same or better performance than they show in natural environments (Gao et al. 1993). Experimentally, it has been demonstrated (Aresta et al. 2005a) that concentrations of CO_2 in the gas phase up to 5% are acceptable for growing macro-algae such as *Gracilaria bursapastoris, Chaetomorpha linum,* and *Pterocladiella capillacea*.

In general, macro-algae (▶Fig. 4.1) require not very sophisticated techniques for growing: coastal farms are the most-used techniques for growing macro-algae.

The world market of seaweeds is remarkable. Aquaculture production is around 11.3 million wet tones. China is the main producer (92% of the world's seaweeds supply) (FAO 2006). Brown seaweeds represent 63.8% of the production, while red seaweeds represent 36.0% and the green seaweeds 0.2%. Approximately one million tons of wet seaweeds are harvested and treated to produce about 55,000 tons of hydrocolloids, valued at almost US$600 million (McHugh 2003).

The adaptation of macro-algae from wild conditions to pond culture is not straightforward. Thalli can be cut and used for starting a new culture. In principle, it is more suitable to cultivate macro-algae using the natural climatic conditions, because the adaptation to different climates may not be easy. The knowledge of physiological conditions is essential for the definition of the best operative parameters (optimized growing conditions) (Aresta et al. 2002).

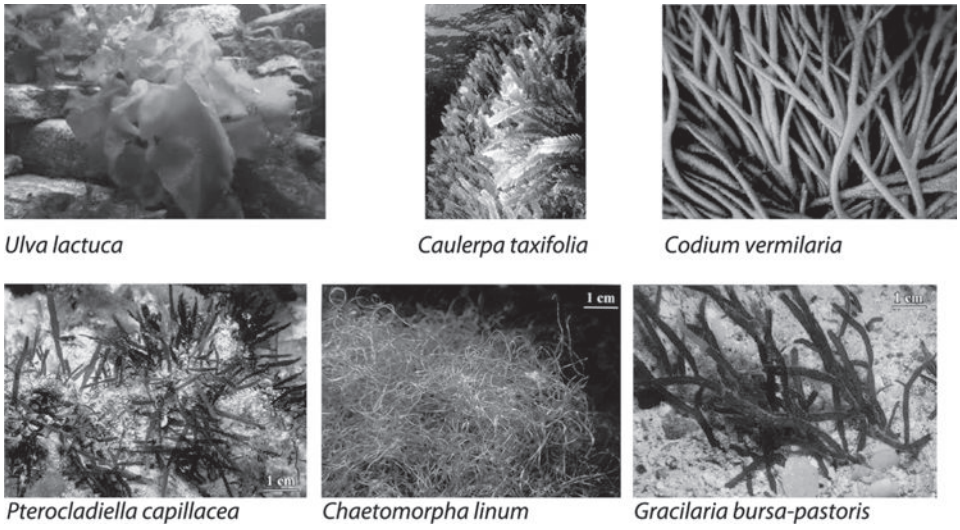


Fig. 4.1: Different types of macro-algae.



Fig. 4.2: (a) Red drift algae. (b) Sargassum floating in the Venice bay (Picture: www.algaebase.org). (c) Drift *Ulva spp* (CEVA).

Very interesting is the use of drift macro-algae (when the production is higher than the capacity of the ecosystem), which may represent a way to convert a waste into an energy source. Actually, macro-algae have been used to produce algae paper and as soil additives in agriculture. ▶Fig. 4.2 shows examples of overproduction of macro-algae that can be harvested and used as an energy source when the economic conditions exist. Additionally, the CO_2 emission into the atmosphere will be reduced with respect to the use of fossil fuels.

4.2.2 Micro-algae

Micro-algae are microscopic organisms and are currently cultivated commercially as feed for fish around the world in several dozen small- to medium-scale production systems, producing from a few tens to several hundred tons of biomass annually. The main algae genera currently cultivated photosynthetically (e.g. with light) for various nutritional products are *Spirulina*, *Chlorella*, *Dunaliella,* and *Haematococcus* (▶Fig. 4.3).

Micro-algae can be grown in open ponds or in photobioreactors(PBR). The culture in open ponds is more economically favorable with respect to photobioreactors (Oilgae 2010) because open ponds cost approximately $100,000 per hectare in capital costs while photobioreactors cost about $1–1.5 million per hectare. However, PBR provide yields that are 3–5 times higher than for open ponds. The latter may raise the issue of land cost and water availability, appropriate climatic conditions, nutrients cost, and production. Moreover, in the open-pond option other cultivation aspects should be taken into consideration, such as the maintenance of long-term growth of the desired algae strain without interference by competitors, grazers, or pathogens. These results also indicate how much the overall production cost depends on the reactor (open or closed) cost (Darzins, Pienkos, and Edye 2010).

Using open-pond systems the nutrients can be provided through runoff water from nearby living areas or by channeling the water from wastewater treatment plants. CO_2 from power plants or industries could be efficiently bubbled into the ponds and captured by the algae. The water is moved by paddle wheels or rotating structures (raceway systems), and some mixing can be accomplished by appropriately designed guides. Typically, micro-algae are cultivated in open ponds (horizontal or circular) as shown in ▶Fig. 4.4.

Methods to cultivate algae have been developed over the years. Recent developments in algae growth technology include vertical PBRs (Hitchings 2007) and bag reactors (Bourne 2007) made of polythene mounted on metal frames, reducing the amount of land required for cultivation.

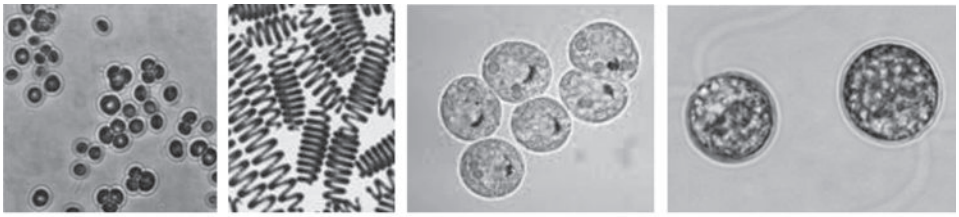


Fig. 4.3: Different types of micro-algae.

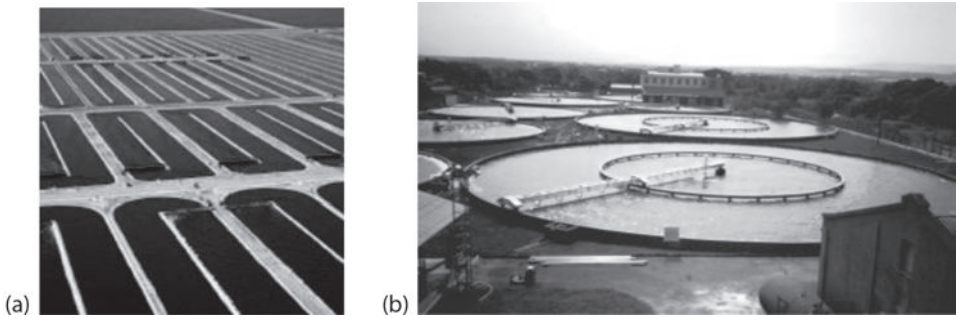


Fig. 4.4: (a) Raceway ponds, (b) circular ponds.

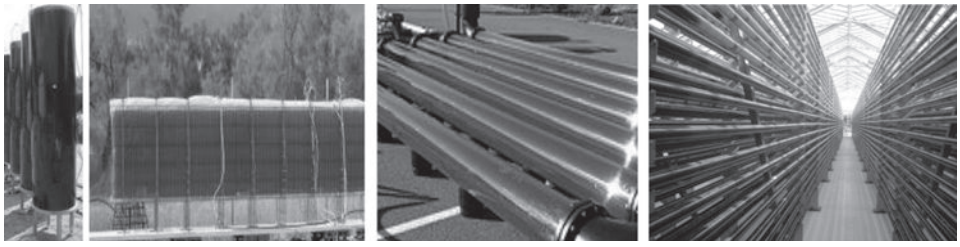


Fig. 4.5: Photobioreactors.

Using such bioreactors, micro-algae can grow under light-irradiation and temperature-controlled conditions, with an enhanced fixation of CO_2 that is bubbled through the culture medium. Algae receive sunlight either directly through the transparent container walls or via light fibers or tubes that channel the light from sunlight collectors. A number of systems with horizontal and vertical tubes, bags, or plates are made of either glass or transparent plastic exposed to the sun either in the free air or in greenhouses (►Fig. 4.5).

Using these kinds of reactors, several micro-algae production facilities have been set up as shown in ►Fig. 4.6.

The production of micro-algae in open ponds depends on the climatic conditions. Solar irradiation and temperature are the most important factors affecting the farming

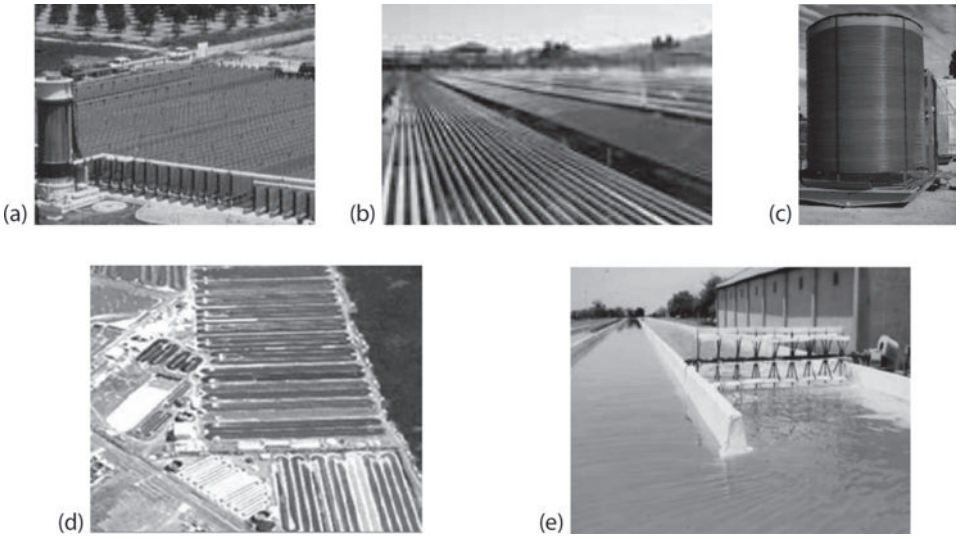


Fig. 4.6: (a) *Dunaliella* production in Spain. (b) *Haematococcus* production in Israel. (c) A 1,000 L helical tubular photobioreactor at Murdoch University, Australia. (d) Cultivation of *Spirulina* and *Haematococcus* in the United States. (e) *Dunaliella salina* production in India.

process and its productivity. These two parameters drive the growing period and, thus, the economics of the process.

The availability of land and water are the key factors for developing open-pond cultures. So far, semidesert flat lands that are not suitable for tourism, industry, agriculture, or municipal development were selected – also if in such areas the biomass cultivation is strongly affected by the supply of CO_2 and water. In fact, either CO_2 or water becomes a limiting factor.

In an open-pond system, the loss of water is greater than in closed tubular cultivation or bag cultivation methods. The water can be ground saline water, local industrial water, or water drained from agricultural areas and recycled after harvesting algae. CO_2 for algae growth can be distributed using pipelines that transport purified CO_2 or directly flue gases from power plants or any other gas rich in CO_2.

Nutrients (N- and P-compounds, micronutrients) represent one of the major costs for algal growth. The use of wastewater (sewage, fisheries, some industrial waters) rich in N- and P-nutrients is an economic option with a double benefit represented by the recovery and utilization of useful inorganic compounds and the production of clean water that, finally, can be reused or discharged into natural basins. Should nutrients be added to water, the biomass will not produce a zero-emission fuel, as the production of nutrients bears with it an associated large emission of CO_2. Therefore, the use of wastewater rich in N- and P-compounds is a must for growing algae in pounds or PBR. The direct use of flue gases as CO_2 providers requires that algae should be resistant to the pollutants that are usually present in the flue-gas stream, namely nitrogen- and sulphur-oxides. Studies have shown that 150 ppm of NO_2 and 200 ppm of SO_2 do not affect the growth of some algal species (Zeiler et al. 1995).

It must be noted that the resistance to NOx and SOy is not a common feature of all algal species, and this may represent a limitation to the direct use of flue gases. Another

point that demands clarification is the optimal concentration of CO_2 in the culture, as CO_2 addition lowers the pH of the medium. Although the response to the pH change generated by the concentration of CO_2 may be different for the various algal species, operating at a pH close to 6 may, in general, strongly affect the algal growth. However, one of the key points in culturing micro-algae, or algae in general, is to generate the optimal concentration of CO_2 in the gas and liquid phase. CO_2 can be supplied into the algal suspension in the form of fine bubbles. A drawback of this methodology is the residence time in the pond: it must be sufficient to allow CO_2 to be uptaken (Becker 1994). In general, in this way, a lot of CO_2 is lost to the atmosphere and only 13%–20% of CO_2 is usually used. A different method to supply CO_2 is the gas exchanger, which consists of a plastic frame that is covered by transparent sheeting and immersed in the suspension. CO_2 is fed into the unit and the exchanger is floated on the surface. CO_2 needs to be in a concentrated form and 25%–60% of it is distributed and used (Becker 1994). Also, if this is the a most effective method, it presents as a drawback the need to use very concentrated and pure CO_2, which is trapped under the transparent plastic frame with a very little amount of CO_2 lost into the atmosphere. The growth rate of microalgae is dependent on the temperature and the season (high growth rate in the summer and low growth rate in the winter).

Micro-algae may easily adapt to the culture conditions (Collins, Sueltemeyer, and Bell 2006; Cecere et al. 2006), also if several parameters that influence the rate of growth and cell composition of micro-organisms must be kept under strict control in order to guarantee a constant quality of the biomass, a parameter particularly important for the biomass exploitation.

Another factor that influences the growth of micro-algae is irradiation. Both in ponds and in bioreactors the light availability is of paramount importance. Shadow or short light cycles may cause a slow down of the growth rate; conversely, intense light (as may occur in desertic areas or bioreactors) does not guarantee fast growth and may modify the cell functions (Dibenedetto and Tommasi 2003; Ono and Cuello 2002, 2007).

Tropical or semitropical areas are the most practical locations for algal culture systems (Borowitzka and Borowitzka 1988). Before starting to build a culture system it is necessary to consider several aspects, because the evaporation rate may represent a problem in dry tropical areas. Here, the evaporation rate is higher than the precipitation rate: a high evaporation rate increases the salt concentration and pumping costs due to water loss (Collins, Sueltemeyer, and Bell 2006). A high precipitation rate can cause dilution and a loss of nutrients and algal biomass. With low relative humidity, high rates of evaporation occur that can have a cooling effect on the medium (Richmond 1986), while with high relative humidity and no wind, an increase of the temperature of the medium may occur (even up to 40°C). Finally, a location must be chosen where there is a constant and abundant supply of water for the mass culture pond systems.

4.3 Harvesting of aquatic biomass

4.3.1 Macro-algae

The harvesting of macro-algae and plants requires more immediate and not very sophisticated technologies. The technique depends on whether the biomass is grown floating-unattached or attached to a hard substrate. In the former case, the biomass can be easily



Fig. 4.7: Harvesting of macro-algae: (a) Hand harvesting of Ascophyllum (M Guiry/Algaebase), (b) Scoubidou system used in France (CEVA), (c) Harvest of drift seaweeds at Sacca di Goro (IT).

collected using a net (as in fishing), and in the latter case it must be cut from the substrate. Automated or manual devices can be used for the collection (Morineau-Thomas et al. 2004).

Harvesting of macro-algae is carried out in different ways. The manual harvesting (▶Fig. 4.7a) is common for both natural and cultivated seaweeds. Mechanized harvesting methods (▶Fig. 4.7b, 4.7c), which can involve mowing with rotating blades, suction, or dredging with cutters, have been developed.

4.3.2 Micro-algae

In contrast to macro-algae, micro-algae, due to their size and, sometimes, fragility, demand sophisticated equipment and handling operations.

The choice of harvesting methods depends on a few factors, such as:

- Type of algae that has to be harvested (filamentous, unicellular, etc).
- Whether harvesting occurs continuously or discontinuously.
- What the energy demand is per cubic meter of algal suspension.
- What the investment costs are (Collins, Sueltemeyer, and Bell 2006; Ono and Cuello 2002, 2007; Pulz and Gross 2004).

The technologies primarily used with micro-algae are: centrifugation, sedimentation, filtration, screening and straining, and flocculation.

Various flocculants have been used, covering a large variety of chemical structures such as: metal compounds (Bare, Jones, and Middlebrooks 1975), cationic polymers (Tenny et al. 1969), and natural polymers such as chitin (Venkataraman 1980). They have been employed not only at the laboratory scale but also at the industrial scale. Such "induced flocculation" may be accompanied by a "spontaneous- or auto-flocculation" that can be caused by a pH variation of the culture medium upon CO_2 consumption. For example, an increase of pH may cause the precipitation of phosphates (essentially Ca-phosphate), which causes flocculation of algae. Aggregation of algae, produced by organic secreted substances (Benemann et al. 1980) or aggregation with bacteria (Kogure, Simidu, and Taga 1981; Salim et al. 2011) (▶Fig. 4.8) may also occur that facilitates their sedimentation.

Centrifugation is a very popular technique today, but still it presents some drawbacks, such as the rate of separation, and generally is considered expensive and electricity consuming. It is, however, the best-known method of concentrating small unicellular algae (Grima et al. 2003). Benemann recommends in Sazdanoff's (2006) report to

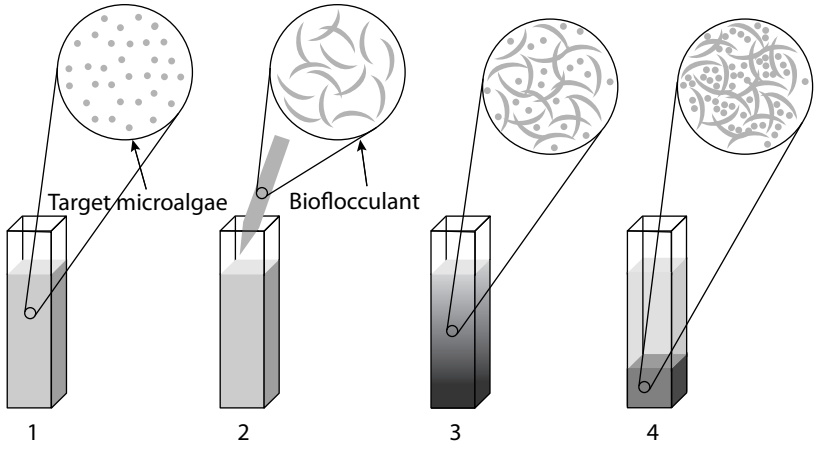


Fig. 4.8: Schematic view of bioflocculation (Salim et al. 2011).



Fig. 4.9: Alfa Laval CH-36B GOF Separator Centrifuge.

use centrifugation after pond settling, and a specific centrifuge (▶Fig. 4.9) that has an acceptable energy consumption.

Recently, new technologies have been developed that lower energy consumption (Boele and Broken 2011). Most advanced technologies are based on the use of membranes (tubular, capillary, or hollow-fiber membranes) that are becoming more and more popular (Mohn 1980). The size of the pore decreases in the order from tubular (5–15 mm) to capillary (1 mm) to hollow-fiber (0.1 μm) and the risk of plugging increases with the decrease of the pore diameter.

4.4 Composition of aquatic biomass

Aquatic biomass contains several pools of chemicals at different concentrations depending on the physical stresses or genetic manipulation induced on the organism.

►Tabs. 4.1 and 4.2 show the categories of many products produced by micro-algae and macro-algae, respectively.

In general micro- and macro-algae can be used in different sectors:

- Energy (hydrocarbons, hydrogen, methane, methanol, ethanol, biodiesel, etc.).
- Food and chemicals (proteins, oils and fats, sterols, carbohydrates, sugars, alcohols, etc.).
- Other chemicals (dyes, perfumes, vitamins/supplements, etc.).

Aquatic biomass can be used as a raw, unprocessed food because they are rich in carotenoids, chlorophyll, phycocyanin, amino acids, minerals, and bioactive compounds.

Besides their nutritional value, these compounds have applications in pharmaceutical fields such as immune-stimulating, metabolism-increasing, cholesterol-reducing, anti-inflammatory, and antioxidant agents (Singh, Kate, and Banerjee 2005). Also, they are rich in omega-3 fatty acids, which have significant therapeutic importance inherent in the ability to act as an anti-inflammatory to treat heart diseases.

Due to the high product-distribution entropy, the extraction of a single product may have an economic benefit only in cases in which the product represents several tens of percent of the global dry mass. If it is present at the level of a few units percent, then it should have a high market value for meeting the economic criteria. As mentioned

Tab. 4.1: Products from micro-algae.

Class of products	Chemicals	Applications
Coloring substances and antioxidants	Xantophylls (astaxantines and canthaxanthin, Lutein, β-carotene, vitamins C and E)	Health, food, functional food, feed additive, aquaculture, soil conditioner
Fatty acids (FA)	Arachidonic acid (AA), eicosapentenoic acid (EPA), docosahexaenoic acid (DHA), glinolenic acid (GCA), linoleic acid (LA)	Food and feed additives, cosmetics
Enzymes	Superoxide dismutase (SOD), phosphoglycerate kinase (PGK), luciferase and luciferin, restriction enzymes	Health food, research, medicine
Polymers	Polysaccharides, starch, poly-β-hydroxybutyric acid (PHB)	Food additive, cosmetics, medicine
Special products	Peptides, toxins, isotopes, amino acids (praline, arginine, aspartic acid), sterol	Research, medicine

Tab. 4.2: Products from macro-algae.

Class of products	Chemicals	Extraction technology	Commercial use
Proteins			Pharmacology
Aminoacids		Phenol-acetic acid-water	Food industry
Lipids		Sc-CO_2, organic solvent, liquefaction, pyrolysis	Biofuels, food, and pharmaceutical industry
Essential oils	Geraniol, geranyl formate or acetate, cytronellol, nonanol, eucalyptol	Distillation	
Alcaloyds		Solvent extraction	
Sterols	Cholesterol		
Pigments: chlorophylls, carotenoids, Xantophylls	Isoprenoids	Solvent extraction	
Amines	Methylamines, ethylamines, propylamine, isobutylamine		Pharmaceutical industry
Inorganic compounds	Iodides, bromides, sulphates, nitrates, etc.		Pharmaceutical industry

previously, the ability of algal organisms to concentrate a type of resource (proteins, starch, lipids) on stress may help to reduce entropy and to increase the concentration of a given product in the biomass. This issue is particularly relevant when the use of aquatic biomass for energy purposes is considered. Due to the cost of cultivation, in case of application as an energy source, producing biomass with a high content of energy products should be a must.

4.5 Bio-oil content of aquatic biomass

A great interest is increasing today in the use of micro-algae for the production of biodiesel, although this is not the only producible fuel: biogas can also be produced, as well as bioethanol or biohydrogen or hydrocarbons. The quality and composition of the biomass will suggest the best option for the biofuel to be produced. A biomass rich in lipids will be suitable for the production of bio-oil and biodiesel, while a biomass rich

Tab. 4.3: Yields of fuels for various types of biomass.

Biomass	Yield (L ha^{-1} y^{-1})
Corn	170
Soybeans	455 to 475
Safflower	785
Sunflower	965
Rapeseed	1,200
Jatropha	1,890
Coconut	2,840
Palm	6,000
Micro-algae	47,250 to 142,000

in sugars will better be suited for the production of bioethanol. The anaerobic fermentation of sugars, proteins, and organic acids will produce biogas.

Several species of micro-algae are very rich in lipids (up to 70%–80% dry weight, with a good average standard of 30%–40%) and this makes a given species strain more or less suitable for bio-oil production. The highest values are relevant to particular growing conditions. In a commercial culture, what is of interest is the productivity of a pond, that means the production per unit time.

▶Tab.4.3 shows, as a comparison, the amount (L) of oil per hectare per year produced by different types of biomass, including micro-algae (Briggs 2004; Riesing 2006).

Macro-algae, in general, present a lower content of lipids than micro-algae and a larger variability (Aresta et al. 2005b). The lipid content largely depends on the cultivation technique and on the period of the year macro-algae are collected (Khotimchenko 2003; Al-Hasan, Hantash, and Radwan 1991). These are, thus, key issues to be taken into consideration in the development of a commercial exploitation of such biomass.

Comparing micro- and macro-algae, it must be considered that macro-algae are produced at lower costs than micro-algae. The energy value of an alga cannot be stated only on the basis of the specific amount of oil produced, but must also consider other very important parameters, such as the quality of it, the possibility to produce other forms of energy from the residue obtained after the lipid extraction, and the production of chemicals. Today micro-algae are not economically viable as a source of fuel. Therefore, a biorefinery approach that may afford chemicals and fuels may be the winning option.

4.6 The quality of bio-oil

Although algae biomass can be thermally processed to afford an oily product, the acidity and composition of the liquid are such that its direct use is not suited and complex processing is needed before its use. The extraction of lipids will be discussed in the following paragraphs. Lipids are a mixture containing more than a single type of fatty

Tab. 4.4: Distribution of fatty acids in lipids present in some macro-algae.

Fatty acid	Species and percentage of a given compound in the species					
Compound Number of Carbon atoms/unsaturated bonds	*Fucus* sp	*Nereocystis luetkeana*	*Ulva lactuca*	*Enteromorpha compressa*	*Padiva pavonica*	*Laurencia obtuse*
Saturated $C_{12} \rightarrow C_{20}$	15.6%	27.03%	15.0%	19.6%	23.4%	30.15%
Monounsaturated $C_{14} \rightarrow C_{20}$	28.55%	15.84%	18.7%	12.3%	25.8%	9%
Polyunsaturated $C_{16/2} \rightarrow C_{16/4}$, $C_{18/2} \rightarrow C_{18/4}$, $C_{20/2}$	55.86%	57.11%	66.3%	68.1%	50.8%	60.9%

acid (FA), most frequently the lipid fraction of algae (both micro- and macro-algae) contains a large variety of FAs, with a different number of unsaturation, as shown in ▶Tab. 4.4. This is an important issue for assessing the energetic value of a biomass. The number of unsaturation in an FA is important because it determines the usability of the compound as a fuel. In fact, the optimal conditions for having a biodiesel with good combustion properties is the presence of only one unsaturation in the C-chains (Renaud and Luong-Van 2006). Therefore, the higher the number of unsaturation, the lower the quality of the biodiesel produced.

An increase of the CO_2 concentration up to 10% in the gas phase can influence the number of unsaturation and can almost double the total concentration of FAs (from 29.1% to 55.5%) and in particular that of FAs 16:0, 18:1, 20:4, and 20:5 in *C. linum* (Aresta et al. 2005a). In general, it has been found that the number of unsaturation may increase with the concentration of CO_2 (Fu et al. 2007; Andersen and Andersen 2006; Aresta et al. 2005a).

Bio-oil, such as extracted, can be directly used in thermal processes or in combustion, but cannot be used in diesel engines because it presents a low enthalpy value (LHV) (8–12 MJ/kg) and a high viscosity and unsaturation. It can be converted into biodiesel through a transesterification reaction in order to increase the LHV to 36 MJ/kg. This conversion can be followed by a partial hydrogenation in order to reduce the number of unsaturation to 1.

From the environmental point of view, biodiesel introduces several benefits including the reduction of carbon monoxide (50%) and carbon dioxide (78%) emissions (Ben-Amotz, Polle, and Subba Rao 2009); the elimination of SO_2 emission, as biodiesel does not include sulphur; and the reduction of particulate. Because biodiesel is nontoxic and biodegradable, its use and production is rapidly increasing, especially in Europe, the United States, and Asia. A growing number of fuel stations are making biodiesel available to consumers, and a growing number of large transport fleets use a fuel that contains biodiesel in variable percentage. ▶Tab. 4.5 reports some fuel properties of different types of bio-oil.

Tab. 4.5: Fuel characteristics of different bio-oils.

	Density (kg/L)	Ash content (%)	Flash point (°C)	Pour point (°C)	Cetane number	Calorific value (MJ/kg)	Reference
Algae	0.801	0.21	98	–14	52	40	Vijayaraghavan and Hemanathan (2009)
Peanuts	–	–	271	–6.7	41.8	–	Knothe, Dunn, and Bagby (1997)
Soya bean	0.885	–	178	–7	45	33.5	
Sunflower	0.860	–	183	–	49	49	
Diesel	0.855	–	76	–16	50	43.8	
Biodiesel from marine fish oil	–	–	103	–	50.9	41.4	Lin and Li (2009)

A new area of application is opening now; that is, the production of avio-fuels. These may include biodiesel and other molecules derived from different fractions of the aquatic biomass.

4.7 Technologies for algal oil and chemicals extraction

Oil and chemicals can be extracted from biomass by using a variety of technologies of different intensity (destructive, semidestructive, and nondestructive) (Aresta et al. 2005b; Dibenedetto et al. 2012). There is a relation between the softness-hardness of the technology used and the complexity of the structure of the chemicals extracted. Softer technologies will affect less the complex molecular structures that will be recovered unchanged. Hard technologies will destroy complex networks and complex molecules.

Biomass is suitable for the production of different products such as: bio-oil, biodiesel, bioalcohol, biohydrogen, and biogas, all related to the production of energy.

The extraction of chemicals from micro- and macro-algae may require different technologies due to the different size and quality of the cell membrane of the algae. First of all, oil from algae cannot be extracted by the more conventional method used in oil seed processing. Algal lipids are stored inside the cell as storage droplets or in the cell membrane. The small size of the algal cell and the thickness of the cell wall prevent simple expelling to release the oil. Depending on the species strain, the cell membrane can be very hard or elastic, so that crushing of the membrane is recommended prior to the extraction. Such crushing is quite effective if performed at low temperatures, typically the liquid nitrogen temperature (183 K). This will obviously increase the cost of the extracted oil and lower the net energetic value of the biomass.

Among the technologies used to produce chemicals from biomass, solvent extraction with conventional organic solvents (with and without in situ transesterification), supercritical fluids, mechanical extraction, and biological extractions are the most used.

4.7.1 Conventional solvent extraction

Solvents, such as hexane, have been used to extract and purify soybean seed oils and high-value fatty acids. These types of solvent-based processes are most effective with dried feedstock or with those with minimal amounts of free water. Of course when aquatic biomass (which has a high water content) has to be treated, the cost of drying significantly adds to the overall production cost and requires significant energy. A limited number of solvents have been evaluated for large-scale extraction of algal biomass with some success, but at the time no effort was made to determine the process economics or material and energy balances of such processes (Nagle and Lemke 1990). The drying of algae wet pastes for the large-scale organic solvent extraction may not be economically feasible or sound in terms of energy for biofuels.

An alternative to the organic solvent-based processes is the extraction by in situ transesterification (Dibenedetto, Aresta, and Ricci 2010). In this approach, and in particular using heterogeneous catalysts and methanol as solvent, the bound lipids are released from the biomass directly as methyl esters. Additionally, the catalyst can be easily recovered.

4.7.2 Supercritical fluid extraction (SFE)

Supercritical CO_2 ($scCO_2$) has both liquid and gas properties, allowing the fluid to penetrate the biomass and act as an organic solvent, without the challenges and expense of separating the organic solvent from the final product. Literature describes successful extraction of algal lipids with $scCO_2$ (Aresta et al. 2005b; Couto et al. 2010), and the resulting conversion into biodiesel. The ability of SFE to operate at low temperatures preserves the algal lipid quality during the extraction process, virtually eliminates the degradation of the product extracted, and minimizes the need for additional solvent processing (sometimes methanol can be added as co-solvent in order to increase the extraction yield). In addition, the ability to significantly vary the CO_2 solvation power by changes in pressure and/or temperature adds operating flexibility to the $scCO_2$ extraction process that no other extraction method, including solvent extraction, can claim (Mendes et al. 2003). Also, for the $scCO_2$ extraction the biomass should be dried, then the cellular wall has to be broken in order to increase the extraction yield (it is possible to use liquid nitrogen, or a different method) (Gaspar and Leeke 2004).

Bench scale supercritical CO_2 experiments on micro-algae have been performed on *Botryococcus, Chlorella, Dunaliella,* and *Arthrospira* from which different types of valuable products have been extracted as hydrocarbons (up to 85% mass of cell from *Botryococcus*), paraffinic and natural waxes from *Botryococcus* and *Chlorella, s*trong antioxidants (astaxanthin, ß-carotene) from *Chlorella* and *Dunaliella,* and linolenic acid from *Arthrospira*.

Supercritical CO_2 may substitute the organic solvent because it has some unique advantages and is considered a good candidate for algae treatment because it is a nontoxic and fully "green" solvent (Singh et al., 2005). Despite the advantages, using $scCO_2$ to extract valuable compounds from micro-algae is not the prevailing technology in use today, even though production costs are of the same order of magnitude as those related to classical processes. In fact, for such a technique, quite anhydrous materials are recommended (water content below 5%), so energy should be consumed to dry the biomass.

However, the capital and operating costs for a high-pressure SFE operation currently limits its potential for biofuel production. Over time, SFE applications have targeted added value products, but are not yet commodity chemicals. Technology development (e.g. gas antisolvent and subcritical fluid extractions) and further reductions in costs may lead to processes applicable to biofuel production.

4.7.3 Mechanical extraction

Mechanical treatments, such as ultrasonication (disruption with high-frequency sound waves) and homogenization (carried out by rapid pressure drops), may be used to disrupt cell walls and lead to enhanced oil recovery. For example, Pursuit Dynamics Ltd. (European Union Patent 2011) manufacture a device based on steam injection and supersonic disruption and claim homogenization of plant material with very low energy input. Systems based on sonication process and centrifugation may provide economic solutions for algal lipid recovery. Very interesting is the application of the reactive extraction using ultrasonication or microwaves in order to have a direct one-pot conversion of biomass into FAMEs (Dibenedetto, Aresta, and Ricci 2010).

4.7.4 Biological extraction

Biological methods that are used to capture and extract lipids offer low-tech and low-cost methods of harvesting and lipid extraction. Demonstrations in large open ponds of brine shrimp feeding on micro-algae to concentrate the algae, followed by harvesting, crushing, and homogenizing the larger brine shrimp to recover oil have been successful (Brune and Beecher 2007). Using crustaceans to capture and concentrate micro-algae would appear to be a promising solution for algae oil recovery. The use of enzymes to degrade algal cell walls and reduce the energy needed for mechanical disruption has also been investigated.

4.8 Conclusions

Wild types of micro- and macro-algae very often are not suitable to produce energy as they have a chemical composition that may vary according with the growing conditions also within the same strain. For this reason, to produce energy it is better to use a selected cultivated strain in order to have an optimal energetic yield. Moreover, aquatic biomass has to be considered as a source of several compounds that can be used as chemicals or to produce energy. The co-production of chemicals and fuels from aquatic biomass can be of great importance in order to make positive the economic balance. In fact, if biomass is used only to produce energy, the cost of fuels derived from it is not competitive with that of fossil fuels. The correct application of the concept of biorefinery may bring to produce fuels at low cost if high-value chemicals are co-produced. In the near future, aquatic biomass might contribute to the production of transport fuels in a significant volume, supposed that the right conditions for its growth, collection, and processing are developed. In any case, it seems that the co-production of chemicals and fuels is necessary for a profitable exploitation of aquatic biomass.

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5 Biomass pretreatment: separation of cellulose, hemicellulose, and lignin – existing technologies and perspectives

Anna Maria Raspolli Galletti and Claudia Antonetti

5.1 Introduction

Biomass fractionation and, more generally, biomass pretreatments involve many different approaches, and the optimum conditions strictly depend on the characteristics of each raw material as well as on the final purpose of the process itself. As a consequence, if the aim of the fractionation/pretreatment is to exploit (hemi–)cellulose fraction, it should increase the accessibility and the reactivity of the cellulose breaking down the semi–crystalline cellulose and hemicellulose, without significant degradation of polysaccharides (Hayes 2009). The most common historical pretreatment method employed dilute acid hydrolysis, but this approach resulted in a considerable amount of polysaccharide decomposition and in the formation of microbial inhibitors, which negatively impacted downstream fermentation. As a consequence, several alternative pretreatments have been developed that can be classified into different categories: physical, physicochemical, chemical, and biological pretreatments (De Costa Sousa et al. 2009).

An effective pretreatment should meet the following requirements (Alvira et al. 2010):

1. overcome lignocellulosic biomass recalcitrance;
2. afford high yields to sugars or chemicals and/or give a highly digestible pretreated solid;
3. avoid sugar degradation;
4. avoid the formation of inhibitory toxic byproducts;
5. allow lignin recovery and exploitation to give valuable co-products; and
6. last but not least, be cost effective, involving reasonable size reactors, low waste amounts, and low energetic requirements.

5.2 Biomass composition

Lignocellulosic biomass mainly consists of three polymeric components: hemicellulose, cellulose, and lignin. Hemicellulose is a complex, branched, and heterogeneous polymeric network based on pentoses such as xylose and arabinose; hexoses such as glucose, mannose, and galactose; and sugar acids. It has a lower molecular weight than cellulose and its role is to connect lignin and cellulose fibers. Cellulose is a long-chain polysaccharide formed by D–glucose units, linked by β–1,4 glycosidic bonds: its structure has crystalline parts and amorphous ones. Lignin is an amorphous polymer made by different phenolic compounds and is the main component of cell walls. Finally, lignin holds together cellulose and hemicellulose fibers and gives support, resistance,

and impermeability to the plant. The composition of the some common lignocellulosic materials and wastes is reported in ▶Tab. 5.1 (Sun and Cheng 2002).

Tab. 5.1: Composition of common lignocellulosic raw materials and wastes (wt % on dry biomass).

	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stems	40–55	20–40	18–25
Softwood stems	45–50	25–35	25–35
Rice straw	35–45	18–25	10–25
Wheat straw	38–45	20–32	7–10
Tobacco chops	22–30	15–20	15–25
Arundo donax	30–38	18–22	8–20
Miscanthus	35–40	16–20	20–25
Newspaper	40–55	25–40	15–30

5.3 Physical and physicochemical pretreatments of biomass

The purpose of physical pretreatments is to increase the accessible surface area and the size of the pores of cellulose and, at the same time, decrease its crystallinity and its polymerization degree. Several types of physical processes have been developed, such as milling, grinding, extrusion, and irradiation (gamma rays, electron beams, ultrasounds, microwaves). These methods are not often satisfactory if used individually, and many times they are employed in combination with chemical methods in order to improve the process efficiency.

5.3.1 Mechanical pretreatments

Milling, grinding, and extrusion represent mechanical methods. Among the milling processes, colloid mill, fibrillator, and dissolver are suitable only for wet materials, such as wet paper from domestic waste separation or paper pulps, whereas the extruder, roller mill, cryogenic mill, and hammer mill are usually employed for dry materials (Taherzadeh and Karimi 2008). The ball mill can be used for either dry or wet materials. Milling can improve the susceptibility to successive enzymatic hydrolysis or to other hydrolysis processes by reducing the size of materials and the degree of crystallinity of lignocellulose (Zeng et al. 2007; Fan, Lee, and Beardmore 1980). It has been observed that in the absence of any pretreatment, corn stover with particle sizes of 53–75 μm was more susceptible to enzymatic hydrolysis than that with larger corn stover particles of 425–710 μm. In addition, due to crystallinity reduction by ball milling, saccharification of more than 50% of straw cellulose with minimal glucose degradation became possible at mild hydrolysis conditions (Sidiras and Koukios 1989). More recently, many mechanical pretreatments have been carried out in combination with other treatments, such as alkali, enzymatic, and hydrothermal (He et al. 2010). An interesting result was obtained in the bioethanol production from bagasse using a combined process of

mechanical pretreatment by ball milling and enzymatic hydrolysis and fermentation (Buaban et al. 2010). Ball milling for two hours proved sufficient for nearly complete cellulose structural transformation to an accessible amorphous form. In order to improve the enzymatic conversion of rapeseed straw to sugars, a process involving milling plus a popping treatment was claimed (Wi et al. 2011). The effectiveness of ball milling combined with steam explosion has recently been applied to the conversion of cellulosic waste biomass into ethanol through enzymatic hydrolysis (Asada et al. 2011). Grinding was more beneficial on digested sludge and on waste-activated sludge from an extended aeration process than on activated sludge with a higher solid retention time (Baier and Schmidheiny 1997; Kopp et al. 1997). Sometimes, grinding and milling can be combined together (Walpot 1986).

Finally, the extrusion process is a novel and very promising physical pretreatment method for biomass conversion, especially for ethanol production. The main step in this procedure consists of heating, mixing, and shearing the biomass material, resulting in physical and chemical modifications during passage through the extruder. Screw speed and barrel temperature are the two most important factors responsible for disrupting the lignocellulose structure, causing defibrillation and shortening of the fibers and thus increasing the accessibility of carbohydrates to enzymatic attack. These parameters are very important in order to achieve the highest efficiency in the process. The extrusion process has been proposed as an alternative method for the pretreatment of wheat bran and soybean hulls with respect to grinding with a hammer mill (Lamsal et al. 2010). The thermomechanical extrusion for lignocellulosic biomass using soybean hulls as substrate has been recently analyzed. Structural changes in substrate and sugar yields from thermomechanical processing were compared with two traditional pretreatments that employed dilute 1% sulphuric acid and 1% sodium hydroxide. Compared with untreated soybean hulls, glucose yield from enzymatic hydrolysis of soybean hulls increased by 69.6%, 128.7%, and 132.2%, respectively, when the samples were pretreated with dilute acid, alkali, and extrusion (Yoo et al. 2011). Another interesting study about the optimization of extruder parameters in order to maximize enzymatic sugar recovery was devoted to the combined effect of alkali soaking and extrusion of big bluestem, using a laboratory scale single screw extruder at various barrel temperatures (45–225°C) and screw speeds (20–200 rpm). The optimum pretreatment conditions found – 90°C as barrel temperature, 155 rpm as screw speed, 2.0% as alkali concentration, and 4 mm as particle size – gave the best glucose, xylose, and combined sugar recovery of 90.1%, 91.5%, and 89.9%, respectively (Karunanithy and Muthukumarappan 2011).

However, the power requirement of these mechanical pretreatments is relatively high and depends on the type of biomass and on the final particle size: beyond a certain particle size these pretreatments become economically unfeasible (Hendriks and Zeeman 2009; Sun and Cheng 2002).

5.3.2 Irradiation

The employment of irradiation, such as gamma rays, electron beams, and microwaves, is largely used in combination with other pretreatments in order to improve the hydrolysis of lignocellulosic materials (Singh et al. 2011; Carrère et al. 2010; Shin and Sung 2010; Mamar and Hadjadj 1990). These authors reported that irradiation can enhance enzymatic degradation of cellulose into glucose. Microwave irradiation has been mainly

studied in more recent years as a pretreatment method, generally in combination with other treatments. A microwave-based alkali pretreatment of switchgrass and coastal bermudagrass allowed the achievement of 82% glucose and 63% xylose yields from switchgrass and 87% glucose and 59% xylose yields from coastal bermudagrass, carrying out, after the biomass pretreatment, the enzymatic hydrolysis under optimal conditions (Keshwani and Cheng 2010). The microwave/alkali pretreatment of rice straw and hulls has been recently investigated: alkali and substrate concentration and irradiation time were the main factors governing the saccharification behavior (Singh et al. 2011).

The impact of dilute sulphuric acid pretreatment on bagasse under microwave heating resulted in a significant disruption of the lignocellulosic structure of the biomass (Chen and Kuo 2011). When the reaction temperature was as high as 190°C, the fragmentation of particles became pronounced and the specific surface area of the pretreated materials grew substantially. Meanwhile, almost all hemicellulose was removed from bagasse and the crystalline structure of cellulose disappeared, whereas the feature of lignin clearly remained. The acid hydrolysis of many different grasses was studied using dilute HCl. A significant increase of the hydrolysis of hemicellulose and cellulose components of *Arundo Donax L.* was ascertained under microwave (MW) irradiation, which allowed us to adopt reaction times of a few minutes (Raspolli Galletti et al. 2009). It is important to emphasize that microwaves can be employed not only in the pretreatment step but also as a very effective heating source in many different reactions of biomass and carbohydrates (Richel et al. 2011).

In conclusion, although irradiation processes do not generally require any chemicals for their applications, most of them are highly energy demanding, expensive, strongly substrate-specific, and are not capable of completely removing the lignin component. Despite these drawbacks, microwave irradiation appears to be a promising irradiation treatment.

5.3.3 Pyrolysis

Thermochemical processes are most commonly employed for converting biomass into higher heating-value fuels. In a typical thermochemical process for efficient utilization of bioenergy, pyrolysis is the necessary step before gasification of biomass. When lignocellulosic materials are treated at temperatures greater than 300°C, cellulose rapidly decomposes to produce gases, primarily CO, H_2, CH_4, C_nH_m, CO_2, tar, and residual semichar (Demirbas and Arin 2002). The relative amounts of gas, liquid (tar), and solid (semichar) products are dependent on the operating conditions, such as biomass type, temperature, residence time, and heating rate, among which, pyrolysis temperature is the most significant parameter. With regard to this aspect, in recent research, the effect of pyrolysis temperature on composition and yield in a typical fixed-bed reactor has been reported, showing that the pyrolysis temperature had a considerable effect on the composition, structure, and heat value of the gaseous, tar liquid, and semichar solid products (Xiao et al. 2010). During pyrolysis pretreatment, most of the oxygen content of the biomass is removed, resulting in the semichar solid of higher energy density. The liquid and gaseous products can also be used effectively. The pyrolyzed solid product may be transported directly or mixed with the liquid product to form a slurry for feeding the gasifier. If the pyrolysis pretreatment is carried out at lower temperatures, the decomposition is much slower and less volatile products are formed. Mild acid

hydrolysis (1 N H_2SO_4, 97 °C, 2.5 h) of the residues from pyrolysis pretreatment resulted in 80%–85% conversion of cellulose to reducing sugars with more than 50% glucose (Fan, Gharpuray, and Lee 1987). The process could be improved in the presence of oxygen.

It should be emphasized that, notwithstanding the increasing relief of pyrolysis in the literature (Van de Velden et al. 2010), this pretreatment has not yet developed enough to be feasible for applications on large-scale processes.

5.3.4 Torrefaction

Biomass torrefaction represents a recent attractive approach for biomass thermal pretreatment, although it has received only modest but increasing interest in past few years and has yet to become an important commercial process (Kumar et al. 2009). Torrefaction is a mild thermochemical treatment consisting of biomass heating to a moderate temperature, generally between 200°C and 300°C, working under inert or nitrogen atmosphere (Prins, Ptasinski, and Janssen 2006). This thermal process mainly removes moisture and low-weight organic components and finally depolymerizes the long polysaccharides. Three temperatures, around 210°C, 250°C, and 290°C, are applied for light, mild, and severe torrefaction, respectively (Chen, Tu, and Sheen 2011). Hemicellulose content was mainly influenced adopting light torrefaction, whereas in severe torrefaction there was a drastic depletion of lignocellulosic materials (Chen and Kuo 2010). The increase of torrefaction temperature decreases solid biochar yield with a contemporary increase of the yield in volatile matters, including liquid and noncondensable gases.

This process improves the characteristics of the treated biomass, markedly reducing its moisture content (Arias et al. 2008) and the hygroscopic raw biomass is converted to hydrophobic material, thus allowing easier storage and delivery (Deng et al. 2009). This aspect is particularly important for herbaceous biomass, thus converting to a more thermally stable product (Bridgeman et al. 2008).

Also, the grindability of the torrefied biomass is significantly improved with consequent energy saving when the material is ground (Repellin et al. 2010). Additionally, torrefied biomass forms more spherically shaped particles during grinding and milling and its energy density is significantly increased, whereas the O/C ratio is reduced (Sadaka and Negi 2009). As a consequence, the usefulness of this biomass as a fuel for industrial furnaces is enhanced.

A recent study on torrefaction of olive pruning for the first time has evidenced the possibility of enzymatically hydrolyzing and fermenting the torrefied biomass to ethanol without inhibition (Chiaramonti et al. 2011). Yields comparable with grinded untreated biomass were ascertained together with energy savings. Nonetheless, when energy consumption for ethanol production of a biomass-torrefaction grinding treatment was compared with steam explosion, the latter still showed a significant advantage. This result underlines that this very recent torrefaction process still needs further investigation and optimization.

5.3.5 Steam explosion and liquid hot water

Steam explosion (SE) is the most commonly used pretreatment of biomass and uses both physical and chemical methods to break the structure of the lignocellulosic material

through a hydrothermal treatment (Kumar et al. 2009). The biomass is treated with high-pressure steam at high temperatures for a short time, then it is rapidly depressurized and the fibril structure is destroyed by this explosive decompression. This defibration and the remarkable autohydrolysis significantly improve the substrate digestibility and bioconversion as well as its reactivity toward other catalytic reactions. The successive sudden decompression reduces temperatures, quenching the process. Temperatures ranging from 160°C to 260°C (and pressures of 0.7–5 MPa) are adopted for residence times ranging form one minute to few minutes, then the explosive decompression terminates the process. During this treatment, lignin is depolymerized, while hemicellulose is hydrolyzed and also a remarkable autohydrolysis can be ascribed to the released acetic acid (Kaar, Gutierrez, and Kinoshita 1998) as well as to the very mild acid character of water at high temperatures (Baugh, Levy, and McCarty 1988). When the reaction conditions are particularly harsh, a modest cellulose hydrolysis to glucose is also observed (Jorgensen, Kristensen, and Felby 2007). Additionally, the quick flashing to atmospheric pressure causes the fragmentation of the materials, which become more accessible to enzymes or to inorganic catalysts due to large pore volumes and increased surface area (Brugnago, Satyanarayana, and Wypych 2011).

The efficiency of the steam explosion depends on several parameters, such as temperature, residence time, particle size, and moisture content (Wright 1998). In particular, particle size plays a key role on the effectiveness of the process. Ballesteros has studied the effect of this parameter in the steam explosion of a chipped herbaceous biomass (*Brassica carinata*) (Ballesteros et al. 2002). Relatively larger particle sizes (8–12 mm) gave the best yield in sugars in the successive enzymatic hydrolysis, a valuable result considering the consequent modest mechanical processing of raw materials and lower energy costs. It has been estimated that the conventional mechanical comminution requires 70% more energy than SE to reach the same size reduction (Holtzapple, Humprey, and Taylor 1989). Another parameter, sometimes underestimated, that can influence the performances of SE, is steaming pressure: the thermal stability of cellulose-rich fractions is increased by steam explosion at an elevated pressure (Wang et al. 2009).

On the other hand, the process generates some toxic derivatives that can inhibit the successive hydrolysis and fermentation steps. In particular, furan derivatives, such as furaldehyde and 5-hydroxymethyl-2-furaldehyde, and phenolic compounds (deriving from lignin depolymerization) act as inhibitors (Alvira et al. 2010). In order to remove these inhibitors it is necessary to wash the pretreated biomass with water, although this wash reduces of about 20%–25% the saccharification yields, removing soluble sugars such as those derived from hemicellulose hydrolysis (Sun and Cheng 2002).

An optional addition of an acid has been adopted in SE in order to decrease contact times and temperatures. Dilute acids (H_2SO_4, and also SO_2, oxalic acid, and CO_2), generally 0.5–3.0 wt %, not only improve the hydrolysis step, leading to the complete removal of the hemicellulosic fraction, but also allow the decrease in the formation of inhibitory compounds. The addition of the acid catalyst is determinant when SE is applied to softwoods and to lower acetylated materials: the performances are significantly influenced by acid type and loading. On the other hand, the addition of the acid causes many drawbacks related to equipment corrosion, higher amounts of degradation products, and the necessary step of acid neutralization with the consequent formation of wastes.

SE has been extensively tested for many lignocellulosic raw materials (such as poplar, sugar cane, corn stover, wheat and barley straw, bamboo, and woody hemp) and also for agricultural wastes such as olive tree pruning. This last residue has been submitted to SE in the temperature range of 190–240°C, with or without previous impregnation by water or acid, and the influence of pretreatment conditions was investigated on sugar and ethanol yields by enzymatic hydrolysis and saccharification/fermentation of pretreated solids (Cara et al. 2008a): the best conditions resulted in impregnation by 1% H_2SO_4 and steam treatment at 230°C. Further improvement of sugar recovery can be reached if a water extraction stage previous to SE is adopted: this extractive removal is determinant because their presence hinders the accessibility of cellulose lowering the enzymatic hydrolysis yield (Ballesteros et al. 2011).

When liquid hot water (LHW) at high temperatures (180°C–230°C) and high pressures is employed instead of steam, with contact times from a few minutes to one hour and solids concentration <20 wt %, a process similar to SE is performed. This process has also been named aqueous fractionation, aquasolv, or hydrothermolysis (Kumar et al. 2009) and has been shown to improve cellulose digestibility for different types of biomass. This chemical-free process dissolves about 50% of the total biomass, completely removing hemicellulose, about 5%–20% of cellulose and 30%–60% of lignin. Acetic acid and other released acid components catalyze the autohydrolysis, but, with respect to SE, carried out without chemicals, LHW generates lower concentrations of inhibitory derivatives due to higher water input (Hendriks and Zeeman 2009). LHW and SE were compared using the same batch reactor for both processes in the pretreatment of sugar cane bagasse for bioconversion to ethanol (Laser et al. 2002). LHW pretreatment allowed better performances in terms of conversion and xylan recovery, and no inhibition of glucose fermentation. On the other hand, LHW requires higher energy costs over SE due to the higher pressures and larger amount of water input and the severity of the process strictly depending on the type of employed biomass.

LHW was then compared with NaOH soaking in the pretreatment of soybean straw: the chemical-free treatment was more effective for improving cellulose digestibility of soybean straw (Wan, Zhou, and Li 2011).

LHW was also compared with two different pretreatments (NaOH pulping and ethanol organosolv) in the bioconversion of rye straw (Ingram et al. 2011): at biomass loading up to 15 wt %, cellulose conversion of LHW and organosolv-pretreated materials was almost equal, while soda pulping showed lower carbohydrates and lignin recoveries. Lignin derived from LHW showed interesting properties for polymer applications (Wörmeyer et al. 2011).

5.3.6 Ammonia fiber explosion

The ammonia fiber explosion (AFEX) approach is similar to SE: biomass is exposed to liquid ammonia under high temperatures and pressure and then the pressure is quickly released. Typically 1–2 kg of ammonia/Kg of dry biomass are employed, working at temperatures ranging from 90°C to 100°C with residence times of 5–10 minutes (Kumar et al. 2009). The optimal conditions can change in severity depending on the type and maturity of the adopted biomass: for example, woody materials requiring very drastic conditions to reach high sugar yields (up to 200°C with 30 minutes of residence time).

AFEX modifies the biomass structure without generating liquid-dissolved fractions: an almost complete solid recovery is ascertained (Lee, Jameel, and Venditti 2010). The biomass derived from AFEX has an increased digestibility due to many different combined factors: cellulose decrystallization, partial hemicellulose depolymerization, deacetylation of acetyl moieties, and cleavage of lignin bonds. The surface area of treated materials is enhanced as well as their wettability, thereby the rate of enzymatic hydrolysis is significantly increased.

Four main parameters (ammonia loading, water loading, reaction temperature, and residence time) influence the optimization of AFEX treatment (Bals et al. 2011). In particular, ammonia loading and also residence time have the highest impact on the economics of the process. In fact, ammonia must be recovered and recycled after the pretreatment and the cost of the recovery represents a severe limit for large-scale applications.

The effectiveness of AFEX for enzymatic hydrolysis of switchgrass has been extensively studied and another interesting effect has been evidenced: each harvest time and ecotype/location responded differently to the pretreatment, although all harvests successfully produced fermentable sugars (Bals et al. 2010). These results evidenced that it is necessary to consider an integrated approach between agricultural production and biomass successive processing in order to ensure optimal productivity.

5.3.7 CO_2 explosion

Carbon dioxide explosion is a biomass pretreatment that uses CO_2 as a supercritical fluid (SC–CO_2) (Zheng et al. 1995). This technique was developed in order to adopt lower temperatures than those usually used in SE and to reduce the cost in comparison with AFEX. Supercritical pretreatment conditions can effectively remove lignin, increasing substrate digestibility and the addition of co-solvents such as ethanol, water, or acetic acid, can further improve the delignification process (Pasquini et al. 2005). Supercritical CO_2 has been mostly employed as an extraction solvent, but now it is also considered for nonextractive purposes due to its many advantages, like availability at relatively low cost, nontoxicity, nonflammability, easy recovery after extraction, and environmental acceptability (Schacht, Zetzl, and Brunner 2008). In aqueous solution, CO_2 forms carbonic acid, which favors the biomass hydrolysis. CO_2 molecules are comparable in size to those of water and ammonia and thus they can penetrate in the same way the small pores of lignocellulose. This mechanism is facilitated by high pressures. After the explosive release of CO_2 pressure, disruption of cellulose and hemicellulose structure is observed and, consequently, the accessible surface area for enzymatic attack increases.

The employment of lower temperatures compared to those used in other pretreatments prevents monosaccharide degradation, but in comparison to steam and ammonia explosions, the obtained sugar yields are lower. Nevertheless, a comparison of different pretreatment methods on several and different substrates shows that CO_2 explosion is more cost effective than AFEX, and the formation of inhibitors is lower compared to that of SE (Srinivasan and Ju 2010). The explosion affected the cellulose crystallinity and the glucose or ethanol yield from the subsequent enzymatic hydrolysis or simultaneous saccharification and fermentation. These positive effects were reported for aspen and southern yellow pine raw materials (Kim and Hong 2001) and also for other types of

biomass, such as switchgrass, corn stover, big bluestem, and mixed perennial grasses (Luterbacher, Tester, and Walker 2010).

In conclusion, although there are many advantages to the SC–CO_2 process, such as nontoxicity, nonflammability, easy recovery, low cost, the possibility of using high solid concentrations in pretreated materials, low pretreatment temperatures, and the ability of increasing the accessible surface area, this method does not yet guarantee economic viability. In particular, the high capital cost for high-pressure equipment may represent an obstacle to the commercialization of this lignocellulosic pretreatment.

5.4 Chemical pretreatments

5.4.1 Alkaline hydrolysis

This treatment employs alkaline solutions, such as sodium hydroxide, calcium hydroxide, or ammonia for the treatment of biomass, in order to remove lignin and part of hemicellulose and to efficiently increase the accessibility of cellulose: it is basically a delignification process, where a significant amount of hemicellulose is also solubilized. The use of an alkali causes the degradation of ester and glycosidic side chains, resulting in structural alteration of lignin, cellulose swelling, partial decrystallization of cellulose, and partial solvatation of hemicellulose (Ibrahim et al. 2011; Sills and Gossett 2011; Cheng et al. 2010; McIntosh and Vancov 2010). In general, alkaline pretreatment of lignocellulosic materials causes swelling, decrease of polymerization degree and crystallinity, increase of internal surface area, disruption of the lignin structure, and separation of structural linkages between lignin and carbohydrates. This pretreatment can be carried out at lower temperatures and pressures than other pretreatment technologies, but, especially if performed at room temperature, long times and high concentrations of base are required. In comparison with acid processes, alkaline ones cause less sugar degradation and many of the caustic salts can be recovered and/or regenerated. The mechanism is believed to be a saponification of intermolecular ester bonds, crosslinking xylan hemicelluloses and other components, such as lignin and other hemicelluloses. Alkaline reagents can also remove acetyl and various acid substitutions on hemicellulose, thus reducing the accessibility of hemicellulose and cellulose to enzymes. The effectiveness of the alkaline pretreatments depends on the type of substrate and the treatment conditions. Alkaline treatment is usually more effective on hardwood, herbaceous crops, and agricultural residues with low lignin content than on softwood with high lignin content. Sodium, potassium, calcium, and ammonium hydroxides are suitable alkaline agents, sodium hydroxide being more deeply studied (Wu et al. 2011). Sodium hydroxide pretreatment is able to improve the enzymatic digestibility of solid digestate fibers, enhancing glucose and ethanol yields from enzymatic hydrolysis and fermentation steps (Teater et al. 2011). A dilute NaOH pretreatment followed by enzyme saccharification was applied to cereal residues. After the pretreatment, both solids and lignin content were found to be inversely proportional to the severity of the treatment itself: higher temperatures and alkali strength were fundamental for maximizing sugar recoveries from enzyme saccharifications. In particular, the alkaline pretreatment is able to extract oligoxylans and lignin, thus improving simultaneously cellulose hydrolysis.

However, the selection of an appropriate pretreatment requires a compromise between maximizing glucose yield and minimizing the formation of inhibitors: sorghum and wheat straw resulted excellent feeds for the production of ethanol because of their abundance and their high sugar potential (Vancov and McIntosh 2011). The high digestibility improvement has been related to the alkali disruption of the lignin-carbohydrate matrix (Wu et al. 2011).

Another agent widely employed for the alkaline pretreatment is calcium hydroxide (lime pretreatment) (Fu and Holtzapple 2011; Nachiappan, Fu, and Holtzapple 2011). It is possible to recover calcium from the aqueous reaction system as insoluble calcium carbonate by neutralizing it with inexpensive CO_2; the calcium hydroxide can subsequently be regenerated using established lime kiln technology. The process of lime pretreatment requires slurrying the lime with water, spraying it onto the biomass material, and accumulating the material in a pile for a period of time from hours to weeks. After the treatment, the particle sizes of the biomass are typically 10 mm or less. Elevated temperatures can reduce contact times. Also in this case, lignin removal improves enzyme effectiveness by eliminating nonproductive adsorption sites and by increasing access to cellulose and hemicellulose. A novel lime pretreatment (CaCCO process) for subsequent bioethanol production from rice straw was recently developed (Park et al. 2010). This method did not require a solid-liquid separation step, but after pretreatment, lime was neutralized by carbonation, resulting in a final pH of about 6. $CaCO_3$ obtained by the process was kept in the reaction vessel and no significant inhibitory effects on enzymatic saccharification and fermentation were observed. In this method, solubilized carbohydrates, such as xylan, starch, and sucrose were also kept in the vessel, enabling high recoveries of monomeric sugars. Simultaneous saccharification and fermentation of pretreated rice straw achieved 74% of the theoretical yield from glucose and xylose.

Sometimes the alkaline pretreatment is carried out in combination with irradiation, such as microwaves and radio frequencies. In particular, the microwave-based alkali pretreatment of switchgrass and coastal bermudagrass was investigated in order to improve the production of fermentable sugars from enzymatic hydrolysis. Pretreatments were carried out by immersing the biomass in dilute alkali reagents and exposing the slurry to microwave radiation at 250 watts for residence times ranging from 5 minutes to 20 minutes. Sodium hydroxide was the most effective base for microwave pretreatment of switchgrass and coastal bermudagrass (Keshwani and Cheng 2010).

Finally, ammonia has also been used as a pretreatment reagent to remove lignin. The main effect of ammonia treatment of biomass is delignification without a significant effect on carbohydrate contents. It is a very promising pretreatment reagent, in particular for substrates with low lignin contents, such as agricultural residues and herbaceous feedstock. The ammonia method is suitable for simultaneous saccharification and cofermentation because the treated biomass does not lose cellulose and hemicellulose (Kim, Gupta, and Lee 2009). Ammonia is a proven delignification reagent and the lignin content of the biomass can decrease to a very low level. This aspect is very important because it increases the efficiency of enzyme action, reducing irreversible bindings between enzymes and lignin. Unlike most alkaline pretreatments, ammonia treatment does not cause a substantial loss of carbohydrates and its use leads to the fractionation of biomass by separation of lignin from biomass. It is also important to emphasize that this lignin is sulphur- and sodium-free, unlike that obtained from other pretreatment processes. It is generally of high quality and thus it is considered a higher value

byproduct. Unfortunately, ammonia pretreatment shows some disadvantages: the most revealing one is the consumption of ammonia due to the interaction with lignin and its neutralization by acetates and other buffering agents present in the biomass. Most of the ammonia is recovered and reused in the process: in general, only ammonia equivalent to 2%–5% of dry biomass is irreversibly consumed during the pretreatment. The most widely used ammonia pretreatments are: (1) the ammonia recycle percolation (ARP), which is a high severity, low contact time process, and (2) the soaking in aqueous ammonia (SAA), which is a low severity, high contact time process. In order to reach a sufficient level of delignification and to limit lignin recondensation, liquid/solid ratios of four or higher are normally employed in the SAA process. Because of low process energy and equipment cost, the total processing expense of SAA is lower than that of ARP, but it has limited applications. In fact, it is possible to adopt this process for feedstock having low lignin contents, such as agricultural residues of annual plants (corn stover, surgar cane bagasse, wheat straw, etc.). With regard to this, ARP treatment of corn stover removed about 73% of lignin, solubilized about 50% of xylan, but retained > 92% of cellulose (Kim and Lee 2005b). The same authors also studied the soaking in aqueous ammonia treatment of corn stover, SAA process, which removed 55%–74% of lignin but retained about 100% of glucan and 85% of xylan under mild conditions, at room temperature, and after 10–60 days of pretreatment (Kim and Lee 2005a).

To summarize, it is possible to conclude that, in comparison with other pretreatment technologies, alkali pretreatment usually involves lower temperatures and pressures, even up to room-temperature conditions. Pretreatment time, however, is recorded in terms of hours or days, a duration is much longer than those of other pretreatment processes. Another considerable drawback of alkaline pretreatment is the conversion of alkali into irrecoverable salts and/or the incorporation of salts into the biomass during the pretreatment reactions, making the treatment of a large amount of salts a challenging issue for the alkaline approach.

5.4.2 Acid hydrolysis

Acid pretreatment can be performed with diluted or concentrated acids, but the concentrated acids are more hazardous, highly corrosive for reactors and equipments, and must be recovered after the pretreatment. Moreover, if the pretreatment precedes the enzymatic hydrolysis, drastic acid conditions favor the formation of degradation and inhibiting compounds and cause the fast condensation and precipitation of solubilized lignin (Liu and Wyman 2003). For these reasons, only diluted acid pretreatment appears attractive for large-scale applications.

An efficient mild acid pretreatment completely solubilizes the hemicellulosic component of the biomass and only a little part of the cellulose (at low acid concentration), thus making undissolved cellulose more accessible to enzymes. The most recent studies have been devoted to the optimization of the mild hydrolysis conditions in order to reach high yields of xylose from xylan, an important biomass component that has to be exploited.

The most commonly employed acid is sulphuric one, generally in concentrations below 4 wt %, applied to a wide range of lignocellulosic biomass, ranging from poplar (Wyman et al. 2009) to corncob (Lee and Jeffries 2011) to switchgrass (Digman et al. 2010).

When the acid pretreatments of olive tree pruning and successive enzymatic saccharification were studied, the maximum sugar yield was obtained pretreating the biomass at 180°C for 10 minutes with 1 wt % sulphuric acid concentrations (Cara et al. 2008b). Higher temperatures and acid concentrations caused cellulose solubilization and formation of furan byproducts (furfural and HMF) and of levulinic acid, which can have an inhibitory effect on successive enzymatic hydrolysis.

Another factor can play a negative role on fermentation: it has been ascertained that after acid hydrolysis at temperatures above 130°C, the surface of residual corn stover is covered of droplets of lignin and of lignin/carbohydrate complexes (Selig et al. 2007).

The ^{13}C CP–MAS spectra of poplar wood treated with dilute sulphuric acid for times up to 20 minutes and at temperatures ranging from 120°C to 150°C allowed them to evidence at a molecular-level modification of the biomass structure not only the dominant hydrolysis/depolymerization of hemicellulose but also of holocellulose and lignin (Kobayashi et al. 2011).

Other types of acids have also been applied, such as hydrochloric, phosphoric, and nitric acid and organic acids have also been tested (Kumar et al. 2009).

Very recently the hydrolysis of lignocellulosic biomass, such as rice straw and Japanese cedar sawdust, has been studied in the presence of concentrated aqueous solutions of highly negatively charged heteropolyacids, such as $H_5BW_{12}O_{40}$. The saccharification efficiently produced a mixture of saccharides with yields >77% based on holocellulose (Ogasawara et al. 2011).

Promising results have been recently attained with dicarboxylic acids, such as maleic and oxalic acids, which were compared with sulphuric one for corncob hydrolysis and successive fermentation (Lee and Jeffries 2011). The dicarboxylic acids were more efficient than sulphuric one in the hydrolysis of hemicellulose, and more ethanol is produced from residual solids.

Considering that acid hydrolysis involves expensive materials for plants, high pressures, neutralization, and conditioning of the residual biomass before an eventual successive enzymatic step, it is necessary to carefully evaluate the proper dilute acid treatment.

5.4.3 Ozonolysis

Pretreatment of lignocellulosic materials can be carried out using ozone, which can effectively degrade lignin and part of hemicellulose. In fact, ozone is a powerful oxidant, soluble in water and readily available. In addition, it is also highly reactive toward conjugated double bonds and functional groups with high electron density. Therefore, the moiety most likely to be oxidized in ozonization of lignocellulosic materials is lignin, because of its high content of C=C bonds. Ozone attacks lignin, releasing soluble compounds of low molecular weight, such as organic acids, formic and acetic ones, which can cause a decrease in pH from 6.5 to 2 (Garcìa-Cubero et al. 2009). Ozone applications have considerably increased both in number and diversity during the past two decades, such as for the treatment of biological waste water (Battimelli et al. 2010), or for the treatment of palm oil mill effluent (Chaiprapat and Laklam 2011), or for pulp bleaching in the paper industry (Shatalov and Pereira 2008). Regarding lignocellulosic biomasses, research was developed to study the main parameters that affect the

ozonolysis pretreatment (Garcìa-Cubero et al. 2009; Neely 1984). The main factors were the moisture content of the sample, the particle size, and the ozone concentration in the gas flow. Among these parameters, the most important one is the percentage of water in the feed because it has a significant effect on the solubilization. The optimum water content was found to be around 30%, corresponding to the saturation point of the fibers. In particular, Garcìa-Cubero et al. studied the pretreatment with ozone of wheat and rye straw in order to enhance the enzymatic hydrolysis extent of potentially fermentable sugars. Operating in a fixed-bed reactor, moisture content and type of biomass showed the most significant effects on ozonolysis. Moisture is a reaction-controlling parameter for values below 30%. Wheat straw proved to be easier to hydrolyzed than rye, although a similar content of residual lignin after ozone pretreatment was obtained for both samples. The main advantages of ozonolysis are the lack of any degradation product that might obstruct the subsequent hydrolysis or fermentation, the efficient removal of lignin, the absence of toxic residues for the downstream processes, the possibility of carrying out the reaction at room temperature and pressure, and, finally, the fact that ozone can be easily decomposed by using a catalytic bed or increasing the temperature, minimizing in this way the environmental pollution (Sun and Cheng 2002). On the other hand, the main drawback is the demand for a large amount of ozone, making the process expensive and not suitable as an application on an industrial scale.

5.4.4 Organosolv processes

Organosolvation (organosolv) treatment represents a very promising approach for solubilizing lignin in an organic medium, thus providing a residual cellulose suitable for enzymatic hydrolysis. On the other hand, after precipitation, the recovered lignin is a relatively pure co-product to be used for many purposes. The solvents more frequently used in organosolv processes are acetone, methanol, ethanol, phenols, ethylene glycol, and tetrahydrofurfuryl alcohol (Zhao, Cheng, and Liu 2009).

In some cases the contemporary addition of an acid catalyst, generally H_2SO_4, HCl or oxalic acid, is reported: this combined approach allows the easier depolymerization of hemicellulose bonds, high yields of xylose are reached, and it is also useful to break the internal lignin bonds.

On the other hand, the acid addition can be avoided by applying higher process temperatures ($T > 180°C$): the released acetic acid lowers the pH, thus favoring the hydrolysis, and significant delignification is obtained without corrosion and acid consumption.

The lignol process is based on aqueous ethanol organosolv: it uses an aqueous solution (50 wt %) of ethanol at 200°C and about 2.75 MPa to extensively extract lignin from wood. The obtained pulping liquor is then flashed up to atmospheric pressure and diluted with water: lignin is recovered as fine powder (Pan et al. 2005). When pine sawdust was employed as biomass at 150°C–250°C, the optimum conditions for lignin extraction appeared to be at 180°C with an ethanol/water 1/1 wt/wt mixture. The obtained lignin was suitable for the synthesis of phenol-formaldehyde resol resins (Wang, Leitch, and Xu 2009).

Removal of the organic solvents is compulsive for economic reasons and also because they could act as inhibitors to the downstream enzymatic hydrolysis and fermentation (Sun and Cheng 2002). The solvent is removed from the reactor, evaporated,

condensed, and finally recycled to the reactor in order to minimize the operational costs. For economic reasons aqueous ethanol is generally the preferred solvent, having a low boiling point, toxicity, and cost.

5.4.5 Ionic liquid pretreatments

A very recent approach to the pretreatment of biomass involves the use of ionic liquids (ILs) as solvents (Brandt et al. 2010). ILs are salts generally formed by large organic cations and small inorganic anions, which are liquid at low temperature and can be used as nonaqueous alternatives to traditional organic solvents (Alvira et al. 2010). They generally have low toxicity, high chemical and thermal stability, are nonflammable, have low vapor pressures, and remain liquid in a wide range of temperatures. In the context of green biorefinery, cheap ILs derived from renewable raw materials and particularly from sugars appear particularly promising (Marra, Chiappe, and Mele 2011). On the other hand, ILs are characterized by a very high viscosity, which represents a serious drawback to mass and phase transfer. Their very high solvating properties have been used for dissolving cellulose, lignin, and also raw biomass, such as hardwoods, softwoods, and grasses (Mora-Pale et al. 2011). In particular, imidazolium-based ionic liquids have been applied for hardwood and softwood dissolution, which is strongly influenced by particle sizes. Biomass solubilization is due not only to the swelling of the plant cell wall, with disruption of inter- and intra-molecular hydrogen bonding between lignin and cellulose, but also to the possible electronic interaction of the organic cations and the aromatic rings of lignin (Zavrel et al. 2009). Cellulose and hemicellulose are then selectively recovered by precipitation with water from the completely dissolved lignocellulose and are then submitted to enzymatic hydrolysis.

ILs can completely dissolve biomass and an interesting alternative is represented by their selective extraction of a single biomass component. For instance, acetate-based ILs are able to extract lignin from recalcitrant maple wood flour, while cellulose is not dissolved but its crystallinity is reduced (Doherty et al. 2010). As a consequence, this residual cellulose can be suitably applied for successive saccharification. Toxicity to enzymes and fermentative microorganisms must be deeply studied, and in general IL residues are to be removed from residual cellulose. Pristine lignin obtained from IL pretreatment can be exploited to produce not only special polymers but also high value phenol derivatives by oxidative depolymerization (Stark et al. 2010).

Before ILs can be applied on a large industrial scale, their recovery and ability to be recycled must be improved because the price is generally high. On the other hand, it is evident that recycling ILs can not be performed indefinitely because of the accumulation of impurities, and intermediate steps of adsorption on activated carbon and organic solvent washing must be inserted for IL regeneration.

5.5 Conclusions and perspectives

The separation of the three main components of lignocellulosic biomass is severely limited by many factors, such as lignin content, cellulose crystallinity, water content, and available surface area, factors that also influence the future exploitation of the pretreated materials. The choice of the best pretreatment strictly depends on the downstream use of

Tab. 5.2: Influence of the main pretreatment processes on lignocellulose structure.

	Milling	Torrefaction	SE	LHW	AFEX	CO_2 explosion	Alkaline	Acid	O_3	Organosolv	ILs
Increase of accessible surface area	H	H	H	H	H	H	H	H	H	H	H/–
Cellulose decrystallization	H	n.d.	–	n.d.	H	L	H	–	n.d.	n.d.	H/–
Hemicellulose solubilization	–	L	H	H	L	L	L	H	H	H	H/L
Lignin solubilization	–	–	L	L	H	L/–	H	L	H	H	H/–
Generation of inhibitors	–	–	H	L	L	–	L	H	–	–	–
Alteration lignin structure	–	L	H	L	H	L/–	H	H	H	H	H/–

H: high effect; L: minor effect; n.d.: not determined.

the pretreated fraction itself. This statement is explained by ▶Tab. 5.2, where the effects of the most important pretreatments on the structure of lignocellulose are summarized, while in ▶Tab. 5.3 the main advantages and drawbacks of the different approaches are reported.

Tab. 5.3: Main advantages and disadvantages of different biomass pretreatments.

	Main advantages	Main disadvantages
Milling	Reduces cellulose crystallinity; increases surface area	Needs to be combined with other treatments; high energy consumption
Torrefaction	Easier biomass storage; no formation of inhibitors; moderate energy consumption; easier grindability	Needs to be combined with other treatments; still incomplete investigation
Steam explosion	Increase of accessible surface area; higher substrate digestibility; depolymerization of lignin; solubilization of hemicellulose	Needs to be combined with other treatments; formation of inhibitors
LHW	Enhanced substrate digestibility; low formation of inhibitors; low-cost plant	High energetic requirements; high water input
AFEX	Low formation of inhibitors; increase of accessible surface area	High cost of plant and ammonia
CO_2 explosion	No toxicity; easy recovery; increase of accessible surface area; efficient hydrolysis of hemicellulose	High cost of plant; high pressure involved lignin remains
Alkaline	Hemicellulose and lignin hydrolysis; mild conditions; increased substrate digestibility	Long reaction times; salts formation and incorporation; base consumption
Acid	Increased substrate digestibility; hemicellulose solubilization	Formation of degradation products; formation of inhibitors; corrosion; need for acid recovery
Ozonolysis	No toxicity; no formation of inhibitors; lignin solubilization	High cost of ozone
Organosolv	Hemicellulose and lignin solubilization	High cost for plant and solvents
ILs	Low toxicity and flammability; high selective solubilization of biomass components	High cost for plant and ILs; high viscosity

To overcome the disadvantages of every method, the most recent literature suggests the usefulness of combined approaches, which can lead to the optimal fractionation of all the different components. In fact, an efficient integrated process must allow the exploitation of all the three main components of biomass, including the up-to-now underutilized lignin. In the context of combined processes, torrefaction and microwave irradiation appear particularly promising if joined with other chemical pretreatments.

It must be emphasized that up to now an exhaustive quantitative economic comparison of the main consolidated pretreatments, evaluating their capital and operating

costs on the basis of mass balances, is still lacking and is very deficient for combined approaches.

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6 Conversion of cellulose and hemicellulose into platform molecules: chemical routes

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6.1 Introduction

First-generation biofuel production technologies use easily accessible edible biomass, thereby impacting the supply of food for humans and animals, and so their extensive and continued production does not seem to be a sustainable solution. Therefore, new alternatives for a more sustainable production of biofuels (and also of chemicals according to the biorefinery concept) must be developed, using widely available biomass feedstocks instead of edible starch and triglycerides. The best source for such alternative biofuels is lignocellulose, since this polymer is the most abundant form of biomass on the planet and is widely available – as waste biomass, as conventional wood, and as a fast rotation crop.

Two main routes exist for the conversion of lignocellulose into biofuel: the thermochemical route and the sugar route. The first approach involves thermochemical processing of lignocelluloses at high temperatures and/or pressures (e.g. pyrolysis, gasification, and liquefaction). The thermal deconstruction of biomass yields upgradeable intermediates such as bio-oils by pyrolysis and synthesis gas by gasification ($CO+H_2$ mixtures, denoted as syngas). Thermal processing is coupled with the subsequent chemical/catalytic upgrading to produce fuel-range hydrocarbons. In the sugar route, lignocellulose must be separated into its constituents lignin (15%–30%), cellulose (35%–50%), and hemicelluloses (25%–30%), which are then depolymerized to the corresponding building blocks.

Lignin is formed by aromatic alcohol building blocks. However, controlled lignin depolymerization is rather difficult on a technical scale and it has not yet been efficiently solved. Controlled cellulose depolymerization results in glucose, whereas the hemicelluloses are depolymerized into a mixture of different sugars, consisting mostly of pentoses. These sugars are the key molecules for the production of fuels starting from lignocellulosic biomass. Fuels from sugars can be obtained by conventional fermentation resulting mainly in the formation of bioethanol, an excellent alternative to gasoline. However, this conversion involves drawbacks, especially in terms of atom economy, as well as taking into account the low energy density of ethanol and its relative low boiling point. Alternatively, via a number of direct chemical catalytic conversion processes, fuel-type molecules can be synthesized by controlled dehydration reactions and subsequent conversions.

The previously mentioned processes require the controlled degradation of natural polymers and the development of highly selective transformations of sugars into target molecules in aqueous solutions. Therefore, the challenges faced include the need to selectively convert highly functionalized molecules and the control of phase effects. Approaches to solve these challenges usually involve novel catalytic materials as well as novel reaction systems.

This chapter considers two main pathways for the conversion of cellulose and hemicellulose into chemicals and fuels by means of chemical transformations. The first involves the selective conversion of sugars into platform molecules, in which dehydration processes play a relevant role, followed by oxidation, hydrogenation, and acid/base catalyzed reactions. The second pathway comprises a variety of processes for the aqueous-phase conversion of cellulose, hemicellulose, and derivatives into liquid hydrocarbons that could be used as transportation fuels.

6.2 Selective transformation of sugars to platform molecules

Conversion of biomass into functionalized, targeted platform molecules is unique to hydrolysis-based methods and allows the production of a wide range of fuel components and chemicals. Among the different platform molecules that can be so obtained, furfural (2-furaldehyde), 5-hydroxymethylfurfural (5-HMF), and levulinic acid (LA) are of high interest for the production of industrial solvents, polymers, and fuel additives.

6.2.1 Dehydration of hexoses into furan compounds: 5-HMF and derivates

Dehydration of hexoses in acid media leads to the formation of 5-HMF, which is a significant intermediate for the synthesis of a great variety of chemicals and biofuels. In the following sections, the different strategies of 5-HMF synthesis from hexoses will be discussed, addressing also their catalytic transformation into valuable biofuels and chemicals.

6.2.1.1 Synthesis of 5-HMF: dehydration of hexoses

Dehydration of hexoses to HMF has been carried out using a great variety of catalytic systems: homogenous organic acids (*p*-toluenesulfonic acid, H_2SO_4, and HCl) as well as heterogeneous catalysts (ionic exchange resins, H-form zeolites, vanadyl phosphate, and ZrO_2) and in the presence of different solvents. Reaction conditions range from temperatures between 100°C and 200°C using conventional heating (reaction times up to 48 hours depending on the catalytic system) as well as microwave heating operating with short reaction times, usually in the range of minutes (Rosatella et al. 2011). In principle, solid acid catalysts are more desirable for this reaction and display significant advantages in comparison with liquid acid catalysts. These heterogeneous catalysts can be easily separated from the product and recycled, and allow working under higher temperatures, which leads to shorter reaction times and to an avoidance of 5-HMF decomposition due to prolonged reaction times. Likewise, the adjustment of their surface acidity provides a better control of the 5-HMF selectivity.

Several reaction media have been used in the dehydration of hexoses. Water media is a suitable candidate from an ecological point of view, but unfortunately 5-HMF under aqueous acidic conditions rehydrates to undesired side products such as levulinic and formic acids as well as self-condensate to form both soluble polymers and insoluble humins. In order to minimize these secondary reactions and increase the yield toward 5-HMF, the use of high-boiling organic solvents has been described in the literature.

For instance, pure dimethyl sulfoxide (DMSO) in the presence of acid resins gave a 5-HMF yield of over 90% starting from fructose, whereas in water media the yields are hardly over 60% (Morikawa and Nakamura 1980). Likewise, biphasic systems (water-organic solvent) have been used in the synthesis of 5-HMF with the purpose of solving the low solubility of sugars in organic solvents while the continuous extraction of formed 5-HMF from the aqueous phase prevents its degradation. These systems have been deeply studied by Dumesic and coworkers in order to improve the selectivity toward 5-HMF formation from fructose (Roman-Leshkow, Chheda, and Dumesic 2006; Chheda, Roman-Leshkow, and Dumesic 2007). Both homogeneous and heterogeneous catalysts have been assayed with this biphasic system, including HCl, H_2SO_4, H_3PO_4, ion-exchange resins, and niobium phosphate catalysts. For instance, fructose and glucose were dehydrated to 5-HMF with selectivities of 89% and 53%, respectively, with high sugar conversions in a system comprised of a reactive aqueous phase modified with DMSO, combined with an organic extracting phase (mixture of methyl isobutyl ketone [MIK] and 2-butanol) at 130°C.

Another relatively new catalytic system to produce 5-HMF involves the use of ionic liquids (ILs). Several works have been reported in the literature combining ILs with homogeneous and heterogeneous catalysts (Zakrzewska, Bogel-Lukasik, and Bogel-Lukasik 2011). However, the main drawbacks associated with the use of ILs are the need for purification steps after recycling, potential sensitivity to moisture and impurities, as well as their high cost, which hinders commercial applications.

Dehydration processes are more efficient and selective for 5-HMF when starting from fructose than from glucose. Thus, the most efficient method for the preparation of 5-HMF is the acid-catalyzed dehydration of fructose, which can be obtained by acid-hydrolysis of sucrose and inulin as well as by means of glucose isomerization. However, glucose is more abundant and readily available and hence a more appealing feedstock for the production of 5-HMF. Thus, there is an important incentive to transform glucose into 5-HMF with high yields. Takagaki et al. (2009) and Ohara et al. (2010) have developed a new strategy to obtain 5-HMF from glucose based on the combination of a basic catalyst (Al/Mg hydrotalcite) and an acid catalyst (Amberlyst-15). The basic catalyst is responsible for the isomerization of glucose into fructose and the acid catalysts promote the subsequent dehydration to 5-HMF. The authors reported a 5-HMF selectivity of 76% with a glucose conversion of 60% using this mixture of catalytic systems.

Finally, the use of polyssacharides, cellulose, and lignocellulose directly as feedstocks for the production of 5-HMF is more appealing from a commercial point of view. The processing of these highly functionalized polysaccharides, which are inexpensive and abundantly available, eliminates the need for obtaining simple carbohydrate molecules by acid hydrolysis in a separate processing step. This approach has been poorly described in the literature but there are some works that deserve to be mentioned. Chheda, Roman-Leshkow, and Dumesic (2007) achieved good selectivities for 5-HMF at high conversions from sucrose, starch, cellobiose, and xylan using a mineral acid as catalyst and a biphasic reactor. More recently, Mc Neff et al. (2010) have described the continuous production of 5-HMF from simple and complex carbohydrates using a fixed-bed porous metal oxide-based catalytic process (ZrO_2 and TiO_2) and using methyl isobutyl ketone as a solvent. For instance, they obtained a cellulose conversion of 87% and 5-HMF selectivity of 35% using this catalytic system.

6.2.1.2 Synthesis of 5-HMF derivates: levulinic acid and γ-valerolactone

Levulinic acid (LA, 4-oxopentanoic acid) is an important biomass derivative that can be obtained by acid hydrolysis of lignocellulosic wastes, such as paper mill sludge, urban waste paper, and agricultural residues, through the Biofine process (Fitzpatrick 1990, 1997). The biomass feedstock is mixed with sulfuric acid (1.5–3 wt%) and introduced into a first plug-flow reactor where hydrolysis of the carbohydrates to intermediates (HMF) takes place at 483–493 K and 25 bar with a short residence time (12 s) to minimize the formation of degradation products. Subsequently, in a second reactor, the intermediates are converted into levulinic acid and formic acid at 463–473 K and 14 bar, with a residence time close to 20 min. These conditions have been optimized to remove both formic acid and the furfural arising from dehydration of the C_5 sugars present in the biomass. Yields toward levulinic acid are around 70%–80%, which corresponds to 50% of the mass of C_6 sugars being the rest of the mass collected as formic acid (20%) and a solid residue (humins). Levulinic acid can be subsequently converted to γ-valerolactone (GVL) by catalytic hydrogenation. This reaction is carried out at relatively low temperatures (373–543 K) and high pressures (50–150 bars) and using both homogeneous and heterogeneous catalysts. The reduction usually uses external hydrogen, but the transformation of formic acid into hydrogen, obtained as a byproduct in the production of levulinic acid, is a promising alternative. Recently, several works have reported a simple process for the production of GVL, which integrates hydrolysis/dehydration of the carbohydrates to form LA and the subsequent hydrogenation to GVL in a single step (Heeres et al. 2009).

6.2.1.3 Catalytic transformation of 5-HMF and derivates into oxygenated biofuels

The catalytic upgrading of these platform molecules into second-generation biofuels, maintaining the carbon skeleton integrity, is currently of great interest. This route could avoid the energy losses and CO_2 emissions that typically occur in the production of ethanol by fermentation. ▶Fig. 6.1 outlines the possible reaction pathways in the conversion of 5-HMF toward oxygenated biofuels.

Avantium company has recently patented biofuels based on 5-HMF derivatives, in particular 5-alkoxymethylfurfural ethers (Gruter and Dautzenberg 2007a) and esters (Gruter and Dautzenberg 2007b) manufactured by reacting a glucose-containing starting material with an alcohol or an organic acid in the presence of an acid catalyst (named Furanics compounds). For instance, the energy density of ethoxymethylfurfural (EMF, a Furanics example) is 8.7 kWh/L. This energy density is as good as that of regular gasoline (8.8 kWh/L), nearly as good as that of diesel (9.7 kWh/L), and significantly higher than that of ethanol (6.1 kWh/L). The high energy density of Furanics compounds makes them very interesting biofuels. Likewise, the catalytic hydrogenation/hydrogenolysis of 5-HMF leads to 2,5-dimethylfuran (DMF) and 2-methylfuran (2-MF), both showing a high octane number, limited oxygen content, and good miscibility with gasoline. The catalytic hydrogenation of the aldehyde group in HMF leads to the corresponding alcohol, which can be further etherified with alcohols to yield biodiesel components.

Levulinic acid can be converted to methyltetrahydrofuran (MTHF), a fuel extender and part of P-series fuels. MTHF can be blended up to 70% with gasoline without modification of current internal combustion engines. The lower heating value of MTHF

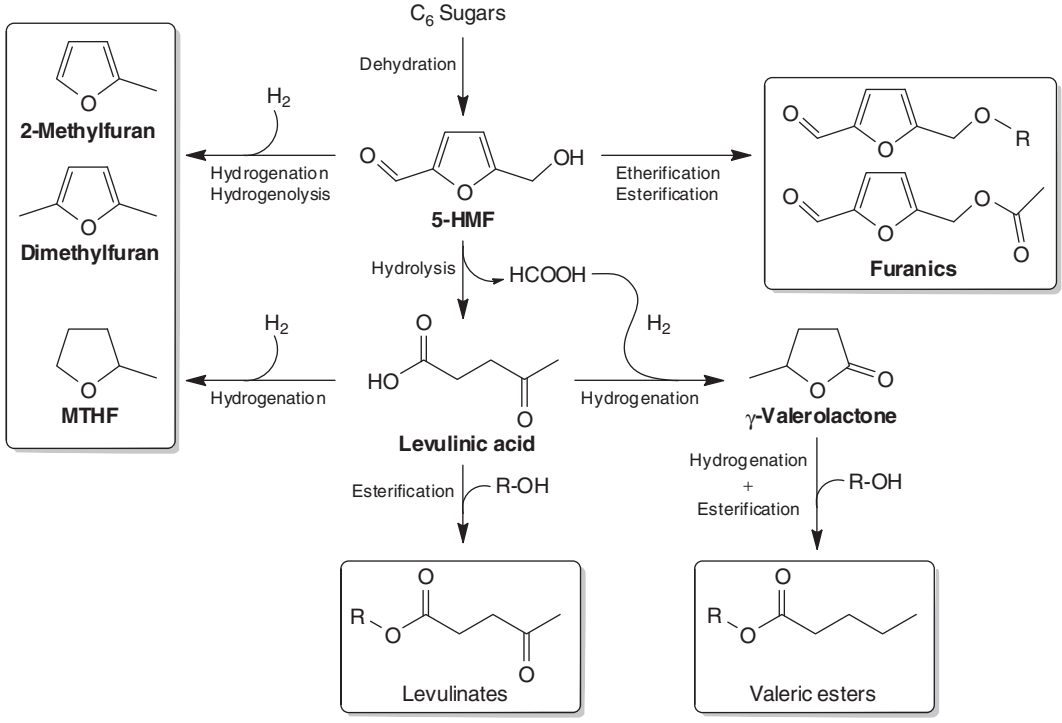


Fig. 6.1: Routes for the production of oxygenated biofuels from 5-HMF platform molecules.

compared with gasoline is compensated by its higher specific gravity, which results in similar mileage to that achieved with gasoline. Direct conversion of LA to MTHF is possible. However, improved yields can be achieved through indirect routes, which proceed through the production of γ-valerolactone as an intermediate. γ-valerolactone can be reduced to 1,4-pentanediol and subsequently dehydrated to MTHF with a total consumption of three moles of external H_2 from LA to MTHF (Elliot and Frye 1999).

Esters of LA produced from either methanol or ethanol have significant potential as blend components in diesel formulations. LA esters are quite similar to the biodiesel fatty acid methyl esters (FAME) that are used in some low-sulphur diesel formulations, but they do not have their principal drawbacks (cold flow properties and gum formation). The addition of ethyl or methyl levulinate to FAME would be expected to alleviate these problems. The most studied among the LA esters is a low-smoke diesel formulation developed by Biofine and Texaco that uses ethyl levulinate (made by esterifying LA with fuel-grade ethanol) as an oxygenate additive. The 21:79 formulation consists of 20% ethyl levulinate, 1% co-additive, and 79% diesel and can be used in regular diesel engines. The oxygen content of ethyl levulinate (EL) is 33 wt%, giving a 6.9 wt% oxygen content in the blend, resulting in a significantly cleaner-burning diesel fuel (Texaco/NYSERDA/Biofine 2000). The ethyl levulinate blend originates lower sulphur emissions than does regular diesel. This is due to the fact that ethyl levulinate contains no sulphur. The sulphur level of diesel is reduced in the refinery using a hydrotreating process; this causes an undesirable removal of some of the lubricity components from the fuel and hence a decrease in diesel lubricity. The addition of EL, with high lubricity, will therefore mean that diesel blend stocks of low lubricity, and hence lower S content, can be used without decreasing the overall lubricity of the end product. Importantly, the significant losses of engine efficiency (a decrease of up to 15% in the distance driven per volume unit is found with other diesel oxygenates such as ethanol) do not occur with ethyl levulinate. This is due to the high energy content of the 21:79 formulation. Finally, the production of levulinic acid esters from LA formed by the Biofine process has an added advantage over conventional bioesters because there is no co-production of glycerol, which would have to be disposed of. Recently, a dual catalytic system has been reported for the one-step synthesis of methyl levulinate from cellulose. In this work, the combination of two homogenous catalysts, metal triflates (Lewis catalyst), and sulfonic acids (Brönsted acids) lead to a yield of methyl levulinate up to 75% under the best reaction conditions in the presence of methanol at 180°C (Tominaga et al. 2011).

GVL can be hydrogenated to valeric acid and subsequently esterified with alcohols to yield alkyl valerate esters (valeric biofuels) (Lange et al. 2010). Gasoline blended with 10% and 20% of ethylvalerate (EV) largely comply with European gasoline specifications and even EV blends show an enhancement of some gasoline properties (increasing of octane number and lowering of aromatics, olefins, and sulphur contents). Likewise, EV also offers the advantages of possessing higher energy density and lower blending volatility than ethanol. Heavier esters, such as butyl and pentylvalerates, exhibit polarity, volatility, and ignition properties that are suitable for diesel.

6.2.1.4 Catalytic transformation of 5-HMF and derivates into chemicals

5-HMF has a high potential demand at the industrial scale since it is a versatile molecule that can be converted into several derivatives with multiple applications

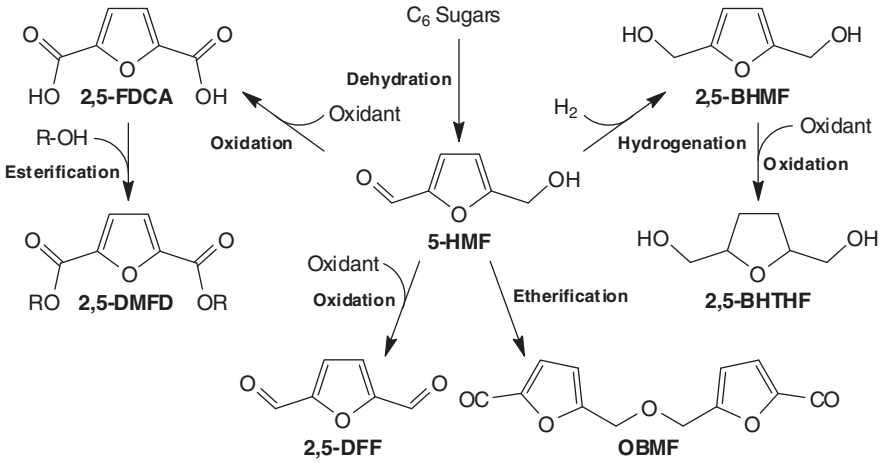


Fig. 6.2: Routes for the production of valuable chemicals from 5-HMF platform molecules.

(pharmaceuticals, fungicides, and polymer precursors; Climent, Corma, and Iborra [2011] and Tong, Ma, and Li [2010]). ▶Fig. 6.2 outlines the possible routes of transformation of 5-HMF into chemicals.

2,5-Furandicarboxylic acid (2,5-FDCA) and dimethyl ester (DMFD) are able to replace terephthalic, isophthalic, and adipic acids in the manufacture of polyamides, polyesters, and polyurethanes. Recently, the oxidation of 5-HMF to these target compounds has been successfully carried out with air using Au supported catalysts (Casanova, Iborra, and Corma 2009; Gorbanev et al. 2009). 2,5-Furandicarboxaldehyde (2,5-DFF) is a versatile compound, and there are numerous reports describing various useful applications as a monomer and as a starting material for the synthesis of pharmaceuticals, fungicides, and new polymeric materials. 2,5-DFF is obtained by oxidation of 5-HMF and, in particular, air oxidation over vanadium oxide catalysts in the presence of different solvents has shown interesting results (Moreau et al. 1997). 2,5-Bis(hydroxymethyl) furan (2,5-BHMF) is used in the manufacture of polyurethane foams, and the fully saturated 2,5-bis(hydroxymethyl)tetrahydrofuran (2,5-BHTHF) can be used as an alkyl diol in the preparation of polyesters and as coating solvents. Both compounds are obtained by reduction under high temperatures (140°C–200°C) and hydrogen pressures (70–75 bar) using conventional Cu/Pt and Ni/Pd catalysts. Finally, 5,5-(oxy-bis(methylene)) bis-2-furfural (OBMF) is an interesting precursor for the preparation of imine-based polymers and hepatitis antiviral precursors. The route leading to OBMF takes place through etherification. Although homogenous catalysts have been reported, such as using NaOH (Williamson etherification) and *p*-toluenesulfonic (acid catalyzed reaction), the large amount of waste, which is formed from acid and base neutralization, is an important drawback. Recently, the use of micro- and mesoporous aluminosilicates with Brönsted and Lewis sites has been reported, for instance Al-MCM-41 working with trifluorotoluene as solvent at 100°C gave a 99% OBMF yield in just one hour of reaction (Casanova, Corma, and Iborra 2010).

On the other hand, the family of chemical compounds available from LA is also quite broad. For instance, LA could be used for the production of acrylic acid and succinic

acid via oxidative processes. The production of LA-derived lactones offers the opportunity to enter into a large solvent market, as these compounds may be converted into analogs of N-methylpyrrolidinone. Complete reduction of LA leads to 1,4-pentanediol, which could be used for the production of new polyesters.

6.2.2 Dehydration of pentoses into furans: synthesis of furfural and derivatives

Hemicellulose is one of the main structural components of plants. Chemically, it can be described as a rather heterogeneous polymer of pentoses (xylose, arabinose, etc.), hexoses (mannose, glucose, galactose), and sugar acids. Hemicellulose can account for more than 80% of leaves, although it is present in lower amounts (30%–40%) in woody biomass (Mohan, Pittman, and Steele 2006). In contrast with cellulose, hemicellulose can be easily hydrolyzed with dilute acids under moderate conditions, yielding a mixture of sugars. Among them, xylose is one of the most abundant, as it constitutes up to 30% of the hydrolyzate of corn stover (Kumar et al. 2009). In a similar way to the formation HMF from hexoses, dehydration of pentoses results in the production of furfural, which has been proposed as a viable platform chemical to be integrated in biorefineries (Bozell and Petersen 2010).

6.2.2.1 Synthesis of furfural: dehydration of xylose

Furfural is usually obtained from agricultural raw materials rich in pentoses (e.g. corncobs, oat hulls, bagasse, etc.). Subsequently, furfural can be used as a raw material for the synthesis of several nonpetroleum-derived chemicals such as furfuryl alcohol, methyltetrahydrofuran (MeTHF), and furan (▶Fig. 6.3). Currently furfural is produced in a hydrolysis process using ground-up biomass pretreated with sulfuric acid and hot steam (Xing, Qi, and Huber 2011). In this process, furfural must be removed to avoid further reaction dehydration to solid carbonaceous byproducts called humins. The overall theoretical yield for this process is 0.73 kg of furfural per kg of pentose, but in practice only around 33% of the theoretical yield is achieved.

When employing pure xylose solutions, biphasic reactors have proved to be very effective for the selective production of furfural. Thus, a biphasic reactor using methylbutyl ketone and acidified water can achieve 85% furfural yield, while the treatment of the pure aqueous solution results in a yield of only 30%. This behavior is due to the fact

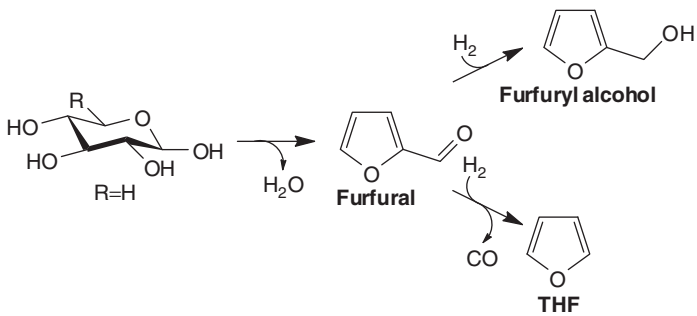


Fig. 6.3: Routes for the production of valuable chemicals from furfural.

that furfural is dissolved in the organic phase that, consequently, avoids the formation of undesired carbonaceous compounds (Weingarten et al. 2010). In these experiments the use of microwave heating increased slightly the efficiency of the process, while the addition of salts to the aqueous solution promoted the extraction of furfural to the organic component. Although most of the tests with biphasic media have used batch-type reactors, recently the application of continuous reactor systems to this process has been reported (Xing, Qi, and Huber 2011). In this process, furfural yields of over 90% can be achieved using a hemicellulose extract from hardwood chips treated in hot alkaline solutions. According to author estimations, the cost of furfural obtained from this method is about 25% that of the market value of this product, so it may become competitive.

Dehydration of xylose into furfural has also been studied using a great variety of heterogeneous catalysts from supported heteropolyacids to ion exchange resins. In general, the selectivity of the dehydration was moderate, consistent with the low yield usually attained for the conversion of xylose to furfural in diluted acids. In general, it has been found that, although all types of acidic sites catalyze dehydration of C_5 sugars, Brønsted acidity enhanced the selectivity to furfural. In contrast, Lewis centers decrease the yield of furfural because they promote the formation of humins (Weingarten et al. 2011). Biphasic systems also provide better results when using heterogeneous catalysts. Thus, treatment of xylose in a toluene-water mixture at 160°C using modified acidic zirconia catalysts gave a 45% selectivity toward furfural at 95% conversion. Recently, higher yields of furfural (up to 74%) have been obtained using composite catalysts consisting of zeolite beta nanocrystals (Si/Al = 12) embedded in a purely siliceous TUD-1 mesoporous matrix (Lima et al. 2010).

6.2.2.2 Catalytic transformation of furfural into chemicals

The main product prepared from furfural with industrial relevance is furfuryl alcohol (FFA), which is obtained by catalytic hydrogenation. This product is widely used for polymer production, fine chemicals, and especially for applications in agriculture. The production of FFA is expected to increase on average at a rate of 5% annually during next few years, being currently led by China, which produces more than 55,000 tons per year (Mammam et al. 2008). Gas-phase hydrogenation is adopted in most chemical plants, while liquid-phase hydrogenation is more commonly used in Chinese facilities.

During the hydrogenation of FFR, the main byproduct formed is 2-methyl furan, which results from further hydrogenation of the alcohol. In addition, successive decarboxylation and hydrogenation may lead to tetrahydrofuran (THF). The presence of catalysts plays an important role in these processes, as they can improve the selectivity. In general the best results have been obtained using copper-based catalysts. Copper chromite was traditionally used for this process but new formulations have lately been developed due to the toxicity of chromium. Recently, a comparison between Cu, Ni, and Pd catalysts supported on SiO_2 for the hydrogenation of furfural has been carried out (Sitthisa and Resasco 2011). This work shows that Pd and Ni favors decarboxylation and ring hydrogenation and consequently presents a higher yield to furan and THF. In contrast Cu/SiO_2 shows a very high selectivity to FFA (>98%) and relatively high conversion (69%) at 230°C at atmospheric pressure. Remarkable selectivity to FFA can also be obtained using amorphous metallic alloys for furfural hydrogenation in ethanol solutions. Thus, good results at very mild conditions have been attained using Ni-P-B

alloys, leading to selectivity toward FFA larger than 80% at 50% conversion working at 80°C under atmospheric pressure (Lee and Chen 1999).

6.3 Catalytic routes for the aqueous-phase conversion of sugars and derivatives into liquid hydrocarbons for transportation fuels

In the past few years, new routes for the transformation of a variety of biomass derivatives, such as sugars, into liquid fuels in aqueous media and using different catalysts have been proposed. Especially remarkable in this direction are the contributions and processes developed by the group led by Professor J. Dumesic (Serrano-Ruiz and Dumesic 2011). The fundamental advantage of these routes, in comparison with traditional gasification and pyrolysis processes for the transformation of biomass, is the use of mild reaction conditions, which allows for a better control of the selectivity toward the targeted products. However, catalytic treatments of aqueous solutions are relatively complex, they require a series of pretreatments of the biomass and produce lignin residues, which should be energetically valorized by combustion. In any case, it is foreseeable that further research and development of these novel routes could overcome some of the current drawbacks, and they can become competitive for specific applications.

The production of hydrocarbons from chemicals derived from biomass implies profound chemical transformations in order to decrease the functionality provided by the high oxygen content of these products of biological origin. Another significant limitation is that sugar molecules are formed by five or six carbon atoms, but liquid hydrocarbons for transportation fuels have a larger chain (up to C_{20} for diesel). Consequently, very efficient catalysts for deoxygenation and oligomerization processes in aqueous solutions must be developed. In addition, two aspects are crucial to ensure the economic feasibility of the aqueous phase route: (1) reduction of the number of processing steps and (2) deoxygenation should proceed with minimal consumption of hydrogen from external sources.

6.3.1 Conversion of HMF and furfural platform chemicals into hydrocarbon fuels

Furfural and HMF can be used as feedstocks for the production of n-alkanes, adequate for formulating diesel and jet fuels, by means of successive reactions of dehydration, hydrogenation, and aldol-condensation. The different alternatives existing in this way in the case of HMF are displayed in ▶Fig. 6.4. In aldol condensation reactions, which are essential for obtaining hydrocarbons with longer chains, the carbonyl group in the furan molecules reacts with other carbonyl-containing molecules, such as acetone, which can also be obtained from biomass-derived sources (Serrano-Ruiz, Wang, and Dumesic 2010). These reactions are performed typically in aqueous solutions using base catalysts such as NaOH or Mg-Al oxides. The condensation reaction must take place several times to obtain chemicals with larger carbon chains and in order to adjust the properties of the final fuel. The process may also require hydrogenation reactions to remove C=C groups. The bulky compounds generated from aldol condensation present a reduced polarity, and consequently they are separated spontaneously from water solutions. This fact can be further promoted using biphasic reactors with an aqueous and an organic

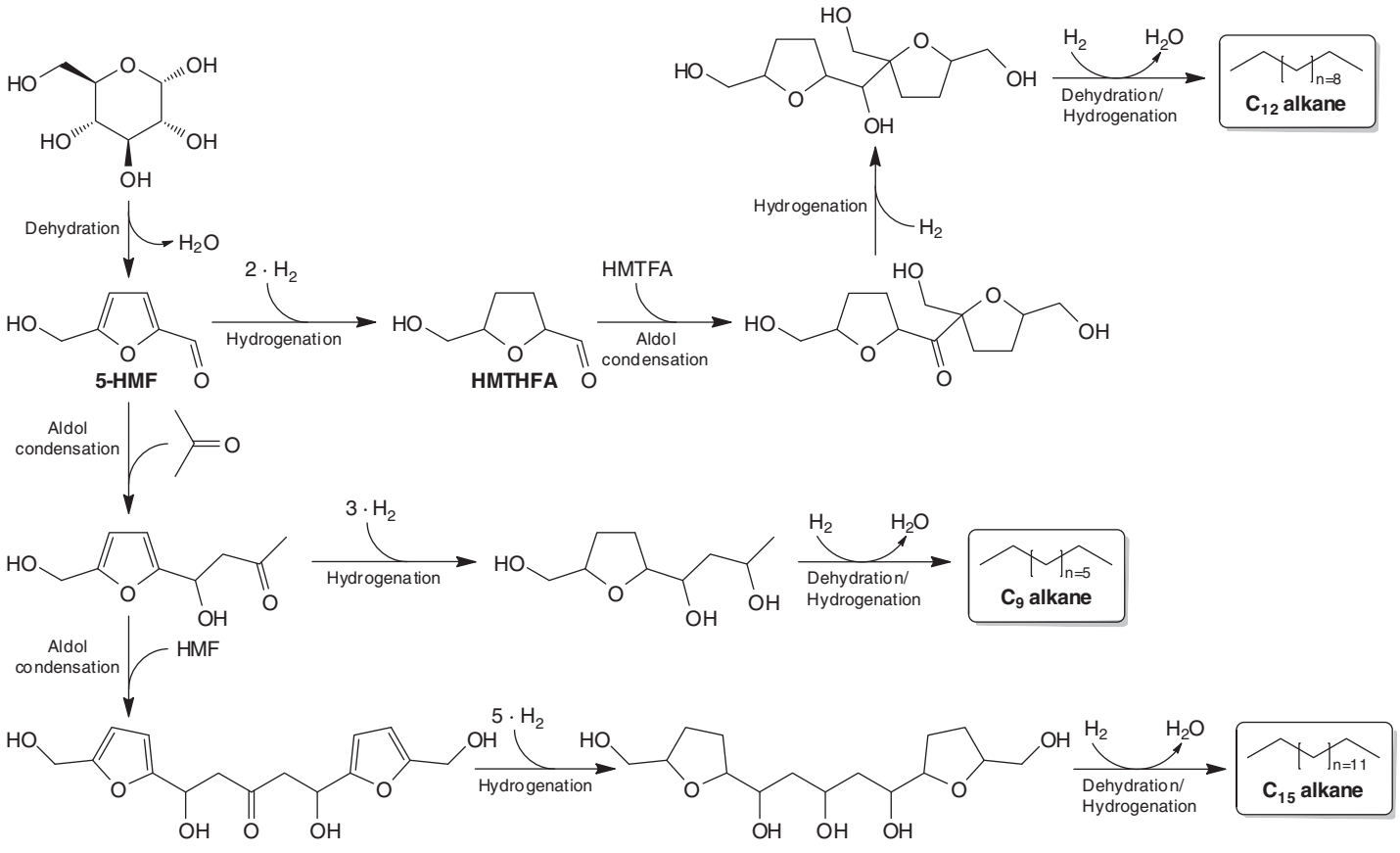


Fig. 6.4: Routes for the production of hydrocarbons from HMF in an aqueous solution.

phase (e.g. THF), which accumulates the products of the condensation, shifting the equilibrium. In order to deal with the complexity of this process it is convenient to use bifunctional catalysts formed by both a metal with hydrogenation activity and support with base sites. In this respect, the use of the water-stable Pd/MgO–ZrO_2 catalyst has provided an overall carbon yield of about 80% (Barret et al. 2006).

The last step of the process involves the production of hydrocarbons, which makes necessary the removal of the oxygen present in the furan ring. This process takes place through aqueous-phase dehydration/hydrogenation (APD/H) reactions, requiring multiphasic reactors and the use of catalysts with both metallic and acidic centers. Among them, the most promising results have been obtained using a Pt/$NbPO_4$ catalyst (Serrano-Ruiz, Wang, and Dumesic 2010), which leads to the production of liquid hydrocarbon fuels having molecular weights within the targeted (C_9–C_{15} for HMF and C_8–C_{13} for furfural) with an overall carbon yield of 60%. However, despite these encouraging results, the inherent complexity of this process with multiple steps and multiphasic processes makes this route difficult to implement at a commercial scale.

6.3.2 Aqueous phase reforming of sugars

One of the main drawbacks of the synthesis of hydrocarbons from biomass feedstocks is the need to consume large amounts of hydrogen. This fact is detrimental for the overall CO_2 emission balance of the process because hydrogen is produced at present mainly by natural gas reforming, and it also contributes to increasing the operation costs. In order to decrease the demand for hydrogen, an alternative is the catalytic reforming of oxygenated chemicals from sugars (Davda and Dumesic 2004) in liquid water under moderate-temperature conditions, This process is known as aqueous phase reforming (APR), and it allows large quantities of hydrogen to be generated in liquid phase. Cleavage of C–C, C–H, and O–H bonds are the initial sources of hydrogen production by APR, although further enrichment is achieved due to the fact that a water-gas-shift reaction is favorable in these conditions, resulting also in very low amounts of carbon monoxide.

The starting point of APR is an aqueous solution typically formed by sugars and polyols, which in a two-step process are transformed into liquid hydrocarbons (Kunkes et al. 2008) according to the route depicted in ►Fig 6.5. First, glucose and related molecules are converted into a mixture of oxygenated compounds (e.g. acids, alcohols, ketones, and heterocycles) in the C_4–C_6 range, which are sequestered in the organic component of the biphasic reactor. This step is carried out at temperatures of about 230°C over a Pt–Re/C catalyst, which can remove up to 80% of the oxygen present in the feedstock by means of C–O hydrogenolysis reactions activated by the hydrogen generated in situ. In fact, a Pt–Re/C material acts simultaneously as reforming and hydrogenation catalysts. However, complete deoxygenation is not pursued at this stage because functional groups formed from the hydrogenolysis of sugars are necessary for the subsequent C–C coupling. For this last purpose, different processes can take place depending on the chemical nature of the intermediates, including oligomerization, aldol-condensation, and ketonization. In this way, alcohols can be converted over H-ZSM5 zeolite at atmospheric pressure to yield 40% of C_{6+} aromatic gasoline components. Ketones can be upgraded to larger hydrocarbon compounds (C_8–C_{12}) with low branching by means of aldol-condensation reactions over bifunctional (metal and base) Cu/$Mg_{10}Al_7O_x$ catalysts.

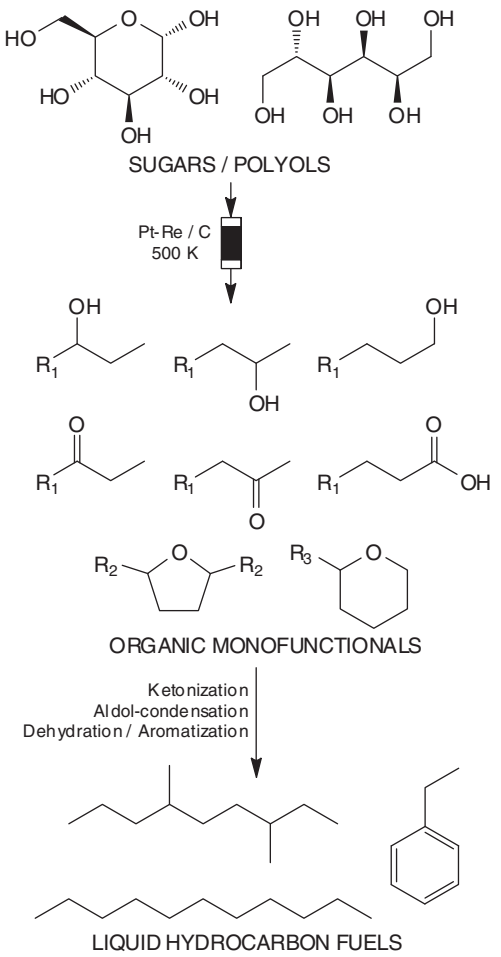


Fig. 6.5: Scheme of the process for the catalytic conversion of sugars and polyols into liquid hydrocarbon fuels by APR.

More problematic is the treatment of carboxylic acids, which cause deactivation of the basic catalytic sites. Consequently, it is necessary to transform these compounds, which are present in high proportions when using glucose in the feed, by ketonization before subsequent aldol condensation (Serrano-Ruiz and Dumesic 2011). Coupling of acid and ketones can be performed with high yield at very mild conditions (250°C and atmospheric pressure) using ZrO_2-CeO_2 catalysts (Gaertner et al. 2010).

Although the hydrogen production by means of biomass-derived APR is an attractive option, the alkane synthesis pathways have attracted much attention recently. Evidence of this interest is the process licensed by Virent Energy Systems, the Bioforming process (Dumesic and Roman-Leshkov 2009). Preliminary economic analysis suggests that converting sugars into conventional liquid fuels using this technology can economically compete with petroleum fuels at crude oil prices greater than $60/bbl.

6.3.3 Conversion of levulinic acid platform into hydrocarbon fuels

Levulinic acid (4-oxopentanoic acid) has been identified as one of the top 10 platform molecules for the production of value-added chemicals and liquid transportation fuels in biorefineries (Bozell and Petersen 2010). As mentioned in section 6.2, this compound can be produced from the acid treatment of C_6 sugars with relatively high yield (higher than 60% but accompanied by an equal molar amount of formic acid), whereas its isolation and purification is a complex process. Recently, the group led by Dumesic has proposed an interesting route for the conversion of this compound into hydrocarbons via hydrogenation leading to γ-valerolactone (GVL). This process can achieve very high yields (96%) when operating at about 150ºC and high pressure (35 bars) using non-acidic catalysts, such as Ru/C, for avoiding coke formation (Serrano-Ruiz, Wang, and Dumesic 2010). Subsequently, aqueous solutions of GVL can be upgraded to liquid hydrocarbon fuels by following either of these two pathways: the C_9 route and the C_4 route, as shown in ▶Fig. 6.6. In the former route, GVL is first transformed into pentanoic acid by means of ring-opening (on acid sites) and after hydrogenation reactions (on metal sites) at moderate temperatures and pressures. Using a Pd/Nb_2O_5 catalyst, a yield of 95% can be obtained. Pentanoic acid is subsequently ketonized to 5-nonanone. Since this process takes place at a different temperature, optimal results (90% yield) can be obtained by using a dual catalyst bed with Pd/Nb_2O_5 for the formation of the acid and $Ce_{0.5}Zr_{0.5}\ O_2$ for the ketonization. 5-nonanone spontaneously separates from water, being subsequently hydrogenated into the corresponding alcohol. Finally, the C_9 alcohol can be further transformed via hydrogenation/dehydration over the Pd/Nb_2O_5 catalyst into n-nonane. Alternatively, the 5-nonanol can be upgraded using acid catalysts into a number of hydrocarbons, including different isomers and long-chain alkanes obtained by oligomerization.

More recently, a promising route to upgrade aqueous solutions of GVL into jet fuels through the formation of C_4 alkenes has been developed by Bond et al. (2010). The process is based on a dual reactor system. In the first catalytic reactor, the GVL feed undergoes decarboxylation at relatively elevated pressures (e.g. 36 bars) over a silica/alumina catalyst, producing a gas stream composed of butene isomers and CO_2. In a second reactor, connected in series, the gaseous butene stream is passed over an acidic catalyst (H-ZSM5, Amberlyst 70) that promotes the oligomerization of butene monomers, yielding a distribution of alkenes with a maximum contribution for C_{12}. In order to avoid the poisoning of the acidic sites, water must be removed before the second stage. The maximum overall yield to C_{8+} alkenes reaches 75%. Accordingly, this can be considered a very promising process with low hydrogen consumption and is potentially competitive with other technologies.

6.4 Future outlook

The feasibility of transforming carbohydrates into valuable compounds by dehydration followed by oxidation, hydrogenation, and acid/base catalyzed reactions has been clearly evidenced in this chapter. In order to improve these processes and enhance their commercial viability is important to avoid costly separation and purification steps, which could be achieved by the conversion of the carbohydrate

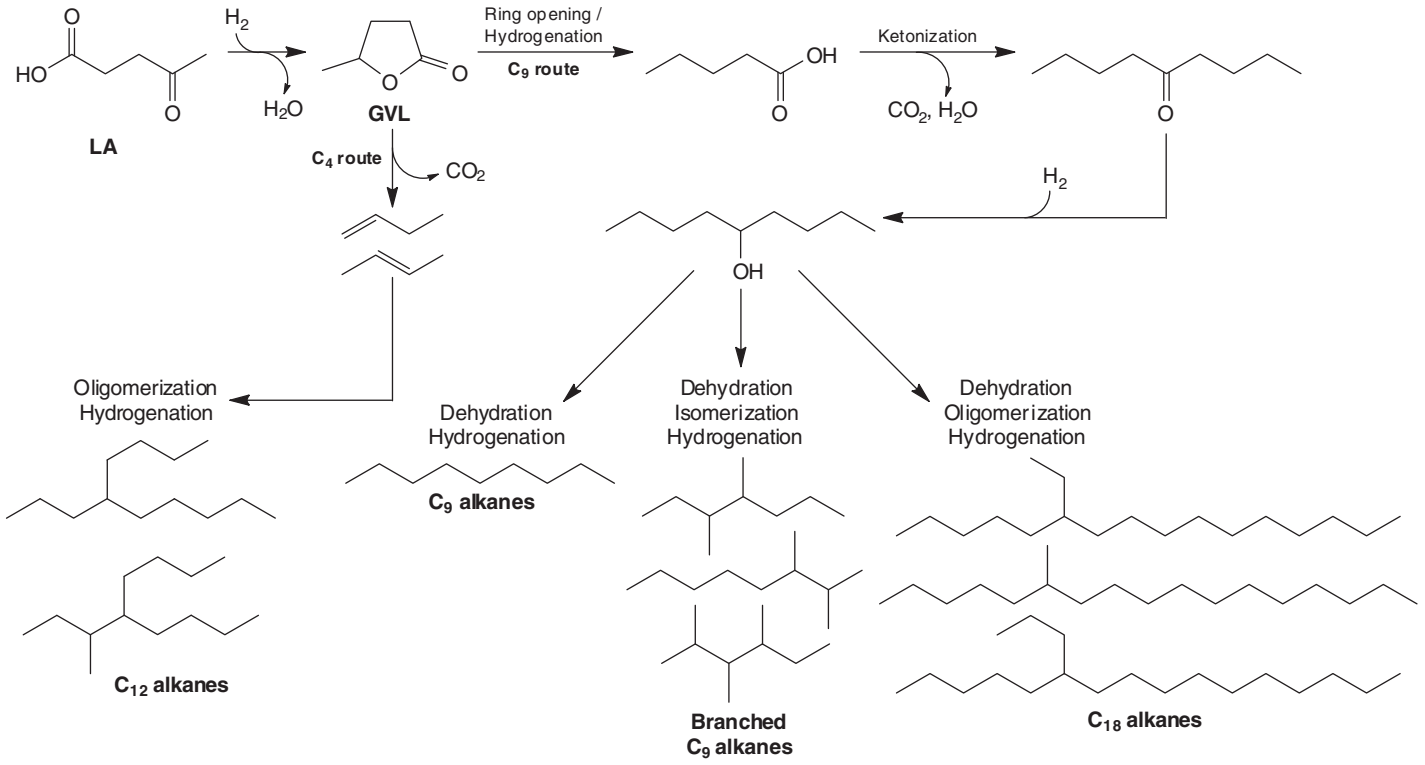


Fig. 6.6: Scheme of the process for the catalytic conversion of levulinic acid into liquid hydrocarbon fuels.

(or, even better, of the raw polysaccharide) in a one-pot reaction. In this sense, the design of novel multifunctional catalysts, suitable to work efficiently in water or biphasic media, is a field that offers a great potential for novel developments in the future. Conversion of biomass into functionalized targeted platform molecules is unique to hydrolysis-based methods and allows the production of a wide range of fuel components and chemicals. Among the different platform molecules that can be obtained, furfural (2-furaldehyde), 5-hydroxymethylfurfural (5-HMF), and levulinic acid (LA) are of high interest for the production of industrial solvents, polymers, and fuel additives.

On the other hand, recent works have shown the interest of new routes for the catalytic transformation of some biomass derivatives in the aqueous phase, such as sugars, into liquid fuels. The fundamental advantage of these routes, in comparison with gasification and pyrolysis processing of biomass, is the mild reaction conditions employed, which provide a better control of selectivity. However, catalytic treatments of aqueous solutions are relatively complex, they require a series of biomass pretreatments, and produce lignin residues. The need of optimizing these processes in terms of number of treatments is evident for developing processes that are competitive regarding the traditional ones and that can be applied at a commercial scale.

The production of hydrocarbons from biomass-derived compounds implies profound chemical transformations in order to decrease the functionality provided by the high oxygen content of these products of biological origin. Another significant limitation is originated by the fact that sugar molecules are formed by five or six carbon atoms, because liquid hydrocarbons for transportation fuels have a larger chain (up to C_{20} for diesel). Consequently, very efficient catalysts for deoxygenation and oligomerization processes in aqueous solutions must be developed. In addition, two aspects are crucial to ensure the economic feasibility of the aqueous phase route: (1) reduction of the number of processing steps and (2) deoxygenation with minimal consumption of hydrogen from an external source.

In achieving these goals, it is foreseeable that these novel routes may become competitive alternatives to traditional processes for the transformation of biomass into biofuels and chemicals.

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7 Conversion of cellulose, hemicellulose, and lignin into platform molecules: biotechnological approach

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7.1 History of bioethanol from wood

As far back as 100 years ago, production of bioethanol from lignocellulosic biomass was in full operation. Hemicellulose in spruce contains around 80% hexoses. When using spruce as feedstock in acidic sulfite pulping, hemicellulose is dissolved and hydrolyzed to monosaccharides. Typical compositions of such spent sulfite liquors (SSL) are shown in ▶Tab. 7.1. In SSL samples from spruce there are high amounts of hexoses, which can be fermented by baker's yeast (*Saccharomyces cereviciae*) to ethanol.

The first plant to produce sulfite ethanol is claimed to be the Skutskär sulfite plant in Sweden, which started production of sulfite ethanol in 1909 (Persson 2007). In Sweden, total capacity peaked in 1950 at 85,000 m^3 of ethanol. In all, there have been 33 such plants in operation in Sweden, of which only one (Domsjö) is still in operation today. In Finland, a total of 17 sulfite ethanol plants were in operation sometime between 1927 and 1990, but none are in operation today (Kaukoranta 1981; Niemelä 2008, 2010). In Norway, four sulfite ethanol plants have been in operation, of which only Borregaard still operates today. Attizholts in Switzerland produced sulfite ethanol from 1912 to 2008. In Canada, Tembec is still in operation. Georgia-Pacific closed down their sulfite ethanol production in Bellingham, United States, in the end of 2001. Several Russian sulfite mills have also produced ethanol from hydrolyzed hemicellulose until quite recently. Their status is not known to the authors, but nonconfirmed rumors indicate that the Kirov plant is still in operation. The Borregaard plant in Norway is the largest producer of second-generation bioethanol produced from lignocellulosics today, with an annual capacity of 20,000 m^3. Kimberley-Clark plans to start up SSL fermentation at their mill in Everett (Washington State, USA) to produce bioethanol and has, in addition, plans to hydrolyze cellulose fines rejected from their processes to sugar solutions to boost their ethanol production (Ross, Sande, and Asbe 2010). Nippon Paper, at their Gotsu mill in Japan, has plans to start sulfite ethanol production of 10,000 m^3 capacity, and M-Real in Hallein in Austria is evaluating the start of sulfite ethanol production of 6,000 m^3 capacity in 2016.

Bioethanol has also been produced from the cellulose part of wood. In the period from 1935 to 1985 in the former Soviet Union, wood was hydrolyzed by weak sulfuric acid at 130–150°C in one or two steps to form sugars in solution. This was the basis for 18 ethanol plants, 16 single-cell protein (SCP) plants, and 15 furfural and xylitol plants (Rabinovich 2009). Feedstock was both softwood and hardwood, and from 1960 it was also potatoes. These plants have all been stopped since they were not profitable due to the fact that the process gives low yields and produces high amounts of lignin side streams that are hard to utilize, even for energy, because of the acid contamination.

There are many excellent recent review papers in the field of second-generation bioethanol and lignocellulosic biorefineries (Sims et al. 2008; Haigwood and Durante

Tab. 7.1: Typical sugar content of spent sulphite liquors (SSL) from eucalyptus and spruce in weight % of dry matter (DM). Analysis performed by the Borregaard quality control laboratories.

Monosaccharide	% of DM in SSL from eucalyptus	% of DM in SSL from spruce
Arabinose (C5)	0.3	0.8
Xylose (C5)	21.9	5.3
Galactose (C6)	1.6	2.1
Rhamnose (C6)	0.6	0.2
Glucose (C6)	1.6	3.7
Mannose (C6)	1.0	14.6

2009; Pandey 2010), and this chapter will not repeat that work; rather, this chapter will emphasize some conclusions from the point of view of optimizing the total output of a range of valuable chemicals (i.e. the biorefinery concept). Steam explosion, often combined with a chemical treatment (dilute acid, ammonia, sulfur dioxide, etc.), seems to be the most common pretreatment process for opening up the cellulose structure and preparing for the hydrolysis in the next process as promoted by SunOpta BioProcess (now Mascoma) and others (BEAN 2011; BioGasol 2011). Many industries and scientific groups around the world are, despite the long history of low yield and noneconomical acid hydrolysis pretreatment of lignocellulosics to bioethanol (U.S. Department of Energy 2011), working on weak acid hydrolysis of lignocellulosic biomass as a pretreatment and hydrolysis technology. According to the U.S. Department of Energy the upper limit for sugar conversion by weak acid hydrolysis of lignocellulosic biomass was established at 70% in the 1980s. A few companies are developing strong acid pretreatment processes with regeneration of the acids by solvent extraction (Weyland), ion exchange resins (BlueFire), or membrane technology (TNO). Enzymatic hydrolysis has attracted more attention over the past few years since higher yields are easier to achieve. The cost of enzymes is still a challenge. New or modified pulping processes also seem to attract more attention. Most development in this field is focused on increasing the yield and reducing the cost of bioethanol production. A few demonstration plants produce a range of products like Inbicon's demo plant in Kalundborg in Denmark (Inbicon 2011).

Whenever there is a possibility to produce chemicals, materials, and other products from lignin and pentoses with a higher value than just the energy value of these side streams, and the increase in value more than covers the additional processing costs, there is potential for improved profitability. This way of thinking has been perfected by the oil refineries and it has already been pointed out that biorefineries must follow the same route (Bozell 2010). Unfortunately, there seems to be an overvaluation of the lignin products from many processes and even a widespread ignorance of the wide range of properties of lignins depending on plant species and processing conditions. Basically, many of the pretreatment processes render lignins unsuited for anything other than energy because of their high temperatures and chemical conditions. Condensation and removal of reactive sites as well as large amounts of impurities are often the results of the pretreatment and hydrolysis process, leaving lignins insoluble in any solvent and thus very hard to modify chemically.

7.2 Case history: 40 years experience from running a biorefinery

7.2.1 From commodity pulp to a range of specialty chemicals

Borregaard top management stated in the late 1950s that the company's strategy was to maximize the output of products from the wood it was processing. This was later changed to maximizing the output of chemicals from spruce. Pulp for paper from cellulose was produced from the very beginning in 1889 (▶Fig. 7.1). From 1938, the monosaccharides from hemicellulose (mainly mannose) were fermented to ethanol for chemical use (solvents and disinfectants, etc.). In 1967, when a process line for lignin and vanillin was installed, chemical products were produced from all of the three main components of spruce. At that time, other sulfite mills were already manufacturing lignosulfonates. Marathon Corporation (now Borregaard) in Wisconsin, United States, already produced vanillin from softwood lignosulfonates by the technology Borregaard later licensed from Du Pont to start their own vanillin production. Marathon later had to stop their vanillin production when the pulp mill supplying the SSL changed feedstock from softwood to hardwood.

In the period 1960–1980 a wide specter of products was produced from biomass, of which many were competing directly with fossil equivalents. The main reason that many of these product lines were stopped is due to competition from low-price fossil products or from countries with lower production costs. It is hard to compete on a global market on commodity products, like pulp and base chemicals, that can easily be produced at a lower cost in other places. Hence, Borregaard was forced to choose a niche strategy or move production to low-cost countries for production of commodities. Both have been attempted, but in the long term, only the niche strategy has turned out to be successful for Borregaard.

Looking at the history map of the Borregaard biorefinery (▶Fig. 7.1), the starting point was cellulose for paper. Later, by forward integration, fine paper was also produced on site. Quite early, there was a move to improve the business, so specialty cellulose was defined as a way to top the profitability seen in the 1920s. This is now the main product line and pulp for paper is no longer produced. For some time, textile fibers were produced and even spun from cellulose. This production was closed down when the textile industry moved to Asia. Still, specialty cellulose for fiber production is produced and even exported to Asia.

The hemicellulose process line is particularly interesting from a long-term development point of view. Ethanol production started in 1938, and was diversified to produce acetic acid and derivatives of acetic acid such as ethyl acetate and vinyl acetate. Even poly vinyl acetate (PVAc) was produced. The acetates were soon outcompeted by fossil equivalents and production stopped. Since the company still had a market position in the vinyl acetate and PVAc markets, it kept the production of the downstream products, and purchased the base chemical (acetic acid) they had just stopped producing on the open market. Thus, market position was a good basis for a harvesting strategy in a market segment that was no longer a main focus area.

Even more process lines based on ethanol were operational for many years. A range of branched higher alcohols were produced from ethanol by aldol condensation (▶Fig. 7.2). Borregaard also used to be a substantial supplier of dioctyl phthalate (DOP) for PVC plasticizers by esterification of phtallic acid with 2-ethyl-hexanol, a branched alcohol made from ethanol.

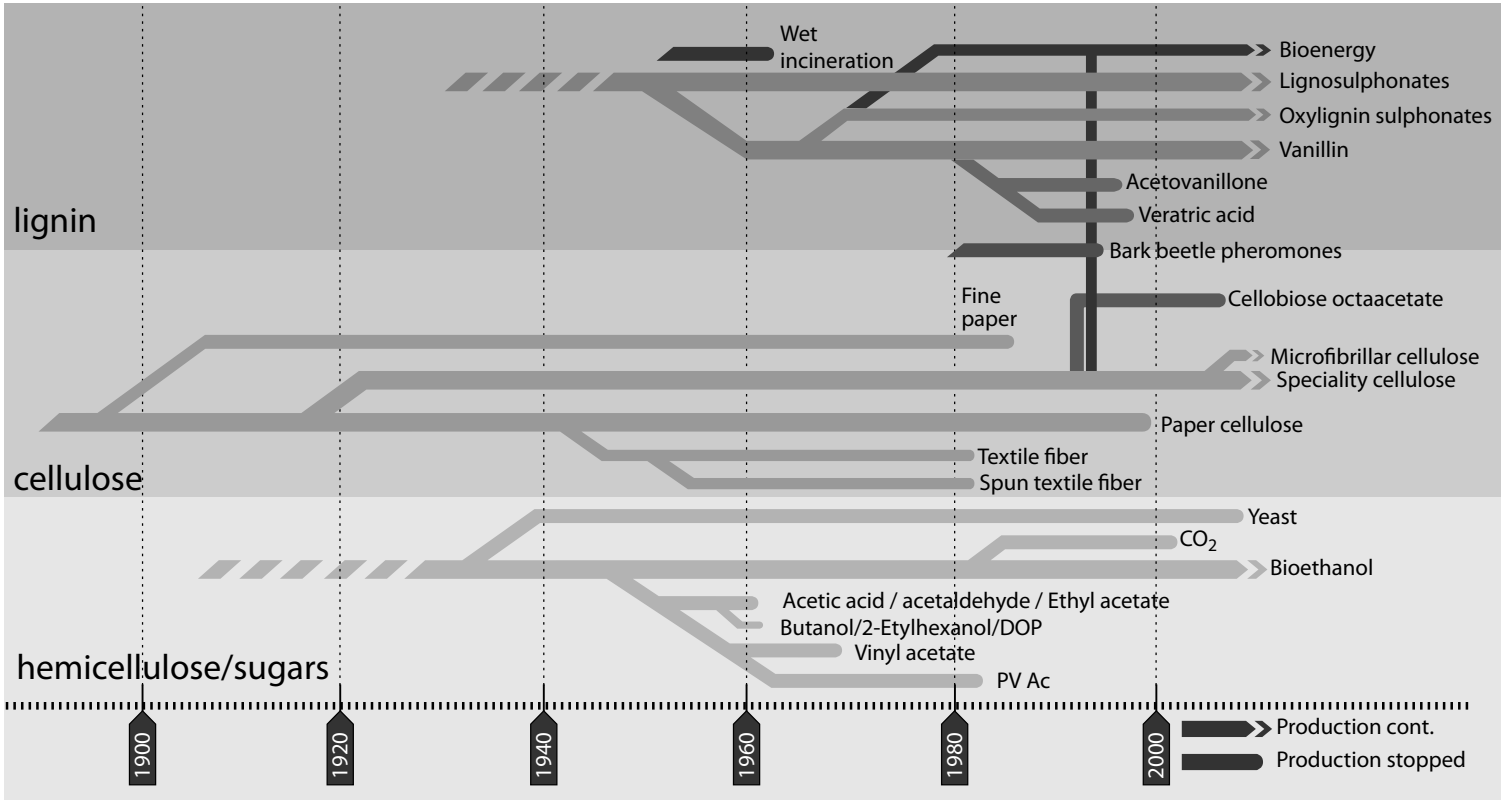


Fig. 7.1: Dynamics of the 120-year history of the Borregaard biorefinery.

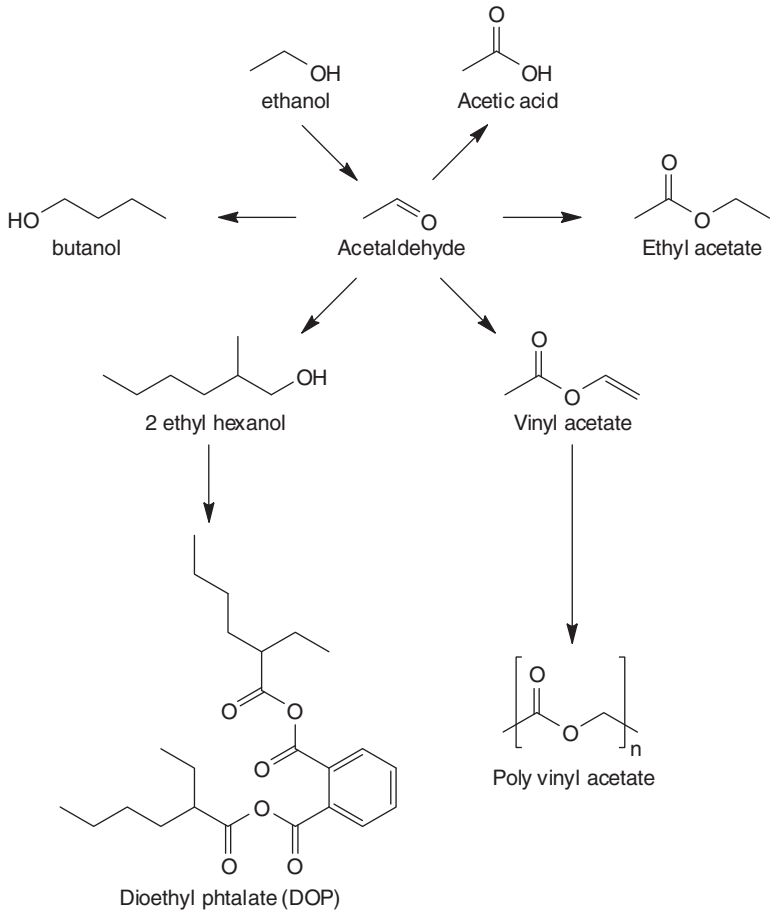


Fig. 7.2: Product tree from ethanol by aldol condensation reactions. Borregaard, 1960s and 1970s.

Vanillin is produced from purified lignin by air oxidation with a catalyst (Bryan 1954; Bjørsvik and Minisci 1999). At some stage, the petrochemical route to vanillin and ethyl vanillin seemed to outperform the biomass-based route because of cost efficiency. Fortunately, now the vanillin from lignin is preferred in some markets due to quality and the "green" image.

7.2.2 Profitability from a range of co-products

Over the years, the demands in the markets have become dynamic. During some periods one product line is the most profitable, and in other periods the same product line may be less profitable. As long as the product lines do not enter the same markets, their demand and price in the market may possibly be out of phase. This is a challenge for the manufacturing side, but substantially stabilizes the company performance from a business point of view.

From the viewpoint of one product line, there are several strategies to survive market fluctuations in a biorefinery, and one needs to be prepared to use them all. Transforming products to energy by incineration is one option, another is building stock to stabilize markets and reduce price fluctuations. In some markets there is a choice between products of different chemical composition but equal performance. Others may have the possibility to manage without using any of the products, likely at the cost of reduced performance. This will, of course, set a ceiling to their willingness to pay for the product. Price setting can, of course, also be used to alter the demand. All these options work only to a limited extent and must be used with care. It will still create quite a fluctuation in profitability for each single product line. The Borregaard biorefinery, having four main product lines (specialty cellulose, ethanol, lignins, and vanillin), runs these strategies in quadruple, which adds another level of complexity in deciding the optimal production level in times of surplus for some product lines and undersupply for others. In addition, being a global market leader, the company also needs to take on the responsibility of stabilizing markets and leveling out supply and demand. Again, the reward for taking on such a complex business model is a more stable profitability, as can be seen from ▶Fig. 7.3. Over the past few years, the pulp and paper industry in Europe as a whole has reached 5% return on capital employed (ROCE) at best, while Borregaard has achieved double that percentage.

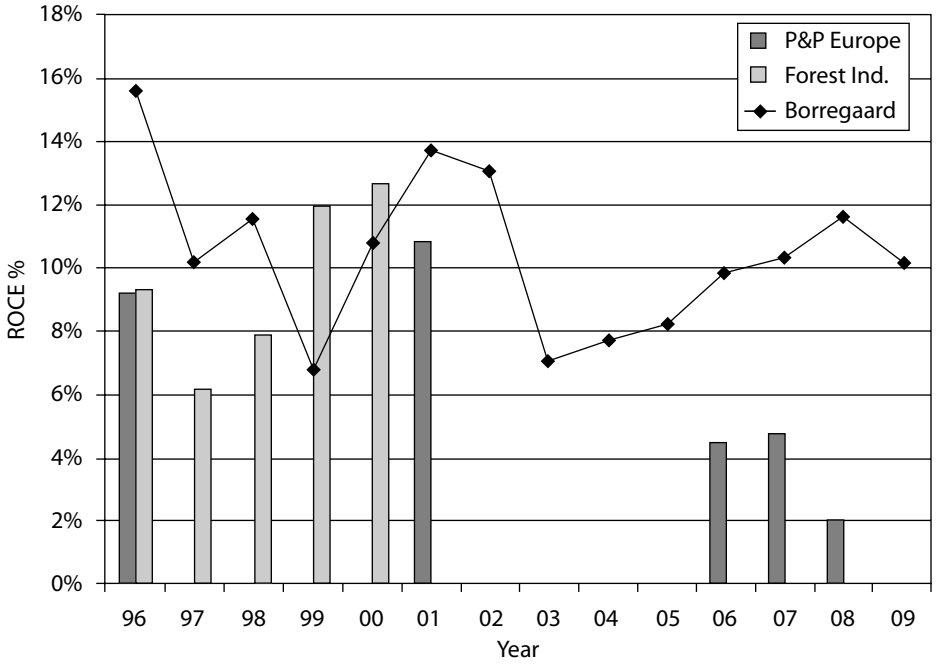


Fig. 7.3: Return on capital employed from Borregaard wood-based biorefinery compared to the traditional pulp and paper industry. P&P Europe figures gathered from CEPI (2011). Forest Ind. are figures from the global forest products industry gathered from Pöyry (2011).

7.2.3 Composition of feedstock is given – demand is never in balance

When processing biomass, the composition of the feedstock is given – there is a given ratio between cellulose, hemicellulose, and lignin in the biomass entering the plant. Since there is little possibility to swap output products based on different components, the main volumes of the output products are also given. The demand for these products is never in balance and it changes continuously. Because of natural dynamics in markets, the demand for some products will completely end, others will be more cyclic, and again others will increase steadily for periods of time. This is a major problem that every biorefinery needs to solve. In particular, for second-generation bioethanol, most processes do not have a valuable application for lignin or pentoses/xylans. This is not a sustainable solution.

7.2.4 Continuous need for product development

As mentioned, because of the dynamics in the markets, there will never be a balanced demand for all product lines in a biorefinery. From time to time, the demand for a product will just drop to zero permanently or be outcompeted by less-expensive equivalents and completely replaced. This can happen quite fast and even without much warning. First of all, it is very important to be in close contact with the market to catch these signals as early as possible. What is even more important is to develop new applications and products to take over in good time. It is normally too late to start this process when the changes happen, since development of new products and applications often takes 3–7 years from project start to full-scale production and sales. This timeline is valid only if the company already has experienced scientists in place. Otherwise it will take much longer. Thus, a biorefinery with a large range of specialty products depends heavily on both technical customer service and efficient and proactive research and development.

7.2.5 High-value biomass for products – low-value organic waste for energy

Every process needs energy. In a biorefinery, not only should the feedstock converted to products be from renewable resources but also the energy. High-value products often need high-value feedstock. Wood is likely the most costly biorefinery feedstock and should only be used for the final products, while side streams and other inexpensive biomass sources should be used for steam production. Since 2000, the Borregaard biorefinery has had a strategy to reduce the consumption of fossil energy in two ways. First, reduction of overall energy consumption, and second, by shifting more and more of the fossil-based energy to biobased energy. Electricity is produced from the plant's own hydropower plant, and steam is now produced by incineration of municipal waste, bark, and wet incineration of organic side streams. From the water purification plant, biogas is supplied to the spray driers for lignins. Currently only the top load of steam (from the boiler house) is supplied from fossil sources. This constitutes about 20% of the total heat/steam consumption. Plans are already in place to replace this by a combined heat and power (CHP) plant based on biomass by 2013. By then, all major input factors to the biorefinery (except for transports) will be from renewable resources.

7.2.6 Long-term commitment to sustainability has given results

The Borregaard biorefinery has proven to be both environmentally friendly and sustainable in several recent studies. Alife cycle assessment (LCA) of all the major product lines from the Borregaard biorefinery in Sarpsborg has been reported by Ostfold Research (Modahl, Brekke, and Lyng 2009) and is summarized in ▶Tab. 7.2.

This study was carried out using (LCA methodology based on the ISO standards 14044/48 for the products cellulose, ethanol (95% and 99.9%), lignin (liquid and powder), and vanillin from the Borregaard plant in Sarpsborg, Norway. The functional units have been 1 metric ton for cellulose, lignin, and vanillin and 1 m^3 for ethanol. The analysis has been performed on a dry basis. For ethanol, this means that the burdens are not allocated to the water content of the product. The study is a cradle-to-gate analysis.

An update of this LCA study published in December 2010 showed a slight improvement mainly due to the start up of a second steam production plant from municipal waste (▶Tab. 7.3; Modahl and Vold 2010). One of the main global warming potential burdens comes from electricity purchased from the net, since Norway does import some coal-based power from Europe. Borregaard sell its hydropower to the net, and purchase standard Norpool mix power from the power net. In addition, the company is selling green power certificates (RECS, LECS) from hydropower production.

Tab. 7.2: Environmental burdens from cradle to gate for Borregaard's products, from Ostfold Research (Modahl, Brekke, and Lyng 2009).

Environmental impact category[a]	Unit	Cellulose[c] 1 ton	Ethanol[c] (96 %) 1 m^3	Ethanol[c] (99 %) 1 m^3	Lignin[c] (liquid) 1 ton	Lignin[c] (powder) 1 ton	Vanillin[c] 1 ton
Global warming potential (GWP)	kg CO_2-eqv.	1,211	335	691	704	1,227	1,343
Acidification potential	kg SO_2-eqv.	11.3	3.8	6.5	7.1	10.4	11.7
Eutrophication potential	kg PO_4^{-3}-eqv.	3.26	0.95	1.35	1.64	2.75	2.47
Photochemical ozone creation potential (POCP)	kg C_2H_4-eqv.	0.70	0.24	0.41	0.42	0.69	0.76
Ozone depletion potential	kg CFC-11-eqv.	8.9E-05	2.6E-5	5.2E-05	4.3E-05	1.1E-4	9.7E-5
Cumulative energy demand (CED)	MJ LHV	33,000	8,700	18,100	18,200	31,500	36,500
Waste[b]	kg waste	57.8	26.8	31.9	37.8	59.6	82.8

[a]Transport to customer is not included in this table.
[b]Solid and nonradioactive.
[c]On dry basis. For ethanol, this means that the burdens are not allocated to the water content of the product.

Tab. 7.3: Environmental burdens from cradle to gate for Borregaard's products, from Ostfoldforskning (Modahl and Vold 2010).

Environmental impact category[a]	Unit	Cellulose[c] 1 ton	Ethanol[c] (96%) 1 m^3	Ethanol[c] (99%) 1 m^3	Lignin[c] (liquid) 1 ton	Lignin[c] (powder) 1 ton	Vanillin[c] 1 ton
Global warming potential (GWP)	kg CO_2-eqv.	1,160	324	666	666	1,120	1,090
Acidification potential	kg SO_2-eqv.	10.6	4.5	7.2	7.9	10.8	10.5
Eutrophication potential	kg PO_4^{-3}-eqv.	3.56	2.17	2.68	3.04	5.14	3.12
Photochemical ozone creation potential (POCP)	kg C_2H_4-eqv.	0.77	0.29	0.49	0.50	0.78	0.75
Ozone depletion potential	kg CFC-11-eqv.	9.3E-05	2.6E-05	5.1E-05	4.9E-05	1.1E-04	8.9E-05
Cumulative energy demand (CED)	MJ LHV	32,993	8,718	18,084	18,216	31,481	36,490
Waste[b]	kg waste	1,386	408	793	701	1,639	1,330

[a]Transport to customer is not included in this table.
[b]Solid and nonradioactive.
[c]On dry basis. For ethanol, this means that the burdens are not allocated the water content of the product.

The LCA would have looked better if there were no sales of green certificates, but it would be at a financial cost. There are no markets for Borregaard chemicals today that are willing to pay such a premium on the products based solely on a better LCA.

A comparative study of the CO_2 footprints of all Borregaard product lines against the major competitive products showed that the Borregaard products gave smaller CO_2 footprints (cradle to gate) than the products from the competitors (Brekke, Modahl, and Raadal 2008). Cellulose was compared to cotton linters for specialty cellulose, lignosulfonates were compared to synthetic carboxylate superplasticizers, ethanol was compared to Brazilian sugarcane ethanol as well as fossil-based ethanol and vanillin fossil to synthetic fossil based vanillin. In ▶Fig. 7.4 the ethanol CO_2 footprint comparison is shown. Data from ethylene-based ethanol was gathered from Sutter (2007) and data for Brazilian sugarcane ethanol from Jungbluth et al. (2007). Data for Borregaard ethanol were reported in Modahl, Brekke, and Lyng (2009). The Ruter transport company in Oslo, Norway, has chosen to use the Borregaard ethanol (as ED95) instead of Brazilian-imported sugarcane ethanol for their busses because of the better CO_2 footprint. This is unfortunately an exception, most players in the market are not that environmentally conscious, and price and quality are the main competitive factors for such commodity products.

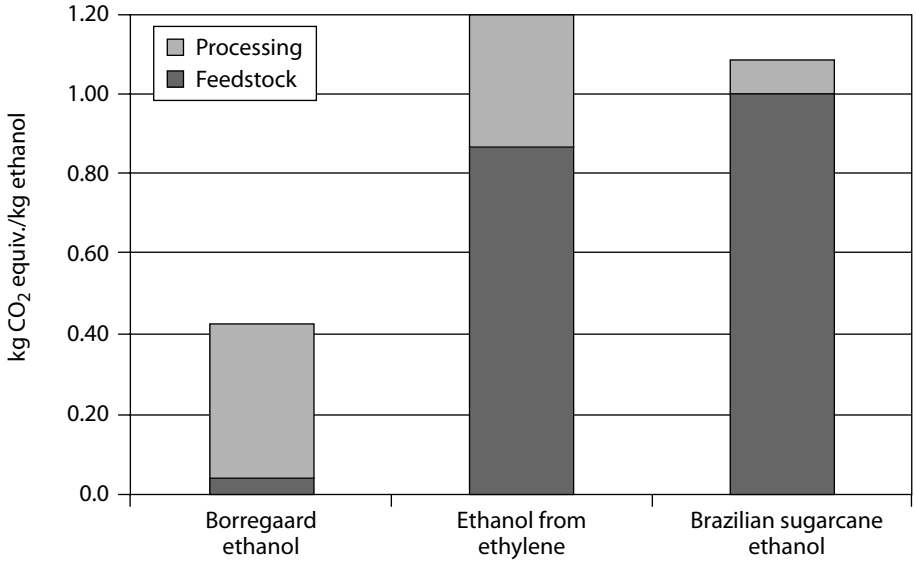


Fig. 7.4: Comparison of CO2 footprints from different ethanol sources (cradle to gate). Evaluation reported by Ostfold Research based on an LCA of Borregaard's production (Brekke, Modahl, and Raadal 2008) and literature data for ethanol from ethylene (Sutter 2007) and Brazilian sugarcane ethanol (Jungbluth et al. 2007).

7.3 The sugar platform – biotechnological approach

When considering transformation of lignocellulosic biomass to biochemicals, biomaterials, biofuels, and bioenergy, there are many optional routes very different in nature. In ▶Fig. 7.5 a general overview of most of these options are presented. First, there is available a wide range of lignocellulosic biomasses of different quality and price. There is also a hierarchy on the product side, with potentially high-value specialty chemicals and materials and low-value energy products. Normally, high-value products are niche products with lower volumes and the low-value products are the volume products. A combination is often beneficial, both to secure outlet of volumes and economy of scale for the manufacturing plant. In addition, it is often high contribution margins from low-volume–high-value products that makes such a biorefinery more profitable, or profitable at all.

In ▶Fig. 7.5 mild processing options are found at the top and tougher options are presented further down, with incineration as the ultimate option at the bottom. One alternative is to preserve the beautiful polymers nature has produced as much as possible, with the option to chemically or mechanically modify them to improve or tailor make properties and performance. Examples of such products are typically pulp, specialty cellulose, and lignosulfonates from the pulping industry. Today there are hardly any hemicellulose polymers commercially available, but many biorefinery projects focus on extraction of hemicellulose and development of applications for this noncrystalline polysaccharide. Another example is microfibrillar cellulose (MFC) where cellulose

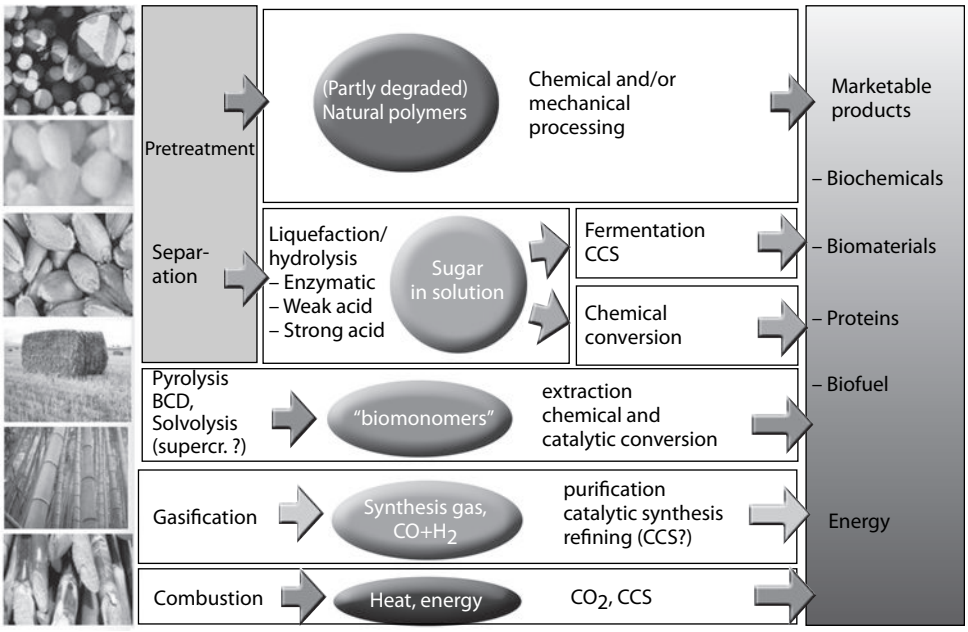


Fig. 7.5: Process routes from biomass to products.

fibers have been defibrillated to nano-size diameters with interesting new properties. They are, for example, excellent viscosifiers that can form clear high-oxygen barrier films.

The sugar platform is an option where the polysaccharides are softly degraded to monosaccharides in aqueous solution. In the biochemical approach, these sugars are then converted to chemicals, fuels, or proteins by fermentation. This will be described in more detail in sections 7.3.1, 7.3.4, and 7.4. The monosaccharides can also be converted by catalytic chemical conversion (the chemical approach).

Pyrolysis is a mild thermochemical conversion that involves heating of biomass to typically 400°C without any oxygen to avoid combustion. This will degrade the biomass to "monomer size" components and split off chemical side groups to form aromatics, lower hydrocarbons, organic acids, and so forth. A lot of char will be formed and the major product will be a pyrolysis oil with a wide range of components, each of very low concentration. Dynamotive (Canada), Ensyn (Canada), and BTG (the Netherlands) are examples of companies working on conversion of biomass to chemicals and fuels by pyrolysis. VTT in Finland has also worked for many years on this technology.

In gasification, the biomass is degraded even further, and the main goal is to produce synthesis gas (CO and H_2), which is a good starting point for catalytic synthesis of Fischer-Tropsch diesel, methanol, dimethyl ether (DME), and a wide range of other chemicals. This is a well-known technology in the petrochemical industry, but the challenge is to start from biomass. Choren in Germany and Chemrec in Sweden are examples of companies leading this development.

7.3.1 Less-expensive feedstocks for low-value products – high-value coproducts from costly feedstocks

Wood, and in particular softwood, contains more fermentable sugars than other biomasses, but it also has other valuable end uses like construction materials, pulp, and bioenergy. However, in many places in the world wood is costly to harvest. All in all this is the basis for higher market prices. Agricultural waste, mainly from annual plants, contains less fermentable sugars and hence will yield less bioethanol and more side streams as depicted in ▶Fig. 7.6.

Depending on the processing technology available, different feedstocks will yield different amounts of ethanol and side streams as illustrated in ▶Fig. 7.7. A theoretical yield of carbohydrates to ethanol of 90% was used for the calculations. In cases where pentoses cannot be fermented to ethanol, annual plants are inferior to softwood. Wood can produce up to 45 liters (35.5 kg) of ethanol from 100 kg of dry biomass, and the same amount of CO_2, at best leaving approximately 30% of the biomass input in side streams. Consumption of biomass for heat and power is not included.

Prices fluctuate over time and by site. Some products are global commodities and render themselves for transport, but many low value products are too costly to transport and prices will be decided in local markets. Heat (and possibly power) is the lowest priced product from biomass in many places in the world, next comes biofuels. Biochemicals and biomaterials are often more attractively priced. Thus, one must make

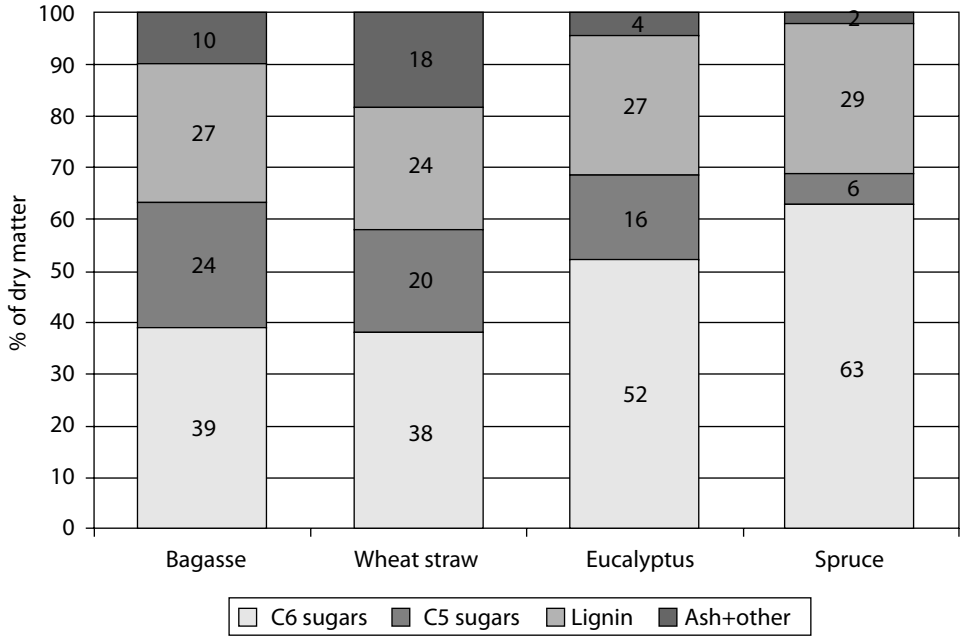


Fig. 7.6: Chemical composition of typical lignocellulosic feedstocks. Compiled from a range of sources and internal analysis. The compositions are used for initial calculations by Borregaard.

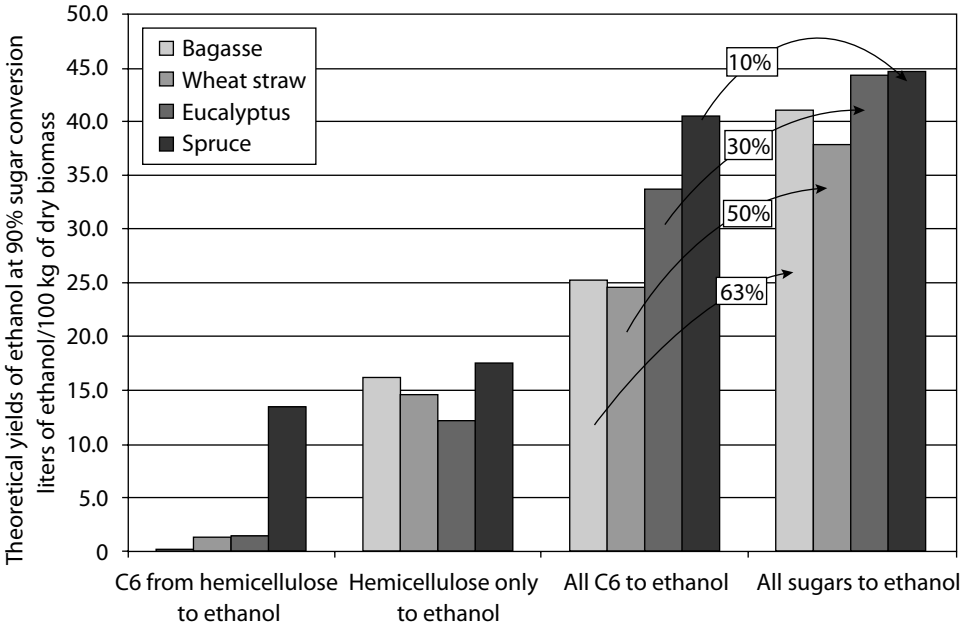


Fig. 7.7: Theoretical yields of ethanol from various lignocellulosic feedstocks depending on processing concepts and based on 90% conversion of sugars to ethanol.

sure not to destroy the potential for making high-value side streams already at the pretreatment stage. In such a setting, the yield of bioethanol is not that important, as long as the combined conversion to valuable products from the feedstock is high.

7.3.2 The sugar platform process train and the major challenges

When biomass enters the processing plant removal of soil, dirt, sand, and pebbles is often necessary to reduce wear on the processing equipment. Since the process encompasses treatments with chemicals and enzymes that need to have access to all the parts of the biomass, grinding and pretreatment is necessary. The different process steps in the biochemical conversion of biomass to ethanol is described in ▶Fig. 7.8 along with a short listing of the major challenges in each process step.

7.3.2.1 Pretreatment and hydrolysis processes

Pretreatment prepares the biomass for the hydrolysis step by opening up the biomass and making as much of the cellulose fibers as possible available for the chemicals or enzymes that subsequently will hydrolyse the cellulose (and possibly the hemicellulose) into monosaccharides in aqueous solution.

The combined pretreatment and hydrolysis processes could be divided into two principally different groups (▶Fig. 7.9):

1. Hydrolysis processes where cellulose is dissolved (hydrolyzed) out of the biomass
2. Pulping processes where lignin is dissolved out of the biomass

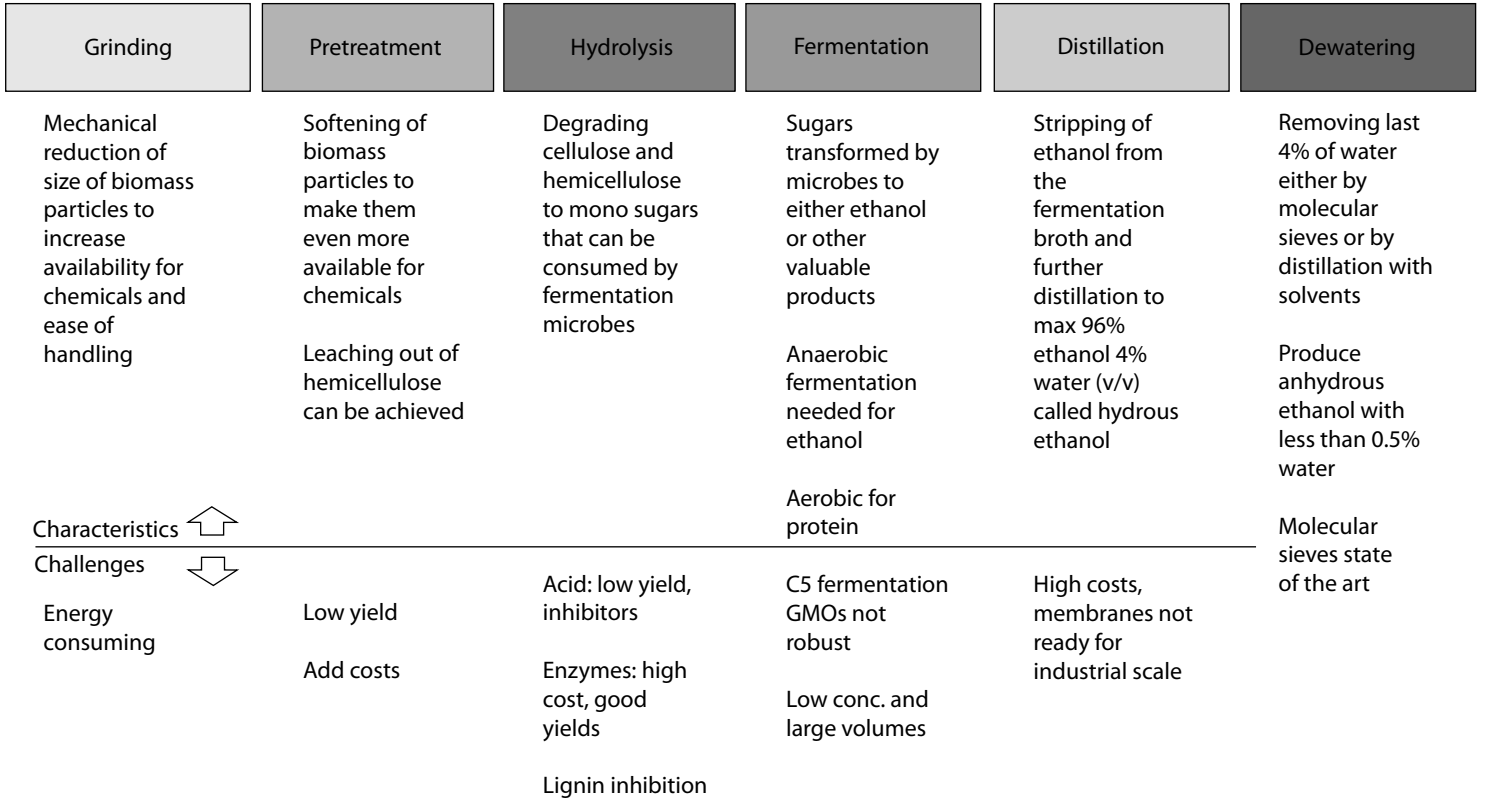


Fig. 7.8: Schematic presentation of the process steps under the sugar platform biotechnological approach.

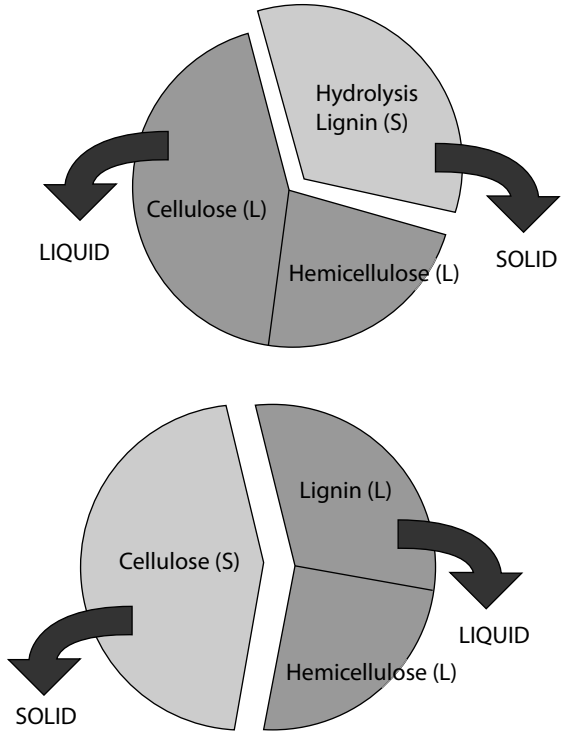


Fig. 7.9: Two groups of pretreatment and hydrolysis processes. Top: hydrolysis processes where the cellulose is dissolved out from the biomass. Bottom: pulping processes where lignin is dissolved out from the biomass.

For hydrolysis processes, weak acids, strong acids, and microbial or enzymatic processes are employed. Weak acids typically use mineral acids like sulfuric acid at elevated temperatures (around 130°C) and pressure. This will create large amounts of furfural, hydroxyl methyl furfural (HMF), acetic acid, and other inhibitors for the microbes during the fermentation step (▶Fig. 7.10).

The strong-acid processes is very old. Versions of it were employed in the first half of the 20th century in Europe, the Soviet Union, and the United States to produce ethanol from wood. The process consumes large amounts of mineral acids (hydrochloric or sulfuric acid). First, the raw material is softened with concentrated acid, then the acid is diluted with water to start the hydrolysis process since the strong acid does not hydrolyse cellulose. Modern processes utilizing strong acid pretreatment include a step for separation and recirculation of the acid either by solvent extraction (Weyland), ion exchange resins (BlueFire), or membrane technology (TNO).

Enzymatic hydrolysis is often combined with steam explosion pretreatment where the biomass in principle is heated with steam to temperatures above 180°C, and then the pressure is released rapidly in a blow tank. This opens up the biomass and dissolves some of the lignin and hemicellulose. Under such conditions, hemicellulose will split off acetate groups and form acetic acid, which will reduce the pH. Fermentation

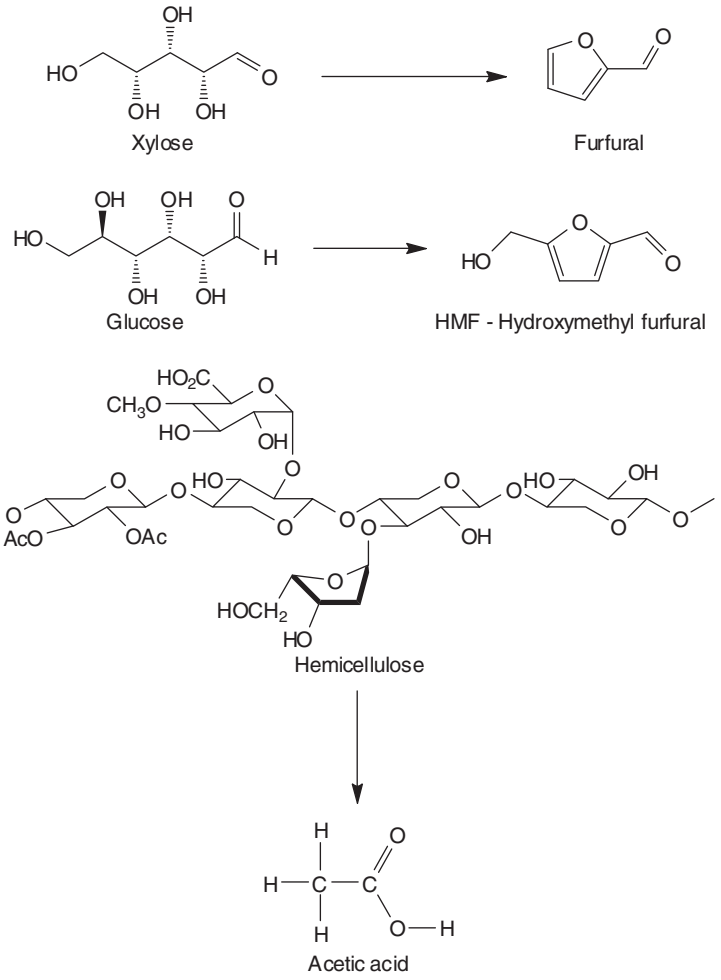


Fig. 7.10: Formation of fermentation inhibitors under conditions of high temperature and low pH.

inhibitors like furfural, HMF, and acetic acid are formed under these conditions (▶Fig. 7.10). Furthermore, the lignins are condensed and degraded to low Mw, creating a highly polydispersed lignin with low O content, low OH content, mostly C-C bonds (few ß-O-4 bonds), and with very low reactivity. This lignin has very low solubility in water or other solvents and contains large amounts of impurities like biomass, unhydrolyzed carbohydrates, minerals, enzymes, resins, and so on. Several versions of this process are used. Some use a two-step process where step one is milder with the purpose of extracting hemicellulose without producing too much inhibitors. Others adds acids or SO_2 to reduce the pH.

An interesting process is developed by PureVision. The whole pretreatment and separation is done in an extruder, where the first stage is a counter-current water extraction at a temperature of around 200°C. Hemicellulose is dissolved together with some

lignin, and acetic acid is split off from the hemicellulose sidechains. In the second stage, a caustic dissolution of lignin separates lignin and cellulose. At the end of the extruder is a blow tank that gives almost the same effect as a steam explosion on the cellulose. The whole processing time only takes minutes, thus producing less inhibitors and producing three separate streams of mainly xylan (oligomers from hemicellulose), lignin, and cellulose.

Some players such as Mascoma let the microbes do the whole job of degrading the biomass polysaccharides to monosaccharides and ferment to ethanol. Thus there may be no mechanical or chemical pretreatment. Of course one could foresee a range of combinations, where solid-state fermentation is part of the concept.

In all pulping processes, both in the pulp and paper industry and in biorefineries, lignin is dissolved out of the biomass. In traditional pulping, the quality of the cellulose and the cost of the process are in focus. The use of the pulping-type processes as pretreatment and separation for biofuels and biorefineries does not face the challenge of producing high-quality pulp. Thus, many new pulping processes, some old processes that never worked for pulp and paper, and a few modified commercial pulping processes are explored. Both Kraft pulping and soda pulping have been evaluated by Inventia of Sweden. The BALI process by Borregaard that is part of the EuroBioRef project (Dumeignil 2011) and the SPORL process (Zhu et al. 2009) by Forest Products Laboratory uses modifications of sulfite pulping. Many organosolv processes are employed, like the old Repap organosolv process modified by Lignol, or the CIM-V process in France. The Lignol process produces pure and reactive lignins that may be used for phenol replacements.

At Borregaard, a new pretreatment process, BALI, (Sjöde et al. 2010) for production of second-generation bioethanol is under development This process is characterized by low enzyme consumption at the subsequent hydrolysis step, high yields of sugars in solution, and valuable products from all main components of the biomass. The BALI pretreatment and separation processes are used as the first lignocellulosic process steps in the EuroBioRef project.

Enzymatic hydrolysis of cellulose is currently one of the top issues in biorefinery research. The cost of enzymes is still high and reduction of enzyme costs is a high-priority topic addressed by large international enzyme companies like Novozymes, Genencor, DSM, Iogen, and several others. In a batch process, the pretreated biomass of 10%–20% DM during feeding is still solid and hard to handle. After a few hours, it is liquefied when the enzymes have started to digest the material and the cellulose and hemicellulose are partly degraded. Increased DM in the hydrolysis reaction is a topic for development, and, for instance, Inbicon's demonstration plant in Denmark uses a simple but brilliant patented process to solve this problem. In batch processes, the state of the art enzymatic hydrolysis takes typically more than 48 hours. All pretreatment processes leave all or some lignin with the cellulose. Lignin is known to inhibit enzymes by adsorption and irreversible binding, thus creating a larger need for enzymes. The BALI process by Borregaard produces water-soluble lignins that do not inhibit enzymes.

7.3.3 The challenge of making chemicals and materials from lignin

All commercial lignin products on the market today are water soluble. BALI and SPORL are the only known pretreatment processes that produce water-soluble lignins. This

section analyzes the mass balance of a typical ethanol production based on a hydrolysis pretreatment process like the one below:

Steam explosion → enzymatic hydrolysis → fermentation → distillation

Each process step has a yield in the range of 80%–90%, which means each step leaves 10%–20% of the material unreacted. These combined side streams end up in the waste, which is often referred to as "lignin." Such a lignin stream can contain large amounts of unreacted biomass, nonhydrolyzed cellulose, unfermented pentoses, and some unfermented hexoses, minerals, insolubles, resins, fat, proteins, enzymes, and so on. Besides that, the lignin has been put through high temperatures at acidic conditions and is condensed and insoluble in most solvents (particularly water) and is very unreactive. It is very hard to do anything other than incinerate such a side stream.

This problem is exactly what the BALI process was designed to solve. By focusing on the possibility of producing products from every major component of the biomass and not destroying the possibilities at the pretreatment stage, the BALI process produces water-soluble lignins, residual lignins that do not inhibit enzymatic hydrolysis, and high yields of fermentable sugars as well as low amounts of fermentation inhibitors.

Converting biomass to drop-in fuels like hydrocarbons creates the need for the removal of oxygen and the addition of hydrogen. Chemical compounds can be plotted into a Van-Krevelen diagram as in ▶Fig. 7.11. Carbohydrates like cellulose and hemicellulose are found in the upper right corner of the diagram, because they have the general formula of $(CH_2O)_n$ and thus have an H:C ratio of approximately 2 and an O:C ratio of approximately 1. Different lignin compounds from different pretreatment processes are also plotted. This figure clearly shows that if one wants to make drop-in hydrocarbon fuels from the lignin side stream from biochemical production of chemicals and ethanol, hydrogenation is needed. Pyrolysis of a lignin side stream does not give a push in the right direction in the diagram. The LtL process is a combined pyrolysis and hydrogenation and has a better effect. If there is a source of hydrogen available, the question is, however, whether it is the best choice to upgrade a lignin side stream to drop-in hydrocarbon fuels or instead incinerate it and use the hydrogen for other applications.

7.3.4 Fermentation, distilling, and dewatering

Fermentation of pentoses to ethanol will not be addressed in great detail in this chapter, although it is a major challenge in second-generation bioethanol development. Normal baker's yeast can only convert hexoses like glucose and mannose to ethanol. It is commonly accepted that only GMOs can convert pentoses to ethanol, although Süd Chemie claims to have found a non-GMO microbe that can convert xylose to ethanol. Alternatively, pentoses could be fermented to other products both aerobically and anaerobically. Xylose is today converted to furfural in many places in the world and one of the more well known is Illovo Sugar Mill in South Africa owned by British Sugar.

Contamination is a problem in the fermentation industry that has not received much public attention, but the fact that antibiotics are used to prevent contamination from other microbes indicates that there will be more attention paid to this issue in the future. Biorefineries should be prepared for a ban on the use of antibiotics in the fermentation industry in the future, similar to one that has already been placed on the animal feed industry in many countries.

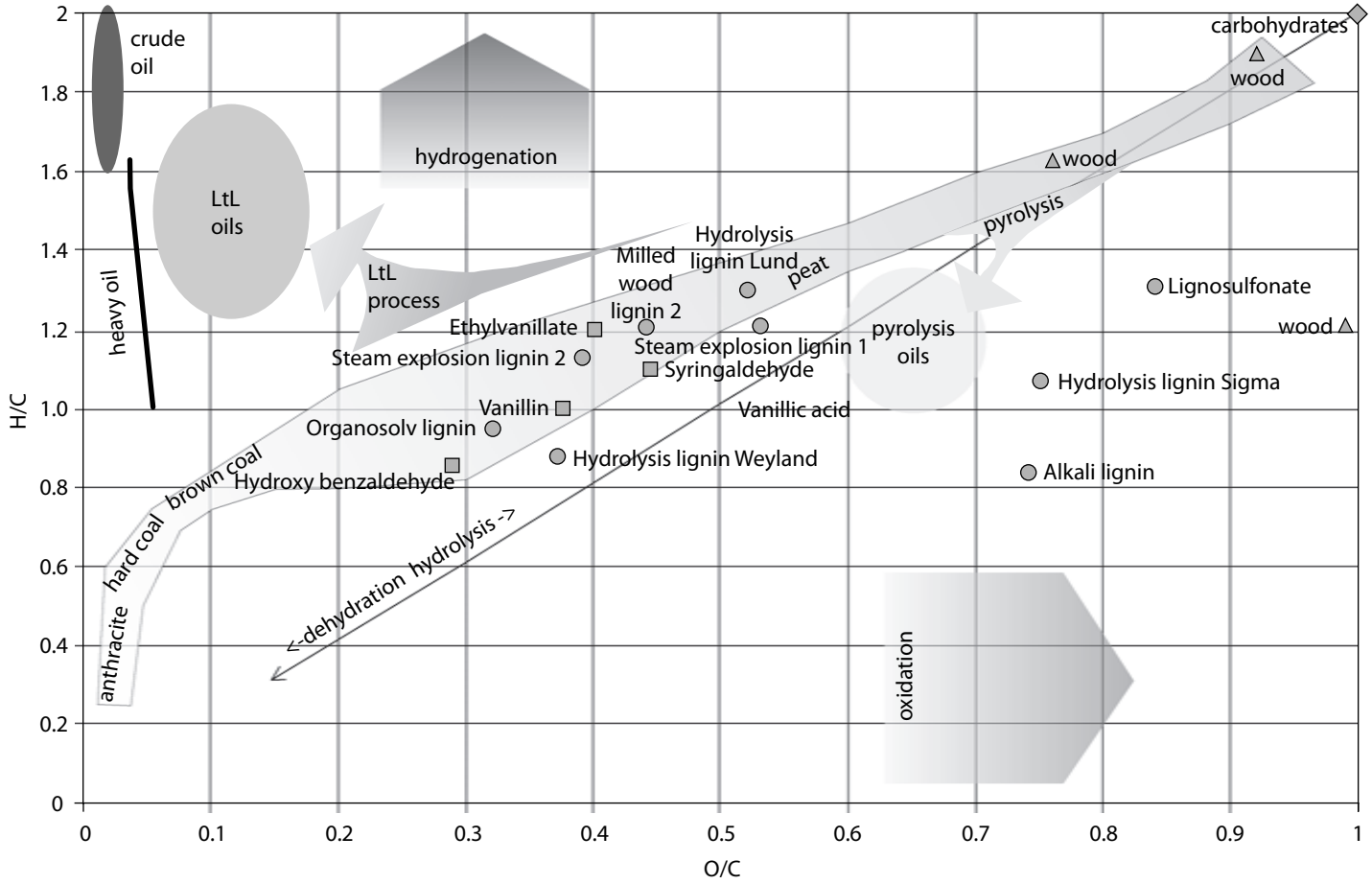


Fig. 7.11: Van-Krevelen diagram of fuels, coal, oil, biomass, pyrolysis oils and lignins.

Distillation and dewatering in the case of ethanol production are well established technologies used in all first-generation bioethanol plants around the world, although there are issues of cost and new membrane technologies.

7.4 The BALI pretreatment and separation process

7.4.1 The BALI process – technical description

The BALI process aims to utilize low-value biomass and convert it to various competitive products. A goal for the process is to utilize at least 80% of the biomass to products, energy excluded. The process consists of four major steps (see ▶Fig. 7.12) (Sjöde et al. 2010).

The first step is a sulfite pretreatment or fractionation where the lignin is made water soluble, the cellulose is made accessible to enzymes, and the hemicellulose is either preserved or hydrolyzed into soluble monosaccharides (see ▶Fig. 7.13).

After the pretreatment, the dissolved lignin (potentially together with monosaccharides) is processed to further increase the value of the product. The lignin is through this turned into a performance chemical with several interesting properties. The monosaccharides (if any) are turned into ethanol or other potentially interesting fermentation products. The cellulose (potentially together with unhydrolyzed hemicelluloses) is enzymatically hydrolyzed. The hydrolysis process has proven to benefit from the BALI pretreatment, even more than anticipated with regard to the lignin content of the solid fraction.

After the enzymatic hydrolysis, the sugar solution is fermented to valuable products. The fermentation has also been shown to benefit from the fractionation in the pretreatment, since the level of inhibitors in the hydrolysate is very low.

One of the great advantages with the BALI process is the flexibility in raw material. With minor adjustments several different raw materials, such as bagasse, straw, willow, and spruce, have been treated and turned into valuable products. Furthermore, a much higher yield of marketable products is reached compared to other processes, mainly due to the isolation and utilization of a marketable lignin product.

7.4.2 The BALI process – beneficial enzymatic hydrolysis

After the pretreatment the solid phase, containing mainly cellulose, is enzymatically hydrolyzed. Enzymatic hydrolysis of the BALI pretreated material has been seen to be relatively independent of the lignin content of the substrate, as shown in ▶Fig. 7.14, and thus one can conclude that the lignin left in the substrate is not inhibiting the hydrolyzing enzymes.

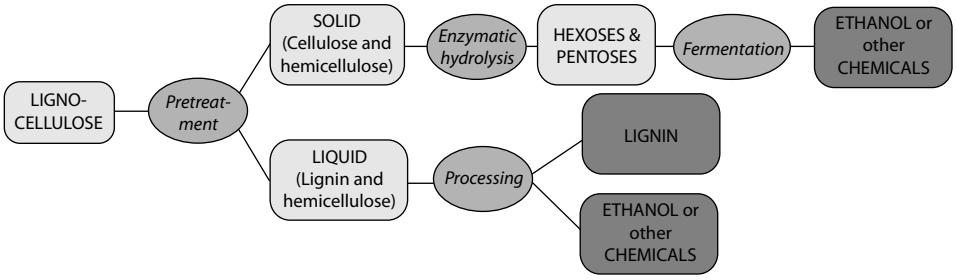


Fig. 7.12: Schematic description of the BALI process.

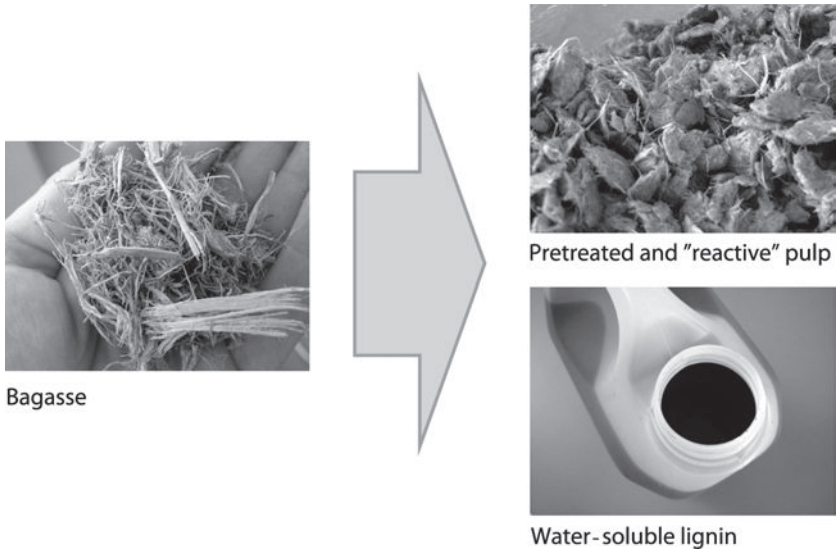


Fig. 7.13: Graphical presentation of the pretreatment step in the BALI process.

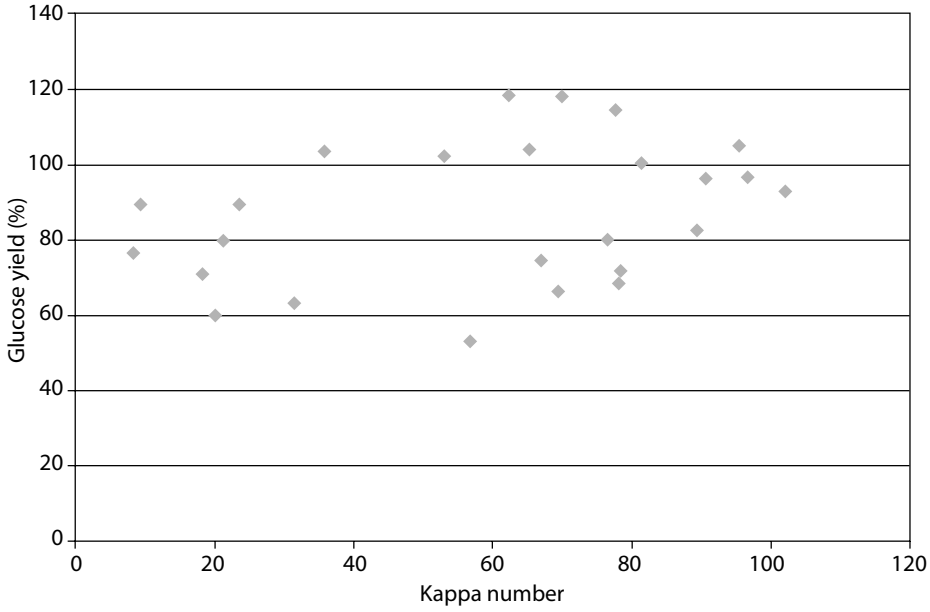


Fig. 7.14: Correlation between Kappa number (lignin content) of BALI-treated bagasse and glucose yield after enzymatic hydrolysis. The results indicate that the residual lignin in the substrate does not inhibit enzymes.

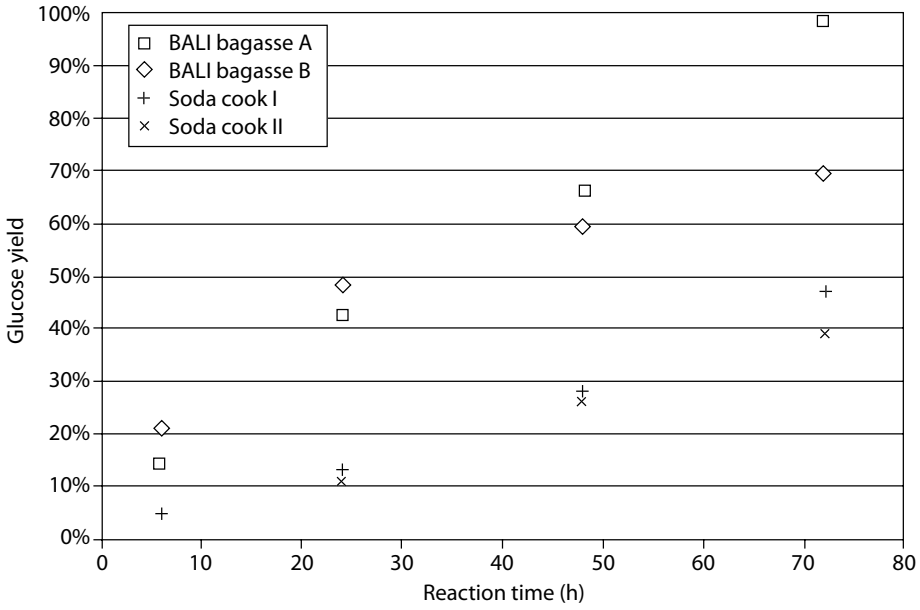


Fig. 7.15: Enzymatic hydrolysis of different cellulose substrates of sulfite-pretreated and soda-cooked pulps with Celluclast (Novozymes). The lignin content of the substrates was for BALI A 5%, BALI B 11%, soda cook I 4%, and soda cook II 5%.

The BALI pretreated substrates have been shown to be easily hydrolyzed. In a comparison between BALI pretreated materials and soda-cooked pulps, it was seen that the BALI pretreated materials were superior (see Fig. 7.15). It is a general idea that there is a strong correlation between enzymatic digestibility and lignin content for pretreated materials (Mooney et al. 1998; Lu et al. 2002). In this comparison between soda-cooked and BALI-pretreated material, this anticipated correlation was not observed. Absence of correlation between the amount of lignin and digestibility under enzymatic hydrolysis has also been observed by others using a similar pretreatment (Zhu et al. 2009; Takahshi et al. 2010).

Several different enzyme cocktails from leading suppliers have been tested on the BALI materials with good to excellent results. One example is given in ▶Fig. 7.16, where BALI substrates reach complete carbohydrate conversion at a relatively low enzyme dosage.

The good results can be attributed to the fact that the residual lignin in the BALI-treated substrate show a very low inhibition of enzymes and probably also that the cellulose has been efficiently opened to give easy access for the enzymes.

7.4.3 The BALI process – high-value products from all three main components of the lignocellulosic feedstock

The BALI process makes it possible to convert all the main components in lignocellulosic biomass into valuable products. The cellulose is converted into glucose and then further processed. Since the hydrolysate is almost free from inhibitors, several fermentation processes have been observed to be successful. Examples of organisms tested are *Saccharomyces cerevisiae*, *Kluyveromyces marxianus,* and *Pichia jadinii*. Although the

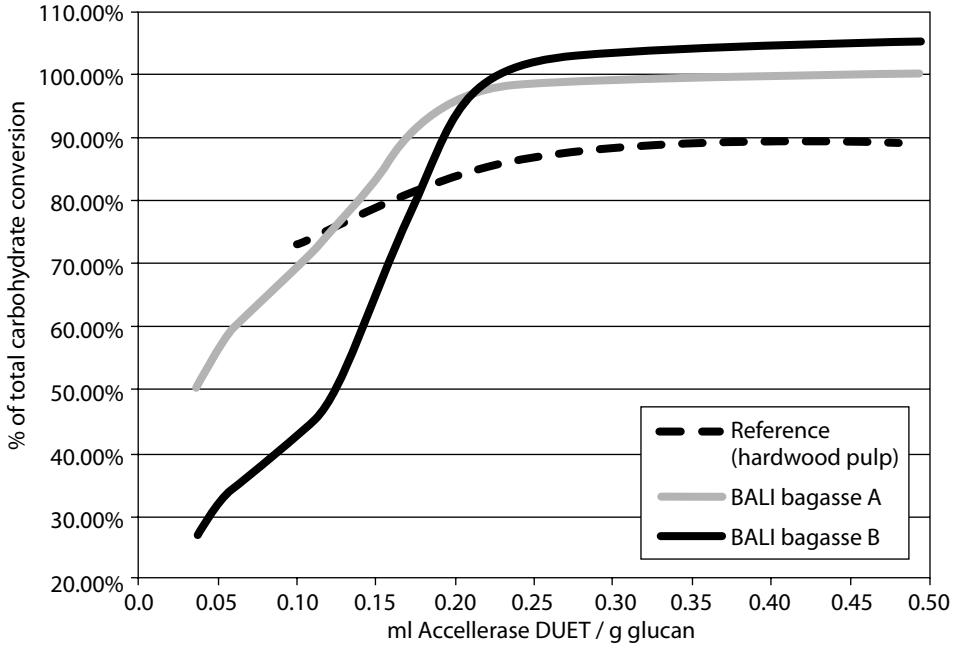


Fig. 7.16: Dose response of carbohydrate conversion of different cellulose substrates. Two BALI cellulose substrates from bagasse (two extreme processing conditions) compared to a standardized hardwood cellulose substrate (unbleached hardwood pulp, delignified to Kappa 10.1). Experiments performed by Genencor at 7% cellulose w/w, 50 °C, pH 5.0, 72 h and using Accellerase® DUET™.

tested organisms all are yeasts, there are no indications that other organisms such as bacteria or fungi should have any problems fermenting the hydrolysate, and such tests are under evaluation. The hemicellulose may also be turned into valuable products. Depending on the raw material, several options are possible. We have focused our initial efforts on the production of biomass with high protein content. This has been shown to be successful for both hexoses and pentoses.

The BALI pretreatment process yields water-soluble lignins, and development of applications for these to expand to the existing markets for lignosulfonates is also occurring. This will make a biorefinery based on the BALI process competitive, profitable, and sustainable. By making the lignin water soluble, several options for further transformations open up. Generally, lignin is a stable molecule with interesting properties. One of the most interesting potentials of the modified lignin is the dispersing property, which can lead to valuable applications as a specialty chemical after chemical upgrading and modification.

A model structure of a softwood lignosulfonate is depicted in ▶Fig. 7.17. The actual structure of a lignin produced by the BALI process depends on the raw material used and the pretreatment conditions. ▶Fig. 7.17 shows, however, the main functional groups and main backbone structure of the polymer. The amount of functional groups, such as sulfonate, as well as their location will depend on the processing conditions, and the ratio between the three propane-phenyl monomers in the backbone will depend on the biomass species.

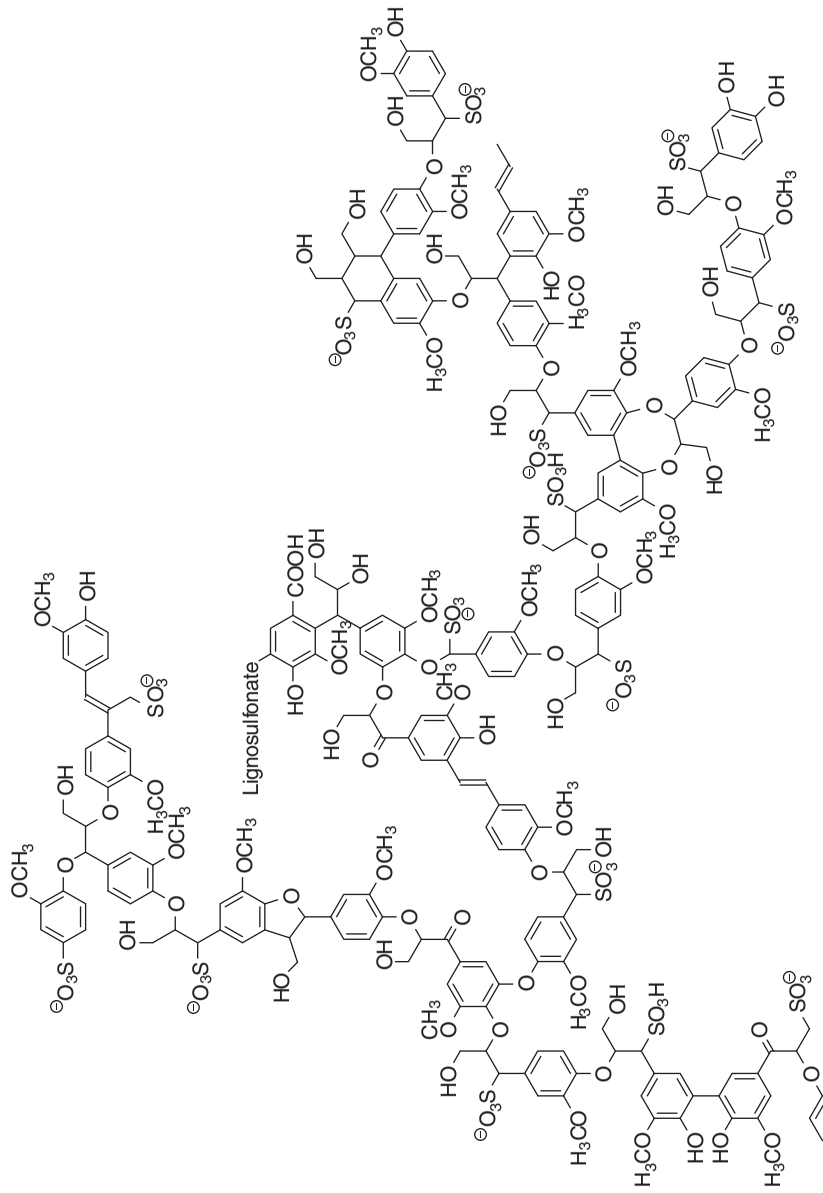


Fig. 7.17: Model structure of lignosulfonate.

7.5 Demo plant for the BALI process

Construction of a demo plant for demonstration of the BALI process started in June 2011 and the budget for this project is NOK 130 mill (EUR 16 mill). The demo plant is expected to be finalized in the second quarter of 2012 and be operational at the third quarter 2012. The demo will be used to demonstrate the scale-up of the BALI process and will make it possible to optimize process parameters, test out some specific process equipments, and spot cost reductions as well as producing large samples of different products for large-scale testings. In particular, this demo is expected to produce samples for further development work within the EuroBioRef project (Dumeignil 2011).

Acknowledgements

The new biorefinery development programs and investments have received support from several Norwegian governmental bodies as well as the European Union. In the very beginning, the Norwegian industrial R&D support program SkatteFunn acknowledged Borregaard with tax reductions. Based on initial results, a NOK 18 mill funding for a four-year biorefinery development program was granted for the project Biomass-2Products (B2P) by the Norwegian Research Council. Later, the BALI pretreatment and separation process received a EUR 3 mill funding from the EU FP7 Programme – The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007–2013) under grant agreement n° 241718 EuroBioRef. Finally, Borregaard received a grant from Innovation Norway for funding a demo plant for exploration and demonstration of the BALI technology. All these grants and supports have been received with great appreciation and gratitude. The progress in this project would not have been possible without such support.

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8 Conversion of lignin: chemical technologies and biotechnologies – oxidative strategies in lignin upgrade

Silvia Decina and Claudia Crestini

8.1 Introduction

The global energy system is currently dominated by fossil fuels. In recent years interest in the development and exploitation of renewable and alternative energy sources has become of paramount importance to reduce our dependence on oil. Biomass plants are readily renewable alternative sources, so the research has focused on their exploitation. Biomass has a very complex composition due to carbohydrates, lipids, proteins, fats, and a wide range of substances such as vitamins, colorants, flavors, and essences. As such, different treatments are needed to obtain chemically pure and simple products to be used in the industry (Werpy and Peterson 2004). The use of biomass provides significant benefits for environmental and socioeconomic impacts because it is one of the most efficient systems to reduce emissions of greenhouse gases and other pollutants resulting from the use of fossil fuels. Lignocellulosic biomass biorefinery processes constitute a facility that produces, in analogy with the petroleum refinery, multiple products including fuels, power, and bulk and fine chemicals. The development of parallel processes for production of both fuels and chemicals constitutes the basis of an economically viable biorefinery. From this viewpoint, the valorization and exploitation of all the biomass components is of crucial importance (Glasser, Northey, and Schultz 1999).

Since lignin is the second-most abundant renewable polymer, the lignocellulosic biorefinery streams will receive enormous amounts of lignin. As such, the valorization of lignin for the production of fuels and chemicals is pivotal for the development of sustainable biorefineries.

To date, processes for lignin conversion and applications other than heat production are lacking. As such it is necessary to develop new technologies for lignin conversion to value-added chemicals (Glasser and Sarkanen1988).

▶Fig. 8.1 shows a biorefinery scheme focused on lignin.

Plant materials contain, besides cellulose, hemicellulose and lignin and also water, soil, salts, extractives, and other materials. The biomass has to be separated into its components by suitable pretreatments in order to produce feed streams. Biomass origin and pretreatment methods determine the composition of feed streams and have to be adapted to local environments (Lebo, Gargulak, and McNally 2001).

Lignin can then be treated by conventional or new technologies. Pyrolysis or gasification yield syngas, which by current use in petroleum technology, can be converted to fuels and chemicals (Johnson 2002). A second possibility is cracking to platform chemicals by elimination of most functional groups present in lignin. In this way it is possible to obtain platform chemicals to be further converted by petroleum technologies into fuels and block and fine chemicals (Aden 2005).

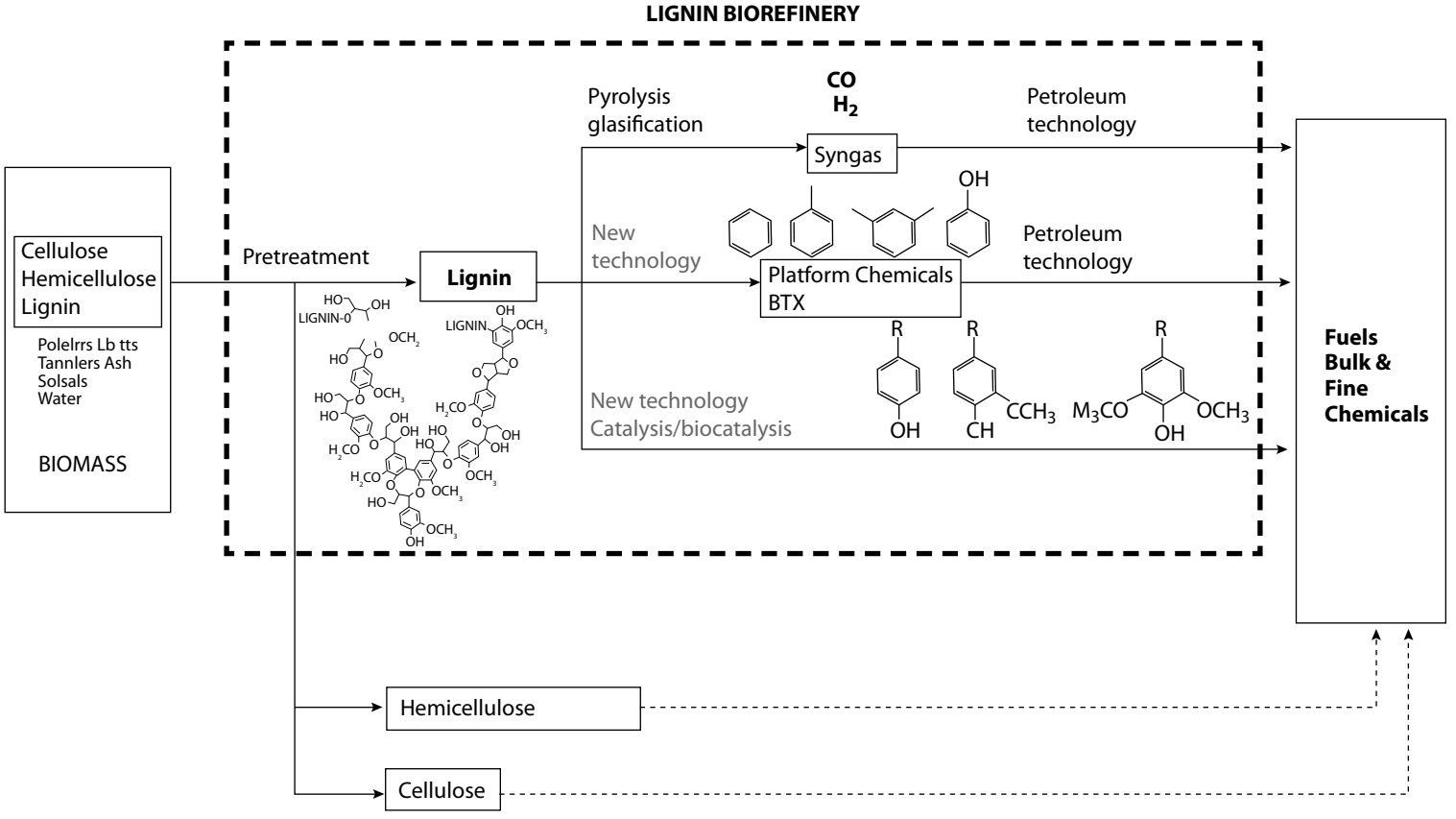


Fig. 8.1: Lignin biorefinery scheme.

A third approach consists of milder catalytic treatments of lignins aimed at yielding modified polymers or functionalized monomers.

8.2 Lignin structure, pretreatment, and use in the biorefinery

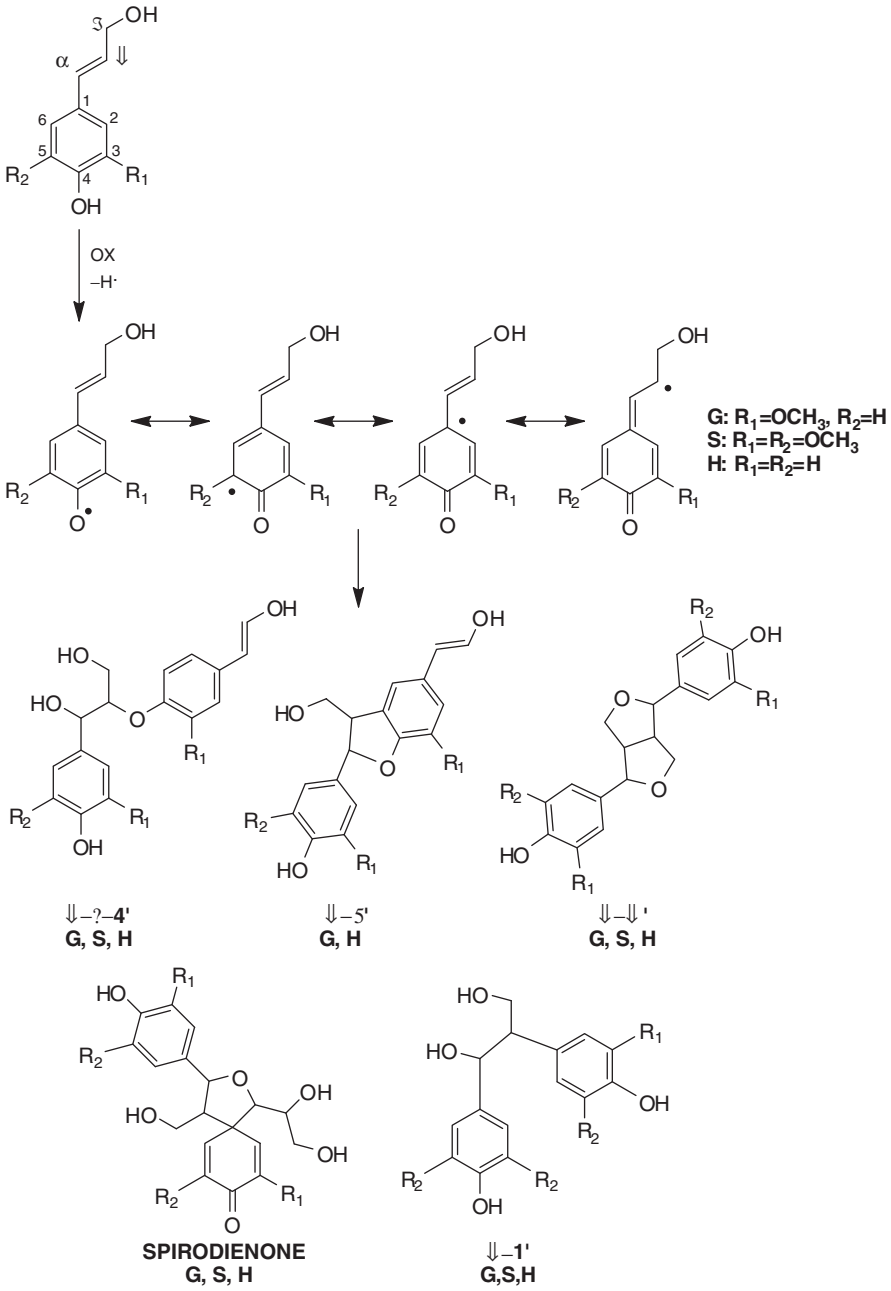
8.2.1 Lignin structure

Lignin is an extremely abundant raw material contributing as much as 30% of the weight and 40% of the energy content of lignocellulosic biomass (Sakakibara 1980). Lignin's native structure suggests that it could play a central role as a new chemical feedstock, particularly in the formation of supramolecular materials and aromatic chemicals. Lignin is a hydrophobic substance in cells that interacts with other matrix components and chemically and physically links the polysaccharide components of the wall, resulting in increased impermeability, mechanical strength, and rigidity of the cell wall. It gives the wall greater resistance to microbial attack. The distribution of lignin in cell walls is not uniform (Lapierre, Pollet, and Monties 1995). The concentration of lignin in the middle lamella and primary wall is higher than in the secondary wall. However, the total amount of lignin present in the plant is significantly higher in the secondary wall, given its considerable volume. In woody tissues, about 75%–85% of the total lignin is in the secondary wall, while 15%–25% is in the middle lamella and primary wall.

The amount of lignin present in various plants is widely variable. While in the woody lignin, content ranges from 20% to 30% in hardwoods, softwoods, as well as many herbaceous angiosperms, monocots are less lignified. Lignin is a highly complex phenolic biopolymer in nature, the nature of which varies depending on the plant species. Its function is to give support to the plant and protect it from attack (Lin and Lin 1990).

Lignin shows an heterogeneous composition and, to the best of the current knowledge, lacks a defined primary structure. It is a random three-dimensional phenyl-propanoid (C9) polyphenol mainly linked by arylglycerol ether bonds between the monomeric phenolic p-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S) units. Gymnosperms have a lignin that consists almost entirely of G (G-lignin); dicotyledonous angiosperms lignin is a mixture of G and S (GS-lignin), and monocotyledonous lignin is a mixture of all three units (GSH-lignin). All lignins contain small amounts of incomplete or modified monolignols (Yean and Goring 1955). Lignin structure is the result of a biosynthetic pathway that occurs via oxidative radicalization of monolignols followed by radical coupling of two monomer radicals that form a dehydrodimer (▶Fig. 8.2). Coupling is favored at monolignol β positions resulting in arylglycerol-β-aryl ether (β-O-4′), pinoresinol (β-β′), phenylcoumaran (β-5′), spirodienone (SD), and diphenylethane (β-1′) dimers formation. In principle, dilignol coupling at positions 4 and 5 could occur yielding diaryl ether (4-O-5′) and diphenyl (5-5′) dimers formation, as shown in ▶Fig. 8.2.

In a subsequent step the dimer is newly dehydrogenated to a phenoxy radical, and then it can couple with another monomer radical in an end-wise coupling mode (Sjostrom et al. 1962). Coupling of two lignin oligomers yields 4-O-5′ and 5-5′ coupling. In turn, 5-5′ subunits undergo α-β-O-4-4′ coupling to dibenzodioxocine units (DBDO)



⇓ couplings: favored as monolignol coupling mode and end-wise polymerization

(*Continued*)

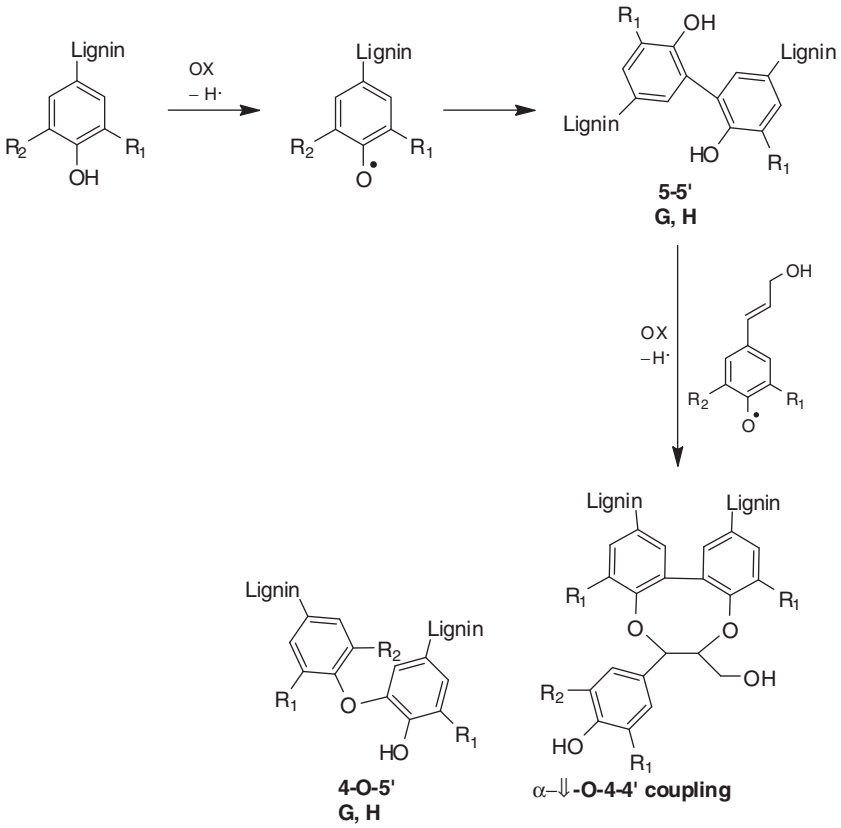


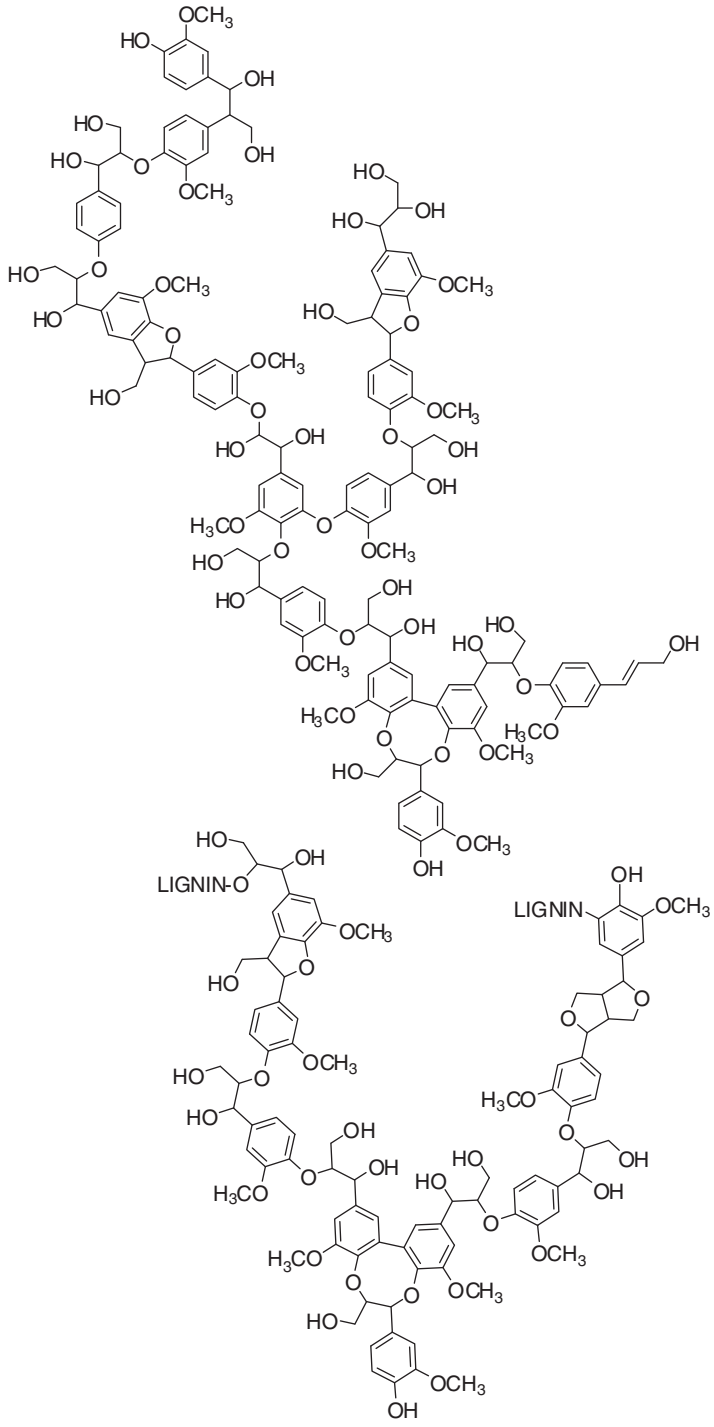
Fig. 8.2: Lignin biosynthesis. Coupling mode for monolignols (a) and oligomeric (b) lignin chains.

(Brogdon and Dimmel 1996). Both dibenzodioxocine and 4-O-5′ coupling modes constitute branching points in lignins. The phenylpropane (C9) units are thus attached to one another by a series of characteristic linkages (β-O-4′, β-5′, β-β′, β-1′, SD, 5-5′, DBDO, and 4-O-5′). ►Fig. 8.3 shows a general picture of lignin structure and main interunit lignin bonding patterns.

Since lignin is a polydisperse polymer with no extended sequences of regularly repeating units, its composition is generally characterized by the relative abundance of H/G/S units and by the distribution of interunit linkages in the polymer.

8.2.2 Lignin pretreatment

The pretreatment of lignin is an important initial step in biorefinery operation. It separates the principal components of the biomass and degrades the extended polymer to


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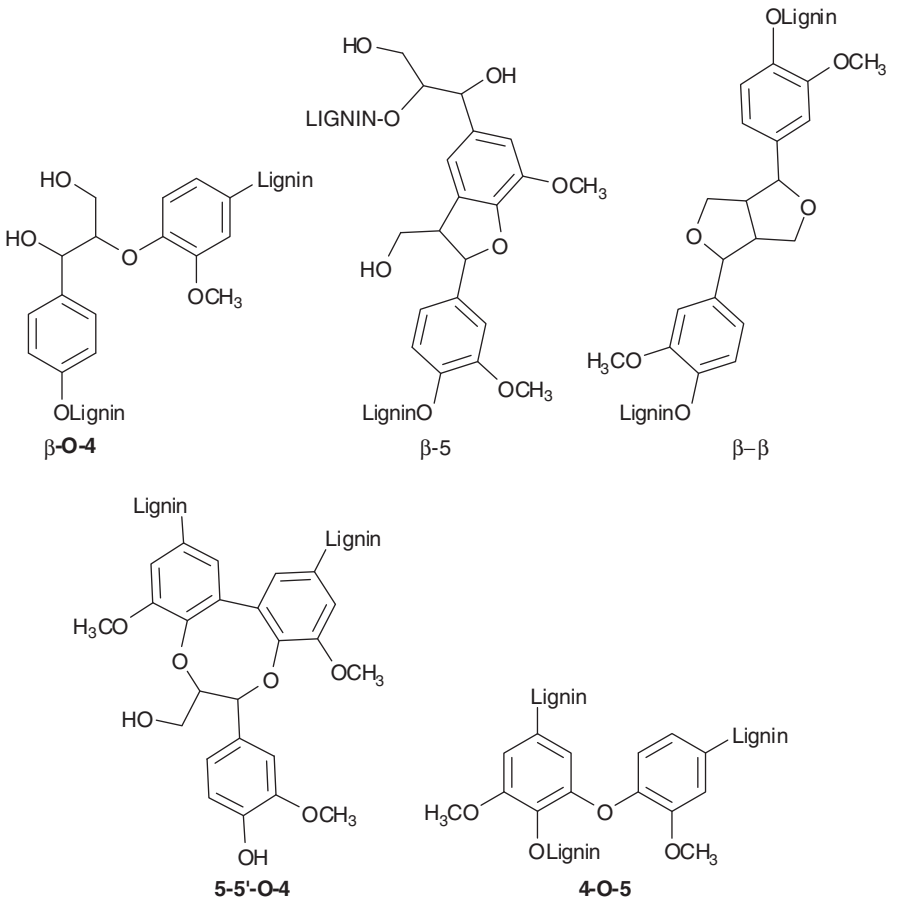


Fig. 8.3: Lignin structure.

smaller compounds. Pretreatment occasionally causes other chemical transformations, depending on the pretreatment method.

The structure of the isolated lignin is highly dependent on the pretreatment nature. Efficient biomass transformation is at the basis of the success of biorefinery streams. Consequently, isolation/pretreatment methods that result in consistent types of lignin of high quality and purity are highly desirable. Several different lignin sources, derived from a specific form of biomass pretreatment, could be potentially used as feedstocks for lignin valorization in a biorefinery. These sources could originate either from pretreatments in the pulp and paper industries (i.e. kraft or lignosulfonate) or new feedstocks specific to the biorefinery scheme (i.e. organosolv) (Smith, Rice, and Ince 2000).

8.2.3 Potential sources of biorefinery lignin

8.2.3.1 Kraft lignin process

Kraft pulping is the main chemical pulping process. The process consists of treatment at 150–180°C with sulfide, sulfhydryl, and polysulfide at high pH. Solubilized lignin is localized in the spent pulping liquor ("black liquor") along with most of the wood's hemicellulose. Lignin contained in black liquor is used as a fuel for the kraft mill after concentration. Lignin is an important fuel for paper and pulp manufacturers because it contributes heavily to a pulp mill's energy self-sufficiency.

Kraft lignin may be recovered from the black liquor by precipitation lowering the pH. Approximately 70%–75% of kraft-isolated lignin is chemically sulfonated. Sulfonylation at aliphatic, benzylic, or aromatic sites confers solubility and surfactant qualities to the lignin.

The degree of sulfonation can be controlled so that products similar to or significantly different than sulfite mill-derived product can be manufactured.

Kraft lignin is soluble in alkali and in strongly polar organic solvents. Its average molecular weight (Mn) is generally between 1,000 and 3,000, but it exhibits a polydispersity typically between 2 and 4. Polydispersity and functional group analysis suggests that the average monomer molecular weight is around 180. A "molecular formula" of $C_9H_{8.5}O_{2.1}S_{0.1}(OCH_3)_{0.8}(CO_2H)_{0.2}$ has been reported for softwood kraft (▶Tab. 8.1), and a model structure for kraft lignin has been reported (▶Fig. 8.4). Nearly 4% by weight is typically free phenolic hydroxy. Kraft pulping of wood constitutes potentially the source of the largest amount of lignin for the biorefinery (Fredheim, Braaten, and Christensen 2002).

Tab. 8.1: Molecular formulas and weights of lignins from various sources.

Type	C9 Molecular Formula	Monomer Molecular Weight
Kraft lignin	$C_9H_{8,5}O_{2,1}S_{0,1}(OCH_3)_{0,8}(CO_2H)_{0,2}$	180
Technical kraft lignin	$C_9H_{7,98}O_{2,28}S_{0,08}(OCH_3)_{0,77}$	176
Unreacted kraft lignin	$C_9H_{8,97}O_{2,65}S_{0,08}(OCH_3)_{0,89}$	190
Lignosulfonated lignin (softwood)	$C_9H_{8,5}O_{2,5}(OCH_3)_{0,85}(SO_3H)_{0,4}$	215–254
Lignosulfonated lignin (hardwood)	$C_9H_{7,5}O_{2,5}(OCH_3)_{0,39}(SO_3H)_{0,6}$	188
Organosolv lignin	$C_9H_{8,53}O_{2,45}(OCH_3)_{1,04}$	nd
Pyrolysis lignin	$C_8H_{6,3-7,3}O_{0,6-1,4}(OCH_3)_{0,3-0,8}(OH)_{1-1,2}$	nd
Steam explosion lignin	$C_9H_{8,53}O_{2,45}(OCH_3)_{1,04}$	188
Dilute acid lignin	$C_9H_{8,53}O_{2,45}(OCH_3)_{1,04}$	188
Alkaline oxidation lignin	$C_9H_{8,53}O_{2,45}(OCH_3)_{1,04}$	188

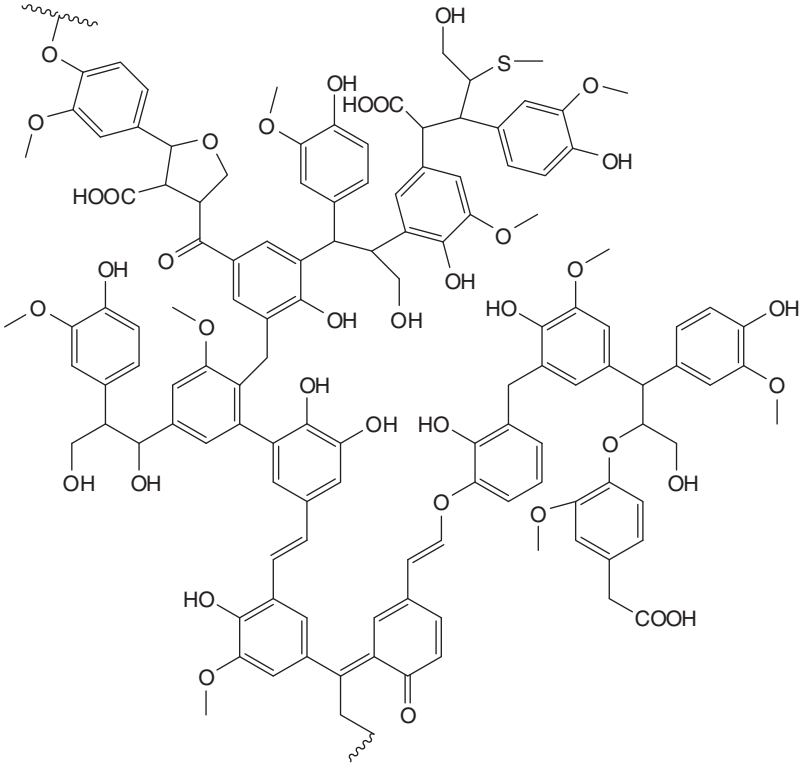


Fig. 8.4: Proposed structure for kraft lignin.

8.2.3.2 Lignosulfonate process

Sulfite pulping is carried out between pH 2–12, depending on the cationic composition of the pulping liquor. Most sulfite processes are acidic and use calcium and/or magnesium as the counterion. Higher pH sulfite pulping is generally done with sodium or ammonium counterions. Because of the nature of the sulfite process, the isolated lignin contains considerable sulfur in the form of sulfonate groups present in the aliphatic side chains. Sulfite lignin generally is soluble throughout the entire pH range so it cannot be readily isolated by simple pH adjustment. Thus, recovery of sulfite lignin (lignosulfonate) is commonly done from waste pulping liquor concentrate after stripping and recovery of the sulfur. Precipitation of calcium lignosulfonate with excess lime (the Howard process) is the simplest recovery method, and up to 95% of the liquor's lignin may be recovered. Sulfite lignin has a higher average molecular weight than kraft lignin. Mw values of 1,000 and even up to140,000 have been claimed, although values of 5,000–20,000 are more common. Their polydispersity is higher than kraft (4 to 9), and they have a higher sulfur content (3% to 8%). Sulfite monomer molecular weights of 215–254 have been calculated. Lignosulfonates are generally soluble in water throughout almost the entire pH range. They are also soluble in some highly polar organic solvents. Approximate "molecular formulas" of $C_9H_{8.5}O_{2.5}(OCH_3)_{0.85}(SO_3H)_{0.4}$

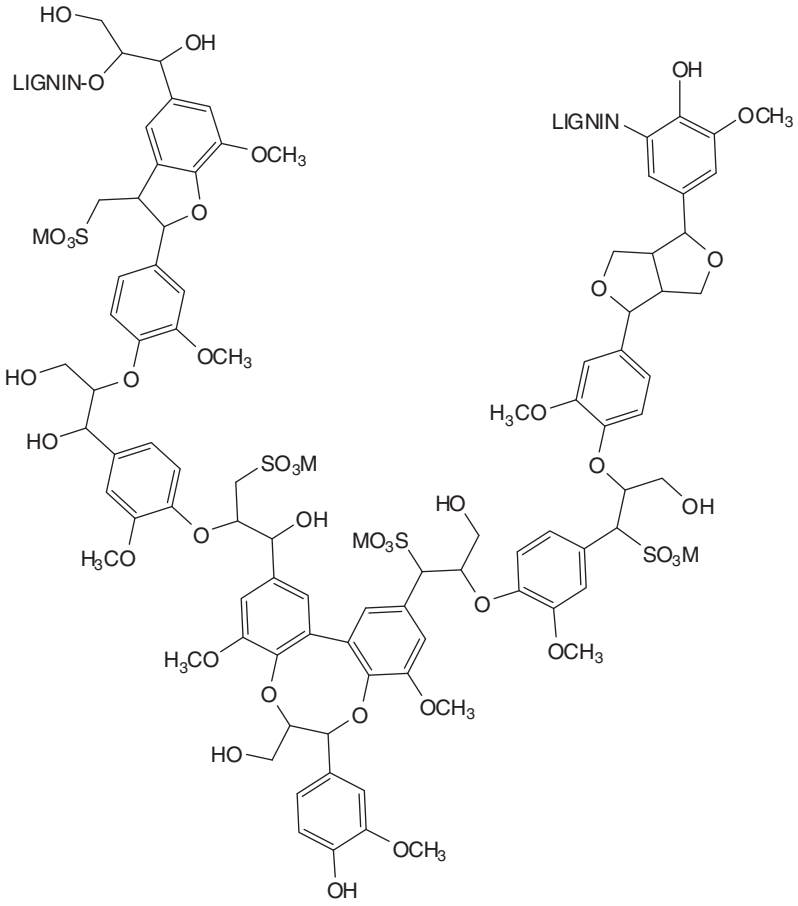


Fig. 8.5: Proposed structure for sulfite lignin.

for softwood sulfite lignin and $C_9H_{7.5}O_{2.5}$ $(OCH_3)_{1.39}(SO_3H)_{0.6}$ for hardwood sulfite lignin have been claimed, and a model lignosulfonate structure has been reported (▶Fig. 8.5) (Buchholz, Neal, and McCarthy 1992).

8.2.3.3 Organosolv lignin

Organosolv pulping is a general term for the separation of wood components through treatment with organic solvents. Such operations normally give separate process streams of cellulose, hemicellulose, and lignin. A wide variety of solvents and combinations have been proposed for organosolv pulping. Many include acids or alkali to enhance pulping rates. The most well known is the Allcel process, which uses ethanol or ethanol water as a solvent.

Organosolv processes offer several possible advantages as sources of biorefinery lignin. In general, the processes result in separate and easily isolated streams of cellulose,

hemicellulose, and lignin. Specifically, organosolv lignin can be easily separated from the pulping solvents either by solvent removal and recovery or a combination of precipitation with water accompanied by distillation to recover the solvent. Most organosolv lignin is insoluble in water between pH 2 and 7, but will dissolve in alkali and many polar organic solvents. Mn values are typically less than 1,000, and polydispersity may range from about 2.4 to 6.4. An approximate molecular formula of $C_9H_{8.53}O_{2.45}(OCH_3)_{1.04}$ and a calculated molecular weight of 188 have been reported (►Tab. 8.1) (Freheim, Braaten, and Christensen 2003).

8.2.3.4 Pyrolysis process

Pyrolytic processes (thermal decompositions occurring in the absence of oxygen) can be used to produce a lignin stream for potential biorefinery use. They require relatively high temperatures (723K) and short vapor residence times, up to 2 seconds.

The byproducts from biomass pyrolysis are char and gas, which are used within the process to provide the process heat requirements. There are no waste streams other than flue gas and ash. The main disadvantage lies in the high carbohydrate consumption required to fuel the process.

The largest difference between pyrolytic lignins and the lignin in biomass is the very low molecular weights of pyrolytic lignin, indicating the high degree of depolymerization caused by the thermal treatment of pyrolysis and suggesting that pyrolysis may be useful as a technology for the controlled molecular weight reduction of lignin. Schulze et al. reported Mw values of 600–1,300 and Mn values of 300–600 for pyrolytic lignins, indicating the presence of dimeric to nonameric phenolic units. Schulze et al. proposed a C8 repeat unit for pyrolytic lignin rather than the C9 unit normally used. The empirical formula was $C_8H_{6.3–7.3}O_{0.6–1.4}(OH)_{1–1.2}(OCH_3)_{0.3–0.8}$ (►Tab. 8.1). these features imply unique opportunities to make specific aromatic hydrocarbons not available from other processes (McDonough and Tappi 1993).

8.2.3.5 Steam explosion lignin

Steam explosion consists of biomass impregnation with steam (180–230°C) under high pressure (200–500 psig) at short contact time (1–20 min) followed by rapid pressure release. The steam explosion process allows the release of individual biomass components, and the process has generally been used as a method for preparing cellulose pulp. Alkali washing or extraction with organic solvents allows recovery of hardwood lignins up to 90%. Steam explosion lignin shows a lower molecular weight and higher solubility in organic solvents than kraft lignin. Thus, steam explosion lignin may be an interesting candidate for selective conversion of lignin to a relatively narrow fraction of mixed phenols.

The steam explosion process provides separated cellulose and lignin streams. As such it is a potentially attractive biorefinery process focused on fuel ethanol, chemicals, and lignin derivatives (Schroeter and Tappi 1991).

8.2.3.6 Other processes

Several other methods have been developed to isolate lignins from biomass. Among them, diluted acid treatments suffer from low yields and corrosion disadvantages

(Varshney and Patel 1988). Pulping can also be done via alkaline oxidation using, for example, O_2 or H_2O_2 . The delignification rates of these processes are, however, slow. Both acid and alkaline treatments provide lignins similar to organosolvent lignins with low molecular weight and high solubility in organic solvents (Aziz, Tappi, and Sarkanen 1989).

8.2.4 The use of lignin in current and future biorefinery schemes

Industrial processes for the exploitation of wood for the production of wood pulp for paper making, and more recently, modern saccharification process for the production of bioethanol from lignocellulosic materials are able to use the cellulose and hemicellulose fraction of wood. Lignin, which comprises up to one third of the wood, is a remnant of work that is not currently valued appropriately, although the lignin resulting from the business cycle of ethanol has an energy content sufficient to support the energy needs of the system. The value of lignin is the key stage in the development of processes for the production of renewable energy (Avellar and Glasser 1998).

Lignin is a highly complex biopolymer, which is the main obstacle to its use because there are not yet available industrial processes that can produce materials from chemically regular or simple molecules, using commercially available products (Shevchenko, Beatson, and Saddler 1999).

Lignin is available commercially as a product of the paper manufacturing processes. It is estimated that, worldwide, from production of 140 million tons of pulp and paper pulp, it revenues every year about 50 million tons. Over 95% of that lignin is burned to recover chemicals used in the process or disposed of in landfills. The two major industrial sources of lignin are composed of lignosolfonate and kraft lignin. Alcell lignin, produced from hardwoods, is available in quantities from the seed industry, representing about 1,500 tons per year (Heytz et al. 1991).

All applications and industrial production of lignin that have been used to date aimed at low value-added. Basically, its polyphenolic structure has not been fully exploited for the production of raw materials for the polymer industry, nor for the development of new materials. This is mainly in the case of composite materials and the low compatibility of lignin with hydrophobic plastics. Lignin-based composite materials show low performance due to such low compatibility. In addition, numerous studies have clearly shown that lignins exhibit interesting antioxidant, antibacterial, and antiviral activities. The biological properties of these materials have not yet been properly exploited (Sun and Cheng 2002).

Agricultural and forestry residues constitute a renewable source of lignocellulosic materials. Industrial use of biopolymers such as cellulose is considerable while lignin, which accounts for 15%–30% of biomass, is an underutilized source of chemical energy. The use of lignin is nowadays limited to thermovalorization processes as filler in composites, a component in binders and coatings, or, at a lower extent, as surfactant/dispersant additives, whereas its potential as a source of valuable phenols in the production of high value-added biopolymers in alternative to petrol chemistry is largely unexploited. Thus, novel processing methods and product concepts are required to extend the role of lignin for future biomass and biofuel application in emerging platforms such as the biorefinery (Torget, Kim, and Lee 2000).

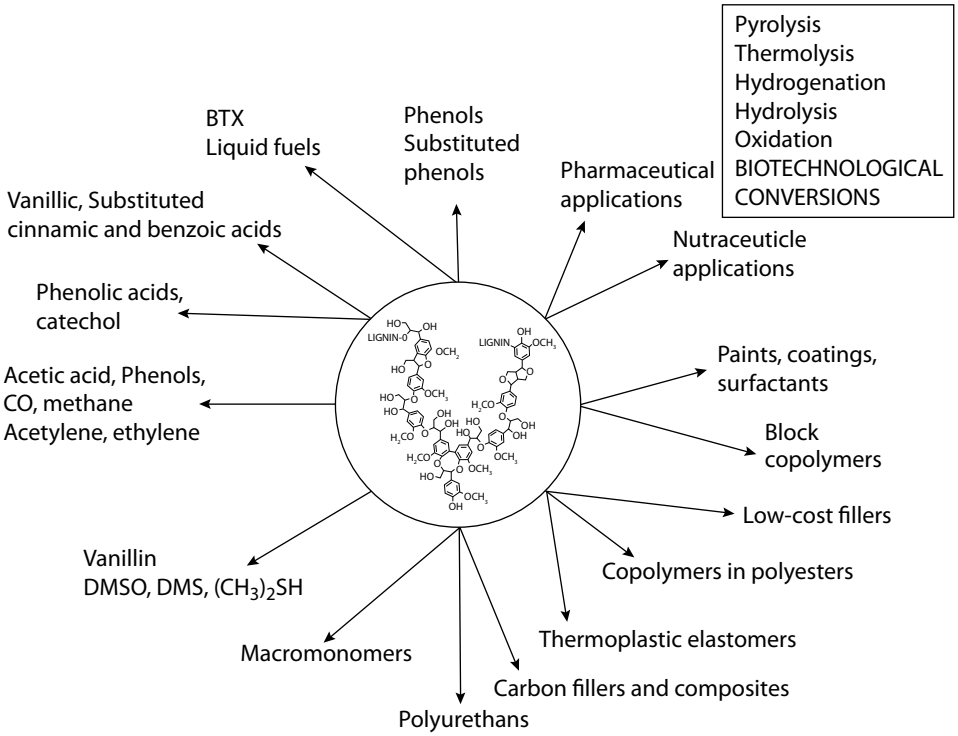


Fig. 8.6: Product opportunities from catalytic lignin transformations.

Lignin valorization to chemicals is an important tool for economic profitability of the biorefinery. Lignin exploitation can be divided into three categories: (1) power, green fuels, and syngas; (2) macromolecules; and (3) aromatics and other chemicals (Dimmel et al. 2002).

The first option focuses on the use of lignin as a carbon source using aggressive means to break down its polymeric structure (Bozell, Hoberg, and Dimmel 2000). The second option aims at valorizing the macromolecular lignin structure in high molecular weight applications (Bozell, Hoberg, and Dimmel 1998). In the third option the macromolecular lignin backbone is broken to obtain aromatic building-block molecules (Bozell, Hames, and Dimmel 1995). ▶Fig. 8.6 shows possible new product opportunities from catalytic lignin transformations.

8.2.4.1 Power – green fuels – syngas

Lignin is currently used primarily for process heat, power, and steam (DeBons and Whittington 1992). Lignin gasification produces syngas (carbon monoxide/hydrogen), the addition of a second phase that uses the technology of water-gas shift (WGS) allows the production of a hydrogen flow "pure" to coform with carbon dioxide. Hydrogen can be used to produce electricity (fuel-cell applications) or by hydrogenation/hydrolysis. Lignin-derived syngas can be used in Fischer-Tropsch (FT) technology to produce green diesel (Kim, Ralph, and Akiyama 2008). The technical requirements for FT include

economical purification of syngas streams and catalyst and process improvements to reduce unwanted products (Boerjan, Ralph, and Baucher 2003).

The dry biomass can be converted to a liquid known as pyrolysis oil or bio-oil by fast pyrolysis. Bio-oils obtained as a product generally are not stable to changes in viscosity and oxidation and this makes them awkward to use as fuel and chemical products. Pyrolysis oils may be included in some of the oil refinery processes after pretreatment and stabilization. The process includes preconditioning prior to pyrolysis oil stabilization (Schiene 2002).

8.2.4.2 Macromolecules

The lignin's polymer and polyelectrolyte properties are important for all current commercial uses of lignin. The targeted applications are: emulsifiers, binders, and antidisperdants. In fact, nearly 75% of lignin products are within these applications. Without modification of lignin these applications remain low added value. Medium-term conversion technologies will be focused at implementation of their performance by targeted lignin functionalization. ▶Tab. 8.2 shows a scheme of possible applications (Ralph et al. 2004).

8.2.4.3 Aromatics and chemicals

Lignin is the only renewable source of an important and high-volume class of compounds – the aromatics. It is easy to conclude that direct and efficient conversion of lignin to discrete molecules or classes of high-volume, low molecular weight aromatic molecules is an attractive goal. As petroleum resources diminish and prices increase, this goal is very desirable, and is perhaps the most challenging and complex of the lignin technology barriers. Bringing high-volume aromatics efficiently from a material as structurally complex and diverse as lignin becomes a challenging but viable long-term

Tab. 8.2: Medium-term conversion technologies: high molecular weight lignin products.

Carbon fiber	Economical purified lignin sources Economical modifications to allow high-melt spin rates High carbon yields Application varied lignin sources
Polymer fillers	Economical modifications to improve solubility and compatibility with other polymers Controllable alteration of molecular weight Control of polymer color Control of polyelectrolyte character Functional group enhancement
Thermoset resins	Molecular weight and viscosity control
Formaldehyde-free resins	Functional group enhancement (carbonylation, carboxylation, de-etherification) to improve oxidative stability, thermal stability, consistent lignin properties, cure rate consistency, and lignin color
Adhesives and binders	

Tab. 8.3: Long-term conversion technologies required for the aromatics market

Aromatic	Lignin required – theoretical (10^9 lb)	Lignin required – current technology (10^9 lb)
BTX	93	930
Phenol	10	80
Terephthalic acid	13	130
Total	**116**	**1,112**

opportunity (Holtman et al. 2003). ▶Tab. 8.3 shows the long-term conversion technologies required for the aromatics market.

These products could be easily and directly used by conventional petrochemical processes. Development of the required aggressive and nonselective chemistries is part of the long-term opportunity but is likely to be achievable sooner than highly selective depolymerizations. In fact, some of the past hydroliquefaction work with lignin suggests that, with further development, this concept is a good possibility (Heikkinen et al. 2003).

Monomeric lignin molecules The breaking of CC and CO bonds leads to a very selective depolymerization that could produce a series of aromatic complex not likely to be obtained through conventional techniques. The barriers that would need to be overcome are to develop technology that would allow a selective cleavage of bonds bearing structures like monomeric lignin and the development of a new market for monomeric building blocks (Zhang et al. 2006).

8.3 Oxidative strategies in lignin chemistry: a new environmentally friendly approach for the valorization of lignin

Lingin's chemical heterogeneity is one of the main reasons for the lack of valorization of lignin residues that emerge from pulp and paper and modern saccharification processes (Capanema, Balakshin, and Kadla 2004). The possible strategies of lignin valorization are focused into two main directions, namely the selective funcionalization of the lignin polymer in order to improve its compatibility and performance in composite and copolymer materials, or, alternatively, in its oxidative polymerization to get polyfunctional monomeric compounds to be used as feedstocks for the polymer industry as an alternative to fossil-fuel derived building blocks (Guerra et al. 2006).

In this context, special emphasis was devoted in the past few years to the study of lignin oxidative functionalization processes, mainly due to the presence of high amounts of side-chain aliphatic OH, terminal phenolic OH groups, and reactive benzylic position, which can be selectively modified (Cole, Clark, and Solomon1990).

Products derived from oxidation of lignin may serve as a platform for organic synthesis because they tend to form aromatic compounds with added features (Shleev et al. 2005). The selective oxidation of lignin can be accomplished by the use of homogeneous and

heterogeneous catalysts. The modulation of metal ligands with the tuning of stereoelectronic properties will influence the reactivity, stability, selectivity, and solubility of the catalysts, thus making possible the selective modification of specific functional groups in lignins. The possibility to spam from robust catalysts that are able to disrupt targeted linkages to selective oxidation of specific functionalities is an important tool for the design of valorization of lignin toward high value-added products (Solomon and Lowery 1993).

8.3.1 Oxidation of lignin by biocatalysis processes

In nature, lignin is selectively oxidized by white-rot fungi. These species excrete a pool of ligninolytic enzymes that activate both dioxygen and hydrogen peroxide at the degradation of lignins. Among them, laccases and peroxidases, more specifically Mn-peroxidase and lignin peroxidases, are the most active. Several studies have been carried out in order to establish their reaction mechanisms and the potentialities for the development of biotechnological routes to lignin oxidation either in the presence or in the absence of oxidation mediators. Strategies for enzyme immobilization and use in mixtures to reproduce natural cascades have also been reported.

8.3.1.1 Laccase

Laccase, benzenediol:oxygen oxidoreductase 1.10.3.2, is a multicopper oxidase that performs the reduction of oxygen to water. The enzyme contains four copper centers, one type 1 Cu (T1), one type 2 Cu (T2), and a coupled binuclear type 3 (T3) Cu centers (Reinhammer and Malstrom 1981). The T2 and T3 sites form a trinuclear Cu cluster onto which O_2 is reduced. The T1 Cu atom oxidizes the reducing substrate and transfers electrons to the T2 and T3 Cu atoms. Laccase is able to oxidize phenolic systems by an outer-sphere electron-transfer process that generates a radical cation, which by fast deprotonaton generates a reactive phenoxy radical (Caldwell and Steelink 1969). The phenoxy radical intermediates formed during this process can further disproportionate and consequently initiate lignin degradation (Lundquist and Kristersson 1985). Laccase shows a high thermal resistance (stable at 60°C) (Call and Mucke 1997), low substrate specificity, and high oxidation rates that make this enzyme an ideal candidate for the development of efficient processes for lignin modification (Kirk and Chang 1990; Higuchi 1990).

The redox potential of laccases depends on the fungal species that have been used for their production. The redox potential (versus NHE [normal hydrogen electrode]) varies from 430 mV for tree laccase from *Rhus vernicifera* to 780 mV for fungal laccase from *Polyporus versicolor* (Elegir et al. 2005). In any case, the oxidation of substrates with blocked phenolic O-H, for example, methoxybenzene derivatives, is prevented by their high redox potential and requires the presence of radical mediators such as 1-hydroxybenzotriazole (HBT) and 2,2-azinobis- 3-ethyl-benzthiazoline-6-sulfonate (ABTS) (Morozova et al. 2007; Bourbonnais and Paice 1992).

In ▶Fig. 8.7 the accepted mechanism for laccase oxidation of phenolic compounds is reported. Pathways B, C, and D are not likely to occur due to the slow kinetics of oxygen addition to phenoxy radical species (Reid and Paice 1994).

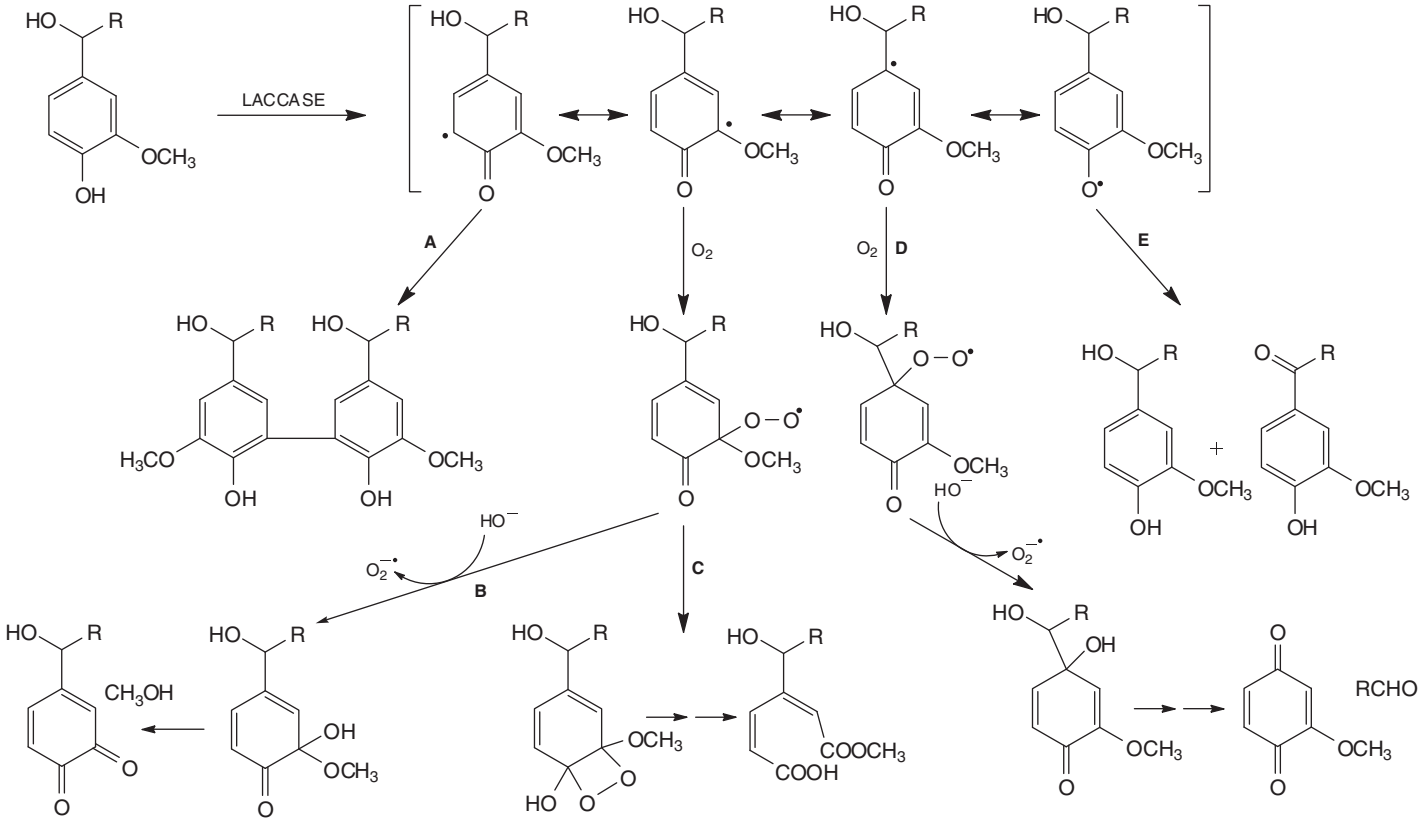


Fig. 8.7: Lignin oxidation mechanism by laccase.

The radical mediator, such as HBT, acts as a diffusible lignin oxidizing agent since it can access inner lignin structures in the cell wall as opposed to the relatively large enzyme (Bourbonnais et al. 1995).

In order to elucidate the delignification mechanism catalyzed by laccase, several studies have been carried out on both phenolic and nonphenolic monomeric, arylglycerol β-O-4, and β-1 ether lignin model compounds (see, e.g. Bourbonnais and Paice 1990; Kawai, Umezawa, and Higuchi 1988). The oxidation of condensed phenolic structures, such as 5-5′, α-5, diphenylmethane, and stilbene units, is also an important tool to be achieved manly because they are among the main units of highly stable (and recalcitrant to oxidation) kraft lignin (Gierer 1985). In order to elucidate the reactivity pattern of a laccase mediator system toward kraft lignins, efforts have been devoted to study the oxidation of different condensed phenolic models with laccase and HBT (Crestini and Argyropoulos 1998).

It has been shown that laccase in the presence of HBT generates the oxybenzotriazolyl radical that can oxidize both phenolic and some nonphenolic lignin models (Potthast, Koch, and Fisher 1997) by a hydrogen atom abstraction process rather than

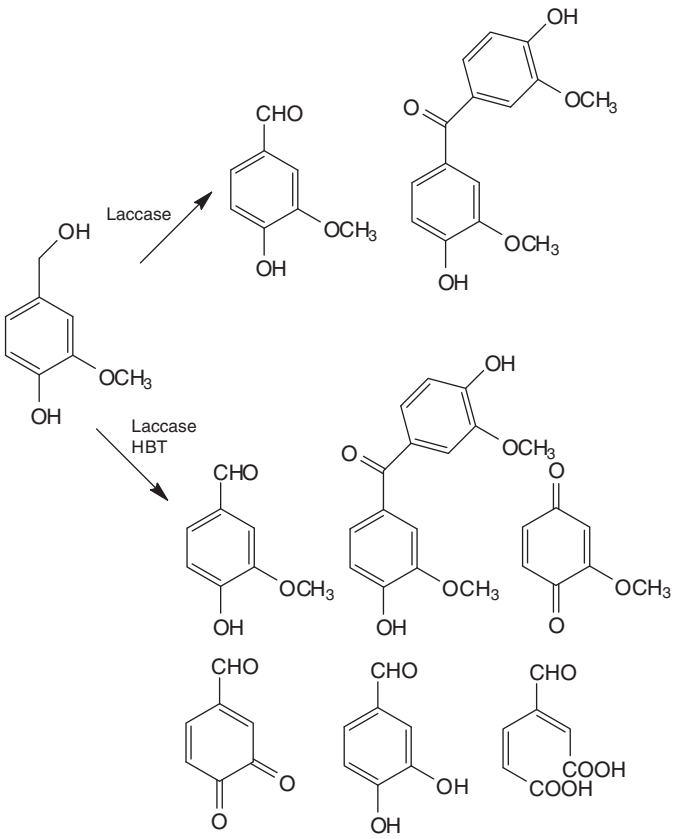


Fig. 8.8: Oxidation of vanillyl alcohol by laccase and the laccase-mediator system.

an electron-transfer process. The oxidation of vanillyl alcohol was then performed with a laccase and laccase mediator (LM) system to further elucidate the role of radical mediators in the modification of phenolic and nonphenolic lignin subunits (Crestini, Jurasek, and Argyropoulos 2003). The oxidation of vanillyl alcohol with laccase produced products of alkyl side-chain oxidation and oxidative coupling, respectively (▶Fig. 8.8). When HBT was added to the reaction medium, a different behavior was observed, and products of aromatic ring oxidation, *ortho*- and *para*- benzoquinones, catechol, and muconic acid, were recovered in appreciable yield.

The formation of these products cannot be explained on the basis of the reaction of a phenoxy radical with oxygen because the kinetics for oxygen addition to phenoxy radicals are slow. On the contrary, the kinetics of the addition of a superoxide anion radical to phenoxy radical species are fast and would explain the formation of such a range of products. In this case the benzyl radical produced would undergo fast oxygen addition and superoxide anion radical elimination as reported in ▶Fig. 8.9. In turn, the superoxide anion radical so generated would react with the phenoxy radical species present in the reaction medium. More specifically, it was evident that laccase treatments induced both side-chain oxidation processes (as shown by the decrease of aliphatic O-H groups present in lignin side chains) and oxidative coupling processes. The last reaction pattern was demonstrated by the increase of condensed phenolic units after the laccase treatment (Rodriguez Couto et al. 2007). On the contrary, the oxidative coupling reaction pattern, extensive aromatic ring cleavage, and alkyl side-chain oxidation were observed when lignin was submitted to LM treatments in the presence of HBT or ABTS (Cho and Bailey 1979).

The industrial use of the laccase or LM system is prevented by both the need to recycle the enzyme and its rather low stability (Krajewska 2004). There are extensive reports in the literature about laccase immobilization (Abadulla et al. 2000). However, the main drawback in the application of such protocols lies in the fast deactivation of immobilized laccases (Ryan et al. 2003). Recently, a new process for the deposition of ultrathin, multilayer, alternatively charged polyelectrolites onto charged substrates, the layer-by-layer technique (LbL), was developed (Kandelbauer et al. 2004).

A first catalyst was prepared by laccase immobilization onto alumina particles by sylanization and cross linking with glutaraldehyde according to classical procedures (Di Serio et al. 2003).

The immobilized laccase was in turn coated by alternate layers of poly(allylamine) hydrochloride and polystyrene sulfonate (Held et al. 2005). The LbL coating of the enzyme resulted in a retained enzymatic activity and in an increased stability with respect to the laccase (▶Fig. 8.10) (Decher, Hong, and Schmitt 1992; Crestini et al. 2010). In a same fashion, LbL poly(allylamine) hydrochloride and polystyrene sulfonate microcapsules were synthesized using a carbonate templates (Peyratout and Dähne 2004). The core dissolution was followed by the opening of pores onto the microcapsule surface by tuning the pH value. At pH 2.8 pores can be opened and the laccase could be loaded inside the microcapsules by coulombic interaction with the oppositely charged polyelectrolyte. Increase of the pH value resulted in the reduction of the pore diameter and enzyme entrapment (▶Fig. 8.11). The laccase microcapsules showed comparable enzymatic activity and stability to coated laccase particles as shown in ▶Fig. 8.10.

Both LbL-coated laccase particles and microcapsules were studied in the oxidation of lignin with laccase and the LM system (Crestini, Perazzini, and Saladino 2010). The

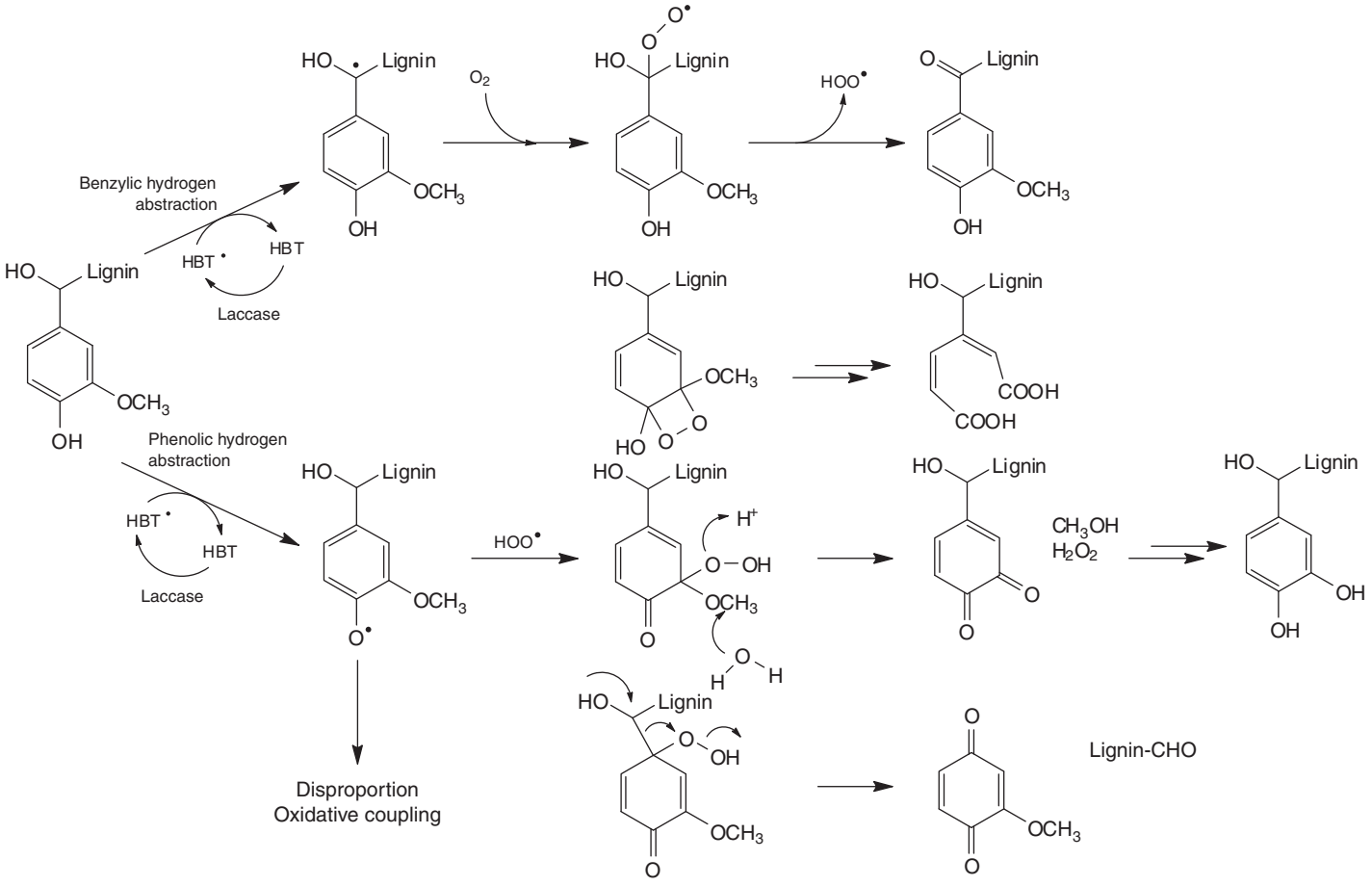


Fig. 8.9: Proposed reaction mechanism for the oxidation of lignin by the laccase-mediator system.

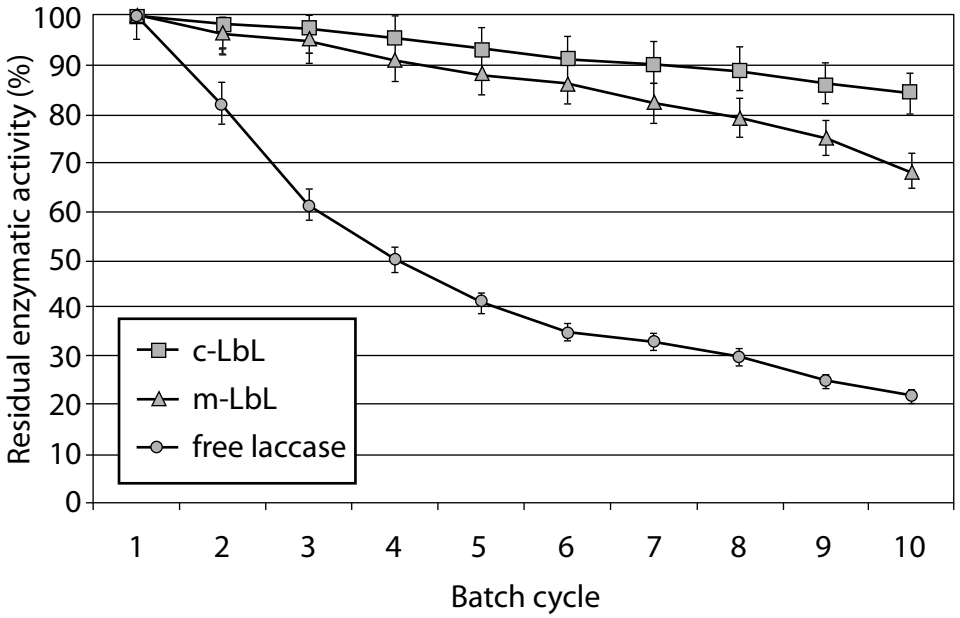


Fig. 8.10: Laccase, LbL-coated laccase, and LbL laccase microparticle residual activity after 10 12-hour reaction batches.

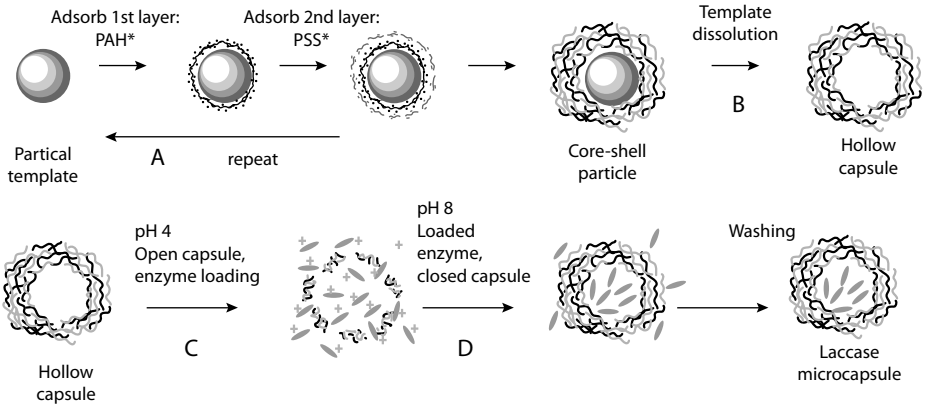


Fig. 8.11: LbL laccase microparticles synthesis.

lignins were oxidized by the immobilized enzymes better than soluble laccase, probably due to the increased stability of the supported enzymes. In the presence of laccase, extensive alkyl side-chain oxidation and aromatic ring oxidative coupling processes were detected as shown by the decrease of the aliphatic OH groups and increase of condensed phenolic units, respectively.

8.3.1.2 Manganese peroxidases

Besides laccases, Mn-peroxidases (MnP) from white-rot fungi showed a high reactivity in the oxidative functionalization of lignins (Paice et al. 1995). This enzyme, which contains one iron protoporphyrin IX as prosthetic group, is able to activate H_2O_2 in the oxidation of Mn(II) to Mn(III), which in turn, after chelation by organic acids, became a freely diffusible oxidizing species. The ultimate oxidation of lignin is performed by generation of reactive phenoxy radicals through a hydrogen abstraction process (Wariishi, Akileswaran, and Gold 1988). Due to its high reactivity, MnP has been used for the oxidation of different lignin model compounds, including phenolic arylglycerol β-aryl ether (Tuor et al. 1992) and diarylpropane derivatives (Wariishi, Valli, and Gold 1989).

Condensed phenolic lignin model compounds, 5–5′, β-5, and diphenylmethane subunits were also efficiently oxidized by MnP (Crestini et al. 2000). In particular, when the 5-5′ was treated with MnP produced by the white-rot fungus *Lentinula edodes* (D'Annibale et al. 1996), an extensive conversion of substrate was obtained to yield products of alkyl side-chain oxidation. It is interesting to note that the β-5 lignin model compound, 2,4′-dihydroxy-3,3′-dimethoxy-5-methyl-diphenylmethane was the most reactive substrate during MnP/H_2O_2 oxidation to afford products of alkyl side-chain oxidation and oxidative cleavage of the carbon bridging position, which are vanillin and vanillic acid (▶Fig. 8.12). These results clearly suggest that the oxidation is selective for the methyl or methylene groups in *para*-position to OH moieties. In the case of the methylene moiety, the cleavage of the carbon bridging position became an operative process.

8.3.1.3 Multiple enzyme treatments

Recently, a number of studies have been reported on the synergic activity of laccases and peroxidases in lignin oxidation. More specifically, it was shown that coimmobilized LbL-coated laccase and HRP are able to efficiently depolymerize lignin by concomitant hydrolytic and oxidative processes, as reported in ▶Fig. 8.13.

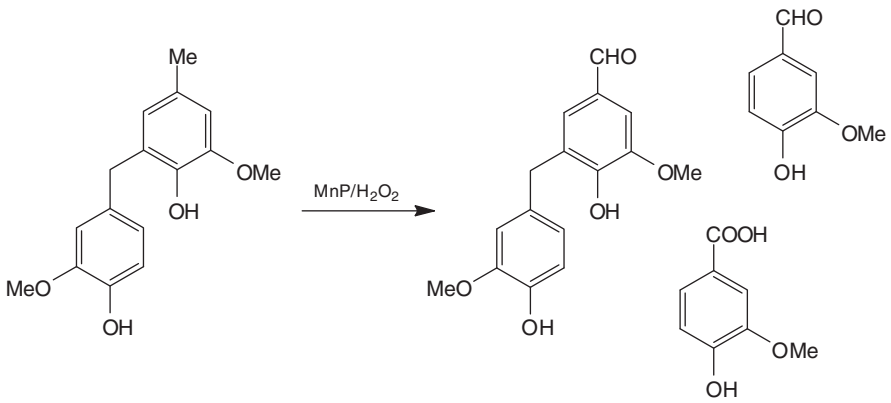


Fig. 8.12: Oxidation of 2,4′-dihydroxy-3,3′-dimethoxy-5-methyl-diphenylmethane by MnP/hydrogen peroxide.

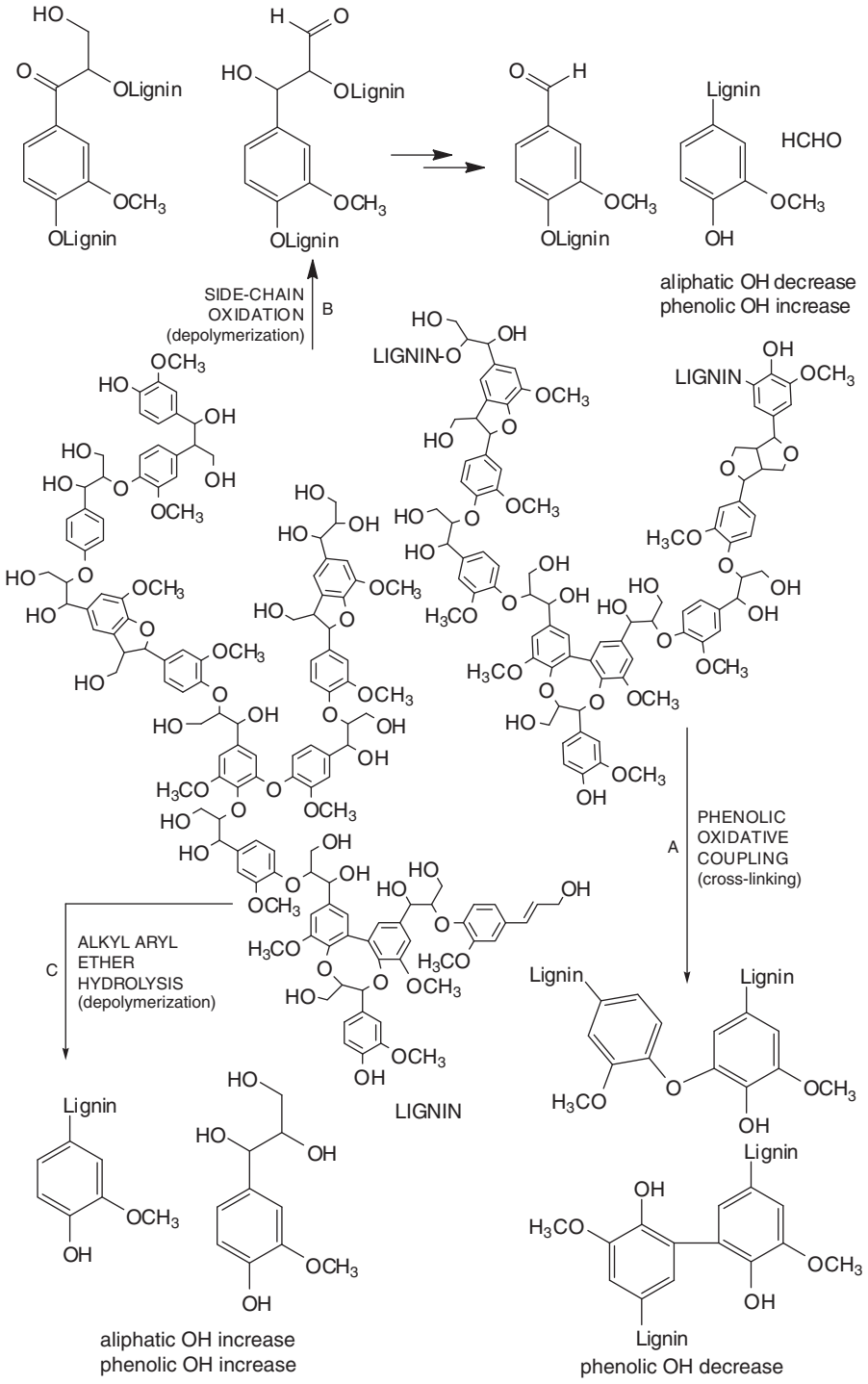


Fig. 8.13: Lignin oxidation by coimmobilized oxidative enzymes.

8.3.2 Catalysis

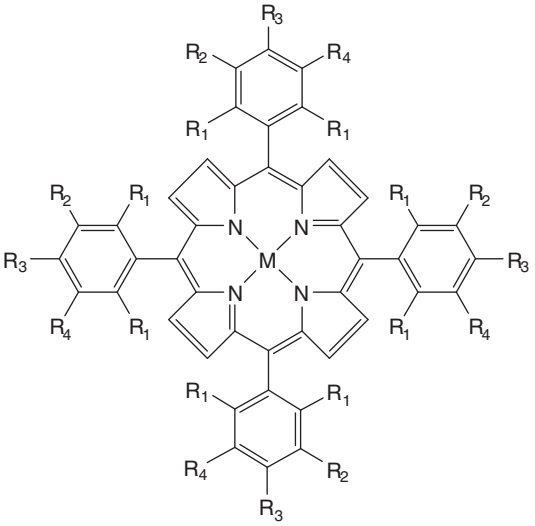
The catalysts used for lignin oxidation can be classified according to the ligand nature. A first class consists in metallopophyrins (Ferm, Kringstad, and Cowling 1972). Such catalysts show high potentials in ligand functionalization and reactivity tuning and constitute interesting biomimetic systems.

Typically, alcohol oxidation has been performed by aid of Schiff-base catalysts, especially Co(salen), which are structurally simpler than the porphyrin ligands (Nayak 1999). Alternatively more robust complexes, extensively used as wood pulp bleaching catalysts, can be used, including iron tetraamido macrocyclic ligand (TAML), manganese 1,4,7- trimethyl-1,4,7-triazacyclononane (TACN), or manganese 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane (DTNE) complexes (Zoia et al. 2008). Polyoxometalates are polyatomic clusters of early transition metaloxy anions and were also used as wood pulp bleaching catalysts (Canevali et al. 2005). Also, simple metal and organometal salts have been used as well as miscellaneous catalysts that employ various ligand systems (Cho and Bailey 1979).

8.3.2.1 Oxidative functionalization of lignin and lignin model compounds by biomimetic catalysis: catalysis by metalloporphyrins

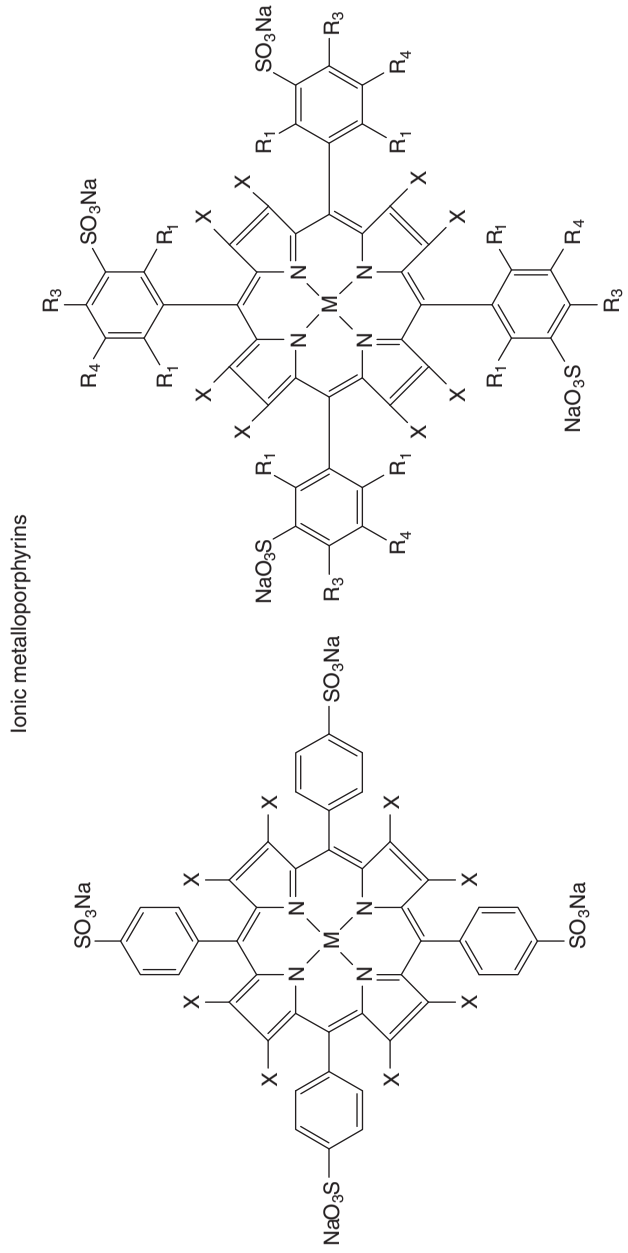
The selective modification of lignin in wood is mainly accomplished by enzymes produced by white-rot basidiomycetes, such as laccases, lignin peroxidases (LiP), and manganese-dependent peroxidases (MnP). Synthetic metalloporphyrins are biomimetic catalysts for LiP and MnP because they can yield highly oxidized metallo-oxo species similar to LiP I and LiP II (Glenn et al. 1983). Highly functionalized porphyrins bearing aryl substituents in the *meso* positions of the ring are catalyst systems stable to oxidants, and their redox-potential, as well as their solubility, can be finely tuned by the stereoelectronic properties of the substituents (▶Fig. 8.14). Several metal porphyrin

Neutral metalloporphyrins

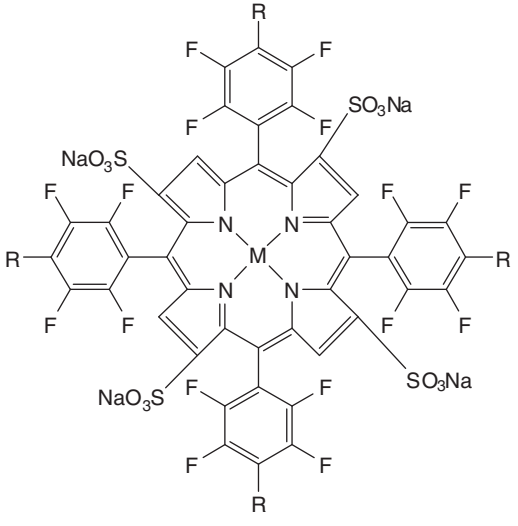


(*Continued*)

Ionic metalloporphyrins



(*Continued*)



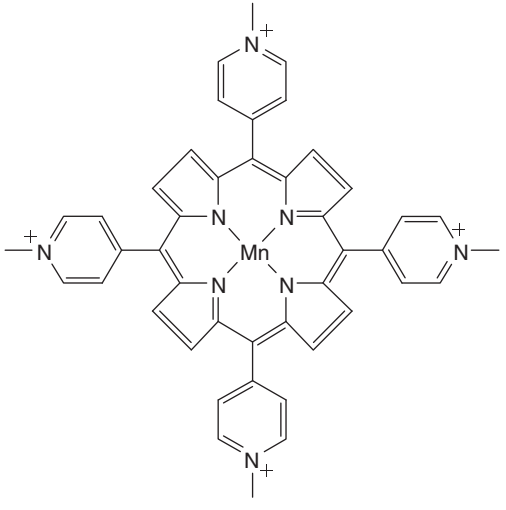


Fig. 8.14: Metalloporphyrins structures.

catalysts were found to be capable of performing the oxidation of lignin and lignin model compounds. There is an extensive review on the oxidation of lignin and lignin model compounds using metalloporphyrin complexes (Crestini et al. 1999; Crestini, Pastorini, and Tagliatesta 2004).

For example, recalcitrant residual kraft lignin and 5-5′ diphenylmethane substituents have been oxidized with H_2O_2 and an array of anionic manganese and iron meso-tetra(2,6-dichloro-3-sulphonatophenyl)porphyrin chloride (TDCSPPMnCl and TDCSPPFeCl, respectively) and meso-tetra-4-sulphonatophenyl porphyrin chloride (TSPPMnCl), and cationic manganese meso-tetra(N-methylpyridinio)porphyrin pentacetate TPyMePMn(MeCOO)$_5$. Irrespective of experimental conditions, the oxidation of the dimeric model compounds afforded products of aromatic ring oxidation to benzoquinone, alkyl-side oxidation (benzyl alcohol derivatives), and demethylation (▶Fig. 8.15).

A comparison between TDCSPPMnCl and TDCSPPFeCl showed that the manganese porphyrin was able to perform a more extensive oxidation than the iron

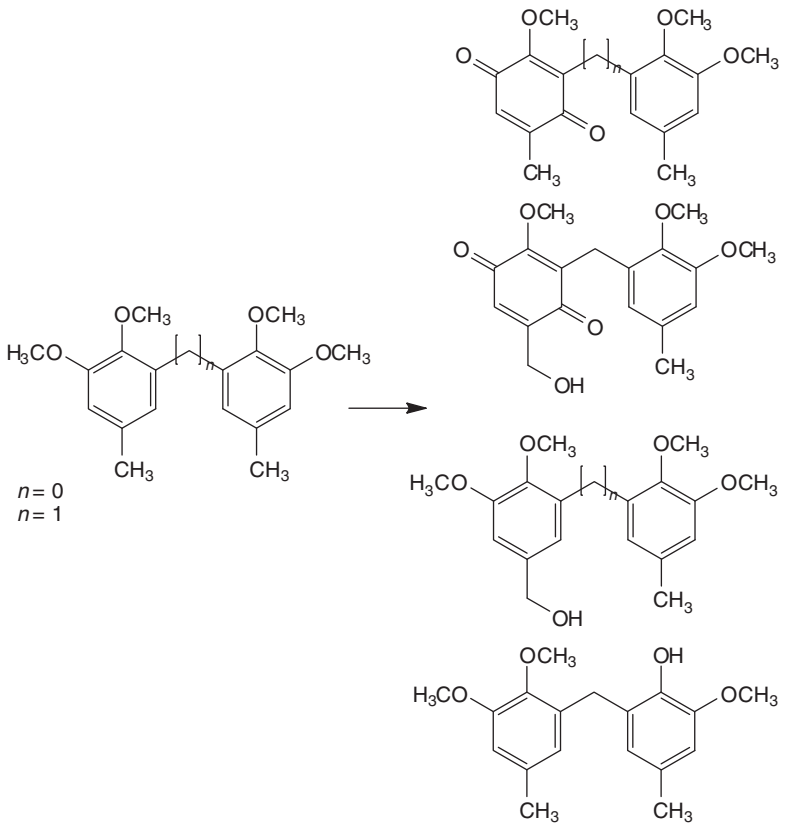


Fig. 8.15: Oxidation of diphenylmethane lignin model compound by Fe and Mn porphyrins.

one. Manganese porphyrins were more efficient in carrying out the oxidative process, producing only a low amount of coupling reactions, as suggested by the presence of low amounts of condensed phenolic OH groups. The comparison between anionic and cationic water-soluble Mn porphyrins TSPPMnCl and TPyMePMn(MeCOO)$_5$, respectively, showed an increased efficiency in the case of the cationic catalysts.

The major disadvantage of this process is at the level of industrial production, the cost caused by the degradation, and loss of the catalysts that sometimes exceeds the advantage due to efficiency. The major need is, therefore, to develop techniques that allow us to obtain restraining stable catalysts that have a high chance of being recycled.

The immobilization protects the catalyst center of natural enzymes so the porphyrin catalyst would be recycled. A further step in the design of robust biomimetic catalysts of LiP based on metalloporphyrins was the immobilization procedure of active species on inorganic supports that mimic the effect of the polypeptide envelope to protect the catalytic center toward deactivation. Among the different supports tested, clays of the smectite family, such as montmorrilonites, have been used to immobilize cationic metalloporphyrins used in the oxidation of lignin and lignin model compounds (Shimada et al. 1977). In this context, the cationic porphyrin TPyMePMn(MeCOO)$_5$ was efficiently immobilized on montmorillonite to yield a novel heterogeneous TPyMePMn(MeCOO)$_5$/clay catalyst and applied for the oxidation with H_2O_2 of a series of lignin model compounds.

For example, the β-O-4 arylglycerol phenyl ether model compound in ▶Fig. 8.16 was treated with the TPyMePMn(MeCOO)$_5$/clay/H_2O_2 catalyst system in dioxane/citrate buffer at 60°C to yield products of side-chain oxidation, para-benzoquinone formation, quinone formation, and products of side-chain cleavage and side-chain cleavage and quinone formation (▶Fig. 8.16).

8.3.2.2 Metallosalen catalysts

In recent years some of the most promising catalysts of lignin were Cobalt(salen) complexes (▶Fig. 8.17) (Peng, Simonsen, and Westermark 1992). They can form cobalt-superoxo complexes and dimeric peroxo complexes upon exposure to molecular oxygen or H_2O_2 (Haikarailen et al. 2001). Advantages in the use of Co(salen) complexes are due to the fact that they are economic, stable, and easy to synthesize (Bolzacchini et al. 1996).

The properties of solubility and reactivity of the catalyst can be modified altering the salen ligand, for example, by adding the sulfonate groups, and are easily reached and change the properties of solubility and reactivity of the catalyst for the oxidation of lignin (Bolzacchini et al. 1997). In particular, it was demonstrated that they were able to oxidize lignin model compounds in high yields (Beatson et al. 1984).

For the oxidation of monomeric and dimeric lignin model compounds with oxygen catalyzed by Co(salen), the reactivity and the characterization of radical intermediates by electron paramagnetic resonance (EPR) spectroscopy suggested that such

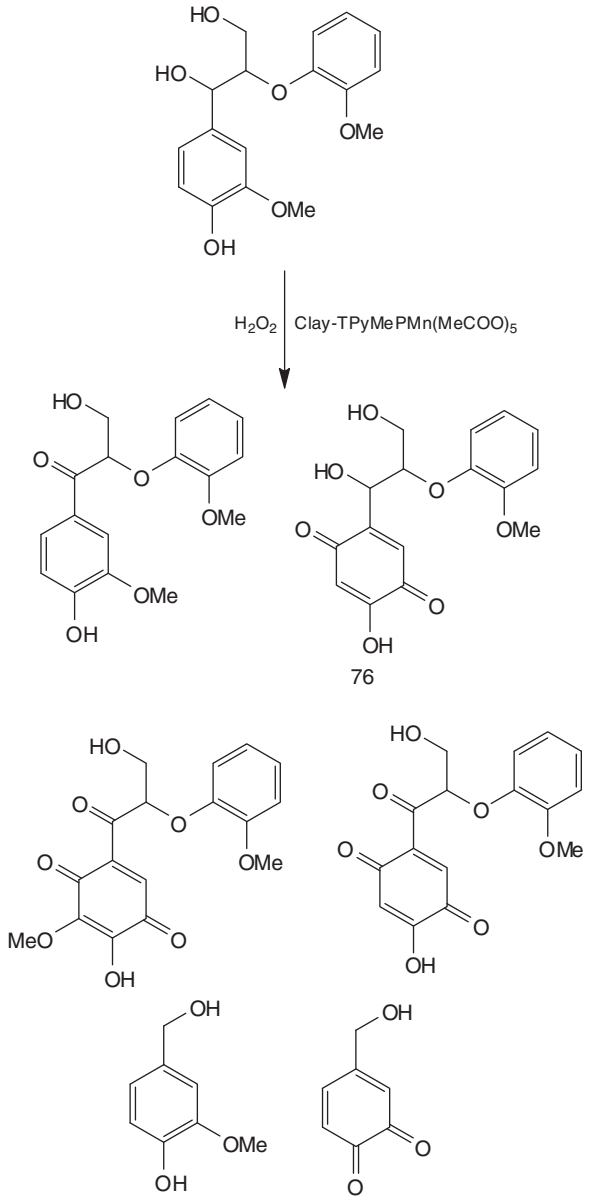


Fig. 8.16: Oxidation of β-O-4 lignin model compound by the biomimetic clay-immobilized porphyrin mediator system.

oxidation occurs through three steps, yielding the formation of a superoxocobalt derivative, phenoxycobalt radical, and phenoxyphenate cobalt radical, respectively (Carnevali et al. 2002). ▶Fig. 8.18 shows the oxidation pathway of dimeric lignin model compounds.

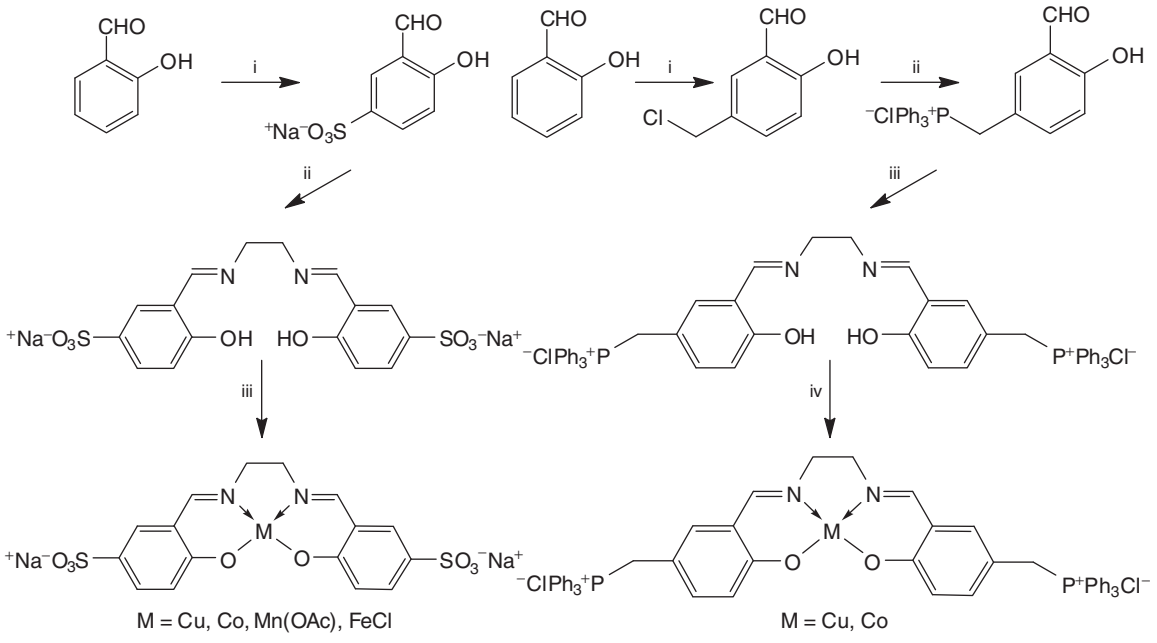


Fig. 8.17: Salen structures and synthesis.

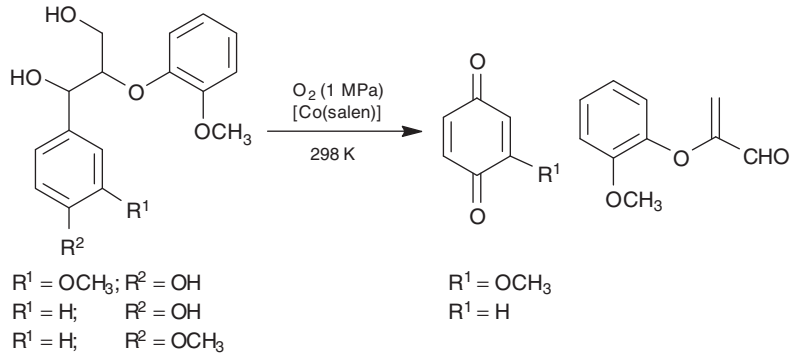


Fig. 8.18: Oxidation of dimeric lignin model compounds by Co(salen) complexes.

8.3.2.3 Metallo-TAML, -DTNE, and -TACN catalysts

Mn-TAML (tetraamido macrocyclic ligand) complexes are active and selective catalysts (Kangaz, Salmi, Kleen 2002). They are highly resistant to oxidative degradation $[(Me_4DTNE)Mn(IV)_2(\mu\text{-}O)_3](ClO_4)_2]$, where DTNE is 1,2-bis-(4,7-dimethyl-1,4,7 triazacyclonon-1-yl)ethane, or $[(Me_3TACN)Mn(IV)_2(\mu\text{-}O)_3](PF_6)_2]$, where TACN is 1,4,7-trimethyl-1,4,7-triazacyclononane (▶Fig. 8.19). Structures of [(Me4DTNE)Mn(IV)2(μ-$O)_3$] $(PF6)_2$ and [(Me3TACN)Mn(IV)2(μ-$O)_3$]$(ClO4)_2$) have been used in the oxidation of lignin model compounds and for bleaching of pine kraft AQ pulp (Koljonen et al. 2003).

8.3.2.4 Polyoxometalate-based catalysts

Polyoxometalates are a family of anionic clusters consisting of d^0 metal cations, particularly W(VI), Mo(VI), V(V), and Nb(V) and oxygen anions arranged in MO_6 octaedral units. POM are low-cost easily available catalysts that can be made readily soluble in water or organic solvents and display high redox potential. One of the most studied POM families is the Kegging-type heteropolyanions $XM'_aM''_{12-a}O^{bm-}$ where X^{n+} is a p or d block heteroatom and M′ M″ are d^n and d0 metal centers, respectively (▶Fig. 8.20). POM can efficiently activate O_2 or H_2O_2 toward lignin oxidation. β-O-4 aryl ether moieties are efficiently oxidized by both homolytic and heterolytic processes. ▶Fig. 8.21 shows the oxidation products of a phenolic β-arylether model compound by HPA/O_2.

8.3.2.5 Simple metal salt-based catalysts

Lignin or lignin model compounds in the presence of oxygen react using simple metals. These catalysts have been developed to catalyze the hydrocarbons originally in a selective manner. Aromatic units form a significant part of the structure of lignin, and that is why it is significant to use these oxidation catalysts to enhance the lignin in kraft pulp, leaving the use of these catalysts for the oxidation of hydrocarbons. Sometimes salt solutions besides Mn(II)/Co(II) combinations are used in the lignin oxidation, such as the use of Mn(III)acetate as a polymerization catalyst of guaiacol to polyguaiacol.

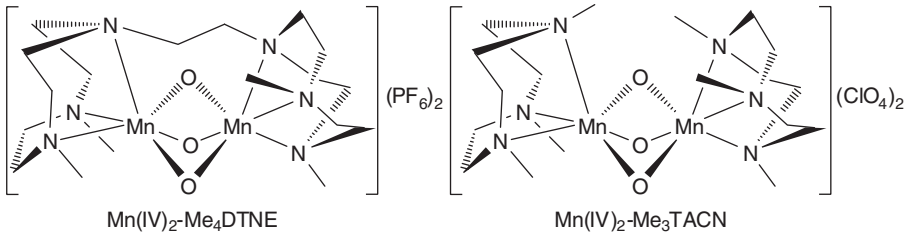


Fig. 8.19: Structures of $[(Me_4DTNE)Mn(IV)_2(\mu\text{-}O)_3](PF_6)_2]$ and $[(Me_3TACN)Mn(IV)_2(\mu\text{-}O)_3](ClO_4)_2]$.

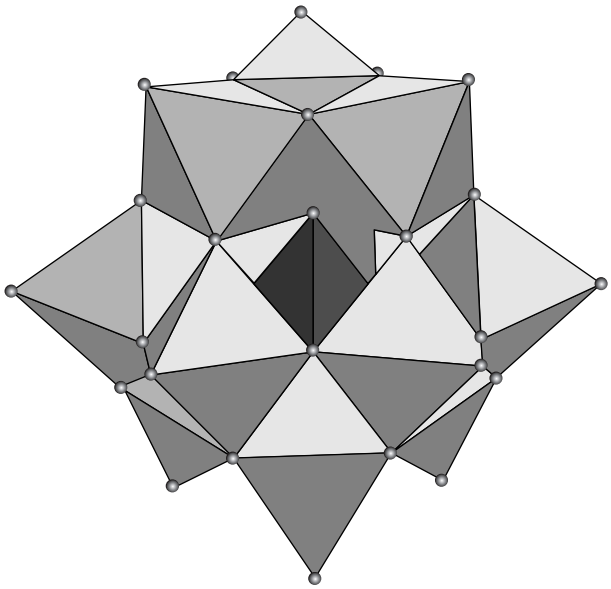


Fig. 8.20: Kegging-type heteropolyanions.

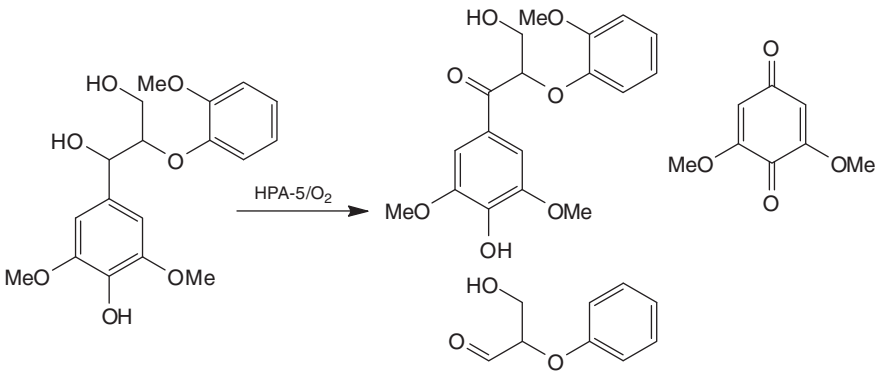


Fig. 8.21: Oxidation of phenolic β-O-4 lignin model compounds by HPA-$5/O_2$.

8.3.2.6 Organometallic catalysis for the oxidation of lignins and lignin model compounds: catalysis by MTO

Methyltrioxo rhenium (MTO) is the simplest organometallic compound containing Re(VII) (Herrmann and Fischer 1995). In recent years, MTO has been used in several organic transformations, including the selective oxidation of natural substances with hydrogen peroxide (H_2O_2) as environmentally friendly oxidants (Genin et al. 1995). The activation of H_2O_2 by MTO requires the formation of two peroxorhenium intermediates, a monoperoxo [$MeRe(O_2)O_2$] and a bis-peroxo [$MeRe(O_2)_2O$] h2-rhenium complex (▶Fig. 8.22) (Hermann et al. 1993), the reactivity and stability of which strictly depends on the specific conditions applied for the transformation. The transfer of the oxygen atom from these peroxo-h2-rhenium complexes to a substrate is achieved by a butterfly-like transition state through a concerted mechanism without formation of intermediate radical species.

The oxidation of monomeric and dimeric lignin model compounds, carried out by treating the appropriate substrate with H_2O_2 and MTO or MTO-supported catalysts (containing 1.0 % w/w of the active MTO) in AcOH proceeded with a similar selectivity, yielding products of alkyl side-chain oxidation, oxidative ring-opening of the aromatic moieties, and oxidation to benzoquinone derivatives, as reported in ▶Fig. 8.23 (Crestini et al. 2006). On the other hand, the mass balance measured for heterogeneous

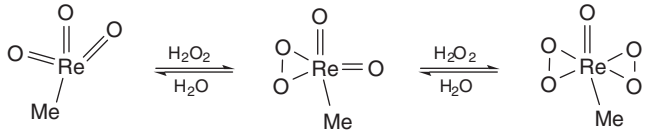


Fig. 8.22: Reaction mechanism of MTO with hydrogen peroxide.

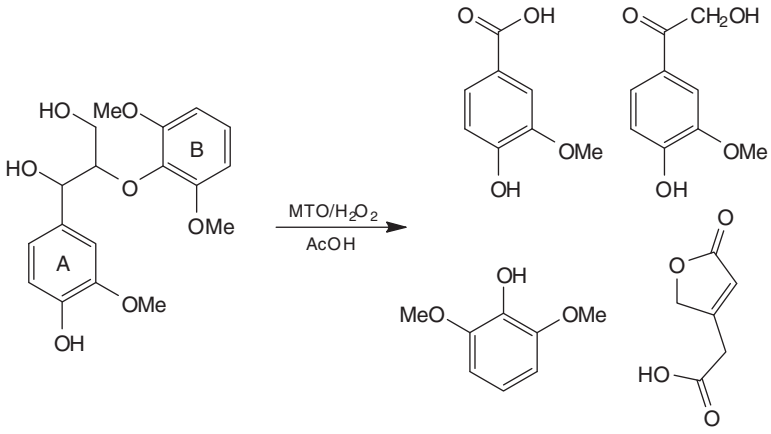


Fig. 8.23: Oxidation of monomeric and dimeric lignin model compounds byhomogeneous and heterogeneous MTO/H_2O_2.

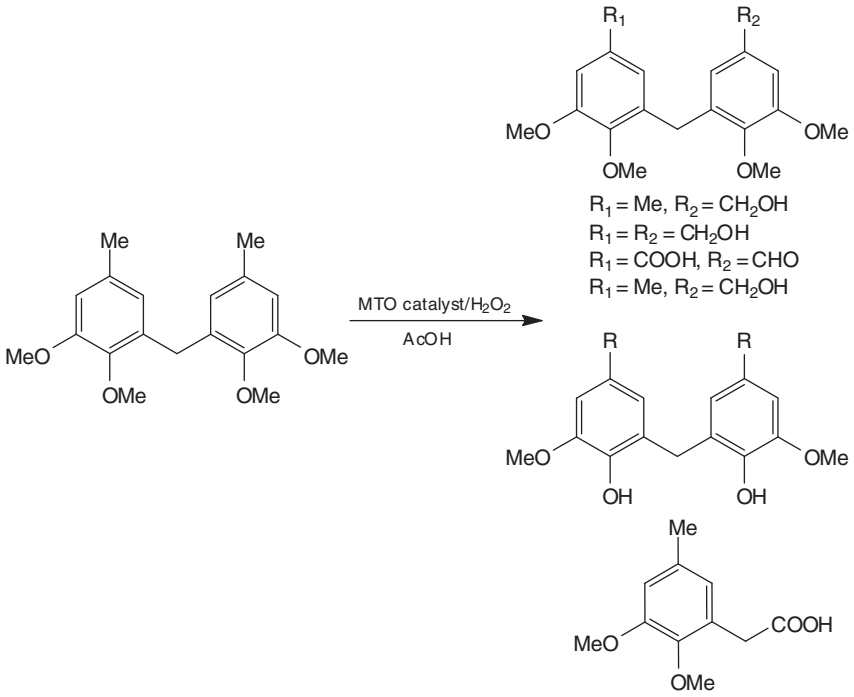


Fig. 8.24: Oxidation of nonphenolic diphenylmethane model compounds by MTO/H_2O_2.

oxidations was significantly higher than that obtained with MTO, suggesting that the supports are able to tune the reactivity of rhenium, avoiding the formation of over-oxidation products (for a general study on the effect of the resin on the selectivity of MTO, see Bianchini et al. 2006). The oxidation was operative also in the case of diphenylmethane dimeric lignin model compounds. As, for example, the oxidation of nonphenolic diphenylmethane lignin model compounds afforded products of alkyl side-chain oxidation to benzyl alcohol, aldehyde, demethylation at the alkyl-arylether moieties, and oxidative ring-cleavage of one of the aromatic rings (▶Fig. 8.24).

The use of MTO and immobilized MTO into polystyrene or polyvinylpyridine resulted in higher conversion yields for both lignin model compounds and lignins than those obtained with laccases. The structure of residual lignins after oxidation showed a similar trend to laccase-mediator catalyzed reactions. However, in the presence of MTO, the poor mass balances obtained indicated an extensive overoxidation of both lignins and lignin model compounds. This drawback has ruled out the possibility of using MTO in the oxidation of lignin for functionalization purposes.

8.4 Concluding remarks

The valorization of lignin represents a crucial step in the development of modern biorefinery processes. Its complex structure offers unique routes to produce fine and

bulk chemicals either by adjustment of already developed petroleum processes or by new technologies. Catalysis plays a major role in the conversion of lignin. A considerable number of efforts have been devoted to the development of catalytic routes for the specific oxidation/functionalization of lignin. Despite this, a general view on the performance of single catalysts on the valorization of lignin is lacking. This is due, on one side, to the heterogeneity of lignin sources and different lignin pretreatments that yield different lignin streams with different potentials and performances. Moreover, lignin streams could contain proteins, inorganic salts, and other potential poisons that generally complicate catalysis. Another factor affecting a possible general understanding of lignin chemistry is the analytical challenge associated with its structural characterization.

Several reports are present in archival literature about lignin model compound oxidations. Although such studies are relevant for the understanding of the general chemistry of the polymer, they do not reflect the structural variability of lignin and the number of possible chemicals obtainable. Obtaining different catalyst's performance information directly on the lignin used is relevant for the development of practical biorefinery processes.

The highly oxygenated nature of biomass feedstocks ($C_nH_mO_o$), which contain various ether linkages, make them more hydrophilic from hydrophobic petroleum feedstocks (C_nH_m). Despite this, several of the catalysts used in lignin valorization were originally developed for petroleum refining. Suitable catalysts specifically designed for the exploitation of the different potentialities of biomass feedstocks should be developed. As an example, the high amount of methoxy groups in lignin represent a potential source of C1 compounds, such as methanol, which is a valuable chemical not as easily obtained from petroleum streams. This C1 product stream can then subsequently be converted into other products with conventional technology, such as the methanol-to-olefins process.

Short- to medium-term biorefinery development will make use of existing petroleum refinery infrastructure and processes to circumvent high capital costs, which may otherwise be prohibitively expensive. From this viewpoint, the crucial challenge is the development separation processes for product streams derived from biomass.

The infancy of petroleum refinery in the 20th century consisted of a few products and little energy production. It was using the previously developed coal technologies. The development of petroleum refinery was a long-lasting process that gradually yielded the highly efficient system that we know today. It took an extensive effort to develop processes and catalysts. In the same fashion, up to now, biorefineries are able to produce only a few chemicals. It will require the development of catalytic technology and new integrated production systems to meet the chemical and fuel requirements of the 21st century. In order for biorefineries to become efficient, highly integrated systems, it is mandatory that the lignin fraction arising from biomass will be fully exploited, since it represents an invaluable source for the production of renewable aromatic compounds on which our industry depends. Lignin has to be transformed from a waste stream for the production of low-quality, low-price products to a high-value feedstock. This can be accomplished by the development of suitable selective catalytic processes.

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9 Process development and metabolic engineering for bioethanol production from lignocellulosic biomass

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9.1 Introduction

The increase of supply problems and of the price of fossil fuels along with concerns about CO_2 emission-driven climate change have prompted in the past decade a dramatic increase in demand for sustainable alternative transportation fuels based on renewable resources.

Ethanol is currently the most important renewable fuel in terms of volume and market value (Licht 2006). In 2010 worldwide biofuel production reached 105 billion liters, 86 billion of which were represented by bioethanol, with the United States and Brazil as the world's top producers accounting together for 90% of global production (Worldwatch Institute 2011). Today's biofuel industry primarily produces ethanol from sweet juice (e.g. sugarcane, sugar beet juice, or molasses) and starch (e.g. corn, wheat, barley, cassava), and biodiesel is generated from vegetable and animal oils. These are the so-called first-generation biofuels.

The major drawbacks of first-generation biofuels are:

- Competition with other crops for land that could be used for food production.
- Rising cost of food due to increased demand of grain crops for biofuel production. These crops are, in fact, the staple grains in the diets of many people, especially in less-developed countries.
- Necessity to irrigate these crops, which in some regions adds to the already high stress put on groundwater sources.
- High input of fertilizers and pesticides, and increased erosion from tillage and putting poor quality land into production.

Second-generation biofuels are produced from lignocellulosic biomass such as agricultural and forestry residues, weeds, waste paper, and so on. In addition, dedicated energy crops are being developed. Second-generation biofuel crops have many advantages over first-generation biofuels, including:

- Lack of competition between feeding and fueling.
- Dedicated energy crops grow on marginal lands that can not support food crops and require less fertilizer and pesticide inputs. This decreases contamination from agricultural lands and reduces impacts to waterways.

Lignocellulosic biomass is composed of cellulose, hemicellulose, lignin, extractives, and several inorganic materials (Morohoshi 1991). Their relative proportion varies according to the specific biomass. Cellulose is the most abundant organic polymer on earth – it is a linear polysaccharide polymer of glucose. The cellulose chains are packed by hydrogen bonds in elementary- and microfibrils (Ha et al. 1998) covered by

lignin. Hemicellulose is a heteropolymer consisting of xylose-linking compounds such as arabinose, glucose, mannose, and other sugars through an acetyl chain. In contrast to cellulose, which is crystalline, hemicelluloses have a random and amorphous structure with little resistance to hydrolysis (O'Dwyer 1934). Lignin is a very complex molecule constructed of phenylpropane units linked in a three-dimensional structure with hemicellulose and cellulose. Lignin is particularly resistant to chemical and enzymatic degradation. Generally, softwoods contain more lignin than hardwoods and most of the agriculture residues.

The process for producing ethanol and other biofuels from lignocellulosic biomass includes four main steps:

- Pretreatment – breaking bonds between lignocellulose constituents.
- Enzymatic hydrolysis and detoxification – transforming cellulose to glucose and removing fermentation inhibitors that originate during pretreatment processing.
- Fermentation – obtaining the desired biofuel through the microbial catabolism of sugars.
- Distillation-rectification-dehydration – separating and purifying the fermentation products.

In this chapter we describe advancements in ethanol production from lignocellulosic biomass with a specific focus on the metabolic engineering of the microorganisms used in the fermentation step. We refer the reader to other chapters of this book for a more detailed description of the whole production process.

9.2 Pretreatment

Pretreatment is required to alter the biomass structure and chemical composition in order to facilitate the hydrolysis of the carbohydrate fraction (Sun and Cheng 2002; Mosier et al. 2005). Pretreatment effects include: an increase of the accessible surface area, cellulose decrystallization, partial cellulose depolymerization, modification of the lignin structure, and hemicellulose and/or lignin solubilization. Pretreatment can be carried out on the basis of mechanical, physical, chemical, physicochemical and biological actions, or a combination of them.

Biological pretreatment is performed by adding lignin-degrading microorganisms, such as white- and soft-rot fungi, to the lignocellulose materials. Although this method is environmentally friendly and energy-saving, the rate of the biological pretreatment processes is too low for industrial use and some material is lost as these microorganisms, to some, extent ferment hemicellulose and cellulose, or lignin (Galbe and Zacchi 2007).

Physical, chemical, physicochemical pretreatment methods are described in other chapters of this book; for a review see Carvalheiro (2008) and Taherzadeh and Karimi (2007, 2008) and references therein.

9.3 Enzymatic hydrolysis and detoxification

Most pretreatments solubilize hemicellulose, either totally or in a very significant quantity, in a oligomeric form. After pretreatment, two main processes are used to hydrolyze cellulose and the remaining part of hemicellulose into monomeric sugar constituents

required for fermentation into ethanol: acid (dilute and concentrated) and enzymatic treatments. Acid hydrolysis is described in chapters 5 and 6.

9.3.1 Enzymatic hydrolysis

Enzymatic hydrolysis of cellulose and hemicellulose is carried out by cellulase and hemicellulase enzymes. The hydrolysis takes place under mild conditions (e.g. pH 4.5–5.0 and temperature 40–50°C). The main advantages of this process are low plant corrosion problems, low utility consumption, and absence of fermentation inhibitors of the hydrolyzates (Chandel and Chan 2007).

Cellulases and hemicellulases can be classified in at least 15 protein families and some subfamilies. Enzymatic hydrolysis of cellulose can be divided into three phases: cellulase adsorption onto the surface of the cellulose, hydrolysis of cellulose to fermentable sugars, and desorption of the cellulase. Cellulase cocktails consist of three major classes of enzymes: endoglucanases, exoglucanases, and ß-glucosidases. These enzymes are usually together called cellulase or cellulolytic enzymes (Taherzadeh and Karimi 2007). The endoglucanases attack the low-crystallinity regions of the cellulose fiber and create free chain ends. The exoglucanases further degrade the sugar chain by removing cellobiose units (dimers of glucose) from the free chain ends. The produced cellobiose is then cleaved to glucose by β-glucosidase. This enzyme can not be considered a cellulase, but its action is very important to complete depolymerization of cellulose to glucose.

Since hemicellulose contains different sugar units, the hemicellulytic enzymes are more complex and include endo-1,4-β-D-xylanases, exo-1,4-β-D-xylosidases, endo-1,4-β-D-mannanases, β-mannosidases, acetyl xylan esterases, α-glucuronidases, α-L-arabinofuranosidases, and α-galactosidases (Chandel and Chan 2007).

Bacteria and fungi are good sources of cellulases and hemicellulases. The enzymatic cocktails that are usually employed comprise mixtures of several hydrolytic enzymes (cellulases, xylanases, hemicellulases, and mannanases). Different enzyme cocktails are currently available. The optimal cocktail depends on the specific biomass and the fermentation process used.

Several lignocellulolytic microorganisms, mainly fungi and bacteria, have been isolated. Nevertheless, *Trichoderma reesei* and its mutants are primarily employed for the commercial production of hemicellulases and cellulases with a few also produced by *Aspergillus niger*. This is partly because *T. reesei* was one of the first cellulolytic organisms isolated in the 1950s. Since then, extensive strain improvement and screening programs have been carried out, and cellulase industrial production processes have been developed in several countries (Howard et al. 2003).

Despite recent advancements, enzyme costs are still considered to be a major impediment to an economically viable production of biofuels from lignocellulose. It is estimated to represent approximately 50% of the total hydrolysis process cost. The low cellulase activity – which is approximately 10–100-fold less than those of amylases, depending on the cellulose pretreatment and hydrolysis process conditions – demands substantial amounts of lignocellulytic enzymes. The production cost of this amount of enzyme still represents a major bottleneck for the entire process. Many research efforts have been focused on lowering the cost of enzymes trying to improve the enzyme-producing strains, screen new organisms, produce more active enzymes, engineer

enzymes, and improve the enzymatic hydrolytic process parameters (Howard et al. 2003).

9.3.2 Fermentation inhibitors

The efficient fermentation (ethanol yield and productivity) of the hydrolysates is limited due to the presence of inhibiting compounds that are generated during pretreatment and hydrolysis of lignocellulosics, which could be classified into three main groups: weak acids, furan derivatives, and phenolic compounds (Almeida et al. 2007). A greater understanding of the inhibitory mechanisms of individual compounds and their interaction effects, as well as the influence of environmental parameters such as pH, are crucial for optimal design of the fermentation process. Rates of bioconversion and the adaptive response of the microorganism to the toxic compounds in the hydrolysate also have to be considered (Palmqvist and Hahn-Hägerdal 2000a).

9.3.2.1 Weak acids

Weak acids (e.g. acetic, formic, octanoic, and levulinic acid) inhibit yeast fermentation by reducing biomass formation and ethanol yields. Acetic acid is formed by the deacetylation of hemicelluloses, while formic and levulinic acids are products of hydroxymethylfurfural breakdown. Formic acid can also be formed from furfural under acidic conditions at elevated temperatures.

Two mechanisms have been proposed to explain the inhibitory effect of weak acids: uncoupling and intracellular anion accumulation (Russell 1992). Undissociated weak acids are liposoluble and can diffuse across the plasma membrane. In the cytosol, dissociation of the acid occurs due to the neutral intracellular pH, thus decreasing the cytosolic pH. The decrease in intracellular pH is compensated by the plasma membrane ATPase, which pumps protons out of the cell at the expense of adenosine triphosphate (ATP) hydrolysis. Consequently, less ATP is available for biomass formation. However, at higher acid concentrations, the ATP demand is so high that cells cannot avoid acidification of the cytosol. According to the intracellular anion accumulation theory, the anionic form of the acid is captured inside the cell and the undissociated acid will diffuse into the cell until equilibrium is reached.

9.3.2.2 Furan derivatives: furfural and HMF

The furan compounds 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde are formed by dehydration of hexoses and pentoses, respectively. The level of furans varies according to the type of raw material and the pretreatment procedure. Furfural is metabolized by *Saccharomyces cerevisiae* by reduction to furfuryl alcohol. Instead, furfural oxidation to furoic acid by *S. cerevisiae* occurs, to some extent, primarily under aerobic conditions. Several mechanisms may explain the inhibition effects of ethanol fermentation by furans. In general, the effects of furans can be explained by a redirection of yeast energy to fix the damage caused by furans and by reduced intracellular ATP and NAD(P)H levels, either by enzymatic inhibition or consumption/regeneration of cofactors. Furfural inhibition of alcohol dehydrogenase (ADH), pyruvate dehydrogenase (PDH), and aldehyde dehydrogenase (ALDH) has been reported (Almeida et al. 2007; Palmqvist and Hahn-Hägerdal 2000a).

9.3.2.3 Phenolic compounds

Phenolic compounds are generated due to lignin breakdown and carbohydrate degradation during acid hydrolysis (Pérez et al. 2002). The amount and type of phenolic compounds depend on the biomass source, since lignin in different raw materials has different degrees of methoxylation, internal bonding, and association with hemicellulose and cellulose in the plant cell wall. Vanillin constitutes a large fraction of the phenolic monomers in hydrolysates of spruce, pine, and willow.

The inhibitory effects of phenols are due to their partition into biological membranes with loss of integrity. However, inhibition mechanisms of phenolic compounds have not yet been completely elucidated, largely due to the heterogeneity of the group and the lack of accurate qualitative and quantitative analyses. Weakly acidic phenolic compounds may destroy the electrochemical gradient by transporting the protons back across the mitochondrial membranes (Almeida et al. 2007; Palmqvist and Hahn-Hägerdal 2000a).

9.3.3 Detoxification

Biological, physical, and chemical methods may be employed for detoxification of lignocellulosic hydrolysates (Palmqvist and Hahn-Hägerdal 2000b). Lignocellulosic hydrolyzates vary in their degree of inhibition, and different microorganisms have different inhibitor tolerances. Detoxification is particularly important when strongly inhibiting hydrolysates are fermented, if high concentrations of inhibitors accumulate in the fermentation unit due to recirculation of streams, or when a fermenting organism with low inhibitor tolerance is used.

9.3.3.1 Biological detoxification methods

Treatment with the enzymes peroxidase and laccase, obtained from the ligninolytic fungus *Trametes versicolor*, led to selective and virtually complete removal of phenolic monomers and phenolic acids (Jönsson et al. 1998). The detoxifying mechanism was suggested to be oxidative polymerization of low molecular weight phenolic compounds. Acetic acid, furfural, and benzoic-acid derivatives were removed from the hydrolysates by the treatment with the filamentous soft-rot fungus *T. reesei* (Palmqvist et al. 1997). Enzymatic detoxification using the lignolytic enzymes laccase or peroxidase could be performed directly in the fermentation vessel prior to fermentation and would thus not require an additional process step (Jönsson et al. 1998). Immobilization would facilitate enzyme recovery and reduce cost. Simultaneous detoxification and enzyme production has been reported to occur when the inhibitor-containing hemicellulose hydrolysate from the pretreatment stage was used as substrate for *T. reesei* (Palmqvist et al. 1997). The enzyme-containing, inhibitor-free liquid can then be used to hydrolyze the cellulose fraction. This detoxification method would improve the process economy because all wood-derived sugars are utilized.

9.3.3.2 Physical detoxification methods

Roto-evaporation of hemicellulose hydrolysate and dilution of the nonvolatile highly inhibitory fraction led to a decrease in the concentration of acetic acid, furfural, and vanillin (Palmqvist et al. 1996). Acetic acid furfural, vanillin, and 4-hydroxybenzoic acid may also be removed by solvent extraction (diethyl ether or ethyl acetate).

9.3.3.3 Chemical detoxification methods

Detoxification of lignocellulosic hydrolysates by alkali treatment (i.e. increasing the pH to 9±10 with $Ca(OH)_2$ (overliming) and readjustment to 5.5 with H_2SO_4) led both to the precipitation of toxic components and to the instability of some inhibitors at high pH (Palmqvist and Hahn-Hägerdal 2000b). The concentrations of furfural and HMF may be reduced by treatment with sodium sulphite (Larsson et al. 1999). Also, combination of sulphite and overliming is an efficient method to detoxify hemicellulose hydrolysate prior to fermentation. The effect of the combined treatment was probably due to decreased concentrations of ketones and aldehydes.

9.4 Fermentation

There are different types of fermentation processes. Fermentation can follow the hydrolysis process or can be simultaneous to it. The main hydrolysis-fermentation formats are:

- Separate hydrolysis and fermentation (SHF)
- Simultaneous saccharification and fermentation (SSF)
- Simultaneous saccharification and co-fermentation (SSCF)
- Consolidated bioprocessing (CBP)

9.4.1 Separate hydrolysis and fermentation (SHF)

In the SHF process, pretreated lignocelluloses are hydrolyzed to monosaccharides and subsequently fermented to ethanol in separate reactors (▶Fig. 9.1).

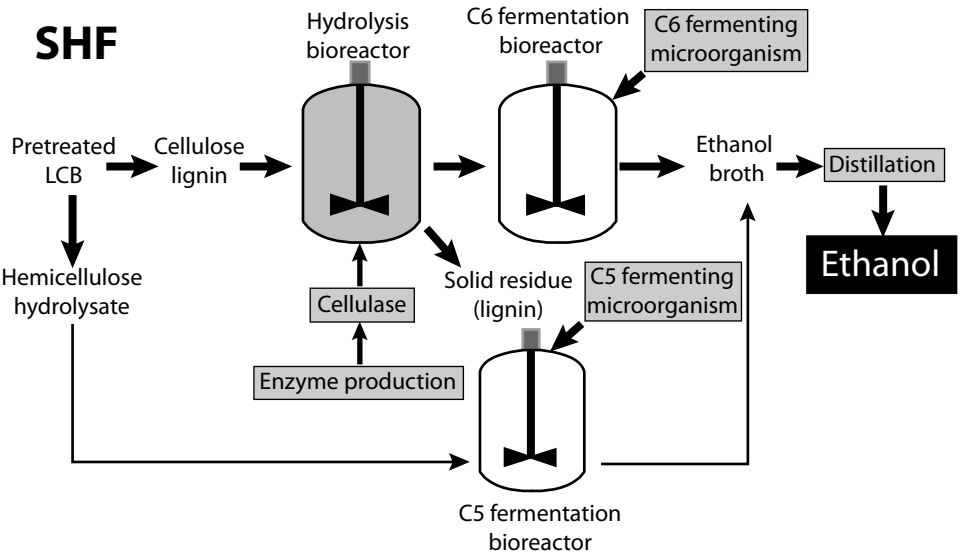


Fig. 9.1: Schematic flowsheet for bioethanol production from lignocellulosic biomass using separate hydrolysis and fermentation (SHF); LCB = lignocellulosic biomass.

This mode of operation makes it possible to perform hydrolysis and fermentation at their own optimum conditions. The optimum temperature for cellulase is usually between 45 and 50°C, whereas that of fermenting microorganisms is between 30 and 37°C (Olsson and Hahn-Hägerdal 1996; Wingren, Galbe, and Zacchi 2003).

This format has two main drawbacks. First is the inhibition of cellulase activity by the released sugars, mainly cellobiose; β-glucosidase is, on the other hand, inhibited by released glucose. Second, SHF is prone to microbial contaminations during the hydrolysis process if cellulase preparations are not sterile. The hemicellulose stream contains a large fraction of pentose sugars, which can be fermented in a separate tank (Taherzadeh and Karimi 2007).

9.4.2 Simultaneous saccharification and fermentation (SSF)

In SSF the glucose produced by the hydrolyzing enzymes is consumed immediately by the fermenting microorganism present in the culture (▶Fig. 9.2).

There are several advantages of SSF compared to SHF. SSF avoids end-product inhibition since the inhibition effects of cellobiose and glucose to the enzymes are minimized by keeping a low concentration of these sugars in the media. Consequently, higher ethanol yields from cellulose have been reported for SSF compared to SHF. Moreover, SSF requires lower amounts of enzyme (Eklund and Zacchi 1995; Karimi, Emtiazi, and Taherzadeh 2006; Sun and Cheng 2002) and shows a lower risk of contamination due to the presence of ethanol. Moreover, SSF requires a lower number of vessels in comparison to SHF, resulting in lower capital costs.

Despite all these advantages, several problems remain to be solved. The most important problem is the difference between optimum temperatures of the hydrolyzing

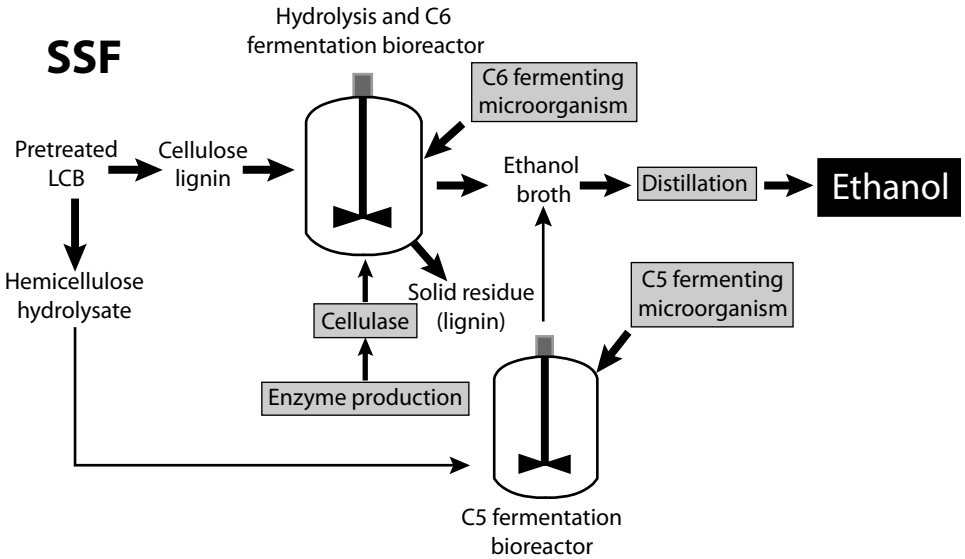


Fig. 9.2: Schematic flowsheet for bioethanol production from lignocellulosic biomass using simultaneous enzymatic saccharification (hydrolysis) and fermentation (SSF); LCB = lignocellulosic biomass.

enzymes and fermenting microorganisms. The optimum temperature for hydrolytic enzymes, whose activity is the rate-limiting step of SSF, is usually between 45 and 50°C, whereas fermenting microorganisms like *S. cerevisiae* have an optimum temperature of between 30 and 35°C and are virtually inactive at more than 40°C. Several thermotolerant bacteria and yeasts (e.g. *Kluyveromyces marxianus*) have been proposed for use in SSF to raise the temperature close to the optimal temperature of hydrolysis. Another problem is the impossibility of achieving high substrate loads consequent to difficulties with mechanical mixing and insufficient mass transfer. As for SHF, and also in SSF, the pentose-rich hemicellulosic stream can be fermented by a pentose-fermenting microorganism in a separate tank (Taherzadeh and Karimi 2007).

9.4.3 Simultaneous saccharification and co-fermentation (SSCF)

SSCF is a variation of SSF in which the fermentation of both five-carbon and six-carbon sugars to ethanol (co-fermentation) is carried out in the same bioreactor (▶Fig. 9.3). The hemicellulose hydrolyzed during pretreatment and the solid cellulose are not separated after pretreatment, allowing the hemicellulose sugars to be converted to ethanol together with the SSF of the cellulose (Taherzadeh and Karimi 2007).

S. cerevisiae recombinant strains capable of fermenting both hexose and pentose sugars are used in this process. Using a recombinant *S. cerevisiae,* industrial-strain ethanol concentrations reaching 40 gl^{-1} and yields up to 80% of the theoretical based on xylose and glucose have been achieved (Ohgren et al. 2006). Also, the recombinant bacterium *Zymomonas mobilis* and the natural pentose fermenting yeast *Pichia stipitis* have been used in SSCF. However, yields obtained were lower and a thorough detoxification of the hydrolizate was necessary (Teixeira, Linden, and Schroeder 2000).

9.4.4 Consolidated bioprocessing (CBP)

CBP is a process in which cellulase production, substrate hydrolysis, and fermentation are accomplished in a single process step by cellulolytic microorganisms (▶Fig. 9.4). It is

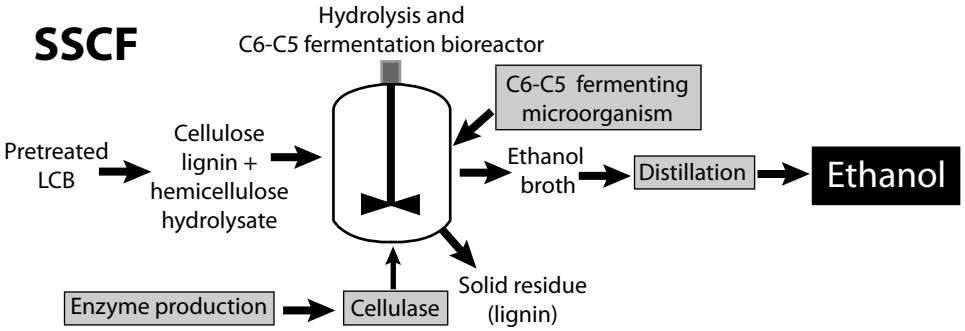


Fig. 9.3: Schematic flowsheet for bioethanol production from lignocellulosic biomass using simultaneous saccharification (hydrolysis) and co-fermentation (SSCF); LCB = lignocellulosic biomass.

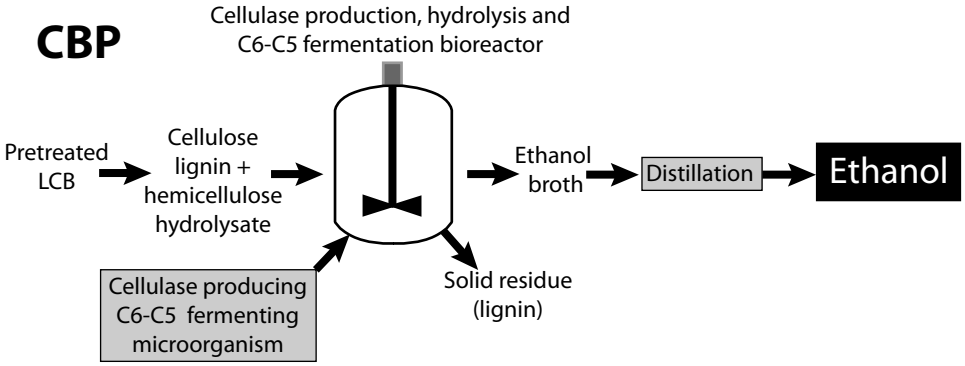


Fig. 9.4: Schematic flowsheet for bioethanol production from lignocellulosic biomass using consolidated bioprocessing (CBP); LCB = lignocellulosic biomass.

based on utilization of mono- or co-cultures of microorganisms that ferment cellulose to ethanol without the addition of cellulases. Although still immature, CBP could become an important technology for producing ethanol commercially and is the logical endpoint in the evolution of ethanol production from lignocellulosic materials. This mode of operation has potentially lower costs and higher efficiency than processes featuring dedicated cellulase production. This results from avoided costs for capital, substrate, and other raw materials and utilities associated with cellulase production. Moreover, higher hydrolysis rates are potentially achievable using thermophilic organisms and/or complexed cellulase systems and cellulose-adherent cellulolytic microorganisms. This can in turn reduce reactor volume and capital investment for purchasing enzymes or to produce them (Lynd et al. 2005).

In order to develop efficient CBP, researchers are trying either to modify excellent cellulase-producing microorganism so that they also become efficient ethanol producers or to express cellulases in fermenting microorganisms. In addition the "ideal" microorganism employed in CBP should be ethanol-tolerant, thermostable, and ethanol-selective and should achieve high production yields (Lynd et al. 2005).

9.5 Microbial biocatalysts

An optimal microbial catalyst involved in biofuel fermentation should: (1) be able to ferment both hexoses and pentoses, which are highly concentrated in hemicellulose and whose fermentation can make second-generation biofuels profitable; (2) have a high tolerance to fermentation inhibitors; (3) be resistant to contamination; and (4) ferment sugars to bioethanol or other biofuels with high yields and productivity. Important properties of the "perfect biocatalyst" are also its capability of producing (hemi)cellulolytic enzymes and its thermostabilty. Some of these features can be natural in most microorganisms; no microorganism, however, displays all of them. Hence, metabolic engineering and directed evolution are needed to improve the biocatalysts (▶Fig. 9.5).

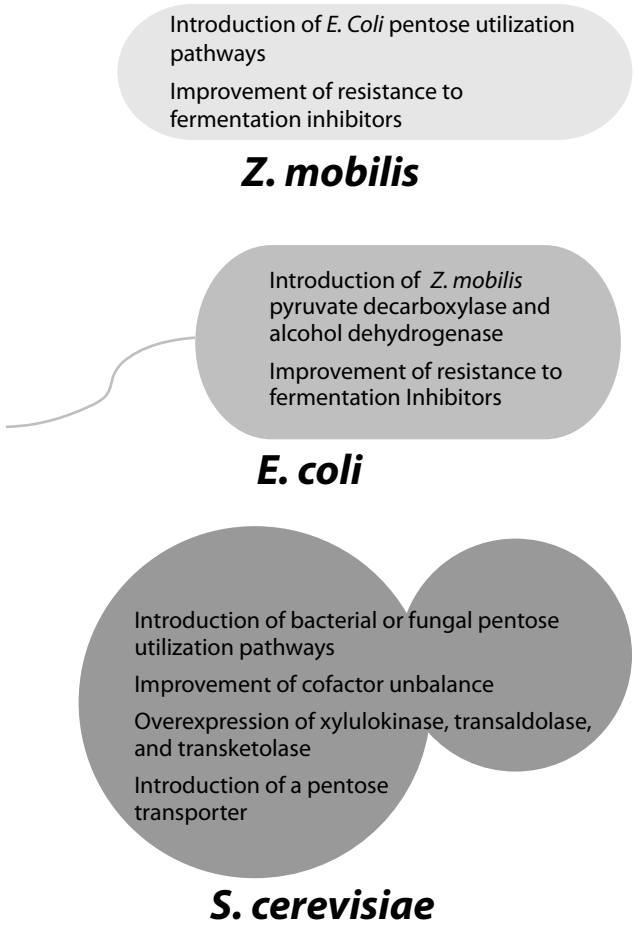


Fig. 9.5: Main metabolic engineering and directed evolution approaches used to enable *Z. mobilis*, *E. coli*, and *S. cerevisiae* to ferment C6 and C5 sugars to ethanol.

9.5.1 *Escherichia coli*

E. coli is a commonly used microorganism in industrial processes; it can ferment hexoses and pentoses but it does not produce ethanol. The introduction in the chromosome of *E. coli* B of *Z. mobilis* pyruvate decarboxyalse and alcohol dehydrogenase II genes generated the strain KO11, which was able to produce ethanol from all the sugars of the hemicellulose hydrolizate with more than 95% theoretical yield (Ingram et al. 1998). The fermentative performance of KO11 and its derivatives varied according the different lignocellulosic fraction employed, obtaining values up to 0.51 g EtOH per gram of sugar (100% theoretical yield) with corn stover after dilute acid hydrolysis achieving 40 g ethanol l^{-1} after 48 h (Asghari et al. 1996). The same strain has been used in a 1,000 l scale bioethanol production using dilute acid–treated house wood, obtaining 0.45 g EtOH per gram of sugar in a 63 h fermentation (Okuda et al. 2007).

A limitation of these recombinant *E. coli* strains is that they are not capable of fermenting simultaneously hexoses and pentoses, preferring glucose over other sugars. Yomano et al. reported that the deletion of mgsA encoding methylglyoxal synthase resulted in the co-metabolism of glucose and xylose, and accelerated the metabolism of a five-sugar mixture (mannose, glucose, arabinose, xylose, and galactose) to ethanol (Yomano et al. 2009).

The major problem that hampers the use of these ethanologenic *E. coli* strains is their lower resistance to fermentation inhibitors, ethanol, and process stress (change in pH, salts, temperature) compared to *S. cerevisiae*. The *E. coli* LY01, derived from KO11, is more resistant to ethanol and fermentation inhibitors than other biocatalysts (Zaldivar, Martinez, and Ingram 1999). Further, random and rational approaches have been carried out in order to improve this trait (Alper and Stephanopoulos 2007; Stephanopoulos, 2007). Results are, however, not yet sufficient to make *E. coli* an industrial ethanol producer.

9.5.2 *Zymomonas mobilis*

This Gram-negative bacterium is a natural ethanol producer. It is a GRAS (generally regarded as safe) microorganism. Moreover, it shows a high ethanol tolerance (up to 120 g/l), a higher ethanol yield (+5%–10%), and higher ethanol productivity (2.5 fold) than that of *S. cerevisiae* (Rogers et al. 1982).

The high ethanol yield and productivity depends on its unique capability of fermenting glucose using the Entner-Doudoroff (ED) pathway. It yields less ATP per glucose than the classical Embden-Meyerhoff-Parnas pathway; consequently, less biomass and more ethanol are formed from the carbon source used. The introduction of the *E. coli* genes xylose isomerase (xylA), xylulose kinase (xylB), transketolase (tktA), and transaldolase (talB) enabled *Z. mobilis* to convert xylose into xylulose-5-phosphate, an intermediate of the pentose-phosphate pathway (Zhang et al. 1995). The recombinant strain obtained, CP5(pZB5), fermented xylose with an 86% ethanol yield. The subsequent introduction of the *E. coli* arabinose operon L-arabinose isomerase (araA), L-ribulose kinase (araB), L-ribulose-5-phosphate-4-epimerase (araD), transketolase (tktA), and transaldolase (talB), allowed the utilization of arabinose (Deanda et al. 1996). Altough the theoretical yield was close to 100%, the fermentation rate was much lower than that observed with the xylose-fermenting strain. Another recombinant strain, AX101, was generated carrying the genes required to ferment both xylose and arabinose integrated into its genome (Mohagheghi et al. 2002). Altough cofermentation was obtained by this strain (yield 84%), it showed a sugar preference, with glucose being consumed first, followed by xylose and arabinose. *Z. mobilis* has proved to be an efficient biocatalist in SSCF. Poplar wood chips pretreated with steam explosion followed by overliming to reduce fermentation inhibitor concentration have been used as SSF substrate. The process was carried out at 34ºC (a compromise between optimal fermentation and enzymatic hydrolysis temperatures) and pH 5.5 for 7 days, obtaining a final ethanol concentration of 30 g/l and achieving 54% conversion of all potentially available biomass sugars (McMillan et al. 1999). The main disadvantage of *Z. mobilis* recombinant strains is their sensitivity to fermentation inhibitors, especially to acetic acid, which is further exacerbated in the presence of ethanol. This problem is particularly difficult to solve for mixed-sugar fermentations (Mohagheghi et al. 2002) because it has been reported that *Z. mobilis* cells display a lower energetic state when grown on xylose (Kim, Barrow, and Rogers 2000).

9.5.3 Other bacteria

Some members of the Gram-positive bacteria genus *Clostridium,* such as *C. thermocellum,* display interesting features for the development of CBP. They are able to hydrolyze many polysaccharides, including cellulose and hemicellulose, thanks to the secretion of the cellulosome, a large multi-enzymatic complex that contains 14–50 polypeptides ranging in size from 37 to 210 kDa and more than 14 different enzymatic activities. Moreover, many clostridia are thermostable; this feature can be important in the SSF process where it is useful to increase the hydrolysis temperature to achieve an optimal enzymatic performance. The main drawbacks of these bacteria are that they are strict anaerobes, the lack of efficient genetic manipulation tools, and their slow growth rate (Weber et al. 2010).

9.5.4 *Saccharomyces cerevisiae*

S. cerevisiae has been used for a long time for the production of ethanol in beverages and first-generation bioethanol. It is a GRAS microorganism, highly resistant to fermentation inhibitors, ethanol, and low pH, which are desirable features in an industrial setting. *S. cerevisiae* is not able to ferment pentoses (mainly xylose and arabinose) either aerobically or anaerobically. Many other yeasts are efficient pentose fermenters. However, most of them can not produce ethanol anaerobically and only in conditions of oxygen restriction (Custers effect). It is very difficult to maintain microaerobic conditions in an industrial fermentation process; if too much oxygen is provided ethanol yields will be lower because it will be respired. Hence, it is important that xylose is fermented anaerobically (van Maris et al. 2006). To make this yeast a good pentose fermenter, two metabolic engineering approaches have been used:

- Introduction of xylose reductase (XR) and xylytol dehydrogenase (XDH) from *P. stipitis* or other natural pentose fermenting yeasts.
- Introduction of a xylose isomerase (XI) from fungal or bacterial origin.

9.5.4.1 Expression of the fungal xylose utilization pathway

S. cerevisiae can not metabolize xylose, but it is able to ferment xylulose. Many yeasts convert xylose into xylulose in a two-step process (▶Fig. 9.6b). Xylose is first reduced to xylitol by a NADPH-dependent xylose reductase (XR). Xylitol is then oxidized to xylulose by a NAD^+-dependent xylitol dehydrogenase (XDH). *S. cerevisiae* presents both enzymatic activities. They are, however, too low to allow the reaction to proceed. Many xylose-fermenting yeasts have very active XR and XDH. The introduction of the *P. stipitis* XR and XDH into *S. cerevisiae* enabled this yeast to grow on xylose; the main product was, however, xylitol and not ethanol (Kotter and Ciriacy 1993). This is mainly due to a cofactor unbalance of XR and XDH. The first consumes NADPH, the second produces NADH. An increase of NADH concentration or of the NADH/NAD^+ ratio inhibits the action of XDH. As a consequence, xylitol accumulates. Xylose-consuming yeast such as *P. stipitis* ferment xylose only in the presence of a small amount of oxygen, which is required in order to oxidize the excess NADH. Moreover, PsXDH displays a dual cofactor specificity for both NADH and NADPH.

In order to overcome the cofactor unbalance problem a number of possible solutions have been tested:

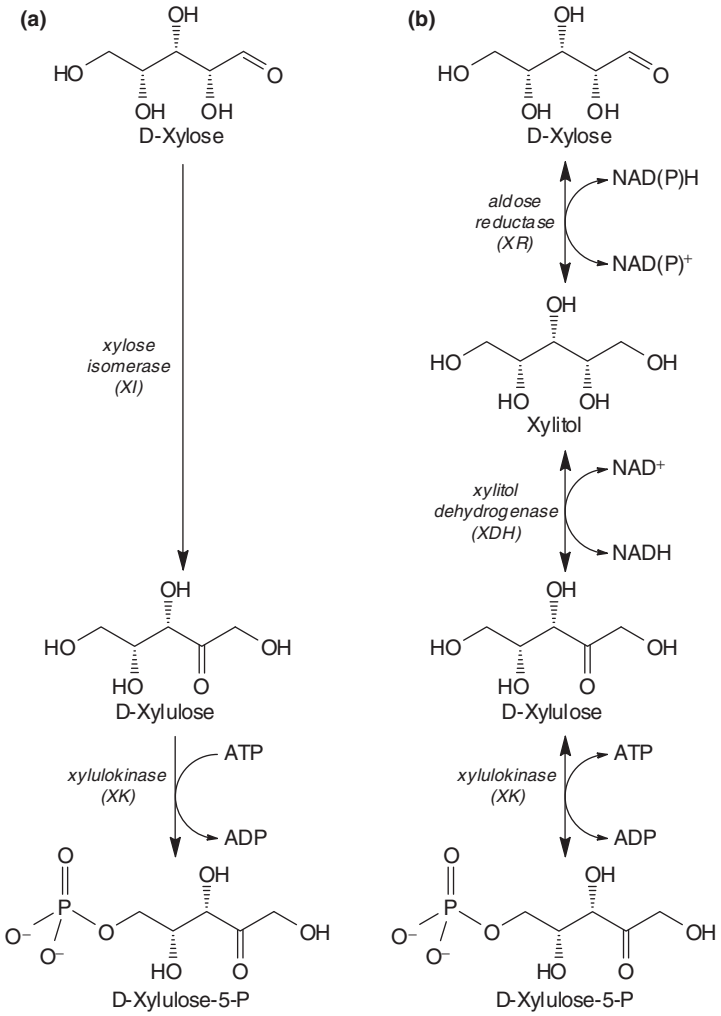


Fig. 9.6: D-xylose catabolism in bacteria (a) and fungi (b). D-xylulose-5-P is further catabolized through the pentose phosphate pathway to fructose-6-P and glyceraldehyde-3-P, which are metabolized in the glycolytic pathway and converted to ethanol.

- Expression of a heterologous transhydrogenase capable of converting NADPH and NAD^+ into $NADP^+$ and NADH. Heterologous expression of a transhydrogenase gene from *Azotobacter vinlandii* in the *S. cerevisiae* xylose fermenting strain TMB3253 reduced xylitol production but increased glycerol rather than ethanol yield (Nissen et al. 2001).
- The overexpression of a heterologous $NADP^+$-dependent glyceraldehyde 3-phosphate dehydrogenases (GAPDH) in xylose-fermenting strains, increasing NADPH, and decreasing NADH has been show to be effective in enhancing ethanol production (Verho et al. 2002, 2003).

- Modification of the ammonia assimilation pathway, obtained by deleting the NADPH-dependent glutamate dehydrogenase gene GDH1 and overexpressing the NADH-dependent isoenzyme gene GDH2 (Nissen et al. 2000), resulted in higher ethanol production and reduced xylitol formation.
- Protein engineering efforts have developed mutated XRs with a decreased affinity for NADPH and a lower Km for NADH. Enhanced ethanol yields accompanied by decreased xylitol yields were obtained in *S. cerevisae* strains carrying these mutated XRs. Flux analysis showed that strains harboring a mutated XR utilized a larger fraction of NADH for xylose reduction. The overproduction of the mutated XR resulted in an ethanol yield of 0.40 g per gram of sugar and a xylose consumption rate of 0.16 g per gram of biomass per hour in chemostat culture (0.06/h) with 10 g/L glucose and 10 g/L xylose as carbon source (Jeppsson et al. 2006).

Many studies have demonstrated that in order to have an effective xylose fermentation to ethanol and a glucose-xylose co-fermentation it is necessary to overexpress xilulokinase (XK) (Ho, Chen, and Brainard 1998). Overexpression of endogenous ScXK with an integrating plasmid enabled *S. cerevisiae* to ferment xylose to ethanol under aerobic and anaerobic conditions (Toivari et al. 2001).

The first xylose-fermenting strains displayed a very low growth rate. This was partially ascribed to the low activity of the PP pathway in *S. cerevisiae* and particularly transladolase (TAL) and transketolase (TKL). Overexpression of TAL and TKL was found to improve the fermentation of xylose both in a strain expressing XR+XDH (Karhumaa et al. 2005) and in a strain expressing XI (Kuyper et al. 2005a). In both strains, the deletion of the endogenous aldose reductase encoded by GRE3 was also found to be useful. GRE3 reduces xylose to xylitol; its deletion lowers xylitol production. However, GRE3 is a stress-regulated gene; hence, its deletion has been found to lower biomass yield and growth rate (Träff-Bjerre et al. 2004). Moreover, the deletion of GRE3 is difficult to perform on industrial *S. cerevisiae* strains.

In *S. cerevisiae* the xylose utilization rate is low compared to that of natural xylose-utilizing yeasts and is much lower than that of glucose. An explanation of its preference for glucose is that *S. cerevisiae* has many transporters for the hexoses (Hxt1, Hxt2, Hxt4, Hxt5, Hxt7, Gal2) but none specific for pentoses. Transport of xylose is completely inhibited by glucose; consequently, the pentose is consumed only after the depletion of glucose (van Zyl et al. 1993). Xylose transport does not limit xylose metabolism in the slow xylose-metabolizing strain TMB3001; in contrast, transports have more than 50% control over xylose utilization in the fast xylose-metabolizing strain TMB3260 (Gárdonyi et al. 2003). Several evolutionary engineering approaches aimed at improving xylose fermenting capability result in evolved strains showing improved xylose transport kinetics (Kuyper et al. 2005b).

Hamacher et al. generated the slow xylose-metabolizing strain TMB3201 in which all the 18 HXT genes were knocked out. Reintroduction of each of them revealed that the high-affinity (Hxt7 and Gal2) and intermediate-affinity (Hxt4 and Hxt5) hexose transporter allowed growth on 2% xylose. Their overexpression, however, did not improve the xylose fermentation rate under anaerobic conditions, probably because TMB3201 was a slow xylose utilizer (Hamacher et al. 2002).

Many transporters from plants, bacteria, and xylose-fermenting yeasts have been expressed in *S. cerevisiae* in order to improve its xylose transport. Significant improvement

has been obtained by the identification and expression in *S. cerevisiae* of *Candida intermedia* GXF1 and GXS1 (Leandro, Gonçalves, and Spencer-Martins 2006). Both of them are efficient xylose transporters. However, they are also efficient glucose transporters, making their use less attractive. The glucose/xylose facilitator Gxf1 from *C. intermedia* was expressed in the recombinant xylose-fermenting *S. cerevisiae* strain TMB3057, obtaining the strain TMB3411. This strain displays improved xylose transport kinetics and specific growth at low xylose concentration (4 g/L), but not at high concentration (40 g/l). Under both aerobic and anaerobic conditions, the Gxf1-expressing strain showed faster xylose uptake and ethanol formation at low substrate concentrations (Runquist et al. 2009).

Also, the *A. thaliana* genes At5g59520 and At5g17010 encoding sugar transporters have been expressed in *S. cerevisiae*. Expression of the transporters increased xylose uptake and xylose consumption up to 46% and 40%, respectively. Xylose co-consumption rates (prior to glucose depletion) were also increased up to 2.5-fold compared to the control strain. Increased xylose consumption correlated with increased ethanol concentration and productivity. During the xylose/glucose co-consumption phase, strains expressing the transporters had up to a 70% increase in the ethanol production rate (Hector et al. 2008). However, At5g59520 expression was not able to sustain growth in a yeast strain deleted of all the HXT transporters (Hamacher et al. 2002).

It has been reported that the endogenous galactose transporter GAL2 is involved in arabinose transport in *S. cerevisiae* (Becker and Boles 2003). Its expression was found to be increased in a strain evolved for arabinose fermentation (Wisselink et al. 2010). Using a yeast strain lacking all of its endogenous hexose transporter genes and expressing a bacterial L-arabinose utilization pathway, Subtil and Boles confirmed this result. Moreover, they showed that the heterologous expression of L-aribinose transporting sugar transporters supported uptake and utilization of L-arabinose, especially at low L-arabinose concentrations, but did not, or only very weakly, supported D-glucose uptake and utilization (Subtil and Boles 2011).

9.5.4.3 Expression of the bacterial xylose utilization pathway

Bacteria are able to convert xylose into xylulose via a one-step reaction catalyzed by xylose isomerase (XI) (▶Fig. 9.6a). XI expression in *S. cerevisiae* has been sought for a long time. It can allow circumvention of the cofactor unbalance problem observed on the expression of XR and XDH.

Many attempts to express a bacterial XI in *S. cerevisiae* were unsuccessful. The first XI functionally expressed in *S. cerevisiae* was *Thermus thermophilus* XYLA. The recombinant strain obtained fermented 3% xylose to ethanol e xylitol with yields of 0.04 $g_{ethanol}$ $g^{(-1)}$ and 0.12 $g_{xylitol}$ $g^{(-1)}$, respectively (Walfridsson et al. 1996). Xylytol was produced by the endogenous XR encoded by GRE3. Xylitol is a powerful inhibitor of XI. Another problem with this strain was the low activity of XI the optimal temperature of which (85ºC) was different from the optimal fermentation temperature. Many metabolic engineering approaches have been carried out in order to improve this performance, including cold adaptation of XI and GRE3 deletion, but without success so far.

The discovery of a eukaryotic XI in the fungus *Pyromyces* sp.E2 and its high-level expression in *S. cerevisiae* (strain RWB202) allowed a very slow growth on 2% xylose under anaerobic conditions. It co-consumed xylose in aerobic and anaerobic

glucose-limited chemostat cultures at rates of 0.33 and 0.73 mmol (g biomass)$^{(-1)}$ h$^{(-1)}$, respectively (Kuyper et al. 2003). In order to improve xylose utilization, RWB202 was subjected to a evolutionary engineering approach through a prolonged cultivation on xylose. The obtained mutant strain (RWB-202AFX) grew aerobically and anaerobically on xylose at specific growth rates of 0.18 and 0.03 h$^{(-1)}$, respectively. The anaerobic ethanol yield was 0.42 g ethanol x g xylose$^{(-1)}$ and byproduct formation was also comparable to that of glucose-grown anaerobic cultures (Kuyper et al. 2004). The fermentative performance of RWB-202AFX was further improved by a metabolic engineering approach: xylulokinase (EC 2.7.1.17), ribulose 5-phosphate isomerase (EC 5.3.1.6), ribulose 5-phosphate epimerase (EC 5.3.1.1), transketolase (EC 2.2.1.1), and transaldolase (EC 2.2.1.2) were overexpressed and GRE3 was deleted to further minimize xylitol production. The resulting strain (RWB217) grew anaerobically on xylose in synthetic media with a μ_{max} as high as 0.09 h$^{(-1)}$: xylulose formation was absent and xylitol production was negligible. The specific xylose consumption rate in anaerobic xylose cultures was 1.1 g xylose (g biomass) $^{(-1)}$ h$^{(-1)}$. Mixtures of glucose and xylose were sequentially but completely consumed by anaerobic batch cultures, with glucose as the preferred substrate (Kuyper et al. 2005a). After a evolutionary engineering protocol in automated sequencing-batch reactors on glucose-xylose mixtures followed by a prolonged anaerobic cultivation, a single-strain isolate (RWB 218) was obtained. RWB 218 rapidly consumed glucose-xylose mixtures anaerobically, in synthetic medium, with a specific rate of xylose consumption exceeding 0.9 g (g biomass)$^{(-1)}$ h$^{(-1)}$ and displayed improved xylose uptake kinetics showing a twofold higher capacity (V(max)) as well as an improved K(m) for xylose (Kuyper et al. 2005b).

Recently Bratt et al. succeed in expressing a prokariotic xilose isomerase (from *Clostridium phytofermentans*); this XI is less inhibited by xylitol and, hence, is a promising alternative to *Pyromyces XI* (Brat, Boles, and Wiedemann 2009).

9.5.4.4 Expression of the arabinose utilization pathway

Arabinose is present in some types of lignocellulosic hydrolyzates. Only a few yeasts are naturally able to ferment arabinose to ethanol. A screening of 116 different yeasts for the ability to ferment L-arabinose found that the following species are able to ferment the sugar: *Candida auringiensis*, *Candida succiphila*, *Ambrosiozyma monospora*, and *Candida sp*. (YB-2248). However, ethanol concentrations obtained were very low (4.1 g/L or less) (Dien et al. 1996). The fungal arabinose pathway comprises aldose (xylose) reductase, L-arabinitol 4-dehydrogenase, L-xylulose reductase, D-xylulose reductase, and D-xylulokinase (▶Fig. 9.7b). This pathway consists of two NAD^+-linked oxidations and two NADPH-linked reductions, resulting in a redox cofactor imbalance under anaerobic conditions (Dien et al. 1996). Overexpression of all the genes of the fungal pathway resulted in the first *S. cerevisiae* strain capable of fermenting L-arabinose to ethanol, but at a very low rate (0.35 mg ethanol g biomass$^{(-1)}$ h$^{(-1)}$ under anaerobic conditions (Richard et al. 2003). The reasons for the low rate of L-arabinose fermentation were probably the cofactor unbalance. Also, bacteria are able to ferment arabinose. The bacterial arabinose pathway does not include any redox reaction and comprises L-arabinose isomerase (araA), L-ribulokinase (araB), and L-ribulose-5-phosphate 4-epimerase (araC) (▶Fig. 9.7a). Becker and Boles introduced into *S. cerevisiae*, *E. coli* araB and araD and *Bacillus subtilis* araA. Moreover, they overexpressed GAL2 encoding a

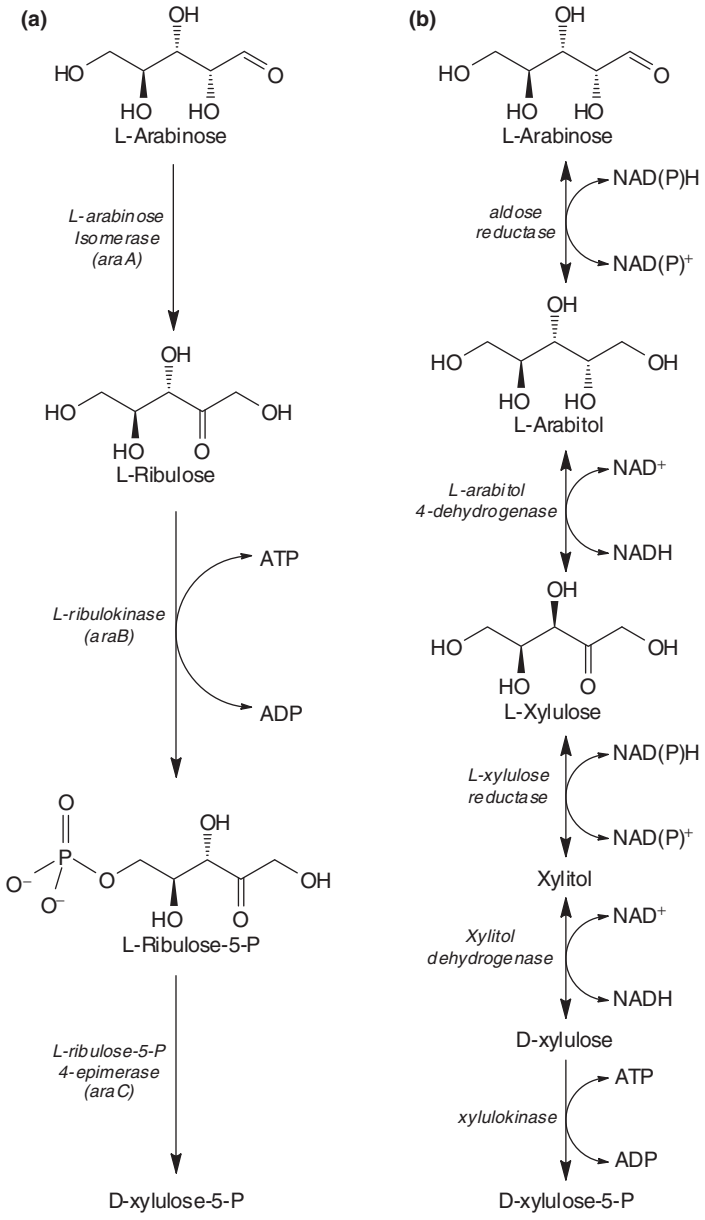


Fig. 9.7: D-arabinose catabolism in bacteria (a) and fungi (b). D-xylulose-5-P is further catabolized through the pentose phosphate pathway to fructose-6-P and glycerhaldeyde-3-P, which are metabolized in the glycolytic pathway and converted to ethanol.

galactose permease, which has been shown to catalyze the arabinose uptake. Through an evolutionary engineering protocol, a strain capable of producing ethanol from arabinose under oxygen-limited conditions at 0.06–0.08 g ethanol g biomass(⁻1) h(⁻1) with a theoretical yield of 60% was selected (Becker and Boles 2003). More recently, an

improvement of the fermentation performances was obtained replacing the *B. subtilis* araA with the enzyme from *Bacillus licheniformis*, leading to a considerably decreased lag phase. Subsequently, the codon usage of all the genes involved in the L-arabinose pathway was adapted to that of the highly expressed genes encoding glycolytic enzymes in *S. cerevisiae*. The ethanol production rate from L-arabinose could be increased more than 2.5-fold, and the ethanol yield could be increased from 0.24 g ethanol (g L-arabinose)$^{(-1)}$ to 0.39 g ethanol (g L-arabinose)$^{(-1)}$ (Wiedemann and Boles 2008).

Arabinose and xylose pathways have been co-expressed in *S. cerevisiae*. Wisselink et al. reported the construction of the first yeast strain capable of fermenting mixtures of glucose, xylose, and arabinose with a high ethanol yield (0.43 g g$^{(-1)}$ of total sugar) without formation of the side products xylitol and arabitol. The kinetics of anaerobic fermentation of glucose-xylose-arabinose mixtures were greatly improved using an evolutionary engineering strategy. Yeast cells were successively cultivated in mixtures of glucose, xylose, and arabinose, allowing them to evolve longer periods on the less-preferred carbon sources. The evolved strain (IMS0010) showed a significant reduction in the time required to completely ferment a mixture containing 30 g liter$^{(-1)}$ glucose, 15 g liter$^{(-1)}$ xylose, and 15 g liter$^{(-1)}$ arabinose (Wisselink et al. 2009).

A different *S. cerevisiae* strain (TMB3664) expressing an improved fungal pathway for the fermentation of L-arabinose and D-xylose was described (Bettiga et al. 2009). During anaerobic fermentation this strain produced biomass and ethanol, L-arabitol (yield: 0.48 g g$^{(-1)}$ of arabinose), and the xylitol (0.07 g g$^{(-1)}$ of xylose). Ethanol yield was 0.23 g/(g sugar) based on total sugars present at the beginning of the fermentation, 0.40 g/(g sugar) based on consumed sugars (Bettiga et al. 2009).

Bera et al. have reported the construction of a recombinant *S. cerevisiae* strain overexpressing the fungal L-arabinose utilization pathway. The resulting strain, 424A(LNH-ST), exhibited production of ethanol from L-arabinose, and the yield was more than 40%. An efficient ethanol production (about 72.5% yield) from five-sugar mixtures containing glucose, galactose, mannose, xylose, and arabinose was also achieved (Bera et al. 2010).

All these studies have employed laboratory yeast strains that are less resistant to inhibitors of fermentation. Moreover, most of them make use of episomal plamsids, which are not stable enough for an industrial use. An improved industrial *S. cerevisiae* strain capable of fermenting both hexoses and pentose was created, integrating in the genome the heterologous genes of the fungal xylose and arabinose pathways. Evolutionary engineering allowed the isolation of an evolved strain TMB3130, displaying improved fermentation performance. Anaerobic ethanol production was increased at the expense of xylitol and glycerol; arabinose was, however, completely converted to arabitol (Garcia Sanchez et al. 2010).

9.5.5 Other yeasts

Pichia stipitis is a natural pentose-fermenting yeast. It is also able to ferment other sugars (e.g. glucose, cellobiose) with good yields (0.31–0.48 g ethanol per gram of fermented sugar). However, compared to *S. cerevisiae* this yeast displays several drawbacks: (1) it produces ethanol only during microaerophilic conditions; (2) sugar consumption rates are slower than in *S. cerevisiae*; and (3) it is sensitive to metabolic inhibitors. The sequencing of the *P. stipitis* genome opens the door to possible genetic engineering approaches to solve these problems (Jeffries et al. 2007).

Two other yeasts (*Kluyveromyces marxianus* and *Hansenula polymorpha*) have been considered for biofuels production, mainly for their ability to ferment many sugars at high temperatures (up to 48–50ºC), which makes them interesting biocatalysts in an SSF process. Both of these yeasts are, however, Crabtree-negative. They do not produce ethanol in the presence of excess sugar and oxygen (Weber et al. 2010).

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10 Catalytic conversion of biosourced raw materials: homogeneous catalysis

Cédric Fischmeister, Christian Bruneau, Karine De Oliveira Vigier, and François Jérôme

With the progressive disappearance of fossil carbon reserves and the growing concern about climate change, biomass is now being intensely investigated as a renewable raw material for the production of valuable chemicals and transportation fuels (Corma, Iborra, and Velty 2007; Clark 2006; Gallezot 2008; Bozell and Petersen 2010; Simonetti and Dumesic 2008). In this context, catalysis plays a pivotal role by offering to chemists efficient tools for selectively converting biomass to more value-added chemicals through economically and environmentally competitive processes.

From the view point of sustainable chemistry, heterogeneous catalysis is more desirable because of the easy recovery and the possible recycling of solid catalysts (Climent, Corma, and Iborra 2011). Historically, heterogeneous catalysis have been developed for the conversion of fossil oils. The low reactivity of the alkanes and alkenes that compose fossil oils has led chemists to design a wide range of solid catalysts that are capable of operating under severe conditions of temperature and pressure. The direct transposition of heterogeneous catalysis from fossil oils to biomass appears as one of the main challenges faced by modern heterogeneous catalysis (Vennestrom et al. 2010). Although fascinating results have been reported either at an academic or industrial level, the direct use of solid catalysts especially designed for fossil reserves to biomass is a difficult task, mainly because of the polyfunctionality or the low solubility of biomass in conventional solvent. Indeed, as compared to fossil reserves, biomass is composed of functional molecules (alcohols, alkenes, ethers, esters, among others) and consequently has to be catalytically activated under mild conditions in order to closely control the selectivity of the reaction. Additionally, starting from lignocellulosic biomass, heterogeneously catalyzed processes are also strongly hampered by the very low solubility of lignocellulosic biomass in common solvents. For all these reasons, particular attention is given to the utilization of homogeneous catalysts for the conversion of biomass. The main advantage of homogeneous catalysts stems from their high activity, which allows designing catalytic processes under milder conditions than with solid catalysts.

Through recent selected examples, we show in this chapter the contribution of homogeneous catalysis for the selective conversion of biomass to higher value-added chemicals. In particular, we highlight the contribution of homogeneous catalysis for the fractionation and conversion of recalcitrant lignocellulosic biomass. Recovery and recycling of homogeneous catalysts is an important issue, and this aspect is also discussed. The synergistic effect between homogeneous and heterogeneous catalysis has recently received a lot of attention, especially for the design of integrated processes. Through recent examples, we show the efficiency of this methodology for the conversion of lignocellulosic biomass to chemical platforms. The second part of this chapter is dedicated to the conversion of fats and oils. On the basis of recent advances reported on the metathesis reaction, we demonstrate the potentiality of homogeneous catalysts for synthesizing

a large range of valuable chemicals from fatty alkenes. Because glycerol is the main co-product of vegetable oil, we also describe the significant contribution of homogeneous catalysis for the conversion of glycerol to safer nonionic surfactants. It is noteworthy that the aim of this chapter is not to provide a complete overview of all works dealing with homogeneous catalysis applied to biomass but, rather, to discuss on recently reported innovative strategies that contribute to convert biomass through eco-efficient routes.

10.1 Lignocellulosic biomass

Lignocellulose is the main component of biomass with an annual production estimated at around 170 billon metric tons. With the depletion of fossil reserves and the dramatic increase of greenhouse gases in the atmosphere, lignocellulose has become of growing interest not only for the synthesis of chemicals but also for the production of transportation fuels. In average, lignocellulose is composed of lignin (15%–25%), hemicellulose (23%–32%), and cellulose (38%–50%) – the exact composition varying according to the origin of biomass (▶Tab. 10.1).

Prior to catalytic conversion, lignocellulosic biomass is subjected to a fractionation process that aims to separate lignin from carbohydrates (hemicellulose and cellulose) from which higher value-added chemicals can be more easily produced.

Up to now, the lignin fraction has been poorly valorized. In most cases, lignin is burnt with the aim of providing heat and electricity to the biorefinery. It should be mentioned, however, that few articles describe the possible use of lignin as a renewable source of phenolic compounds for the synthesis of polymers (Lora and Glasser 2002) or fuels, because the energy content of lignin is about 26.3 MJ/OD kg (Sadler 1993). More information regarding lignin can be found in Chapter 8.

The hemicellulose fraction is mainly composed of xylose together with other carbohydrates such as mannose, galactose, rhamnose, arabinose, glucose, and others. Industrially, hemicellulose is catalytically hydrolyzed to water-soluble sugars that can be further fermented to ethanol or chemical platforms such as xylose or furfural. Reversely, to hemicellulose, the depolymerization of cellulose is more difficult because of its highly crystalline structure assured by a strong cohesive hydrogen bond network. In this context, much effort has recently been paid to the rational design of solid catalysts for the selective depolymerization of cellulose to water-soluble carbohydrates. However, the high crystallinity of cellulose, unfortunately, makes its dissolution in water and in conventional organic solvents very difficult, resulting in a poor contact between

Tab. 10.1: Composition of common lignocellulosic biomass.

Lignocellulosic Biomass	Lignin (%)	Hemicellulose (%)	Cellulose (%)
Hardwood sterns	18–25	24–40	40–55
Softwood sterns	25–35	25–35	45–50
Grasses	10–30	35–50	25–40
Paper	0–15	0	85–99
Cotton seed hairs	0	5–20	80–95

cellulose and solid catalyst surfaces. As a consequence, most reported solid catalysts require harsh conditions, making the control of the reaction selectivity very complex. In order to circumvent this issue, recalcitrant cellulose is generally decrystallized prior to catalytic hydrolysis. Ball-milling and dissolution of cellulose in ionic liquids were recently studied. Although these methods clearly increase the efficiency of solid catalysts in the hydrolysis of cellulose, their industrial emergence is hampered because of their price, high energy input, or environmental problems. Therefore, in the field of cellulose, homogeneous catalysis offers remarkable advantages over solid catalysts. In particular, homogeneous catalysts are capable of diffusing within the recalcitrant cellulose backbone, inducing its depolymerization without the assistance of any pretreatment methods.

In this section we discuss the contribution of homogeneous catalysis for (1) the fractionation of lignocellulosic biomass and (2) the conversion of carbohydrates to higher value-added chemicals. We also discuss recent works highlighting a possible synergistic effect between homogeneous and heterogeneous catalysis, thus offering a promising route for synthesizing valuable chemicals through environmentally friendly processes.

10.1.1 Acid-catalyzed fractionation of lignocellulosic biomass

Fractionation of lignocellulosic biomass is a preliminary and necessary step that aims to release carbohydrates, from which a wide range of chemicals and transportation fuels can be produced (▶Fig. 10.1) (Mosier et al. 2005). Because of the very low solubility of lignocellulosic biomass in conventional media, homogeneous catalysts are generally preferred in order to facilitate a better contact with biomass. Various fractionation processes are reported in the literature. Among them, extraction of lignin with alcohol (organosolv process) and ozonolysis or fractionation in alkaline solution or in the presence of ammonia are commonly used. In this section, we focus on the utilization of acid homogeneous catalysts for the fractionation of lignocellulosic biomass.

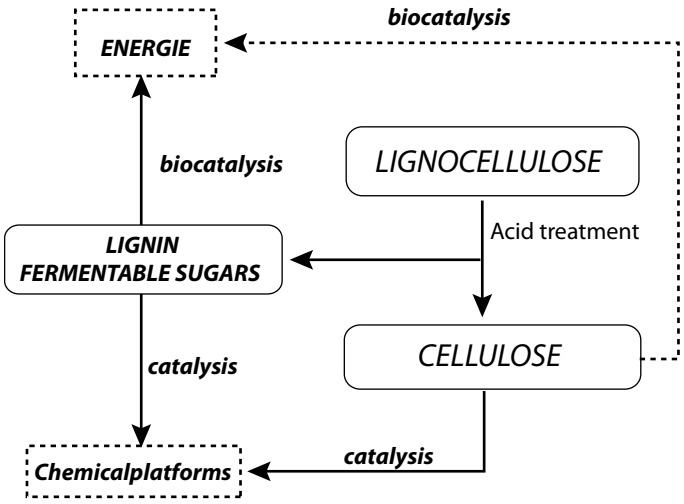


Fig. 10.1: Acid-catalyzed pretreatment of lignocellulosic biomass.

Fractionation of lignocellulosic biomass in the presence of an acid homogeneous catalyst has received considerable attention during the past few decades. According to the acid catalysts (mostly sulfuric acid and phosphoric acid), the fractionation can be performed either at high temperature/low acid concentration (dilute-acid pretreatment) or at low temperature/high acid concentration (concentrated-acid pretreatment). During the fractionation of lignocellulosic biomass, lignin is released and recovered by extraction with an organic solvent while hemicellulose is hydrolyzed to water-soluble carbohydrates (mostly xylose). Because of its high crystalline structure, cellulose remains unaltered during the fractionation process and is recovered as a white powder. It is noteworthy that according to the acid and conditions used (120–180 °C, 30–90 min), cellulose can be partly decrystallized during the acid fractionation of lignocellulosic biomass, thus enhancing its reactivity toward hydrolysis (Zhang et al. 2007).

Although harsh reaction conditions seem beneficial for further enhancing the reactivity of cellulose, it should be pointed out that such conditions can lead to the formation of side products such as furfural, 5-hydroxymethylfurfural (HMF), and aromatic degradation compounds (from lignin). Therefore, up to now, dilute-acid hydrolysis of lignocellulosic biomass is preferred mainly because concentrated acid fractionation results in higher operational and maintenance costs at a commercial scale (Wyman 1996). Furthermore, equipment corrosion problems and acid recovery are significant drawbacks when using concentrated acid solutions.

Very recently, Dominguez and coworkers reported a new process for the fractionation of lignocellulosic biomass (see vom Stein et al. 2011). Originality of this process stems from the utilization of acid and solvent directly available from biomass (vom Stein et al. 2011). In particular, authors have shown that in a biphasic water/2-methyltetrahydrofuran (2-MTHF) system and using oxalic acid as a homogeneous catalyst, fractionation of lignocellulosic biomass smoothly took place. At mild conditions (80–140°C), oxalic acid is capable of (1) hydrolyzing hemicellulose to water-soluble sugars and (2) releasing lignin, which is selectively extracted with 2-MTHF. The insoluble fraction is mainly composed of cellulosic pulp, which can be further converted to glucose using a biocatalytic process. Interestingly, in such a process, authors have found that when the aqueous phase is concentrated, oxalic acid precipitated (nearly 80 wt%) as a pure solid, thus offering an attractive mean for recycling the homogeneous oxalic acid catalyst. This entire process is summarized in ▶Fig. 10.2.

Note that other dicarboxylic organic acids, such as fumaric or maleic acids, have also been previously investigated in the literature, and these acids were also found to be more efficient in terms of activity and selectivity than sulfuric acid (Kootstra et al. 2009; Lee and Jeffries 2011).

10.1.2 Homogeneously catalyzed conversion of cellulose and related polysaccharides

Cellulose is now the topic of intense research mainly because (1) cellulose represents 45% of the worldwide production of biomass (estimated to be 18×10^{10} t/year) and (2) cellulose is not digestible and thus does not compete with human food, which makes cellulose a strategic raw material in chemistry. In this context, many catalytic processes have been designed for the conversion of cellulose to valuable chemicals (propylene

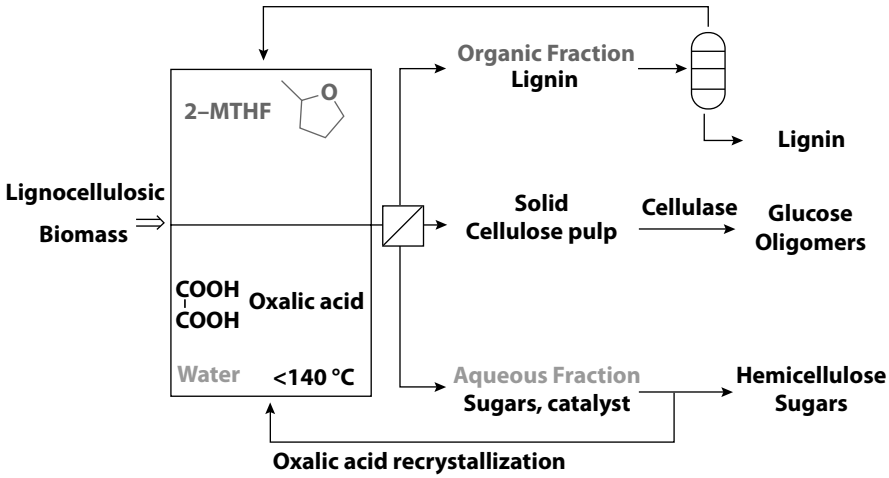


Fig. 10.2: Fractionation of lignocellulosic biomass in the presence of oxalic acid. Reproduced by permission of The Royal Society of Chemistry from vom Stein et al. (2011).

glycol, furan derivatives, etc.), molecule platforms (glucose, 5-hydroxymethylfurfural, levulinic acid, etc.), and transportation fuels (ethanol, butanol, hydrogen, etc.). One should mention that the viability of these processes closely relies on the selective and clean depolymerization of cellulose to water-soluble carbohydrates from which the previously described chemicals, molecule platforms, and transportation fuels are produced.

10.1.2.1 Homogeneously catalyzed hydrolysis of cellulose

Shimizu et al. (2009) have shown that heteropolyacids ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$) and their corresponding metallic salts (M^{n+}) ($M_{3/n}PW_{12}O_{40}$) act as efficient homogeneous catalysts for the selective hydrolysis of cellulose to water-soluble sugars in water. After 2 hours of reaction at 150°C, glucose was obtained with a selectivity of 83% at 18% of conversion of cellulose. Later, Tian et al. (2010) optimized the process. In particular, after 2 hours of reaction at 180°C in the presence of a catalytic amount of $H_3PW_{12}O_{40}$, authors reported a yield of glucose of 50% (i.e. 90% selectivity) starting from a cellulose/$H_3PW_{12}O_{40}$ mass ratio of 0.42 (▶Fig. 10.3). Note that $H_3PW_{12}O_{40}$ was successfully recovered and recycled by means of selective extraction from the water phase using diethylether (Tian et al. 2010).

10.1.2.2 Homogeneously catalyzed hydrolysis of hemicellulose

Catalytic hydrolysis of hemicellulose is of great importance especially with the aim of providing xylose and furfural (▶Fig. 10.4). In this context, Liu and Wyman (2006) have investigated the catalytic activity of $CaCl_2$, $MgCl_2$, and $FeCl_3$ in the conversion of hemicellulose. First, authors described that, at 180°C in water and in the presence of 0.8% $FeCl_3$, 65% of xylose was consumed after only 20 minutes of reaction. On the basis of these results, the same authors (Liu et al. 2009) next extended this process to the

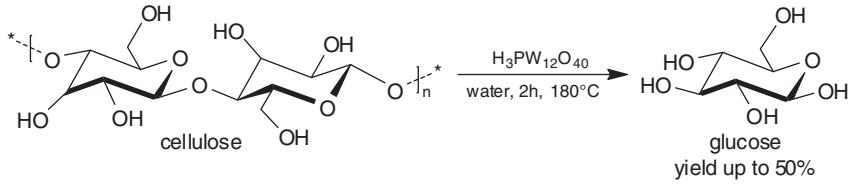


Fig. 10.3: Catalytic hydrolysis of cellulose in the presence of heteropolyacid.

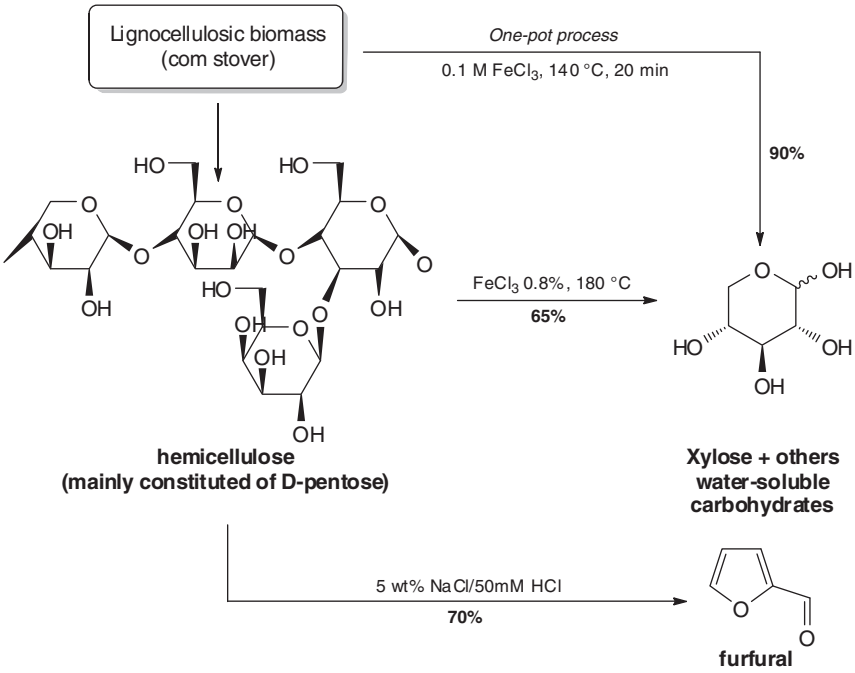


Fig. 10.4: Catalytic hydrolysis of hemicelluloses.

direct conversion of hemicellulose. In particular, they investigated the catalytic activity of $FeSO_4$, $FeCl_3$, and $Fe_2(SO_4)_3$ in the hydrolysis of hemicellulose from corn stover. Optimum conditions were found when the corn stover was reacted with 0.1 M $FeCl_3$ at 140°C for 20 minutes. Under these conditions, xylose was recovered with nearly 90% yield. In 2010 Marcotullio et al. have observed that the addition of 5 wt% of NaCl to a 50 mM HCl aqueous solution not only favored the hydrolysis of hemicellulose to xylose but also promoted its dehydration to furfural, which was obtained in a one-pot process with nearly 70% yield (▶Fig. 10.4).

Clearly, among all tested salts, $FeCl_3$ exhibits superior performance in terms of reaction rate in the conversion of hemicellulose (Marcotullio and De Jong 2010). In 2011 Marcotullio et al. compared the catalytic activity of a dilute aqueous HCl solution with a dilute solution of $FeCl_3$ in the production of hemicellulose-derived carbohydrates from

wheat straw. At 120°C and using 200 mM of an aqueous solution of either HCl or $FeCl_3$, comparable yields of water-soluble carbohydrates were obtained. Under these conditions, hydrolysis of hemicellulose to xylose is nearly complete.

10.1.2.3 Homogeneously catalyzed conversion of cellulose to 5-hydroxymethylfurfural

Direct and catalytic conversion of cellulose to 5-hydroxymethylfurfural (HMF) is a reaction of great interest since HMF is now recognized as a chemical platform for the production of a large number of chemicals such as monomers, solvents, fuels, and so on. Although most catalytic processes (either homogeneous or heterogeneous) involve fructose as a starting material, much effort has been paid to directly convert cellulose, which is available in a much larger scale, to HMF. As mentioned previously, most heterogeneous catalysts are inefficient mainly because of a poor contact between the catalyst surface and recalcitrant cellulose. For this reason, direct conversion of cellulose to HMF is generally accomplished using homogeneous catalysts (▶Fig. 10.5).

In order to overcome the crystallinity and insolubility of cellulose in conventional media, most catalytic reactions involving cellulose are performed in an ionic liquid. In 2008 Zhao et al. described the catalytic hydrolysis of lignocellulose in the presence HCl (Li, Wang, and Zhao 2008). The reaction was performed in butylmethylimidazolium chloride ([BMIM]Cl). After 1 hour of reaction at 100°C in the presence of 7 wt% of HCl in [BMIM]Cl, authors have shown that water-soluble sugars were obtained with 66%, 74%, 81%, and 68% yields from corn stalk, rice straw, pine wood, and bagasse,

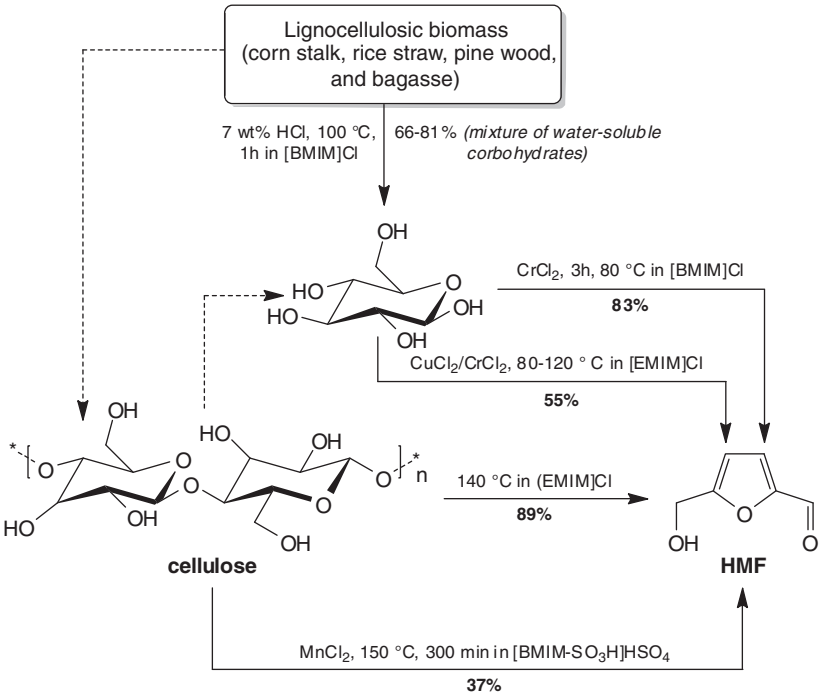


Fig. 10.5: Catalytic conversion of cellulose to HMF in ionic liquids.

respectively (▶Fig. 10.5). Note that among water-soluble sugars, glucose can be then further converted to HMF in [BMIM]Cl. In this context, the same authors reported that in the presence of 6 mol% of $CrCl_2$, glucose can be isomerized to fructose and then dehydrated to HMF (Zhao et al. 2007). After 3 hours of reaction at 80°C, HMF was obtained with 83% yield.

Chen and coworkers reported that cellulose can be directly converted to HMF with 89% yield at 140°C in the presence of $CrCl_2$ in 1-ethyl-3-methylimidazolium chloride [EMIM]Cl (Zhang et al. 2010) (▶Fig. 10.5). Interestingly, Zhang and coworkers have shown that at 80–120°C in [EMIM]Cl, glucose can be converted to HMF with 55% yield in the presence of a mixture $CrCl_2/CuCl_2$ ($\chi_{CuCl2} = 0.9$), thus limiting the dependency of the process to toxic chromium (Hu et al. 2009). In such a process, HMF was selectively extracted with methylisobutylketone, allowing authors to recycle [EMIM]Cl and the $CrCl_2/CuCl_2$ homogeneous catalysts. In 2011 Tao et al. (2011) reported that microcrystalline cellulose can also be converted to HMF in the presence of an acidic ionic liquid such as 1-(4-sulfonic acid) butyl-3-ethylimidazolium hydrogen sulfate ([BMIM-SO_3H]HSO_4). In this process, authors used a catalytic amount of $MnCl_2$ resulting in the formation of HMF with 37% after 300 minutes of reaction at 150°C (▶Fig. 10.5) (Tao et al. 2011).

Unfortunately, hazardous toxicity and the price of ionic liquids currently hampers the industrial emergence of these processes. For these reasons, other media have been explored for the conversion of cellulose. In this context, Raines and coworkers reported the direct conversion of cellulose to HMF in an *N*,*N*-dimethylacetamide (DMA)/LiCl solution (▶Fig. 10.6). After 3 hours of reaction at 120°C, HMF was obtained with 71% yield in the presence of a catalytic amount of CuCl (Binder and Raines 2009). Note that authors found that the conversion of cellulose to HMF is inhibited by the presence of other biomass-derived components, such as lignin and proteins, suggesting that such a process cannot be directly applied to lignocellulosic biomass. Mascal and coworkers investigated the possible conversion of cellulose to 5-chloromethylfurfural (CMF) using concentrated HCl in a water/LiCl solution. In this process, CMF was continuously extracted with dichloromethane (Mascal and Nikitin 2008). After 12 hours of reaction at 65°C, CMF was obtained with 80% yield (▶Fig. 10.6). Although this reaction was not catalytic, the formation of CMF is highly relevant since CMF can be more easily functionalized than HMF, thus opening an interesting route for accessing a broader range of chemicals.

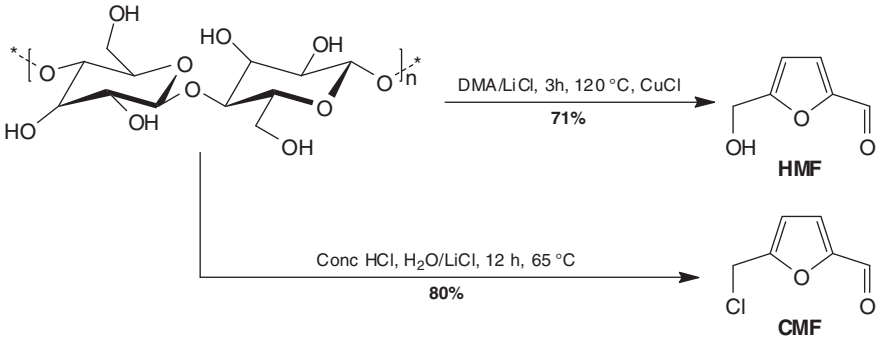


Fig. 10.6: Conversion of cellulose to HMF and CMF.

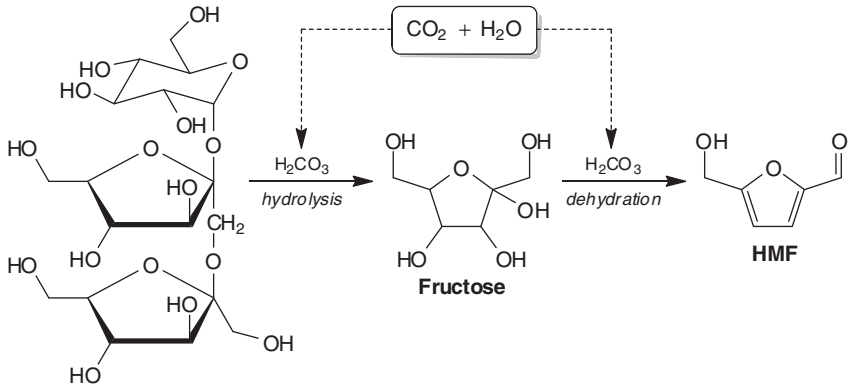


Fig. 10.7: Catalytic conversion of inulin to HMF in the presence of CO_2.

In 2010 B. Han and coworkers reported the effect of CO_2 on the hydrolysis of inulin (a natural polysaccharide of fructose essentially extracted from chicory) (Wu et al. 2010). This process is smartly based on the reactivity of CO_2 with water, which leads to the formation of carbonic acid that can further catalyze the tandem hydrolysis/dehydration conversion of inulin to HMF (▶Fig. 10.7). In particular, authors have shown that increasing the pressure of CO_2 up to 60 bar led to a significant improvement of the HMF yield from 38% (without CO_2) to 53% (180°C, 1.5 h, 5 wt% of fructose).

A further increase of the CO_2 pressure was found to be detrimental to the process. Indeed, at a higher pressure of CO_2, the pH of the solution dropped below 3.5 (optimal pH), resulting in the main degradation of HMF to levulinic and formic acids and humins. The main advantage of this process stems from the absence of work-up generally required for the removal/recycling of homogeneous catalysts.

Note that such a strategy has been previously applied to microcrystalline cellulose, recycled paper, and sugarcane bagasse (Zheng, Lin, and Tsao 1998) or aspen and southern yellow pine (Kim and Hong 2001). In 2011 it was shown that a pretreatment of corn stover with CO_2 led to the production of glucose with 30% yield (3500 psi, 150°C, 60 min), further demonstrating the contribution of the CO_2 technology for the conversion of polysaccharides (Narayanaswamy et al. 2011).

10.1.3 Synergistic effect between homogeneous and heterogeneous catalysis

With the aim of favoring the conversion of lignocellulose in more efficient routes, scientists are now extensively focusing on the combination of homogeneous and heterogeneous catalysts. In these systems, homogeneous catalysts are often used for the fractionation of biomass while heterogeneous catalysts promote the conversion of released products to fine chemicals or transportation fuels. In this section, we discuss the most recent works reported in this field.

In 2011 Dumesic and coworkers reported an integrated biofuel production from lignocellulosic biomass (▶Fig. 10.8) (see Braden et al. 2011). In this process, authors have used sulphuric acid for the deconstruction of biomass to levulinic acid and a series of heterogeneous catalysts capable of converting levulinic acid to hydrocarbons.

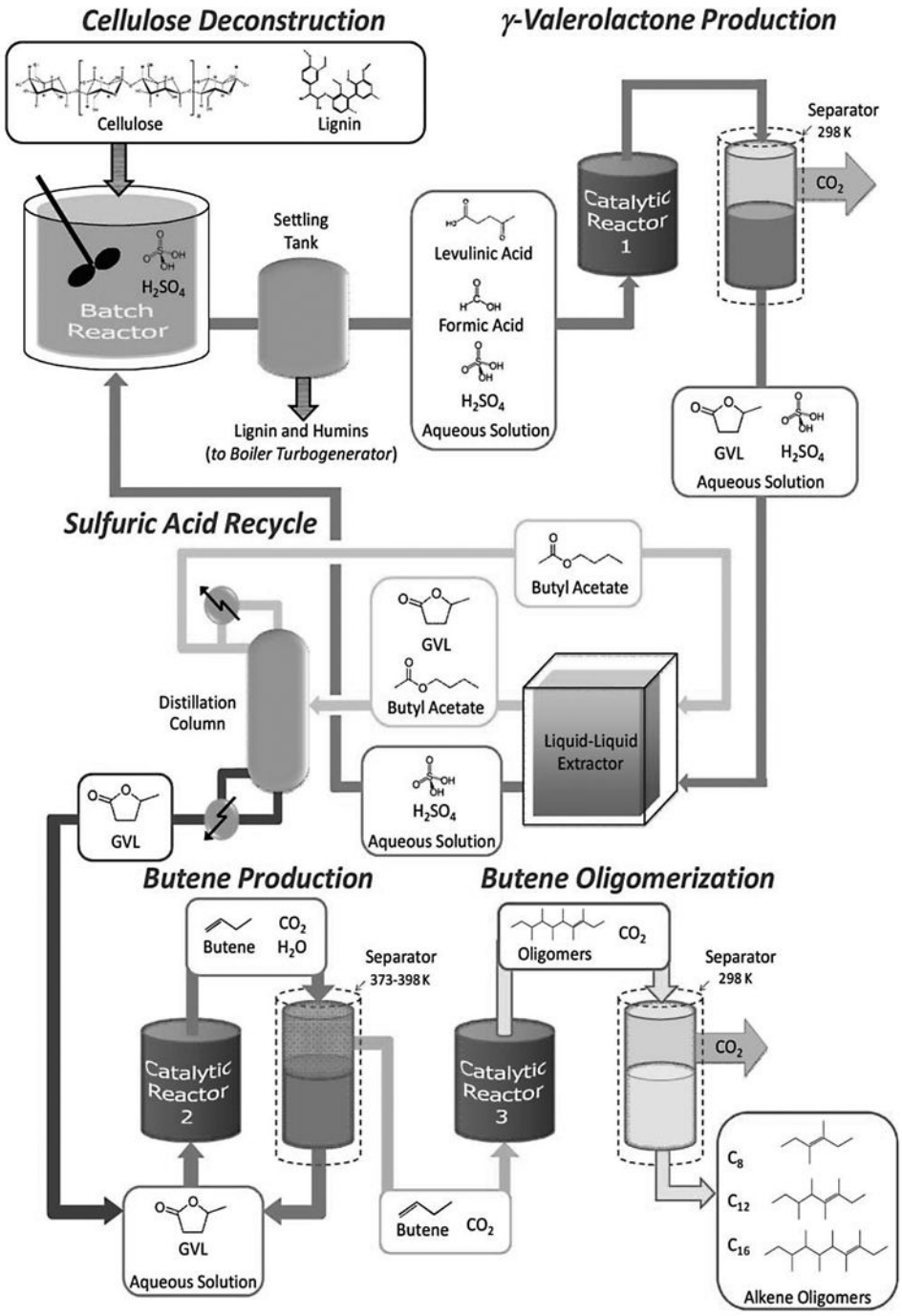


Fig. 10.8: Catalytic conversion of biomass to liquid hydrocarbon fuels. Reproduced by permission of The Royal Society of Chemistry from Braden et al. (2011).

First, the hemicellulose fraction was removed with a dilute acid solution as described previously. Next, cellulose was deconstructed at 150°C with a diluted solution of sulphuric acid (0.5 mol/L), leading to the production of levulinic and formic acids with 55% yield. Insoluble products such as humins and lignin were separated in a settling tank and combined with the xylose fraction (from hemicellulose) prior to being sent in a boiler/tubogenerator for the production of heat and electricity. Then, the acid solution containing levulinic and formic acids was directly passed through a packed reactor filled with a Ru/Re(3:4)/C solid catalyst (heated at 150°C). This heterogeneous catalyst promoted the hydrogenation of levulinic acid to γ-valerolactone (GVL). It is interesting to point out that in this process, hydrogen partly comes from the decomposition of formic acid to hydrogen and CO_2, which concomitantly takes place over the Ru/Re(3:4)/C solid catalyst. GVL is insoluble in water and was selectively extracted with butyl acetate, which was itself removed by distillation and recycled. Importantly, the homogeneous sulphuric acid aqueous phase can be reused for the deconstruction of cellulosic material, thus considerably limiting the environmental impact resulting from the utilization of a homogeneous acid solution. Next, GVL was converted to hydrocarbon by (1) decarboxylation over a silica-alumina-based catalyst (375°C, 36 bar) yielding butene followed by (2) the oligomerization of butene to hydrocarbon over a cation exchange resin. In this process, 99% of GVL was converted to alkenes. This entire process is represented in ▶Fig. 10.8. Even more recently, Dumesic and coworkers optimized the extraction of GVL from the acid aqueous phase using alkylphenol solvents, allowing the recovery of GVL without contamination with sulphuric acid (Alonso et al. 2011).

In 2010 Sels and coworkers investigated the conversion of cellulose to hexitol using a synergistic effect between homogeneous catalysts (heteropolyacid (HPA) $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) and a heterogeneous catalyst (Ru/C) (see Geboerts et al. 2010). In this process, HPA catalyzes the hydrolysis of cellulose to glucose while Ru/C converts glucose to hexitols (mostly sorbitol, mannitol, and sorbitan) (▶Fig. 10.9). After 24 hours of reaction in water at 190°C and 50 bar of H_2, the cellulose conversion reached 82% and the yield of hexitol was 49% (other products stem from the C-C bond cracking of hexitols) using 25 wt% of Ru/C in the presence of a catalytic amount of HPA ($1.22.10^{-2}$ M).

Such an approach was found more efficient than the combination H_2SO_4-Ru/C. The greater efficiency of the HPA-Ru/C system relies on the fast and selective hydrolysis of cellulose to glucose. Interestingly, increasing the hydrogen pressure from 50 to 95 bar allowed suppressing the side C-C bond cracking reaction, resulting in the formation of hexitol with more than 72% selectivity at nearly 80% conversion of cellulose. When using amorphous cellulose (ball-milled cellulose), hexitol was quantitatively produced at complete conversion, thus showing the effectiveness of this process. Very recently, this process has been optimized using caesium salt of HPA. In such a process, caesium salts of HPA were recovered from the aqueous phase by recrystallization, thus making possible the recycling of this semihomogeneous CsHPA (Geboerts et al. 2011a).

In 2011 B. Sels kept working on this concept and reported the catalytic hydrolysis of ball-milled cellulose over a bifunctional Ru/H-USY catalyst in the presence of a catalytic amount of HCl (▶Fig. 10.10) (Geboerts et al. 2011b). Reactions were performed at 190°C, 50 bar of hydrogen, 10 wt% of Ru/H-USY (1.8 wt% of Ru), and 35 ppm of HCl, which corresponds to a pH of 3. In this process, HCl acts as a homogeneous catalyst

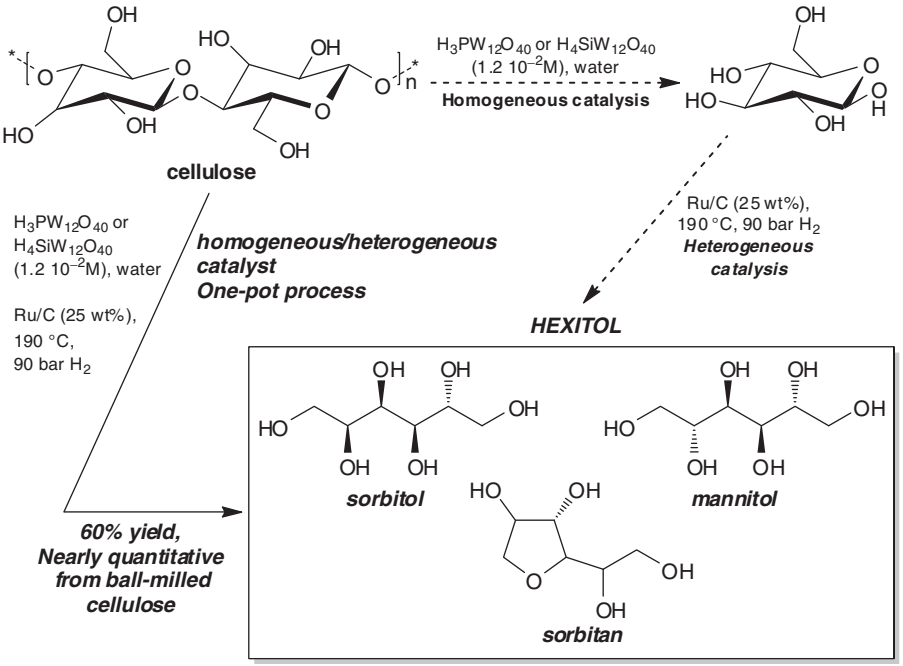


Fig. 10.9: Synergistic effect between HPA and Ru/C for the catalytic conversion of cellulose to hexitol.

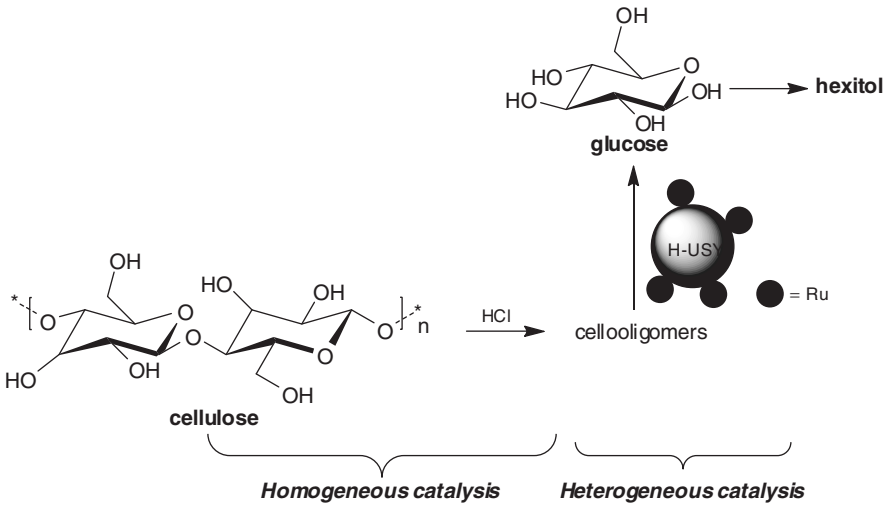


Fig. 10.10: Homogeneous/heterogeneous catalytic conversion of cellulose in the presence of HCl-Ru/H-USY.

and promotes the conversion of cellulose to water-soluble cellooligomers. Cellooligomers were then adsorbed on the acidic surface of H-USY where they were rapidly hydrolyzed to glucose. Next, the large quantity of glucose produced on the catalytic surface was rapidly hydrogenated by ruthenium, affording the desired hexitol with up to 50% yield. Note that when the same reaction was performed with Ru/C, no reaction took place further confirming the key role played by the H-USY support.

In such a process, an optimal balance between the acid/redox properties has to be found. At low pH, in situ–produced glucose is degraded, leading to a drop of the hexitol selectivity. Reversely, when the ruthenium content is too high on the H-USY support, the hydrogenolysis reaction becomes more favorable, leading to the predominant C-C bond cracking of carbohydrates. By means of counter experiments, it was found that using only 106 ppm of HCl combined with 0.2 wt% of Ru dispersed over H-USY, hexitol was obtained with a yield as high as 93%.

Following the same strategy, Zhao et al. (2007) highlighted a possible synergistic effect between a zeolite HY and $CrCl_2$. At 120°C, authors found that it was possible to directly convert cellulose to HMF with 47% yield in [BMIM]Cl. In this case, it was proposed that zeolite enhanced the hydrolysis of cellulose to glucose while $CrCl_2$ promoted the isomerization/dehydration of glucose to HMF (Tan, Zhao, and Zhang 2011).

10.2 Vegetable oils

As compared to lignocellulosic biomass, vegetable oils are a minor fraction of biomass. Although production of vegetable oils represents less than 5% of the annual production of biomass, vegetable oils have attracted considerable attention. Currently, chemical processes based on vegetable oils are even more developed than those based on lignocellulosic biomass. This tendency directly stems from the structure of vegetable oils. Indeed, vegetable oils, or triglycerides, are mainly composed of fatty acid/esters. The structure of these fatty acid/esters (saturated and unsaturated long-chain hydrocarbons) is very close to that of linear hydrocarbons obtained from fossil oils. For this reason, fats and oils have received much attention as biofuels and as alternative sources of raw materials for the chemical industry (Corma, Iborra, and Velty 2007; Marshall and Alaimo 2010; Biermann et al. 2011). In particular, owing to their fatty unsaturated structure, these compounds are of particular interest for the polymer and detergent industries. The fast and recent growth in oleochemistry has in some cases resulted in societal and political problems because some of these oils are also employed in the food industry. Consequently, vegetable oils arising from nonedible plants, such as ricin oil (castor oil) or from micro-algaes, have also attracted much attention as renewable sources of fats and oils (Van der Steen and Stevens 2009; Gunstone 2011; Soh and Zimmerman 2011). The strong interest in fats and oils is in part the consequence of their possible transformation by efficient and selective catalytic methods, in particular olefin metathesis (Hoveyda and Zhugralin 2007). Recently, several reviews have covered this field (Behr, Westfechtel, and Pérez Gomes 2008; Köckritz, Blumenstein, and Martin 2009), and here we focus on the seminal examples as well as on very recent developments concerning the metathesis transformation of fats and oils and other unsaturated renewable resources.

10.2.1 Catalytic conversion of renewable alkenes

10.2.1.1 Metathesis transformations of fatty-acid derivatives

In the early stages of olefin metathesis, ill-defined catalysts were utilized for the transformation of methyl oleate. Initially, the ethenolysis (cross-metathesis with ethylene) of methyl oleate **1** (▶Fig. 10.11) was performed with moderate success with $WCl_6/SnMe_4$ and heterogeneous $Re_2O_7/Al_2O_3/SnMe_4$ catalysts (van Dam, Mittlmeijer, and Boelhouwer 1972; Verkuijlen et al. 1977; Bosma, van Aardweg, and Mol 1981; Sibeijn and Mol 1992).

More recently, well-defined ruthenium-based homogeneous catalysts efficiently promoted the homometathesis (Dinger and Mol 2002), ethenolysis (Burdett et al. 2004; Schrodi et al. 2008; Thurier et al. 2008), and butenolysis (Patel et al. 2006) of methyl oleate (▶Fig. 10.12).

Ethenolysis of methyl oleate is of particular interest because it generates 1-decene **2** and methyl-9-decenoate **3**, the latter having a broad range of applications in the synthesis of lubricants, plasticizers, and fragrances (Warwel et al. 2001; Lu and Larock 2009; Meier 2009). However, the productivity of this reaction is generally hampered by the low stability of the ruthenium-methylidene catalyst. While second-generation catalysts are more active and stable than the first-generation ones, they are significantly less selective due to their capability to promote self-metathesis reactions and double-bond migrations at high temperatures. Nevertheless, Grubbs recently reported a series of new ruthenium complexes bearing unsymmetrical *N*-alkyl,*N*-aryl heterocyclic carbenes that provided the highest selectivity for NHC-based catalysts (see Thomas et al. 2011). For instance, complex **10** promoted the ethenolysis of methyl oleate **1** with 95% selectivity toward the ethenolysis products **2** and **3** (▶Fig. 10.13).

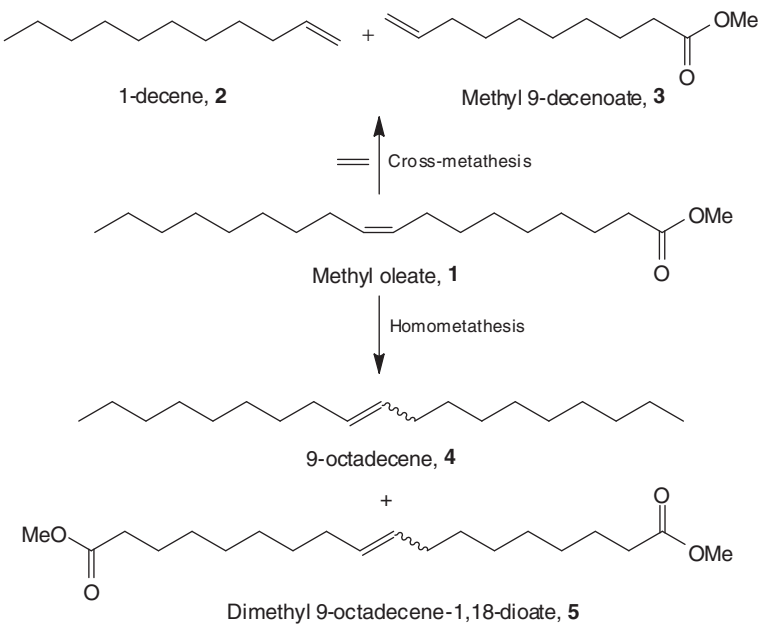


Fig. 10.11: Ethenolysis and homometathesis of methyl oleate.

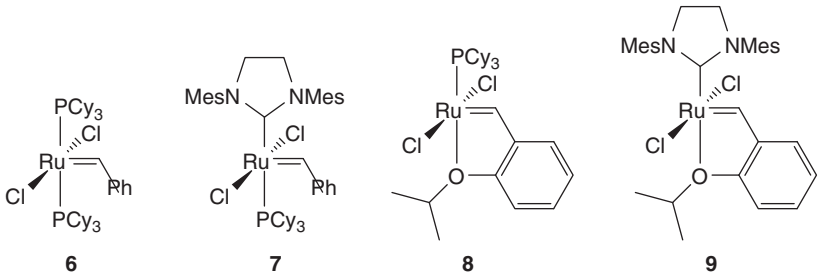


Fig. 10.12: Homometathesis of methyl oleate.

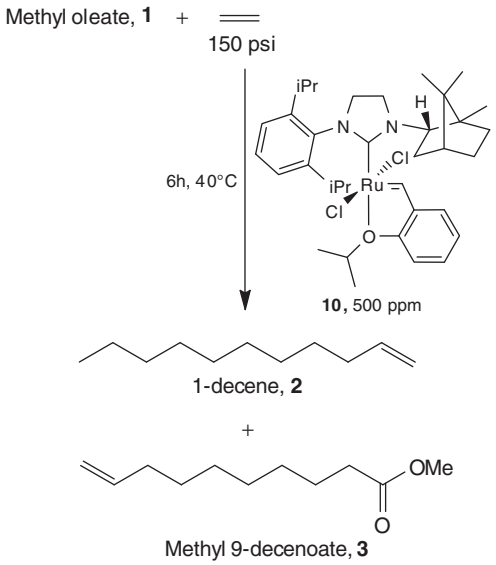


Fig. 10.13: Highly selective second-generation ruthenium catalyst for the ethenolysis of methyl oleate.

A second important class of olefin metathesis catalysts is based on Molybdenum complexes. These are generally very active with a broad range of substrates, but due to their lower tolerance to polar functional groups they have not been extensively used for the transformation of fatty-acid derivatives. However, in 2009 several molybdenum complexes with high efficiency and selectivity were reported. In particular, complex **11** reached 95% conversion with a selectivity for the desired products greater than 99% (▶Fig. 10.14) (Marinescu et al. 2009).

Thanks to the development of very active and functional group-tolerant ruthenium catalysts such as **7** and **9** (Vougioukalakis and Grubbs 2010), the introduction of a polar functionality into fatty-acid derivatives, by cross-metathesis with functional olefin, is now possible. In 2007 Meier and coworkers reported the first cross-metathesis

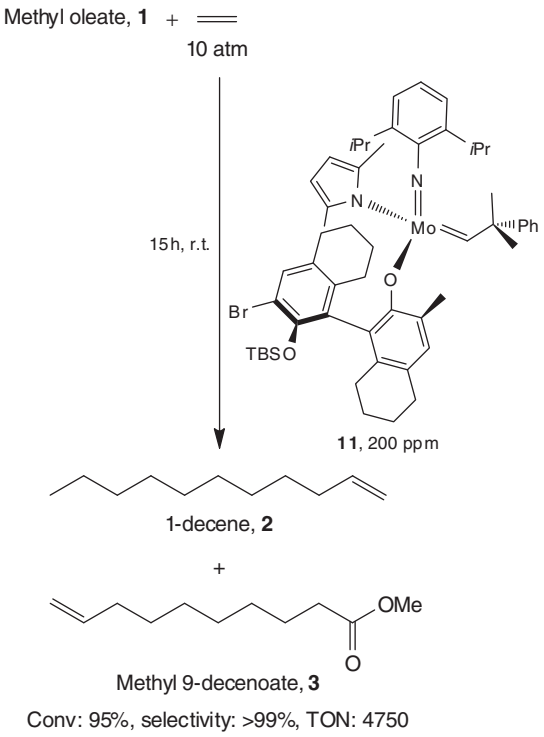


Fig. 10.14: Mo-catalyzed ethenolysis of methyl oleate.

reaction of unsaturated fatty-acid methyl ester with methyl acrylate leading to long-chain diesters such as **13** (see Rybak and Meier, 2007) (▶Fig. 10.15). Such types of compounds were also obtained by cross-metathesis with diethyl maleate (Behr, Pérez Gomes, and Bayra 2011). In 2009 Dixneuf and coworkers described the cross-metathesis of fatty-acid methyl esters with acrylonitrile, leading to ω-cyano fatty-acid esters such as **14** (see Malacea et al. 2009). These types of compounds are valuable precursors of polyamide monomers (▶Fig. 10.15) (Malacea et al. 2009; Van der Steen and Stevens 2009).

As demonstrated so far, olefin metathesis can be used for the transformation of renewable fatty-acid derivatives into valuable compounds, including polymer precursors. Olefin metathesis also offers the possibility to prepare polymers by Acyclic Diene Metathesis (ADMET). This technique was advantageously used by Meier and coworkers for the preparation of high-molecular-weight polyesters. Thus, following the preparation of the fully renewable monomer **15**, obtained from castor oil, the ADMET polymerization was carried out with or without end-capping, leading to renewable polyesters (▶Fig. 10.16) (Rybak and Meier 2008). More recently, the same group used the ADMET polymerization of renewable bioresourced dienes incorporating anhydride or ester linkages thus leading to biodegradable polymers (Türünc and Meier 2011).

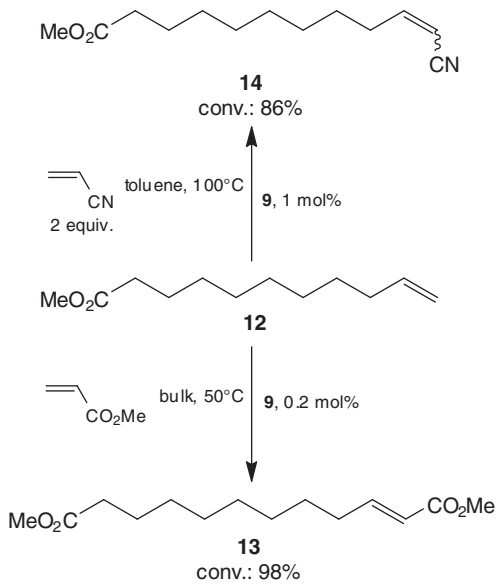


Fig. 10.15: Cross-metathesis of renewable fatty ester **12** with methyl acrylate and acrylonitrile.

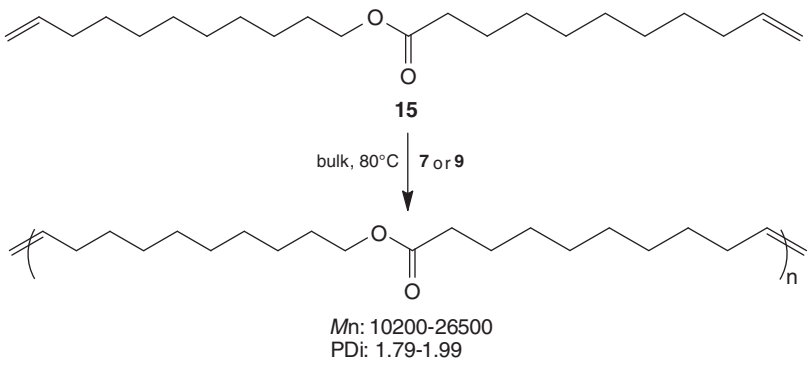


Fig. 10.16: ADMET polymerization of renewable monomers.

10.2.1.2 Sequential transformations involving olefin metathesis

Cleaner and more environmentally friendly transformations and processes have motivated the development of processes involving multiple catalytic transformations followed by a single workup stage with limited emission of wastes (Fogg and dos Santos, 2004). Olefin metathesis catalysts are known to display a broad range of nonmetathesis activity (Alcaide, Almendros, and Luna 2009), but in most cases, following a metathesis step, the metathesis catalysts is decomposed to an unidentified species. In some cases, these species may still display interesting catalytic activity. For instance, the cross-metathesis of

acrolein with 1-undecylenic aldehyde **16**, a renewable material obtained from castor oil cracking, could be followed by the simultaneous hydrogenation of the carbon-carbon double bond and the formyl group, leading to the saturated C12 diol **17** (Miao et al. 2009). In the same manner, tandem self-metathesis of **16** followed by hydrogenation under mild conditions led to the saturated C20 diol **18** (▶Fig. 10.17).

The palladium catalyzed isomerisation-methoxycarbonylation disclosed by Cole-Hamilton in 2005 (Jimenez Rodriguez et al. 2004) was elegantly incorporated in a one-pot sequence beginning with the bunenolysis of methyl oleate **19** (Zhu et al. 2006). Thus, methyl 9-undecenoate **20** and 2-undecene **21**, resulting from the first metathesis transformation, were efficiently converted to dimethyl dodecanedioate **22** and methyl dodecanoate **23** (▶Fig. 10.18). Similarly, the same sequence was applied directly to two vegetable oils (sunflower and linseed), leading to mixtures of mono- and diesters in accordance with the composition of the initial oil.

Cross-enyne metathesis is an efficient tool for the synthesis of conjugated dienes (Diver and Giessert 2004; Fischmeister and Bruneau 2011). This catalytic metathesis reaction has been used for the transformation of renewable compounds such as diester **24** (Le Ravalec, Fischmeister, and Bruneau 2009; Le Ravalec et al. 2010). However, because the direct reaction of an alkyne with an internal olefin was not possible, a one-pot transformation beginning with the cleavage of **24** into terminal olefins by ethenolysis was set up. The transformations were carried out in the greener dimethyl carbonate

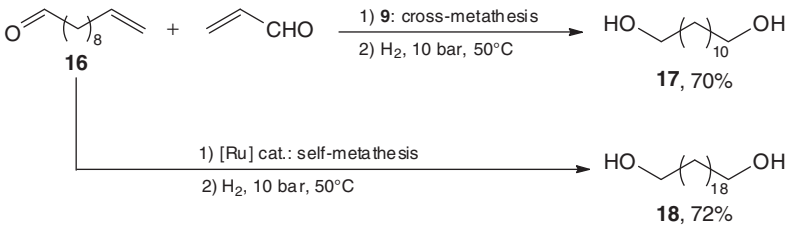


Fig. 10.17: Tandem metathesis/hydrogenation reactions leading to fatty saturated diols.

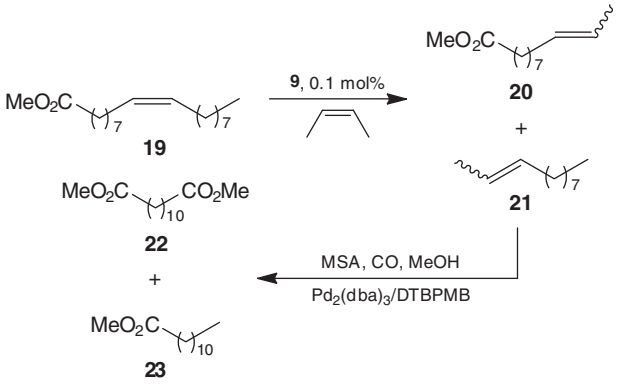


Fig. 10.18: One-pot metathesis-isomerisation-methoxycarbonylation of methyl oleate.

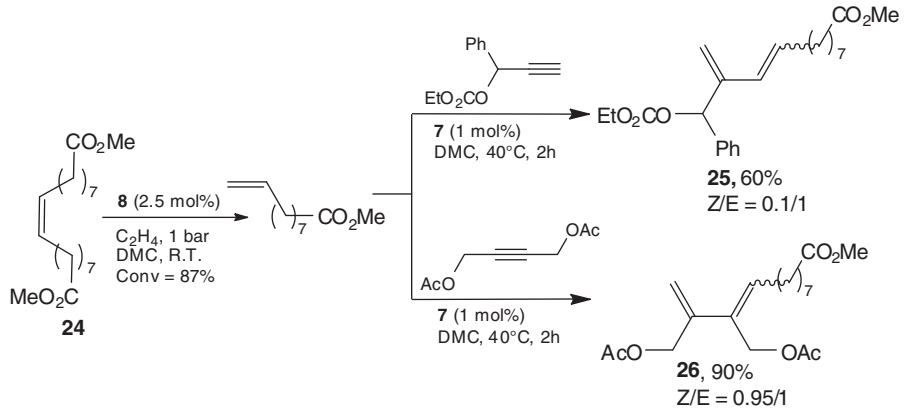


Fig. 10.19: One-pot ethenolysis/cross-enyne metathesis sequence.

(DMC) instead of the less desired dichloromethane or toluene, and several functional dienes such as **25** and **26** were obtained (▶Fig. 10.19).

10.2.1.3 Metathesis transformations of terpenes and terpenoids

Terpenes are a class of natural compounds that have been used for a long time as flavoring and fragrance and in medicinal formulations (Christmann 2010). Recently, terpenes have been shown to be valuable compounds in the context of oil shortages and in the utilization of renewable materials as sources of raw materials for the chemical industry (Luiz, Monteiro, and Veloso 2004; Behr and Johnen 2009). The transformation of terpenes using efficient and selective methods is also of great interest for the preparation of new molecules of potential utility in the perfume or medicinal industry or as synthetic intermediates. Until recently, terpenes such as linalool were used as substrate to extend the scope of new catalysts (Hoye and Zhao 1999; Vieille-Petit et al. 2010). Other terpenes were used and prepared as reaction intermediates, but with moderate efficiency (Yoshikai et al. 2005). The cross-metathesis of citronellol and citronellal with methyl acrylate and methyl methacrylate, leading to new difunctional terpenoids, was reported (Bilel et al. 2011). For instance, compounds **28** and **29** were obtained in high yields from citronellal **27**. When methyl methacrylate was employed as the cross-partner, the terpenic skeleton was retained (▶Fig. 10.20).

Several ruthenium catalysts were evaluated in the cross-metathesis of terpenes containing two double bonds (Borré et al. 2011). To avoid regioselectivity issues, one double bond was masked or protected as a hydrate, such as in dihydromyrcenol **31**, the protected form of citronellene **30**. Thus, using 1 mol% of catalyst **33** in ethyl acetate, the desired product was isolated in 71% yield (▶Fig. 10.21).

As previously mentioned, linalool **34** has sometimes been used as a reagent for the evaluation of the catalytic activity of new catalysts. More recently, linalool was shown to be a potential starting material for the production of jet fuels. Indeed, the linalool RCM product **35** is a precursor of methyl cyclopentadiene **36** that can be further converted into the jet fuel RJ-4. Several catalyst were evaluated to perform the initial RCM of linalool of which **9** showed the best performances (▶Fig. 10.22) (Meylemans et al. 2011).

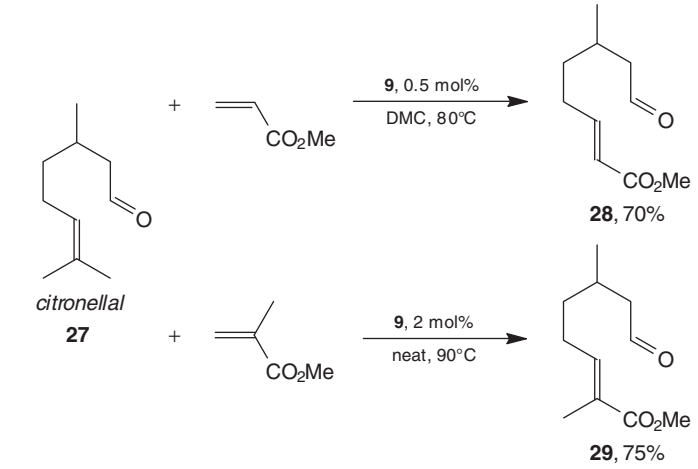


Fig. 10.20: Cross-metathesis of citronellal with methyl acrylate and methyl methacrylate.

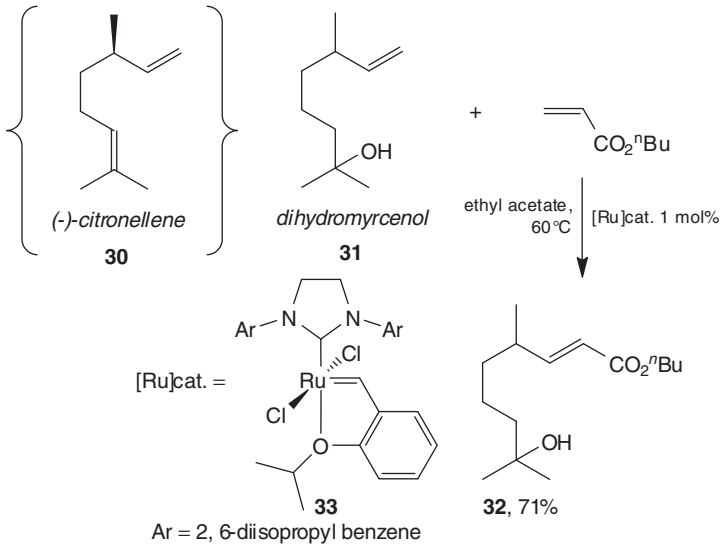


Fig. 10.21: Cross-metathesis of masked terpenes.

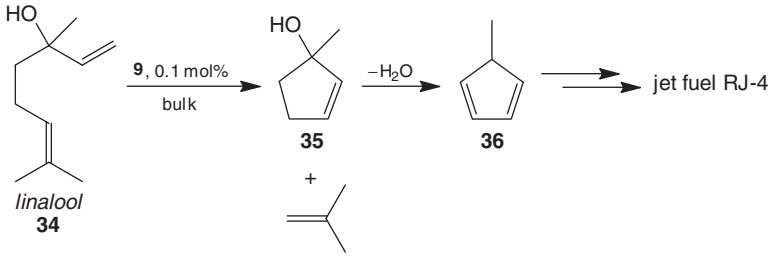


Fig. 10.22: Linalool as a precursor of jet fuel.

10.2.1.4 Metathesis transformations of natural rubber

Very few examples exist for the metathesis transformation of natural rubber (NR). In 2011 β-pinene **37** was evaluated as a chain transfer agent for the metathesis degradation of natural rubber (▶Fig. 10.23) (Gutiérrez and Tlenkopatchev 2011). The molecular weight of the degraded polymer could be tuned by several manifold, such as the reaction time or the amount of β-pinene. During this reaction, degradation of natural rubber by RCM was also observed and several types of polymer chains were detected depending on the chain end, which was either a methylene or a β-pinene group.

The degradation of NR was also investigated by means of ethenolysis; that is, cross-metathesis with ethylene (Wolf and Plenio 2011). For this transformation, several original ruthenium complexes bearing electron-withdrawing NHCs were evaluated. The triterpene Squalene ($C_{30}H_{50}$) was first investigated as model substrate and was fully converted to a mixture of 13 major products (▶Fig. 10.24). The best conditions obtained for squalene were then applied to natural rubber. Although the reaction proceeded fairly well, side reactions such as double bond isomerization occurred to a larger extent than with squalene, and higher amounts of catalyst were needed, likely because of the impurities present in NR. Nevertheless, multigram scale ethenolysis of natural

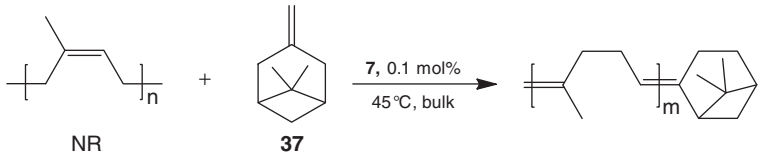


Fig. 10.23: Degradation of natural rubber by cross-metathesis with β-pinene.

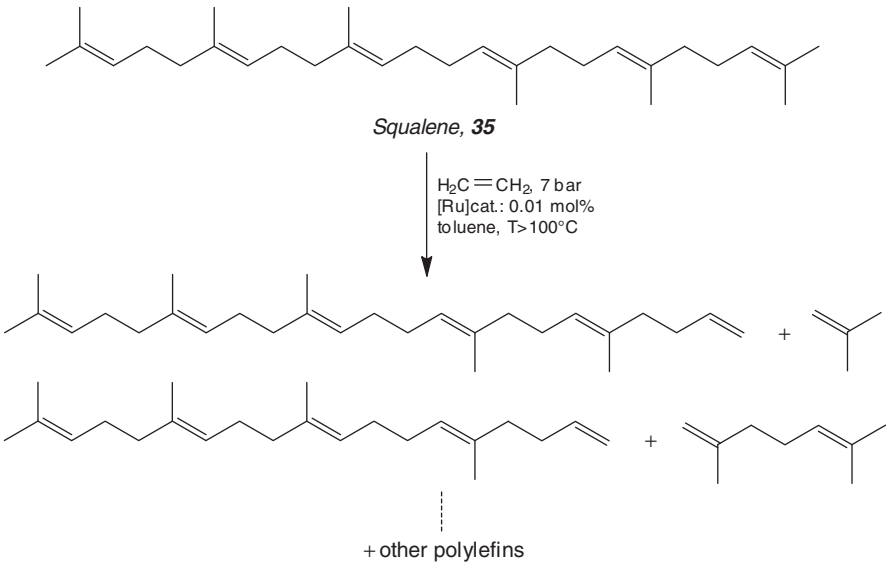


Fig. 10.24: Ethenolysis of squalene.

rubber followed by nanofiltration on membrane and standard column chromatography provided shorter-chain oligomers in high purity (>90%).

10.2.2 Catalytic conversion of glycerol

Although fatty derivatives have attracted considerable attention for the production of valuable chemicals, it should be noted that the economical viability of these processes indirectly relies on the applications found for glycerol. Indeed, glycerol is the main co-product of the vegetable oil industry and its chemical transformation is necessary. One of the biggest markets capable of absorbing a large surplus of glycerol is the market for surfactants, the annual production of which is higher than 10 million tons with a turnover of about $ 19 billion in 2006. Nonionic surfactants, mostly based on ethylene oxide chemistry, represent more than half of the market and ethoxylated lauryl alcohol products alone accounted for $ 2.3 billion each in 2008. As a consequence, production of nonionic surfactants based on glycerol has emerged as a very important issue. To be competitive, such a catalytic transformation should yield amphiphilic glycerol derivatives with similar cost than ethylene oxide–based products (< $5/Kg).

10.2.2.1 Catalytic telomerization of glycerol

To date, esterification and transesterification of glycerol with fatty derivatives have been investigated and these processes yield the so-called amphiphilic monoglycerides. This reaction has already been covered by recent reviews and will not be discussed here (Jérôme, Pouilloux, and Barrault 2008). Although monoglycerides have found many applications, their long-term instability in the presence of water is a serious drawback. For this reason, other strategies have been recently proposed. In this context, telomerization of glycerol with diene have received considerable attention in recent years. This reaction, homogeneously catalyzed by palladium complexes, also affords a direct access to amphiphilic glycerylethers that can be potentially used as water-tolerant nonionic surfactants. Up to now, solid catalysts are not competitive in this reaction. Therefore, in this field of chemistry, homogeneous catalysis occupy a place of choice.

In 2003 Behr and Urschey reported the first example of telomerization of pure glycerol with butadiene (Behr and Urschey 2003). In their work, $Pd(OAc)_2$ (0.06mol%) and a TPPTS ligand (3,3′,3″-Phophinidynetris(benzenesulfonic acid)trisodium salt) (/TTPTS/Pd molar ratio = 5) have been used as catalysts. In this process, water was used as a solvent that allowed not only a better control of the reaction selectivity but also a possible recycling of the homogeneous catalytic system (▶Fig. 10.25). Indeed, in water, monotelomers are not miscible and were consequently continuously separated from the aqueous catalytic phase by simple phase decantation. In such a configuration, the corresponding monotelomers were produced with 58% yield while the yield of ditelomers remained lower than 1%. Although monotelomers were selectively separated from the aqueous catalytic phase, a significant drop of activity was observed when the aqueous catalytic phase was recycled. This phenomenon was ascribed (1) to the oxidation of the TPPTS ligand and the formation of palladium black and (2) to the leaching of palladium in the monotelomer phase (73ppm).

With the aim of stabilizing the palladium-based catalyst in water, Behr et al. have shown that the addition of methylated cyclodextrin (Me-β-CD) in the water phase or

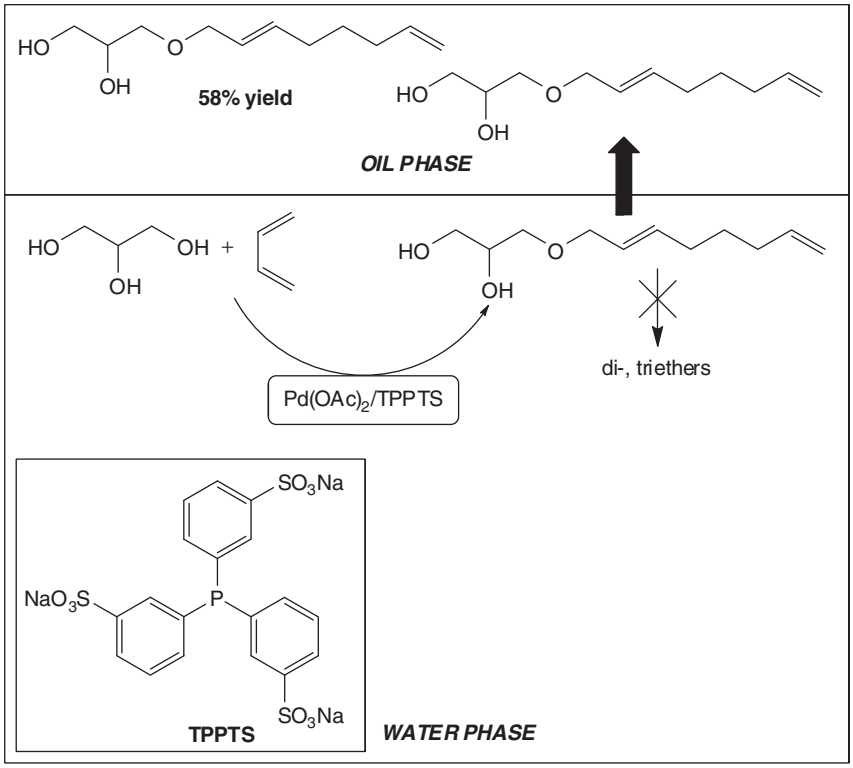


Fig. 10.25: Homogeneously catalyzed telomerization of glycerol with butadiene.

the addition of 2-methyl-2-butanol as an organic solvent allowed for decreasing the leaching of palladium from 73 ppm to 46 and 8 ppm, respectively, while keeping similar catalytic activity (TOF 250h^{-1}) (Behr et al. 2009). Additionally, authors found that the addition of P-octa-2,7-dienyl-P,P,P-[tri(3-sulfonatophenyl)-phosphonium hydrogencarbonate] significantly contributed to stabilizing the palladium-based catalyst in water, which has been successfully used for 230 hours without appreciable loss of activity.

Later, Weckhuysen and co-workers showed that the palladium activity can be dramatically enhanced using tris-(o-methoxyphenyl)phosphine (TOMPP) as a ligand instead of TPPTS (Palkovits et al. 2008a, 2008b, 2009). Thanks to the increase of the palladium electron density caused by the presence of donor methoxy groups on the phosphine ligand, authors have shown that Pd/TOMPP exhibited a TOF of 3,418h^{-1}. Although Pd/TOMPP was found nearly 13 times more active than Pd/TPPTS, the selectivity of the reaction to monotelomers is unfortunately lower (40% yield vs. 58% yield for Pd/TPPTS) due to the higher dissolution of the Pd/TOMPP catalyst in the monotelomer phase leading to the subsequent telomerization of monotelomers to di- and triethers. After further optimization, authors found that a minimum TOMPP/Pd molar ratio of 2 and a butadiene/glycerol molar ratio of 4 have to be used. In such conditions, glycerol ethers were produced with 92% yield along with a selectivity of 40% to monotelomers.

Importantly, one should mention that such a catalytic system is applicable for the direct telomerization of glycerin instead of refined glycerol, thus bypassing the costly and energy-consuming processes required for the industrial purification of glycerol. Remarkably, when glycerine (mixture of glycerol, water, and salt) was directly used as a starting raw material, 73% yield of glycerol ethers, along with a selectivity of 20% to monotelomers, has been obtained.

In 2009 Rothenberg and co-workers investigated the telomerization of glycerol with isopropene, a more attractive diene than butadiene (Gordillo et al. 2009). In this reaction, authors investigated the catalytic activity of a palladium-carbene (0.05mol%), using a mixture polyethylene glycol (PEG-200) and dioxane as solvent (▶Fig. 10.26). Such a mixture has been selected to favor a better contact between glycerol and isopropene phases. Note that the carbene ligand has been generated in situ by a reaction of 0.075 mol% of 1,3-dimesitylimidazolim mesylate with 10 mol% of NaO^{t}Bu. Best results have been collected at 90°C under 20 bar of He and using an isoprene/glycerol molar of 5, a PEG-200/dioxane molar ratio of 1, and a PEG-200/glycerol molar ratio of 2.5. Under such conditions, monotelomers were obtained with 70% yield and the tail-to-head isomer was preferentially produced with 70% selectivity. It should be noted that utilization of PEG-200 as a solvent makes the purification and isolation of glycerol ethers very complex due to the side telomerization of PEG-200.

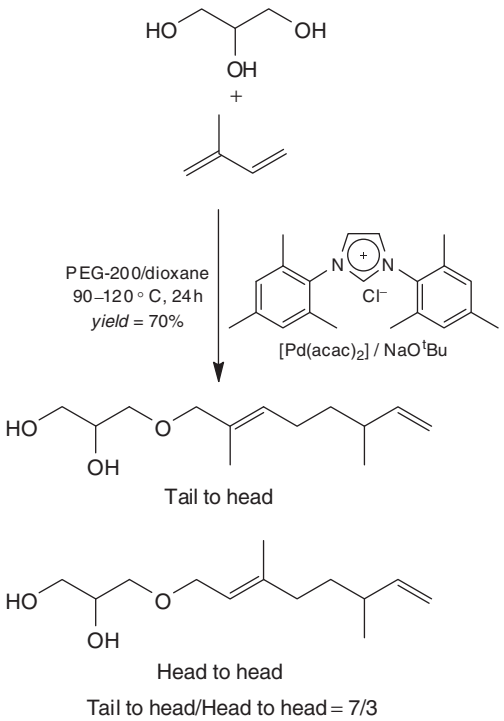


Fig. 10.26: Catalytic telomerization of glycerol with isoprene.

10.2.2.2 Metal-free etherification of glycerol with fatty alcohols

The ability of homogenous catalysis to promote the synthesis of glycerol-based surfactant has been recently taken into account for the etherification of glycerol with fatty alcohols. Glycerol ethers have been successfully obtained by catalytic etherification of glycerol with alcohols such as ethanol (Pariente, Tanchoux, and Fajula 2009), tertiobutanol (Klepacova, Mravec, and Bajus 2005, 2006), or even benzyl alcohol (Gu et al. 2008; Luque et al. 2008) over solid acid catalysts such as zeolite, cation exchange resin, or silica-supported sulfonic sites. However, all attempts to heterogeneously catalyze the etherification of glycerol with fatty alcohols failed. The main reason stems from the low solubility of fatty alcohols in the glycerol phase, inducing important mass transfer problems and dramatically limiting the reactivity of glycerol with fatty alcohols. In this context, Jérôme and co-workers have shown that etherification of glycerol with alkyl alcohols can be successfully performed over a cation exchange resin with a chain length composed of less than six atoms of carbon (Gaudin et al. 2011a). With more hydrophobic alkyl alcohols (1-octanol and 1-dodecanol), this heterogeneously catalyzed reaction is inefficient because of the poor contact between the glycerol and the fatty alcohol phase.

In order to promote the etherification of glycerol with fatty alcohols, Jérôme and co-workers have reported that homogeneous dodecylbenzene sulfonic acid (DBSA), a so-called surfactant-combined catalyst, allowed the formation of an emulsion between the glycerol and fatty alcohol phases, resulting in the formation of the targeted monooctyl- and monododecylglyceryl ethers with 24% and 30% yield, respectively (130°C, glycerol/fatty alcohol molar ratio = 4, 20 mol% of DBSA, 24h) (▶Fig. 10.27). Although yields of the targeted amphiphilic glyceryl ethers are not excellent, this work offers the first route for the synthesis of biobased surfactant from glycerol and fatty alcohols and demonstrate the feasibility of this reaction using homogeneous catalysis.

In the same year, Jérôme and co-workers reported that the direct etherification of glycerol with 1-dodecanol can be also conveniently catalyzed by 1-bromododecane (10 mol%) (Gaudin al. 2011b). In this process, the key step is the catalyst-free coupling of glycerol with a catalytic amount of 1-bromododecane (the so-called Williamson reaction), leading to the formation of the targeted monododecyl glyceryl ethers and the liberation of HBr. Then, 1-dodecanol was in situ brominated by the released HBr regenerating 1-bromododecane (▶Fig. 10.28). Using this homogeneously based strategy, nearly complete conversion of 1-dodecanol was observed and monododecyl glyceryl ethers were obtained with 60% yield. Note that in such a catalytic process, the assistance of cetyltrimethylammonium bromide was needed in order to ensure a better contact between the polar glycerol phase and the hydrophobic 1-dodecanol phase.

10.3 Conclusion

The structural complexity of biomass makes its catalytic conversion rather difficult. One of the main obstacles stems from the crystallinity and low solubility of biomass in common solvents, including water. In this context, homogeneous catalysis offer efficient tools especially for the fractionation of biomass. In particular, homogeneous catalysts are capable of diffusing within the complex structural backbone of biomass, thus allowing

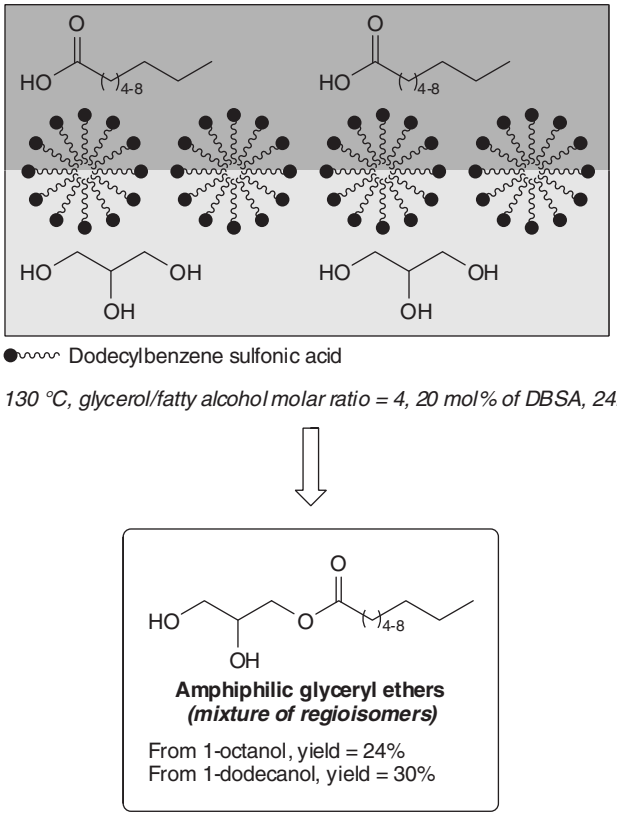


Fig. 10.27: Assistance of dodecylbenzene sulfonic acid as a homogeneous surfactant-combined catalyst for the etherification of glycerol with fatty alcohols.

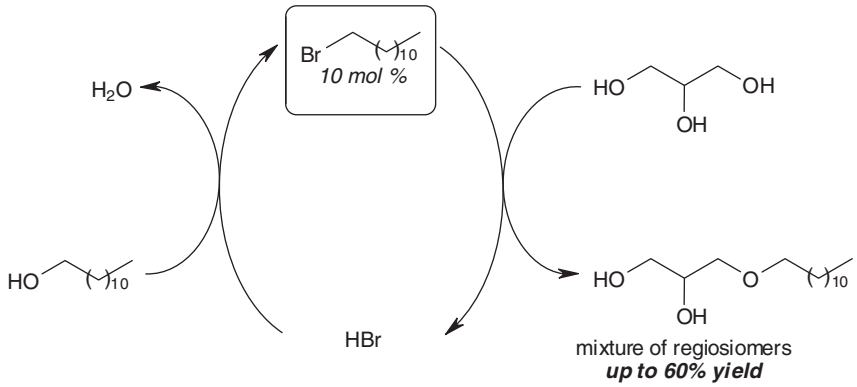


Fig. 10.28: Etherification of glycerol with 1-dodecanol catalyzed by 1-bromododecane.

the release of lignin and carbohydrates from which valuable chemicals and transportation fuels can be more easily produced. In our view, one of the greatest recent advances consists of the smart combination of homogeneous and heterogeneous catalysts, which offers very efficient means for the design of integrated processes where lignocellulosic biomass is fractioned and converted to higher value-added chemicals in a single process. Although homogeneous catalysis allowed accessing a wide range of chemicals or fuels from biomass, it should be noted that the industrial viability of these homogeneously based processes closely relies on the recovery and recycling of homogeneous catalysts. In this context, homogeneous catalysis in a biphasic system clearly appears as a promising approach, the homogeneous catalyst being retained in a liquid phase while products are extracted (sometimes continuously) with a co-solvent from the catalytic phase.

When homogeneous catalysts cannot be recycled, a very low amount of catalysts are generally employed (few ppm or ppb) since, according to the targeted markets, it is not always economically viable to separate homogeneous catalysts from the reaction products. This is typically the case in the synthesis of polymers through a metathesis reaction. Although metathesis reactions allow converting fatty derivatives to a broad range of chemicals, the instability of metathesis catalysts is problematic. For this reason, scientists are now designing more and more active catalysts, which allow for significantly decreasing the loading of catalysts, offering now competitive processes for the conversion of fats and oils.

Clearly, homogeneous catalysis occupy a place of choice for the conversion of biomass. However, it is also the opinion of the authors that the eco-efficient conversion of biomass to higher value-added chemicals will require a smart combination of homogeneous, heterogeneous, and biocatalysis.

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11 Catalytic conversion of oils extracted from seeds: from polyunsaturated long chains to functional molecules

Eva Garrier and Dirk Packet

11.1 Introduction

In this chapter we present the main chemical transformations of terrestrial plant-based oils. Crude vegetal oils extracted from seeds are mainly composed (>98%) of triglycerides. Triglycerides (Karleskind 1992) are formed by the combination of a glycerol molecule with three fatty acids. Each fatty acid is linked to glycerol by an ester bond (▶Fig. 11.1).

Fatty acids differ from one another in terms of chain length and degree of unsaturation.

The distribution of fatty acids depends on the plant. Some contain more saturated fatty chains (e.g. palm oil), some contain more monounsaturated fatty chains (e.g. rapeseed oil), some others have a high content of polyunsaturated fatty chains (e.g. sunflower oil or linseed oil).

The length of the chain may vary from 6 to 24 carbons, most are typically 12–18 C-chains. The number of double bonds varies, usually from 0 to 3. Therefore, triglycerides are molecules having two functional groups, a carboxyl group and double bonds, allowing several transformations to lead to other molecules with different functionalities and/or structures (Gallezot 2007; Behr and Pérez Gomes 2010).

Although triglycerides can be used themselves as starting materials, in general the first step consists of splitting the molecule to release the fatty chains from the glycerol by a transesterification or a hydrolysis reaction.

11.2 Reactions occurring on the carboxyl group of fatty acids/esters

11.2.1 Hydrolysis

A hydrolysis reaction transforms an ester into an acid. Thus, hydrolysis of triglycerides leads to free fatty acids and glycerol (▶Fig. 11.2).

The first examples of chemical hydrolysis were described at the end of the 18th century with the introduction of autoclaves, which allowed reactions under high temperatures and pressures – zinc oxide was used as a catalyst. Chemical hydrolysis is a reversible reaction conducted at elevated temperatures.

Actual industrial processes do not use catalysts. They are performed at high temperatures (230–250°C) and under elevated pressures (30–50 bars), with a yield greater than 98%.

The physical properties of fatty acids depend on the length and the degree of unsaturation of the fatty chain (▶Tab. 11.1).

As the molecular weight of unsaturated fatty acids increases, the melting point increases.

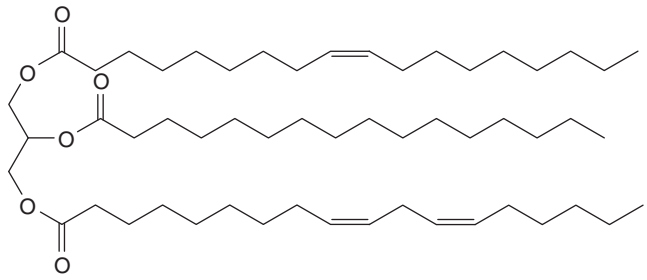


Fig. 11.1: Example of the molecular structure of a triglyceride.

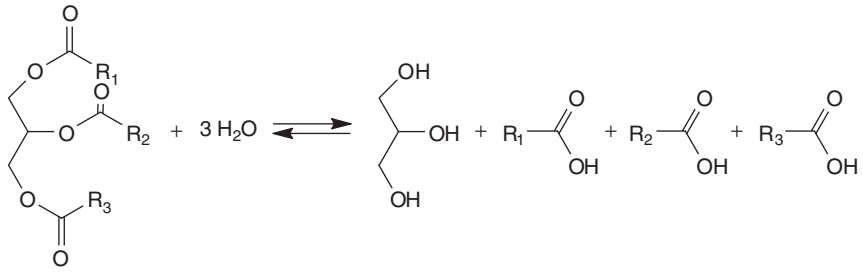


Fig. 11.2: Hydrolysis of a triglyceride.

Tab. 11.1: Physical properties of some major fatty acids.

Fatty acids		Melting point (°C)	Boiling point (°C)
Caprylic acid	C8	17	240
Capric acid	C10	32	270
Lauric acid	C12	44	299
Myristic acid	C14	54	326
Palmitic acid	C16	63	352
Stearic acid	C18	70	383
Arachic acid	C20	75	328
Behenic acid	C22	80	306
Oleic acid	C18:1	16	360
Linoleic acid	C18:2	–5	365
Erucic acid	C22:1	34	381

The unsaturated fatty acids have lower melting points than the saturated fatty acids, due to molecular geometries. The higher the number of double bonds, the lower the melting point.

The fatty acids are platform molecules that can be further transformed via their carboxyl group and/or their double bond(s).

The carboxylic group allows various transformations, like esterification, amidation, and so on, described further on in sections 11.2.3–11.2.6.

11.2.2 Transesterification

The transesterification reaction transforms an ester into another ester. This reaction is especially useful for splitting triglycerides into fatty esters and glycerol.

It is possible to run the reaction without a catalyst, but it requires high temperatures and pressures. Thus, catalytic methods conducted at milder conditions are preferred.

Either acid (sulphuric acid, chlorydric acid, phosphoric acid) or base (alkaline alkoxides, carbonates) homogeneous catalysts can be used. Several heterogeneous catalysts are under investigation. They are more tolerant to high free fatty acids and water contents, but the conversion rates are still moderate compared to the highly active basic homogeneous catalysts (Endalew, Kiros, and Zanzi 2011).

The first transesterification was described in 1942: methanol was added to triglycerides at 80°C in the presence of a sodium methoxide solution (0.1%–0.5%) as catalyst (Karleskind 1992).

This base-catalyzed transesterification is still used today to industrially produce fatty methyl esters. Metal alkoxides are the most effective catalysts due to their high alkalinity.

Each step of the base-catalyzed transesterification mechanism is reversible. The methoxide ion attacks the ester to form an anionic intermediate, which leads to the new ester after the departure of the other alcoholate anion (▶Fig. 11.3).

A large excess of alcohol is necessary to displace to the right the equilibrium of the reaction and to finally produce the desired esters. Using CH_3ONa, high yields are reached (>98%) in a short time (30 min) (Endalew, Kiros, and Zanzi 2011).

This reaction is a major industrial production, which leads to fatty acid methyl esters.

An advantage of this process is that it requires milder reaction conditions than hydrolysis: 70°C at atmospheric pressure for one hour.

Industrially, the methyl ester is produced through a batch process with 22–23 batches per day.

The most important application of fatty methyl esters is biodiesel. Diester Industrie produces its biodiesel with fatty acid methyl esters obtained from rapeseed and sunflower. Diester Industrie has an installed production capacity of three million metric tons of biodiesel in Europe.

Methylesters are also used as solvents or carrier fluids, or they can be converted into other oleochemical derivatives, such as, for instance, fatty alcohols.

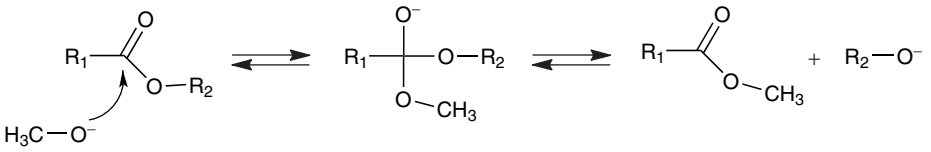


Fig. 11.3: Base-catalyzed transesterification.

However, in the oleochemical industry purified and/or fractionated fatty acids are the preferred starting material for making derivatives such as alcohols, esters, and amines, because most of these derivatives require a specific fatty chain composition, which is different from the fatty chain composition in the vegetable oil.

Another widely used transesterification process is the glycerolysis of triglycerides for the production of mono- and diglycerides, mainly used as food emulsifiers. In this process triglycerides react with an excess glycerol to yield a mixture of approximately 50% monoglycerides, 40% diglycerides, and 10% triglycerides. The monoglycerides may be further concentrated to 90% or more quality by molecular distillation.

11.2.3 Esterification

Fatty esters can also be produced starting from carboxylic acids. The latter are esterified by an alcohol in the presence of an acidic catalyst (strong mineral acids, organic acids, or metal chlorides) (▶Fig. 11.4).

In the presence of an acid catalyst, the fatty acid takes a proton (a hydrogen ion) from the acid catalyst. The positive charge is delocalized over the whole carboxy function, with a fair amount of positiveness on the carbon atom. The positive charge on the carbon atom is attacked by one of the lone pairs on the oxygen of the alcohol. Loss of water from the oxonium ion and subsequent deprotonation produces the ester (▶Fig. 11.5).

The yield of the reaction depends on the nature of the alcohol used. For an equimolar mixture of fatty acid and alcohol, at equilibrium the yield will reach a maximum of:

- 67% in the case of a primary alcohol
- 60% in the case of a secondary alcohol
- 5% if a tertiary alcohol is used

The reaction is reversible. To displace the equilibrium point of the reaction toward the formation of the ester and increase, thus, the yield of the reaction, three methods can be used.

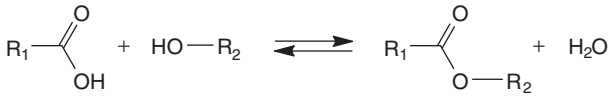


Fig. 11.4: Esterification reaction.

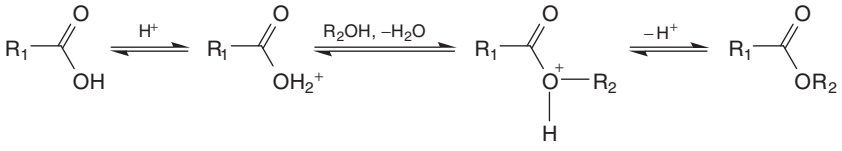


Fig. 11.5: Acid-catalyzed esterification of fatty acids.

- use a large excess of the alcohol, preferably an alcohol that can be easily eliminated from the reaction medium by selective evaporation
- eliminate water continuously, using a volatile solvent that forms an azeotrope with water to avoid hydrolysis of the ester
- distillate the ester as the reaction proceeds

Catalysts typically used are methane sulfonic acid (MSA) or some titanates such as butyl titanate or isopropyl titanate. Tin salts are particularly efficient at 170°C. Yields are up to 97%.

Metal oxides as heterogeneous catalysts have also been described for esterification of fatty acids with 89% yield (Mello et al. 2011).

Fatty esters find applications in many sectors such as in food, metalworking fluids, and cosmetics, depending on the alcohol used. With simple alcohol such as methyl, isopropyl, and so on, fatty esters obtained are used as emollients in cosmetics, solvents, and as metalworking fluids.

Such esters are completely oil soluble and have very good properties, such as emollient, which represents one of the largest markets for the esters. With polyfunctional alcohols such as sorbitol and ethylene glycol, fatty esters are used in foods, paper, personal care, as surfactants, and as functional fluids like lubricants.

11.2.4 Amidation

Amides (Kirk-Othmer 2004) are commonly formed from the reaction of a carboxylic acid with an amine (▶Fig. 11.6). The amides obtained can be either primary amide ($R_2 = H$) or secondary amide ($R_2 \neq H$).

This reaction can be accomplished without a catalyst at elevated temperatures and at very high pressures or with a catalyst at a reduced pressure.

The catalyst activates the carboxylic acid, then the ion pair on the nitrogen of the amine attacks the carboxy carbon, which leads, after dehydration, to the amide.

Short reaction time is preferred in order to achieve a higher yield of amide. Long reaction time promotes dehydration of the amide to nitrile.

Usual catalysts for this reaction include boric acid, alumina, titanium, zinc alkoxides, and various metallic oxides.

Processes requiring a short reaction time at atmospheric pressure have been developed. The catalysts used in such processes are preferably compounds of titanium, zirconium, or tantalum.

For example, it is possible to form a primary fatty amide from oleic acid and gaseous ammonia liberated by urea in the presence of a Lewis catalyst (1 wt %) (Hoong 2006). The reaction is heated up to 190°C for 30 minutes and, in such conditions, the conversion percentage of oleic acid into the reaction product based on acid value is

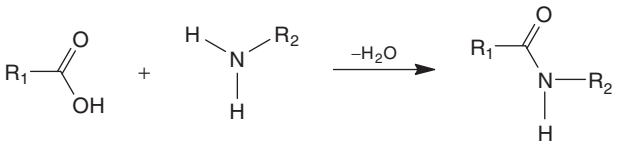


Fig. 11.6: Amidation reaction.

about 95%, using tetra-n-butyl titanate as a catalyst, and 94%, using butyl tin chloride dihydroxy as the Lewis acid catalyst.

Production of mono- and diethanolamides can proceed at 130°C using NaOH/KOH.

Fatty amides have a strong hydrogen bonding, high melting points, and low solubilities in most solvents.

Alkanolamides have many applications depending on their functional properties:

- Foam boosting for detergents and hand cleaning gels. Ether sulfates are the anionic surfactants of choice for formulations of detergents. The interaction between these surfactants and the alkanolamides is the key to the enhancement of formulation properties.
- Emulsification of oils, waxes, solvents for metalworking fluids, lubricants, and plant protection formulations
- Antistatic properties, viscosity modification, and so on

11.2.5 Reduction of the carboxyl function

Fatty acids or fatty methyl esters can be reduced to fatty alcohols by high-pressure hydrogenation (▶Fig. 11.7).

A metal catalyst is necessary to achieve the hydrogenation of carboxylic compounds into their corresponding fatty alcohols.

The hydrogenation is a reversible reaction, and the product's concentration at the equilibrium depends on the hydrogen pressure – at low pressures the alcohols can be converted to their corresponding esters.

High-pressure hydrogenation is carried out at 180–300°C and 200–300 bar using catalysts based on copper, chromium, or copper/zinc-mixed oxides (Suyenty et al. 2007).

Such drastic conditions are required because of the poor solubility of hydrogen and the high mass-transfer resistance in the methyl ester, which leads to a shortage of hydrogen at the catalyst surface.

In the case of unsaturated fatty acids or esters, the selective high-pressure hydrogenation of the carbonyl group in the presence of a double bond in the molecule is particularly difficult to achieve. It is thermodynamically unfavored and, so, it is only possible with a very selective catalyst.

For example,

- CuCr gives the best performance for saturated fatty alcohol
- zinc chromite is preferred for unsaturated starting material due to its high selectivity toward reduction without attacking double bonds

The use of methyl esters is preferred because the catalysts are not always sufficiently resistant to fatty acids.

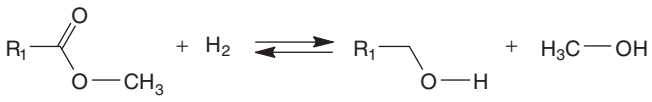


Fig. 11.7: Hydrogenation of fatty acid/ester to fatty alcohol.

Low-pressure vapor-phase hydrogenation, known as Davy Process Technology, offers an alternative route. In this process, oils are first esterified with methanol to give their equivalent methyl esters, which are then converted to fatty alcohols by hydrogenation using a copper-zinc catalyst at 210–235°C and 40 bar.

Oleon developed its own low-pressure technology in the 1980s, using a copper chromium catalyst.

Saturated fatty alcohols, basically C12–C14 fatty alcohols, produced from coconut oil and palm kernel oil, give access to detergents such as fatty alcohol ethoxylates (nonionic detergents), fatty alcohol sulphates, and ether sulphates (anionic detergents). They find applications such as washing and cleaning agents.

Unsaturated fatty alcohols are used in detergents, in cosmetic ointments and creams, as plasticizers, and as defoamers. Oleyl alcohol is also used as an additive in lubricating oils.

11.2.6 Polycondensation

A very interesting polycondensation reaction is the polycondensation between a polyalcohol, a polyacid, and a fatty acid or a triglyceride. This kind of polycondensation leads to the formation of alkyd resins (Meier, Metzger, and Schubert 2007).

A alkyd is a tridimensional macromolecule structure (▶Fig. 11.8).

The first step of this polycondensation is an esterification reaction between the polyalcohol, as glycerol (3 alcoholic functions) or pentaerythritol (4 alcoholic functions), and the polyacid, usually phtalic anhydride or maleic anhydride, to form a polyester. The latter is then modified with unsaturated fatty acids to obtain a polyester with better properties for the final application.

Because raw materials are not miscible, several processes can be used; for example,

- Standard process: The components are heated up to 245°C.
- Monoglyceride process: In a first step, triglycerides are converted to monoglycerides (via a transesterification reaction), which can then solubilize the polyol and the

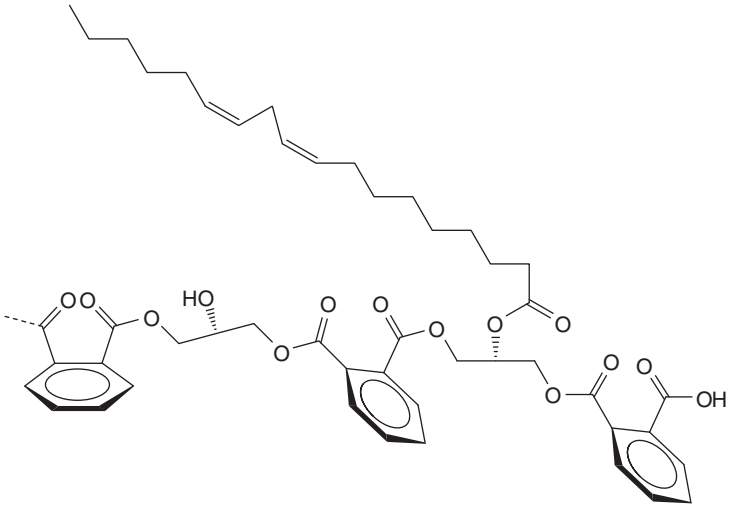


Fig. 11.8: Example of alkyd resin obtained from glycerol, phtalic anhydride, and linoleic acid.

polyacid and the polycondensation can occur. This reaction is alkali (LiOH [lithine]) catalyzed.

- By azeotropic distillation: The water formed during the reaction is eliminated to displace the reaction equilibrium in favor of ester formation. Xylene is commonly used in the industry to form an azeotrope with water at 200°C.

The inconvenience of this process is the requirement of a solvent.

The choice of triglycerides, fatty acids, or polyols depends on the final application of the polymers. These macromolecules are major components in the formulation of bitumen, inks, varnish, and paints.

For example, for application in paints, the addition of polyunsaturated triglycerides/fatty acids will promote drying of the film formed, thanks to their siccativity properties and ability to dry in the air. The higher the number of unsaturations, the more siccatives there are. For example,

- siccative oil: linseed oil
- semi-siccative oils: soja, sunflower, safflower, dehydrated castor oils
- non-siccative oils: castor, palm oils

In accordance with the percentage of oil/fatty acids in the polymer, different applications are possible: with a high content of oil, paints and varnishes will be used in the building trade sector, while with a low content of oil, industrial paints will be produced.

The characteristics of the final resins depend on the choice of polyol used as well. For example, pentaerythritol-based resins are used in the formulation of hard resins with fast drying capability.

The viscosity increases with the degree of advancement of the polycondensation reaction.

11.3 Reactions occurring on the double bond(s) (unsaturation) of fatty acids/esters

11.3.1 Hydrogenation

In a hydrogenation process, hydrogen atoms add across the carbon-carbon double bonds.

A total or partial hydrogenation of either triglycerides (▶Fig. 11.9) or fatty acids is possible.

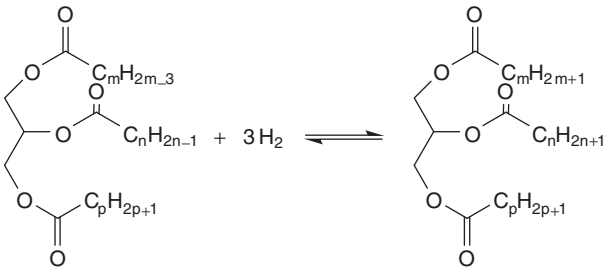


Fig. 11.9: Hydrogenation of fatty chain double bonds.

11.3.1.1 Complete hydrogenation

Hydrogenation of double bonds of fatty chains can be performed starting from triglycerides. A catalyst is necessary to activate the stable dihydrogen molecule. Copper, nickel, and palladium-based catalysts are usually used at a temperature between 140°C and 230°C and a pressure between 10 and 40 bars. These parameters depend on the difficulty to hydrogenate the double bonds.

This is a heterogeneous reaction because three phases coexist: a gas phase with H_2, a liquid phase with the unsaturated fatty compound, and a solid phase with the catalyst.

11.3.1.2 Selective hydrogenation

It is much more difficult to perform a selective hydrogenation, which means hydrogenate only one of two double bonds of linoleic acid, for example.

Catalysts as metal carbonyls; platinum-tin systems; or iron, cobalt, or nickel salts, which need activation by triethylaluminium, can be used for this selective hydrogenation. For selective hydrogenation, a smaller quantity of catalysts and a lower temperature are required.

The formation of trans-fatty acid–like elaidic acid (trans C18:1) is difficult to avoid. Hydrogenation of linoleic acid with palladium-nano catalysts in a solution in propylene carbonate, yield 93% of C18:1, consisting of 55% of oleic acid and 45% of elaidic acid (Behr and Pérez Gomes 2010).

Hydrogenated oils or fatty acids contain less double bonds and are thus more stable toward oxidation. This is an important property for applications in the food sector (e.g. margarine).

Another example is the use of hydrogenated stearic acid for replacing paraffin wax in candle making.

11.3.2 Dimerization

After hydrogenation, dimerization is the most important industrial process occurring on the double bond of fatty chains. Dimerization of unsaturated fatty acids (Gunstone 1999) can proceed in the presence of a radical by thermal activation (T = 260–400°C), or by using a clay catalyst. The latter is used for the actual industrial production of dimer acids. A typical procedure uses montmorillonite clays (2%–10%) at 180–270°C for 4–8 hours. Reaction can occur with monounsaturated and polyunsaturated fatty acids. The resulting product is a mixture of dimers (▶Fig. 11.10) with some trimer acids. Usually, monounsaturated compounds lead to mainly acyclic and monocyclic dimers, while polyunsaturated chains give mono- and bicyclic dimers.

Despite the large industrial production of dimer acids, the exact chemical structure of the mixture obtained is unknown because of some possible hydrogen exchange leading to different derivatives. The dimerized product is fractionated by distillation under high vacuum at high temperature (molecular distillation).

Information on mechanisms are limited to the formation of the dimers. Thermal dimerization is explained both by a Diels-Alder mechanism and by a free-radical route involving hydrogen transfer. Clay-catalyzed dimerization appears to be a carbonium ion reaction based on the observed double-bond isomerization, acid catalysis, chain branching, and hydrogen transfer.

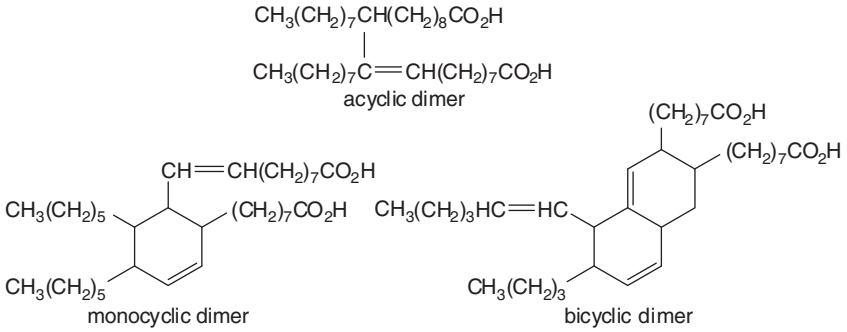


Fig. 11.10: C36 dimer acid possible structures.

For example, the clay-catalyzed intermolecular condensation of oleic and linoleic acid mixtures on a commercial scale produces approximately a 60:40 mixture of dimer acids (C36 and higher polycarboxylic acids) and monomer acids (C18 isomerized fatty acids). These fractions are usually separated by short-path distillation (molecular distillation). Dimer acids can be further separated, also by short-path distillation, into distilled dimer acids (purity >94%) and trimer acids.

Dimer acids are mainly used as polymer (polyamides and polyesters) building blocks. They have special properties, such as elasticity, flexibility, hydrolytic stability, hydrophobicity, and lower glass transition temperatures. Polyamides based on such dimerized fatty acids are used for hot-melt adhesives, in printing inks, and in coatings.

11.3.3 Epoxidation

In the epoxidation reaction, double bonds react with hydrogen peroxide in the presence of a catalyst to lead to the formation of an oxirane via a cis stereospecific addition (▶Fig. 11.11).

The epoxidation of unsaturated fatty acids and triglycerides have been studied testing different types of catalysts (Abdullah and Salimon 2010).

- acids catalysts: the combination of hydrogen peroxide (oxygen donor) with an organic acid, such as acetic acid (active oxygen carrier), in the presence of a catalytic amount of an inorganic acid, which allows the generation in situ of a peracid.

Sulfuric acid, H_2SO_4, was found to be the most efficient inorganic acid.

Maximum conversion of unsaturated fatty acids into fatty epoxides, difficult to obtain by other methods, is obtained using in situ–generated peracetic acid from hydrogen peroxide and acetic acid in the presence of sulphuric acid.

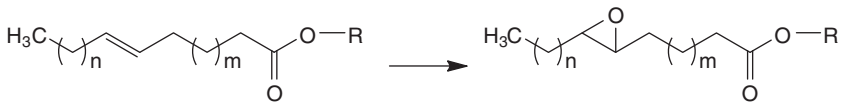


Fig. 11.11: Epoxidation reaction.

Peracetic acid is generated in situ from hydrogen peroxide and acetic acid (▶Fig. 11.12).

m-Chloroperbenzoic and performic acid are more reactive than peracetic, but the corresponding carboxylic acid formed at the end of the reaction is stronger than the hydrogen-bonded peracids and may lead to the ring opening of the oxirane.

For example, up to 78% of double bonds of cottonseed oil can be epoxidized using hydrogen peroxide, glacial acetic acid, and a catalytic amount of H_2SO_4 at a temperature of 60°C.

The epoxidation of mixtures of fatty methyl esters obtained from high oleic sunflower oil, over Ti-MCM-41 (an ordered mesoporous titanium-grafted silica) using *tert*-butylhydroperoxide as oxidant, gives a very high conversion (98%) and selectivity to mono-epoxy compounds (85%).

- Transition metal complexes:
  - Molybden-based catalysts: $Mo(CO)_6$ or $Mo(O)_2(acac)_2$ can catalyze the epoxidation of oleic acid to lead to 9,10-epoxystearic acid with 87% selectivity.
  - Rhenium-based complexes: the complete epoxidation of methyl linoleate could be achieved within 6 hours reaction using 1 mol% of methyltrioxorhenium in pyridine (Meier, Metzger, and Schubert 2007).

The resulting epoxidized plant oil and fatty acids are valuable materials with large application possibilities. They are also interesting intermediates in the synthesis of further substrates.

Fatty epoxides are used in rubbers, resins, and coatings.

The epoxy function presents the advantage for the double bond to be more easily functionalized and consequently widens the field of the possible chemical modifications.

These epoxides are building blocks that can be further transformed into plasticizers, polyols to form polyesters, and polyurethane.

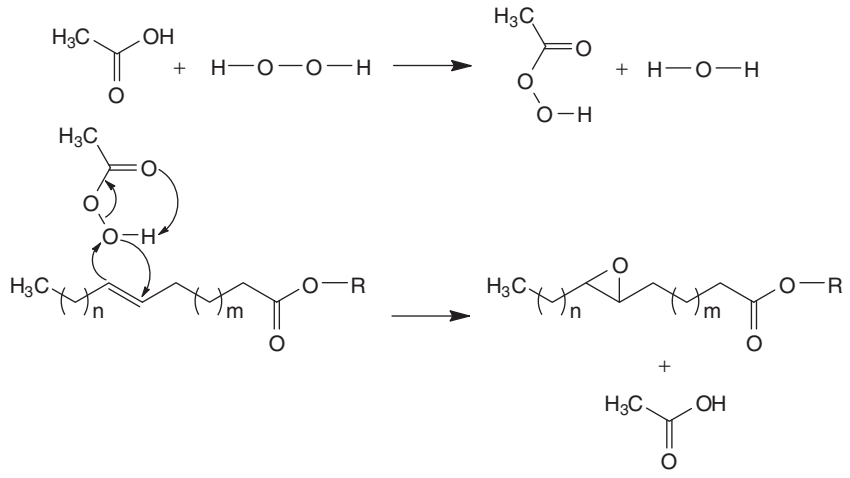


Fig. 11.12: Mechanism of acid-catalyzed epoxidation.

11.3.4 Metathesis

The alkene metathesis reaction is a reversible, transition metal-catalyzed reaction with an exchange of alkylidenic groups ($=CR_2$) between two alkenes. There are mainly two metathesis reaction types generally applied to oleochemicals (Behr and Pérez Gomes 2010):

- the *self-metathesis*: a fatty chain reacts with itself

For example, metathesis of oleic methyl ester leads to an equimolar mixture of 9-octadecene and 9-octadecendioic dimethyl ester (▶Fig. 11.13).

These two products have many different applications, such as polymers, surfactants, and so on.

The triglyceride can be used for this reaction as raw material. Intermolecular self-metathesis leads to "dimeric-triglyceride."

- the *cross-metathesis*: a fatty substrate reacts with another alkene

The most studied one is the ethenolysis, the reaction between a fatty substrate, usually the oleic methyl ester and ethene (▶Fig. 11.14).

The products formed are 1-decene and 9-decenoic methyl ester. The latter is a very interesting molecule because it possesses a terminal double bond, which can be functionalized and gives access to a range of bifunctionalized molecules used in the polymers sector.

It can also undergo a self-metathesis reaction with the formation of an unsaturated diester (▶Fig. 11.15).

Other alkenes are also under investigation to lead to other bifunctionalized compounds with a different number of carbon atoms.

Oleochemical metathesis reactions are catalyzed by homogeneous and heterogeneous catalysts in mild conditions. The principal difficulties are the presence of functional groups on the fatty chain acid (carboxyl function), which deactivate catalytic systems causing a low turnover number (TON) (▶Tab. 11.2). For this reason ruthenium-based complexes are interesting catalysts because they are more tolerant toward the diverse functionalities and present a higher activity in the alkene metathesis.

The molecules formed are new building blocks. For example, the diacids can be used for the preparation of polyesters.

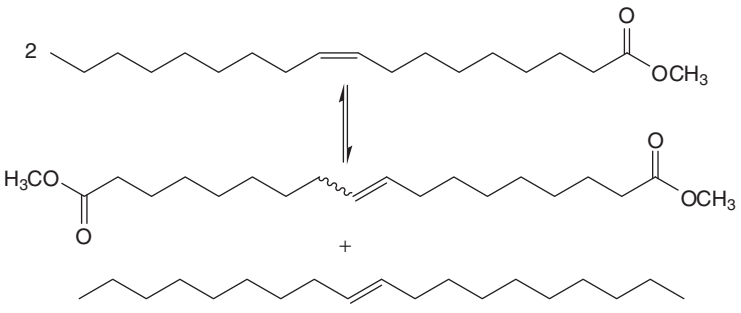


Fig. 11.13: Self-metathesis of oleic methyl ester.

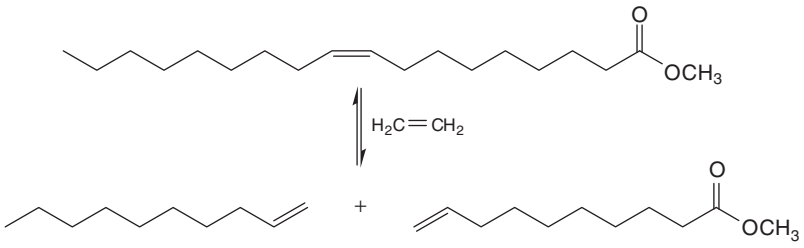


Fig. 11.14: Ethenolysis of oleic methyl ester.

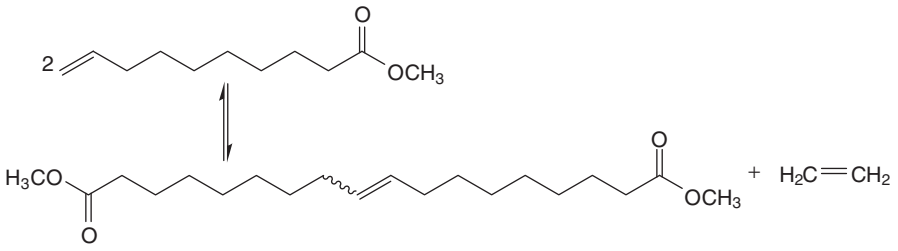
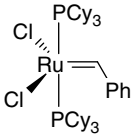
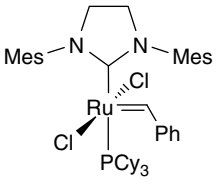


Fig. 11.15: Self-metathesis of 9-decenoic methyl ester.

Tab. 11.2: Example of metathesis catalysts.

Catalysts	Ester/metal atom	T (°C)	t (h)	TON
Homogeneous				
WCl_6 / Me_4Sn	75	110	2	38
$W(OC_6H_3Cl_2\text{-}2,6)_2Cl_4/Bu_4Pb$	50	85	0.5	25
Heterogeneous				
$Re_2O_7/Al_2O_3/Et_4Sn$	60	20	2	3
$Re_2O_7/MoO_3/Al_2O_3/Et_4Sn$	60	20	2	30
$Re_2O_7/B_2O_3/Al_2O_3/Bu_4Sn$	120	20	2	50
$Re_2O_7/SiO_2\text{-}Al_2O_3/Bu_4Sn$	240	40	2	120
$CH_3ReO_3/SiO_2\text{-}Al_2O_3$	100	25	2	27
 Grubbs first generation	5,500	20	48	2,500
 Grubbs second generation	987,000	55	6	440,000

IV

Alpha-olefines can be polymerized and the poly-alpha-olefines obtained are used in the formulations of lubricants.

11.3.5 Isomerization

Fatty chains can contain more than one double bond. Usually two double bonds are separated by a methylene group. Conjugated fatty acids occur as minor component of plant oils.

Isomerization reactions transform a polyunsaturated fatty acid/ester into a conjugated fatty acid/ester.

Actual industrial processes for food-grade conjugated linoleic acid (CLA) uses alcoholate catalysts starting from fatty esters, which are, after the isomerization step, hydrolyzed to yield conjugated fatty acids. Isomerization occurs at 100–130°C with a very good conversion rate (>99%). Direct conjugation for industrial applications is done on sodium soaps of fatty acids, using a molar excess of sodiumhydroxide that also acts as an isomerization catalyst. After conjugation, the soap is split to yield the free conjugated fatty acids.

For example, isomerization of linoleic acid/ester (C18:2 9cis, 12cis) generates a mixture of positional isomers (▶Fig. 11.16), consisting of mainly 9cis, 11trans-form, and 10trans, 12cis form; this latter being the form that is biologically important.

The reaction mechanism is proposed to occur in two steps: first, the alkoxyde takes off an allylic proton (CH11) to yield a carbanion stabilized by resonance. Two forms of stabilization are possible (C9-C11 and C11-C13); each of them leads to the two major isomers after protonation in a second step.

Conjugated linoleic acid (CLA) is known for its biological activity. First isolated as an anti-cancer agent from cooked meat, it is now used for diet food since the discovery of its body-fat-reducing effect.

Industrial-grade conjugated fatty acids have very pronounced siccative properties and they are mainly used in resins for coatings to reduce the drying time.

11.4 Conclusion

More than 150×10^6 tons of vegetable oils are produced each year in the world, and only 15% of them are converted into technical products.

However, oleochemicals are gaining increasing importance as biodegradable substitutes for mineral oils. Due to their surfactant properties, oleochemicals are already

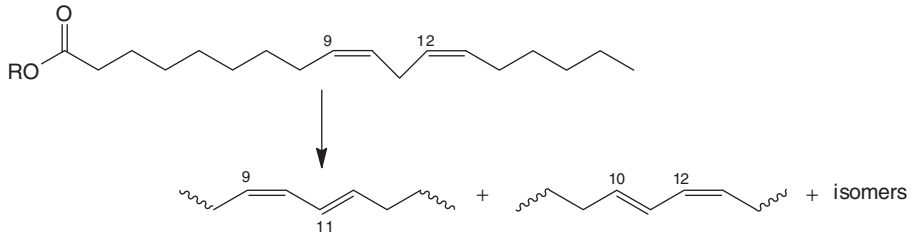


Fig. 11.16: Isomerization of linoleic acid/ester.

well established in detergents, cosmetics, and as food emulsifiers. Other applications are rapidly expanding: biolubricants, materials, plastic additives, coatings, paints, crop protection, and so on.

The challenge to progressively substitute fossil feedstock by materials derived from renewable sources implies not only the development of new original reactions and catalysts but also the adaptation of well-established reactions to the production of new tailor-made compounds capable of producing competitive performance materials.

Actual chemical processes are economically favorable, but enzymatic transformations are getting better and will probably compete with heterogeneous catalysis to develop greener processes.

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12 Heterogeneous catalysis applied to the conversion of biogenic substances, platform molecules, and oils

Angela Dibenedetto, Antonella Colucci, and Carlo Pastore

12.1 Introduction

Heterogeneous catalysis is the strategic approach to the future development of catalytic processes at the industrial scale. It offers several advantages, such as the easy separation of the catalyst (inorganic materials, hybrid materials, supported metallorganic compounds) from the products (lowering, thus, the contamination of the latter), its regeneration and reuse. Issues can be relevant to the contact of solid catalysts with reagents when the latter are not gaseous or liquid: this particular aspect is prominent in the use of heterogeneous catalysts with solid biomass, as, for example, in the conversion of cellulose or hemicellulose or lignin, aspects already discussed in this book. In this chapter, the conversion of products derived from biomass, of platform molecules or oils, will be considered.

Heterogeneous catalysis plays a key role in the conversion of renewable resources into valuable chemicals or fuels, and even into new materials with new properties that are fully biodegradable or compostable, reducing their permanence in the natural environment. The application of catalysis supports the implementation of the basic concept of developing less energy intensive processes with lower carbon consumption (Industrial Technologies Program 2012) along the lines of the sustainable chemical and energy industry.

The approach used so far for biomass treatment and conversion into chemicals or fuels has been based on the "waving of the system entropy," associated with an unavoidable high-energy consumption. In fact, in the business-as-usual technology, any cellulosic biomass undergoes gasification, an endoergonic process, in which the structured matter (C6-unit-based polymers with low entropy content) is converted into destructured-C with high entropy content; that is, syngas or $CO+H_2$. Such a gas mixture is then converted back into low entropy structured-C, such as long hydrocarbons chains or other more complex molecules. At the end of the process, oxygen atoms are lost also if oxygen-free molecules are not the ultimate target for chemicals or fuels. In fact, often species containing only C and H are subjected to oxidation for introducing oxygenated groups. However, both the total elimination of oxygen and the destructuration of natural compounds are not always necessary.

The innovative strategy for biomass exploitation is based on the utilization of biogenic C_n-molecules as "platform molecules" that can be converted into other useful chemicals or fuels by implementing a pathway more conservative in entropy and less energy intensive (Industrial Technologies Program 2012) (▶Fig. 12.1).

This approach will reduce the entropy wave amplitude and will help to develop a more sustainable production of chemicals by lowering the overall energy consumption as well as the waste production.

The use of heterogeneous catalysis in the conversion of cellulosic biomass has already been mentioned in other chapters of this book. In the following sections, a few selected

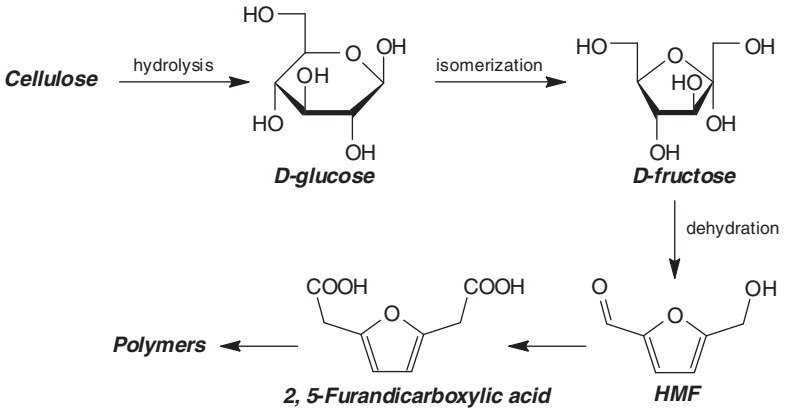


Fig. 12.1: An example of "entropy conservation" biomass in the conversion of a C6 skeleton is maintained in products derived from cellulose that are eventually converted into other polymeric materials.

examples of conversion of natural compounds into molecules that have a specific use will be discussed together with the use of heterogeneous catalysts in the new approach to the water-free simultaneous transesterification of lipids and esterification of free fatty acids (FFAs) contained in bio-oils.

12.2 Use of heterogeneous catalysis in the conversion of biogenic platform molecules

The exploitation of cellulosic and oily biomass has recently progressed quite significantly along the direction of maximizing the entropy conservation in the transformation of the starting biomass. This has identified some platform molecules that can be extracted from the biomass or that are produced in mainstream co-processing of biomass. Such platform molecules are then used as the starting material for the synthesis of several other products that find application as fine chemicals or even as fuels. Examples of such platform molecules are terpenes (obtained directly from plants), sucrose (disaccharide), *d*-glucose (from carbohydrate-containing crops or from depolymerization of cellulose), *d*-fructose (from glucose by isomerization), lactose (from the cheese industry), and glycerol (from transesterification of vegetal glycerides, animal fats, fried oils). C6 and C5 sugars can originate other platform molecules, such as 2,5-hydroxymethylfurfurale (HMF) (from dehydration of *d*-fructose) from which 2,5-furandicarboxylic acid and levulinic acid are originated; furfural (from dehydration of C5 sugars); glycerol; succinic, fumaric, and malic acid (a series of C4 diacids); aspartic acid; itaconic acid; glutamic acid; ethanol (fermentation of glucose); glucaric acid; 2-hydroxypropionic and 3-hydroxypropionic acid; and 1,3-propandiol. All such compounds are mentioned by the U.S. Department of Energy (Werpy and Petersen 2004) as being among the most interesting platform molecules for biosourced chemicals. In the following section a few examples of the catalytic conversion of such molecules will be discussed.

12.2.1 Conversion of terpenes

p-Cymene **1** (▶Fig. 12.2), precursor of p-cresol and other fragrances and flavors, is usually synthesized from aromatic compounds derived from fossil carbon.

Terpenes, such as pinene (α, **2** and β, **3**) and limonene **4**, are quite common natural products characterized by a molecular structure (▶Fig. 12.3) that makes them ideal substrates for the synthesis of p-cymene or its derivatives, such as 8-alkoxy-1-p-menthene **5** (▶Fig. 12.4).

2 and **3** are extracted from turpentine oil, a subproduct of the pulp industry, at a rate of 350 kt/year. **4** has a market of 30 kt/year and is obtained from citrus oil.

The conversion of **2** into **1** was achieved at 573 K in a continuous fixed-bed flow reactor using a 0.5% w/w Pd on SiO_2 (Roberge et al. 2001). Using the same reaction conditions, **4** was converted into **1** in 97% yield: the catalysts was stable for 500 hours (▶Fig. 12.5).

4 was also converted into **5** in the presence of an alcohol at 333 K using a β-type zeolite, characterized by a SiO_2/Al_2O_3=25 ratio, as catalyst. Note that such a conversion is reversible, while the conversion of **2** into **5** (▶Fig. 12.4) is not.

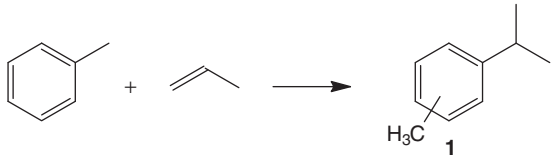


Fig. 12.2: Synthesis of p-cymene from oil feedstock.

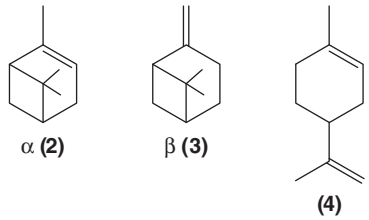


Fig. 12.3: Structure of pinene (**2** and **3**) and limonene (**4**).

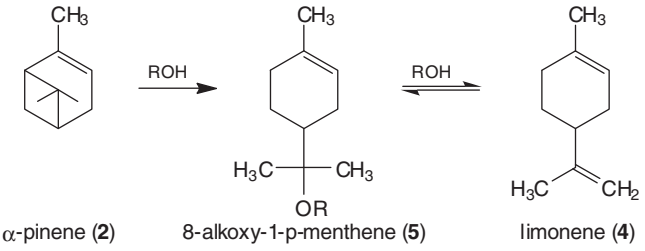


Fig. 12.4: Synthesis of 8-alkoxy-1-p-menthene from limonene or α-pinene.

α-Pinene epoxide **6** can be conveniently converted (100% conversion and >85% selectivity) using USY zeolite (Si/Al=70) at 273 K into campholenic aldehyde **7** (▶Fig. 12.6), which is then used as the starting material for several other fragrances of the sandalwood family.

Besides such use for the production of molecular compounds with high added value, terpenes have also been used as co-monomers in the synthesis of new fully biodegradable and compostable polyesters (Türünc and Meier, 2011).

Sucrose (168 Mt produced in 2011 according to the U.S. Department of Agriculture) and starch (50 Mt/year in 2011, for industrial uses only) are today the major sources of

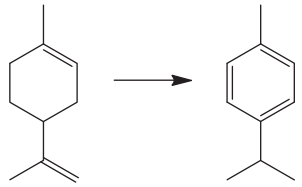


Fig. 12.5: Conversion of α-pinene or limonene into p-cymene.

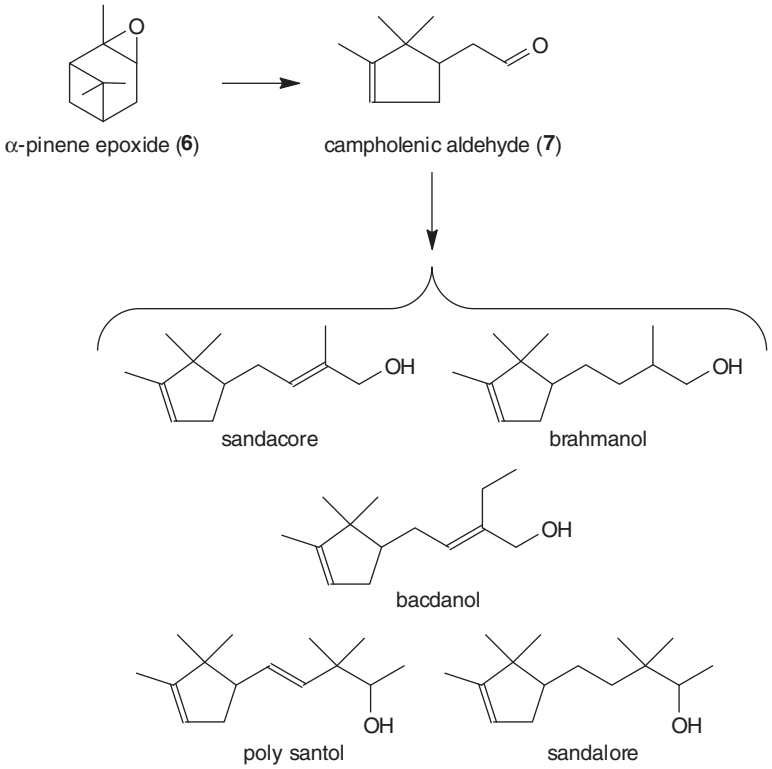


Fig. 12.6: Sandalwood fragrances derived from campholene aldehyde.

C6-polyols; for example, glucose and fructose. In the future, cellulose is expected to become the major source of such platform molecules after enzymatic hydrolysis (see Chapters 7 and 9). C6-moieties are also used to produce C5- and C4-polyols, which are not abundant in nature. So, glucose is oxidatively decarboxylated to afford arabitol, a C5-sugar, used for the production of C4-polyols (▶Fig. 12.7).

The key issue here is avoiding dehydration reactions that would reduce selectivity. The hydrogenation was carried out with high selectivity by using Ru catalysts (Fabre, Gallezot, and Perrard 2002) in the presence of antraquinone-2-sulphonate (A2S), which acted as a surface stabilizer. The catalyst was recycled, maintaining the same activity and selectivity for long time. ▶Fig. 12.8 presents an overview of possible reactions based on heterogeneous catalysis (the relevant catalysts are reported in ▶Tab. 12.1) for the production and conversion of platform molecules derived from cellulose.

In the conversion of cellulose the first step is its depolymerization to afford glucose, which is isomerized into fructose (see Chapter 6). These two operations need an acid and a basic catalyst, respectively. In an attempt to use a single catalyst for the sequential isomerization of glucose-dehydration of fructose, mixed oxides have been prepared that are characterized by tunable acid-base properties, changing the molar ratio of the metals (▶Tab. 12.2) (Pastore, Aresta, and Dibenedetto 2011; Pastore 2011; Aresta, Dibenedetto, and Pastore in press).

Among the many synthesized catalysts, those reported in ▶Tab. 12.2 show comparable activity. Interestingly, the selectivity is 100% in all cases. Both conversion yield and selectivity can be significantly improved, playing with the reaction parameters and shifting from a batch to a flow reactor. Recent papers (Carlini et al. 2004; Benvenuti et al. 2000; Carniti et al. 2006; McNeff et al. 2010) have reported a 26% yield of HMF from fructose, but a direct conversion of glucose into HMF is not a common feature in the literature. Also, the use of water as the only solvent does not seem to favor a high yield of conversion of glucose into HMF: polymeric materials are often formed.

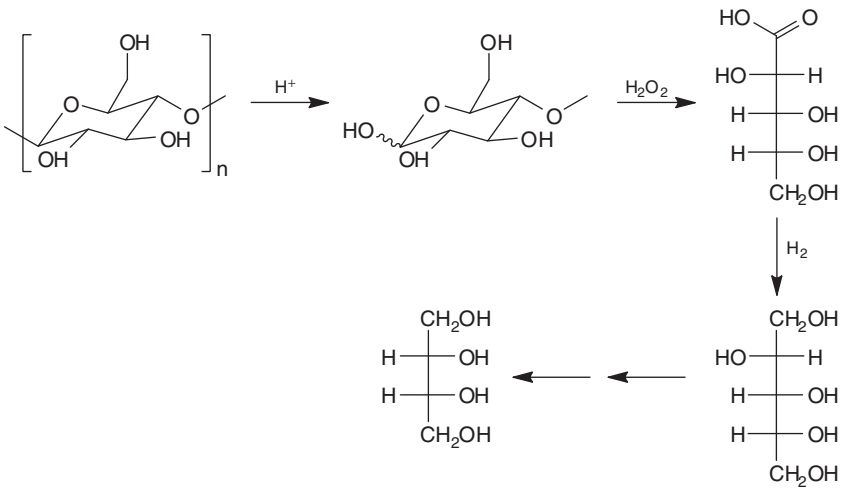
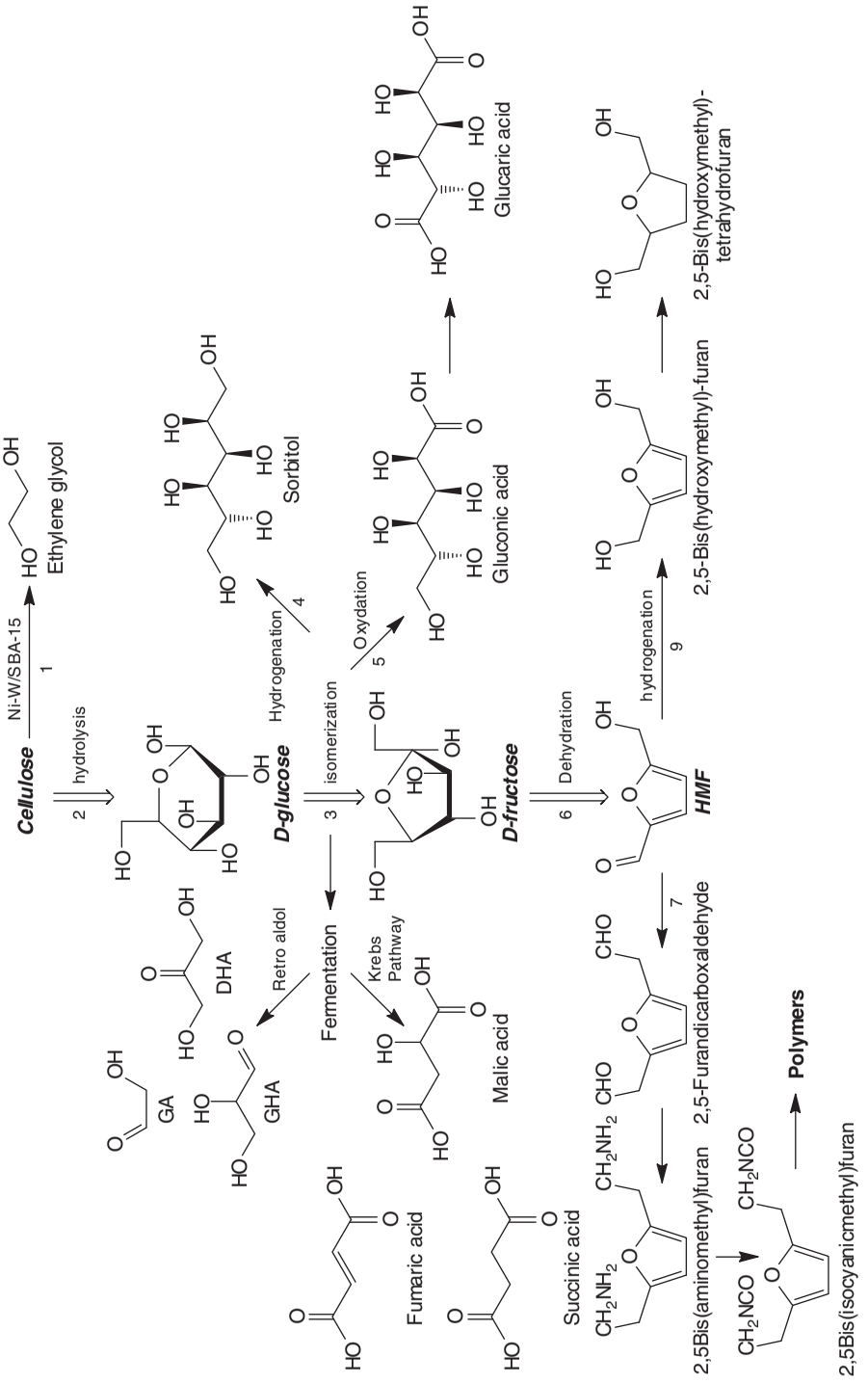


Fig. 12.7: Degradative conversion of C6 into C5 and C4.


Cellulose
Ni-W/SBA-15
1
Ethylene glycol
2
hydrolysis
D-glucose
Hydrogenation
4
Sorbitol
isomerization
3
Oxydation
5
Gluconic acid
Glucaric acid
D-fructose
Fermentation
Retro aldol
DHA
GA
GHA
Krebs Pathway
Malic acid
Fumaric acid
Succinic acid
6
Dehydration
HMF
hydrogenation
9
2,5-Bis(hydroxymethyl)-furan
2,5-Bis(hydroxymethyl)-tetrahydrofuran
7
2,5-Furandicarboxaldehyde
2,5Bis(aminomethyl)furan
2,5Bis(isocyanicmethyl)furan
Polymers

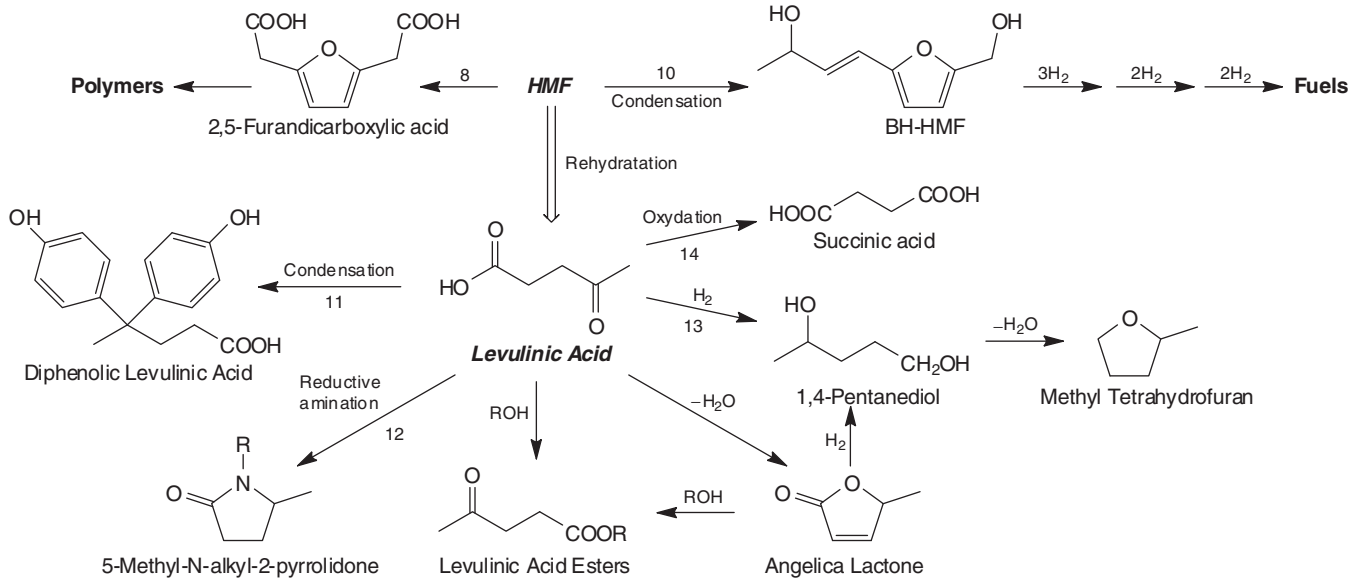


Fig. 12.8: Heterogeneous catalysis applied to the production and conversion of platform molecules derived from cellulose.

Tab. 12.1: Reactions reported in Fig. 12.8 and the relevant catalysts.

Reactions	Catalysts	Reference
1	Ni-W/SBA-15	(Zheng et al. 2010)
2	Carbon-SO_3H-250 423 K, 24h	(Pang et al. 2010)
3	ETS-4 aqueous phase 2-h 373 K in a batch reactor	(Lima et al. 2008)
4	Ru/C in a trickle-bed reactor	(Gallezot et al. 1998)
5	Pd-Bi/C	(Besson et al. 1995)
6	Acid mordenite zeolite with a Si/Al ratio of 11	(Moreau et al. 1994)
7	Pt/C high temperatures and almost neutral pH	(Carlini et al. 2005)
8	Pt/C low temperatures and basic conditions	(Carlini et al. 2005)
9	Raney nickel, copper chromites, and C-supported metals in water as solvent, in relatively short reaction times, at 413 K and 7.0 MPa of hydrogen	(Moreau, Belgacem, and Gandini 2004)
10	Aldol condensation of HMF with acetone	(Huber et al. 2005)
11	Acid-catalyzed condensation with phenols	(Bader and Kontowicz 1954)
12	Pd- and Pt-based catalysts	(Manzer 2004; Manzer and Herkes 2004)
13	Molecular sieves supported TiO_2/SO_4^{2-}	(He and Zhao 2001)
14	PdRe/C catalyst 473–523 K and 10 MPa of H_2 in MTHF	(Elliott and Frye 1998)
15	Vapor phase using dioxygen in the presence of V_2O_5 catalysts at 648 K	(Dunlop and Smith 1955)

Tab. 12.2: Tunable bifunctional catalysts for the isomerization of glucose-dehydration of fructose (423 K, 3 h).

Catalyst	% Glucose	% Fructose	% HMF
CeO_2/SiO_2(8%)	82.7	13	4.3
Al_2O_3/CeO_2	82.3	13	4.7
SnO_2/CeO_2	90.6	5.8	3.6
CaO/Al_2O_3	71.6	25	3.4
CeNb(20%)	85.3	10	4.7

N-based salts (phosphates, mainly) seem to produce interesting conversion, higher than 40%–50%.

Another interesting platform molecule is lactic acid **8**, obtained by fermentation of glucose and polysaccharides. **8** is used for the synthesis of lactide **9**, used for the synthesis of polylactide (▶Fig. 12.9), a biodegradable and compostable polymer.

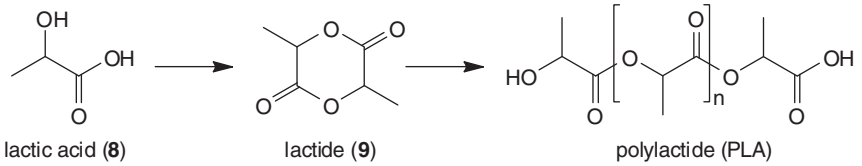


Fig. 12.9: Conversion of lactic acid into lactide and polylactide.

12.3 Conversion of lipids: the established technology

The transesterification of lipids (extracted from seeds or aquatic biomass) to fatty acid methyl esters (FAMEs) is a practice established on a large scale for the production of biodiesel. The principal method of converting biogenic lipids into biodiesel is the transesterification: the viscous lipids (usually a mixture of triglycerides [TG], diglycerids [DG], and monoglycerides [MG]) are reacted with methanol in the presence of a homogeneous catalyst in water to produce FAMEs and glycerol as a co-product (▶Fig. 12.10).

Conventionally, basic catalysts such as NaOH or KOH, carbonates or alkoxides (Felizardo et al. 2006) are used, which are characterized by cost-effectiveness and good performance. The transesterification process is a multi-step reaction mechanism (▶Fig. 12.10) affected by various factors depending on the reaction conditions used, such as the reaction temperature, the ratio of alcohol to vegetable oil, the amount and the type of catalyst, the mixing process, and the raw oils used. One of the key issues with such technology is the fact that if FFAs are present, they will originate soaps upon

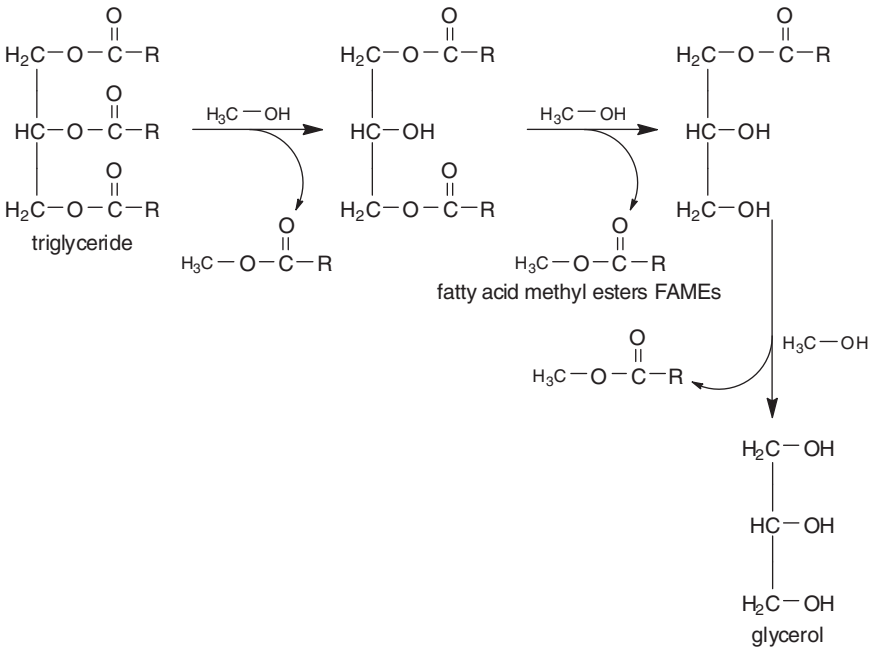


Fig. 12.10: Transesterification of triglycerides into FAMEs and glycerol.

reaction with bases such as NaOH and KOH. The consequence is that emulsions are formed that make difficult the separation of FAMEs. For this reason, refined oils are used that contain a low percentage of FFAs (usually less than 1%). This means that only high-quality oils can be used while used oils (restaurant oils) or low-quality oils (oils from high-pressure processes), which contain a high amount of FFAs, cannot be used – such practice is not economically convenient. However, if aquatic biomass is used as a source of oils this technology is also hardly usable, because such oils usually contain high amounts of FFAs (up to 20%). In fact, algae oil composition depends on the organism, the growing conditions, and the extraction method. In addition, such oil may contain phospholipids, glycolipids, and sulpholipids that must be removed from the oil before processing. ▶Tab. 12.3 gives examples of the composition of different oils sourced from various biomass, seeds, or algae.

12.4 Innovation in the production of FAMEs

FFAs for their conversion into FAMEs require acid catalysts that are not compatible with the basic catalysis used in the transesterification of lipids. Therefore, FFAs need to be removed before the transesterification of lipids. Actually, they are washed out by caustic washing (which forms soaps by reaction of FFAs with the base). Moreover, excess water can also cause undesirable reactions during the cleavage of glycerides ester bonds. The extra processing steps required to avoid saponification in the main reaction vessel are associated with extra costs.

In order to minimize the FAMEs production cost, a number of variations of the transesterification process are introduced by biodiesel manufacturers who will optimize the process for each feedstock by balancing yields against equipment, catalyst, methanol, and energy costs. In the case of algal biofuels, the feedstock composition is uncertain and will likely vary with the species and over time since changes in production temperature, light intensity, and nutrient levels all affect algal lipid composition. Consequently, process optimization (albeit a known art) will need continuous attention in a production environment with the flexibility to deal with varying feedstock composition.

Tab. 12.3: Lipid composition (TG, DG, MG, FFA) of several oils and fats.

	TG	DG	MG	FFA
Brown grease	74.8	11.7	1.5	12.0
Rapeseed oil	99.3	0.7	0	0
Refined palm oil	91.0	9.0	0	0
Crude palm oil	87.7	6.7	0.5	5.0
Lampante olive oil	73.5	5.5	1.2	19.8
Virgin olive oil	99.5	0.3	0	0.2
Oil from Nannochloropsis sp. microalgae	70.8	8.9	3.9	16.4

12.4.1 Hydrolytic esterification of lipids

A possible solution to the problems caused by the co-presence of lipids and FFAs is the hydrolytic esterification process in which the mixture is hydrolyzed in presence of a heterogeneous acid catalyst (Nb_2O_5 is a good catalyst) to afford FFAs and glycerol. After separation, the resulting FFAs are esterified in a subsequent step. The same catalyst (Nb_2O_5) can be used. Such technology is in use in Brazil.

12.4.2 Water-free simultaneous transesterification of lipids and esterification of FFAs

The expansion of the production process increases the cost of FAMEs. The ideal solution would be a single-step transesterification of lipids and esterification of FFAs. To this end, heterogeneous catalysts characterized by tunable acid-base properties can be developed that may at the same time transesterify lipids and esterify the FFAs fraction.

La_2O_3/ZrO_2 mixed oxides have been reported to be active catalysts in the simultaneous transesterification of lipids and esterification of FFAs (Russbueldt and Hoelderich 2010). They use the basic properties of lanthanum oxide and the acid properties of zirconium oxide.

Recently, CeO_2-derived mixed oxides have been reported to act as effective catalysts with tunable properties for the simultaneous transesterification of lipids and esterification of FFAs that can be present in the mixture at a level up to a 20% w/w (Dibenedetto et al. 2011b, 2011c).

▶Tab. 12.4 shows the acid-base properties of some of the mixed oxides and ▶Fig. 12.11 shows how the conversion of the lipids+FFAs mixture is affected by the catalyst composition. The catalysts of composition CaO-CeO_2 and 12CaO7$CeO_2$7Al_2O_3 are the most effective at producing a biodiesel within the EU regulations, starting from an oil with 20% presence of FFAs.

This technology appears quite interesting, supposing that resistant catalysts are produced that are not pulverized on use and can be easily recycled. One of the principal limitations with calcium catalysts is that Ca is leached and lost during application, causing a short life of the catalysts that increases the cost of production of FAMEs.

Tab. 12.4: Acid-base properties of some of the catalysts used in Dibenedetto et al. 2011b.

Entry	Catalysts	BET Surface Area (m^2/g of catalyst)	Volume of NH_3 Adsorbed (mL/g of catalyst)	Volume of CO_2 Adsorbed (mL/g of catalyst)
1	CeO_2	33.2	0.084	0.051
2	0.1 CaO CeO_2	16.9	0.088	0.077
3	0.5 CaO CeO_2	7.7	0.122	0.078
4	CaO CeO_2	3.3	0.179	0.102
5	12CaO7$Al_2O_3$7CeO_2	4.2	0.157	0.098
6	$CaCO_3$	1.4	~0	~0

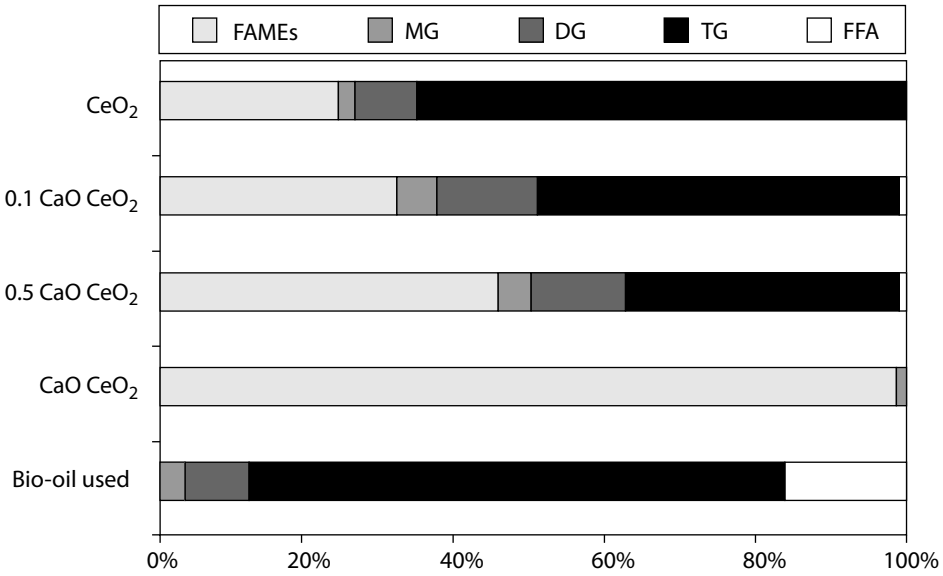


Fig. 12.11: Effect of the composition of catalysts on the conversion of oils of different acidity (Dibenedetto et al. 2011b).

12.4.3 The quality of bio-oil

Bio-oil extracted from biomass of different origin may have quite a variable composition in terms of chain length and unsaturations in each chain. ▶Tab. 12.5 gives an idea of the range of such unsaturations. Polyunsaturated chains are not recommended as components of fuels because they can give rise to gums, which deteriorate engines. Therefore, a treatment is necessary that reduces the number of unsaturations.

The solution to this problem is the (partial) hydrogenation of the polyunsaturated FAs. It is worth recalling that, according to EU regulations, biodiesel may contain up to one unsaturation in a chain and must respond to a maximum Iodine Number (IN) of 115 (German Directive 2007).

The hydrogenation of unsaturated FA is conveniently carried out by using Cu-based heterogeneous catalysts (Ravasio et al. 2002). With such an operation, the quality of FAMEs is raised to the level of usable biodiesel. An alternative route is the conversion of lipids and other hydrocarbons or suitable substrates into molecules that may be used as fuels, as described further on.

12.5 Hydroprocessing

The alternative path to producing liquid fuels from biomass-derived lipids is hydroprocessing, where the oil is treated with hydrogen in presence of an appropriate catalyst to obtain a mixture of alkanes, water, CO_2, and CO (▶Fig. 12.12). The hydrogen required for the reaction is often readily available. The most important source of hydrogen is

Tab. 12.5: Distribution of fatty acids present in lipids of some aquatic biomass in oil derived from seeds and fats.

Species	Saturated $C_{12}\rightarrow C_{20}$ (%)	Monounsaturated $C_{14}\rightarrow C_{20}$ (%)	Polyunsaturated $C_{16/2}\rightarrow C_{16/4}$, $C_{18/2}\rightarrow C_{18/4}$, $C_{20/2}$ (%)
Fucus sp	15.6	28.5	55.8
Nereocystis luetkeana	27.0	15.8	57.1
Ulva lactuca	15.0	18.7	66.3
Enteromorpha compressa	19.6	12.3	68.1
Padiva pavonica	23.4	25.8	50.8
Laurencia obtuse	30.1	9	60.9
Rapessed oil	5.9	62.7	31.4
Refined palm oil	48.7	38.7	13.2
Crude palm oil	53	36.2	10.8
Brown grease	45.1	39	15.9

the catalytic reformer, while the most common method of manufacturing hydrogen is steam-methane reforming.

The alkane mixture can be fractionated to produce a synthetic kerosene jet fuel and hydrogenation-derived renewable diesel (HDRD) or green diesel. HDRD is compatible with petroleum processes and existing fuel infrastructure, and can be blended with petroleum products in any proportion. The glycerol moiety of the TG is converted into propane, which can be either combusted to provide process heat or liquefied and sold as liquid propane gas (LPG).

Attention should be paid to the removal of the gas phase. It can be done through chemical transformation, by a gas cleaning step like an amine wash, or, more simply, by increasing the purge gas rate. If the gases formed are not removed they may give a decreased hydrogen partial pressure, with reduction of the catalyst activity. Further problems with CO and CO_2 may occur due to competitive adsorption of S- and N-containing

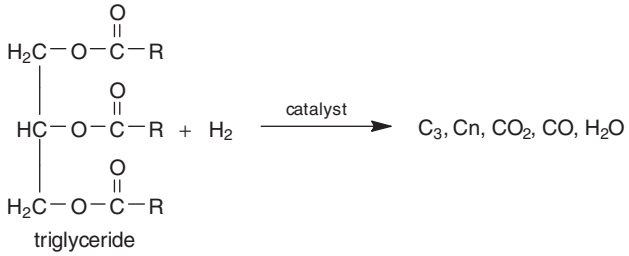


Fig. 12.12: Hydroprocessing of lipids.

molecules on the hydrotreating catalyst. CO, which cannot be removed by an amine wash unit, will build up in the treated gas, requiring a high purge rate or another means of gas purification. In the effluent, CO_2 in water forms carbonic acid, which must be properly handled to avoid increased corrosion rates. Moreover, because both carbon dioxide and carbon monoxide are produced, two additional reactions need to be taken into consideration. Hydrotreating catalysts are known to be active for both reverse water gas shift (Eq. 1) and methanation (Eq. 2).

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (1)$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2)$$

The relative extent of these two reactions accounts for the observed distribution between CO, CO_2, and CH_4. The water gas shift activity of the catalyst makes it difficult to ascertain whether the observed CO and CO_2 are produced by a decarboxylation reaction or by a decarbonylation route (Egeberg et al. 2010). A typical product distribution is shown in ▶Tab. 12.6. In all cases, the product has a very high cetane number (>80) and contains very low amounts of sulfur or aromatics (Holmgren et al. 2007).

The most common catalytic systems used in the process are CoMo, NiMo, and/or CoNi hydrotreating and crystalline silica alumina base with a rare earth metal deposited in the lattice (Pt, Pd, W, Ni).

Vegetable oils and waste animal fats are being processed in petroleum refineries such us Dynamic Fuels, LLC (Environmental Leader 2010) or UOP and Eni S.p.A (UOP 2011) to make HDRD. Many of these projects are based on modifications to existing hydroprocessing reactors at refineries with surplus (or idle) hydrogenation capacity. The conversion of algal oil to synthetic kerosene jet fuel has been demonstrated (US Patent 2010) and the fuel has been tested by a commercial airline.

12.6 Glycerol valorization

As mentioned previously, in the processing of vegetable or animal fats or oils, glycerol is produced at a rate of 10% of the produced FAMEs. Considering the expected large expansion of the production of biodiesel, one can foresee that the production of glycerol will increase much over that actual market capacity. As a matter of fact, bioglycerol is supplanting the synthetic glycerol that is now produced at an ever decreasing rate. Such a situation demands the development of conversion technologies for glycerol into useful products if its accumulation must be avoided. The use of glycerol as fuel is possible

Tab. 12.6: Green diesel product yields.

Feed	Vegetable oil (%)	100
	H_2 (%)	1.5–3.8
Products	Naphtha (vol%)	1–10
	Diesel (vol%)	88–98+
	Cetane number	>80
	S (ppm)	<1

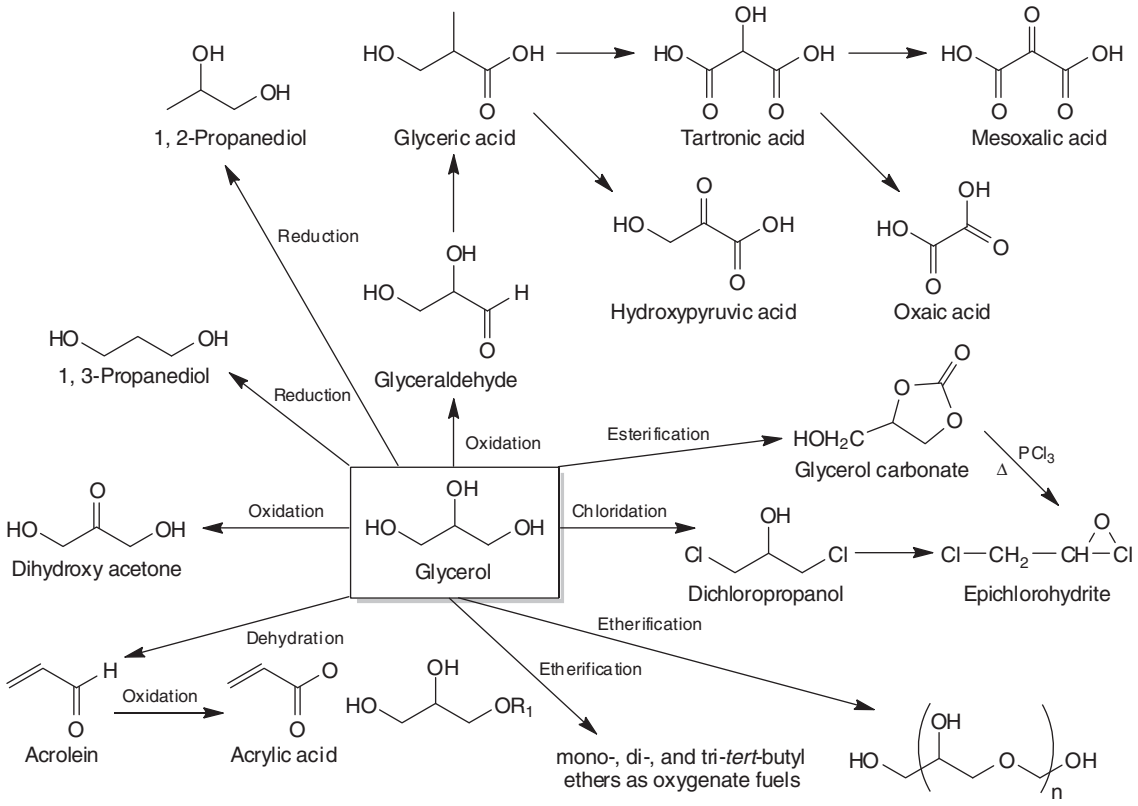


Fig. 12.13: Glycerol conversion into various marketable products.

only into ad hoc designed engines, due to its high viscosity. The McNeil cycle (EP Patent 2009) allows the combustion of glycerol, but such technology has to be proven. Therefore, a lot of interest is growing today about the use of glycerol. ▶Fig. 12.13 shows a number of options for glycerol conversion into chemicals, fuel additives, fuels, and materials.

One of the options is the conversion of glycerol into its carbonate form (Eq. 1, ▶Fig. 12.13). Such conversion has been recently performed using urea, which avoids the use of toxic phosgene. Such biocarbonate can be considered as a platform molecule that can be converted into other useful products (▶Fig. 12.14).

Interestingly, glycerol carbonate can be converted into epichlorohydrin with an overall yield of 70% from bioglycerol under mild conditions (Dibenedetto 2011a).

The conversion of glycerol into H_2 is also an interesting reaction because hydrogen could be used for the partial hydrogenation of polyunsaturated FAMEs. The use of the vapor phase reforming (VPR) is the best chemical technology that used heterogeneous catalysts. Also, bacteria can conveniently convert glycerol into H_2 and organic acids (Aresta and Dibenedetto 2009; Jentis and Aresta 2010).

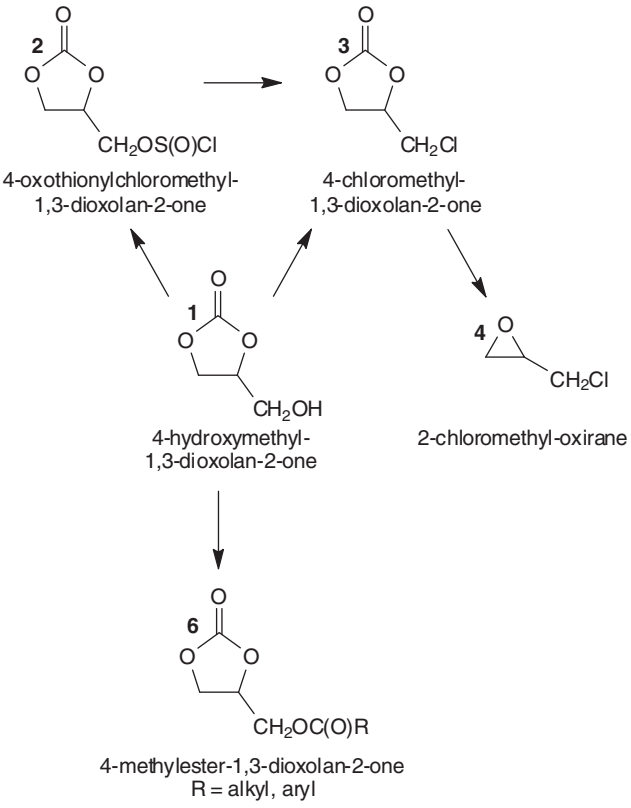


Fig. 12.14: Conversion of glycerol carbonate into new or old compounds.

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13 Biomass gasification: gas production and cleaning for diverse applications – CHP and chemical syntheses

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13.1 Introduction to biomass gasification

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, biofuels, or biomass, into mainly carbon monoxide and hydrogen by processing the raw material at high temperatures with a controlled amount of oxygen and/or steam. The resulting gas mixture is called synthesis gas, or syngas, and is itself a fuel.

Biomass, as a renewable energy source, refers to living and recently dead biological material that can be used as fuel or for industrial production. In this context, biomass refers to plant matter specifically grown for energy purposes or residues such as dead trees and branches, yard clippings, and wood chips biofuel, and it also includes plant or animal matter used for production of fibbers, chemicals, or heat. Biomass may also include biodegradable wastes that can be combusted. It excludes organic material that has been transformed by geological processes into substances such as coal or petroleum. Today's growing interest for the exploitation of renewable energy alternatives to fossil fuels has led research efforts to revamp the gasification technique that was known since the early 1800s – its first commercial application being to produce gas for lighting and to supply local industries (town gas). During the World War II biomass gained ground against coal in a small scale, such as fuel for cars and ships. Technically, the widespread use of gasification of biomass has to overcome two obstacles: (1) the integration of available technologies for cleaning the gas from impurities (particles of ash and char, corrosive gases such as H_2S, HCl) in economically and technically acceptable solutions so that gas can be used in advanced power generation systems, and (2) the uninterrupted availability of facilities able to handle more than one type of fuel without any problems of loss of fluidization.

The advantage of gasification is that using syngas is potentially more efficient than direct combustion of the original fuel, because it can be combusted and expanded at higher temperatures or used in fuel cells so that the thermodynamic upper limit to the efficiency defined by Carnot's rule is higher. Apart from syngas being a fuel for internal combustion engines and gas turbines, it can be used to produce methanol and hydrogen or can be converted via the Fischer-Tropsch process into synthetic fuel. Gasification can also begin with materials that are not otherwise useful fuels, such as biomass or organic waste. In those cases, the high-temperature process refines out corrosive ash elements such as chloride and potassium, allowing clean gas production from otherwise problematic fuels.

Small-scale efficient combined heat and power (CHP) plants based on biomass gasification coupled with emerging technologies for power production, such as micro gas turbines with electrical efficiencies from 20% to 30% of the biomass fuel LHV (lower heating value), have lately gained increasing attention. Internal combustion engines offer higher electrical efficiency with reduced co-generation possibilities and also

exhibit higher pollutant levels. Smaller-scale gasification systems with internal combustion engines have now demonstrated, during several thousands of hours, that they give reasonable electrical efficiencies and limited emissions. For even larger power plants (i.e. >20 MWe) IGCC (Integrated Gasification Combined Cycle) technology is considered the most favorable with electrical efficiencies up to 40% (Maniatis and Millich 1998).

Biomass represents about 4% and about 26% of the primary energy consumption in developed countries and developing countries, respectively. Very high targets are set at the EU level: bioelectricity should contribute about 55 Mtoe together with 19 Mtoe of biofuels introduction (EU Commission 2005). Biomass gasification offers significantly increased efficiencies in electricity production compared to combustion-based systems (which are limited to around 20%), and the possibility to produce biofuels, therefore, is expected to play a significant role in the future of bioenergy schemes in Europe.

13.1.1 Biomass as a feedstock for thermochemical processes

The main feature of biomass as fuel is its high moisture content that can reach up to 95% w/w when fresh. Furthermore, its high oxygen concentrations makes it more reactive than solid fossil fuels. The calorific value (kJ/kg) of biomass is generally weaker than coal. Another important feature of biomass is the heterogeneity of the available types of materials; for example, pellets from wood, sawdust, agricultural residues, and energy plants that may differ greatly in particle size distribution and moisture content. All thermochemical processes for biomass utilization require complex feeding and handling systems. Finally, biomass tends to have high volatiles and ash contents, which create additional constraints: high volatiles create stability problems in thermochemical processes while high ash contents, especially of alkalis, create corrosive aggregates and deposits. ▶Tab. 13.1 brings together a comparison of the elemental analysis and energy content of different fossil fuels and biomasses.

The typical composition of biomass is expressed by the general formula $CH_{1.4}O_{0.6}$ (atomic ratio). Generally, the materials classified as solid biomass are woody, fibrous, or of animal origin. Biomass fibers consist mainly of cellulose ($CH_{1.6}O_{0.8}$) while woody biomass contains significant amounts of lignin ($CH_{1.2}O_{0.4}$). Protein or oily fuels typically have reduced contents of elemental carbon and an increased content of nitrogen and sulfur. ▶Fig. 13.1 shows different fuels based on their relative proportion of carbon, hydrogen, and oxygen in a ternary C-H-O diagram. During combustion or gasification, the individual compounds are shifted to the right due to the addition of oxygen or hydrogen (Gaur and Reed 1998).

Thermochemical processes are greatly affected by the composition and properties of the biomass ash. The inorganic constituents of the plant biomass can be found either in the form of discrete particles or in chemicals bound to the structure of the plant material (Dayton, French, and Milne 1995; Baxter 1993). Silicon (Si) is the most common mineral found in nature and is a dominant component of biomass ash because the plants absorb it from the soil in the form of oxide. Aluminum (Al) is found in lower concentrations, especially when the plant has grown in soils rich in aluminosilicate components. Alkali metals (K, Na) are considered to cause problems for the thermochemical conversion of biomass, such as the melting of ash and agglomeration between particles in fluidized bed processes. Potassium (K) is an element that concentrates in the plants that grow

Tab. 13.1: Elemental, approximate analysis and energy content of different fuels (Gaur and Reed 1998).

Name	Fixed Carbon % w/w db	Volatiles	Ash	C	H	O	N	S	HHV (db) kJ/g
				Woods					
Pine	17.17	82.54	0.29	49.25	5.99	44.36	0.06	0.03	20.02
Birch	12.50	87.10	0.40	49.55	6.06	43.78	0.13	0.07	19.30
Fir	16.58	83.17	0.25	49.00	5.98	44.75	0.05	0.01	19.95
Oak	17.20	81.28	1.52	49.48	5.38	43.13	0.35	0.01	19.42
				Energy Crops					
Eucalyptus	17.82	81.42	0.76	49.00	5.87	43.97	0.30	0.01	19.42
Poplar	16.35	82.32	1.33	48.45	5.85	43.69	0.47	0.01	19.38
Giant reed	14.58	82.94	2.48	46.50	5.71	44.71	0.53	0.01	17.98
				Agricultural					
Olive kernels	18.47	79.12	2.41	51.30	5.80	39.00	1.00	0.00	19.84
Prunings	21.54	76.83	1.63	51.30	5.29	40.90	0.66	0.01	20.01
Corn stover	18.54	80.10	1.36	46.58	5.87	45.46	0.47	0.01	18.77
Straw	19.80	71.30	8.90	43.20	5.00	39.40	0.61	0.11	17.51
Cotton stalks	22.43	70.89	6.68	43.64	5.81	43.87	0.00	0.00	18.26
Rice husks	15.80	63.60	20.60	38.30	4.36	35.45	0.83	0.06	14.89

(*Continued*)

Tab. 13.1: Elemental, approximate analysis and energy content of different fuels (Gaur and Reed 1998. (*Continued*)

Name	Fixed Carbon % w/w db	Volatiles	Ash	C	H	O	N	S	HHV (db) kJ/g
				Liquid Fuels					
Motor gasoline	0.00			85.50	14.40	0.00	0.00	0.10	46.88
Kerosene	0.00		0.01	85.80	14.10	0.00	0.00	0.10	46.50
CH_3OH	0.00		0.00	37.50	12.50	50.00	0.00	0.00	22.69
C_2H_5OH	0.00		0.00	52.20	13.00	34.80	0.00	0.00	30.15
				Pyrolysis Oils					
LBL wood oil			0.78	72.30	8.60	17.60	0.20	0.01	33.70
				Coals					
Coal – Pittsburgh	55.80	33.90	10.30	75.50	5.00	4.90	1.20	3.10	31.75

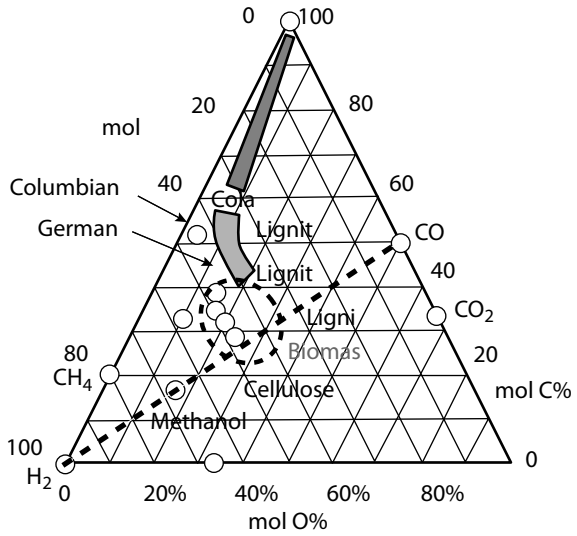


Fig. 13.1: Ternary diagram C-H-O for different fuels and components.

fast – it takes part in the metabolism process. It is situated in the form of ions bound in the organic lattice-to-oxygen-containing groups (carboxyl, carbonyl) (Jensen et al. 2000) and thus in particularly volatile parts of the plant at elevated temperatures. Thus, solid biofuels with high potassium are mainly annual agricultural products or annual energy crops. Sodium (Na) does not play a significant role in plant growth, and even at high concentrations is toxic. Calcium (Ca) is a key component of cell walls of the plant and contributes to its structure. Magnesium (Mg) is found at very low concentrations and is inert toward the significance of the vital functions of the plant. Nitrogen (N) is a nutrient for plants and is introduced by nitrates and ammonium salts, which are transformed into ammonia and thus amino acids. Nitrogen compounds in the biomass are much more volatile than for coal. Chlorine (Cl) is found in low concentration and is required for plant growth. Sulfur (S) enters the plant through atmospheric absorption, or a salt-absorbing sulfur dioxide, and the structure of the plant is found as elemental sulfur or sulfate. Phosphorus (P) is mainly found in fruit kernels and not in all plants. Iron (Fe) plays an important role in the mass transport phenomena taking place in the plant, while the highest percentage is found in green parts and is an important action during photosynthesis. Besides this, the origin of ash in biomass is due to exogenous factors during cultivation, harvesting, processing, and the storage of biomass.

13.1.2 Basics of biomass gasification

Gasification is a thermal process that converts solid fuels into a gaseous fuel mixture of low or medium calorific value using air or oxygen as oxidant or water vapor (H_2O). The difference between air-driven gasification and combustion is the air ratio, which in the first case is substoichiometric ($\lambda < 1$) while in the second case is superstoichiometric ($\lambda > 1$) in relation to the required oxygen for complete combustion. The gasification of biomass can be performed in fixed, moving, or fluidized bed reactors at temperatures

above 700°C. Many of the reactions occurring during gasification are endothermic, and the required thermal energy can be provided by partial oxidation of reactive components (if the gasification agent is oxygen/air or it can be provided indirectly by transferring heat from an external source in the case of steam-driven gasification). In the first case the process is called *autothermal* while in the second case it is called *allothermal*. Overall, the solid fuel is converted mainly to fixed gases (CO, H_2, CO_2, H_2O, and CH_4) and other inorganic compounds with concentrations in the range of ppmv (H_2S, COS, HCl, NH_3, HCN, etc.), as well some small quantity of heavy hydrocarbons (tars), while some small fraction of the original biomass remains in the solid phase as char together with the ash (mainly metallic minerals).

13.1.3 Types of gasifiers

The product gas varies in composition and calorific capacity depending on the gasification system used and the gas reagent with which the process occurs (oxygen, air, or steam). Bridgwater (2002) gave average data for product gas compositions, shown in ►Tab. 13.2. The product gas has to be further cleaned of particles, heavy hydrocarbons, and inorganic traces in specified levels of purity to allow its use in gas boilers, internal combustion engines, and gas turbines and chemical syntheses (Faaij 2006).

13.1.3.1 Fixed-bed gasifiers

Small-scale gasification systems are limited to the type of reactor. Small scale can be defined by capacities of less than 1 MWth. These reactors are often characterized by the direction of the gas flow through the reactor (upward, downward, or horizontal) or by the respective directions of the solid flow and gas stream (co-current, counter-current, or cross-current). In all cases the biomass (in most cases wood or agricultural residues or charcoal produced by slow pyrolysis) is fed on the top and moves downward by gravity, as can be seen in ►Fig. 13.2. Air is supplied by the suction of a blower or an engine.

The updraft gasifiers produce a hot (300–600°C) gas that contains large amounts of pyrolysis tars as well as ash and soot. Steam is sometimes used to provide higher

Tab. 13.2: Composition of the produced gas (Bridgwater 1995).

Process	H_2	CO	CO_2	CH_4	N_2	HHV (MJ/m^3)	Gas Quality	
							Tars	Particles
Fluid bed/air	9	14	20	7	50	5.4	Average	Poor
Updraft/air	11	24	9	3	53	5.5	Poor	Good
Downdraft/air	17	21	13	1	48	5.7	Good	Average
Downdraft/ oxygen	32	48	15	2	3	10.4	Good	Good
Twin bed	31	48	0	21	0	17.4	Average	Poor
Pyrolysis	40	20	18	21	1	13.4	Poor	Good

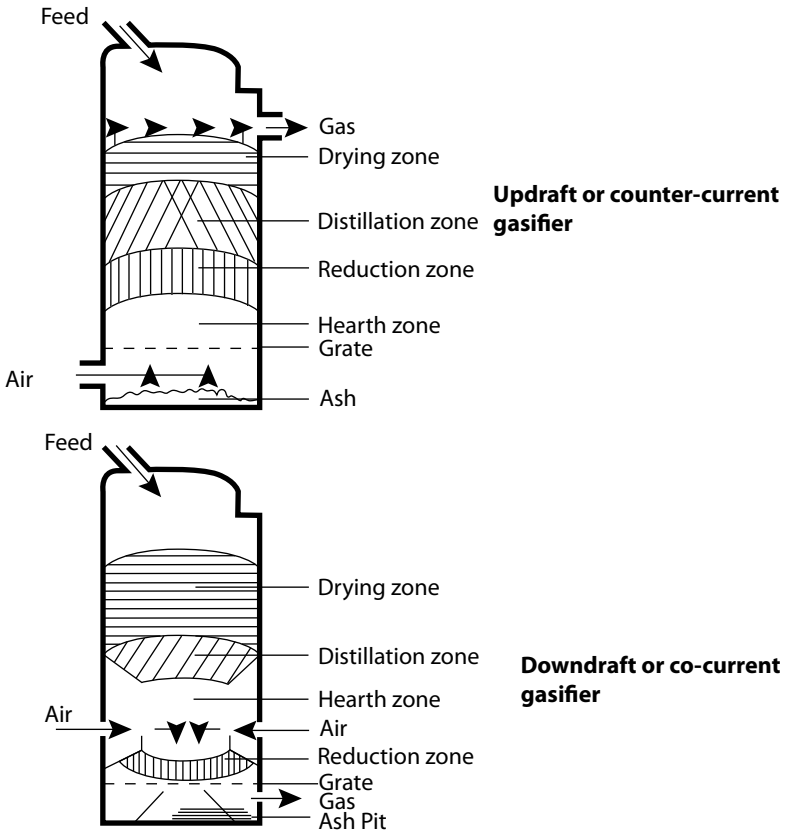


Fig. 13.2: Fixed-bed gasifiers: Updraft and downdraft (Stassen 1995).

hydrogen content in the product gas (Bridgwater 1995). The hot gas is suitable for combustion in a gas burner but for engine applications it needs to be cooled and cleaned of tars, usually by condensation. Because the tars represent a considerable part of the heating value of the original fuel, removing them gives this process low energy efficiency (Stassen 1995).

Downdraft gasifiers produce a hot (700–750°C) tar-free gas. The descending bed is supported across a constriction known as a throat, where most of the gasification reactions occur. The reaction products are mixed in the turbulent high-temperature region around the throat, which aids tar cracking. Some tar cracking also occurs below the throat on a residual charcoal bed, where the gasification process is completed (Bridgwater 1995). After cooling and cleaning the gas is suitable for use in internal combustion engines.

These small-scale gasifiers can produce power with the help of an internal combustion engine (Spark Ignition or Otto engines, or compression ignition or diesel engines). Otto engines can be solely fed with producer gas whereas diesel engines must be fed with mixtures of diesel and producer gases, something that is under research at the moment.

13.1.3.2 Fluidized-bed gasifiers

Fluidized-bed reactors are the only gasifiers with near isothermal operation. The fluidizing material is usually silica sand, although alumina and other refractory oxides have been used to avoid sintering, and catalysts have also been used to reduce tars and modify product gas composition. A typical operating temperature for biomass gasification is 800–850˚C. Some pyrolysis products are swept out of the fluidized bed by gasification products and have to be further converted by thermal cracking in the freeboard region or downstream reactors. Loss of fluidization due to bed sintering is one of the commonly encountered problems depending on the thermal characteristics of the biomass ash. Alkali metal compounds from the biomass ash form low-melting eutectics with the silica of the bed inventory. This results in agglomeration and bed sintering with eventual loss of fluidization and proper operation of the reactor.

Fluidized bed gasifiers have the advantage that they can readily be scaled up with considerable confidence in comparison to fixed-bed reactors. Fluidized beds provide many other features not available in the fixed-bed types, including high rates of heat and mass transfer and good mixing of the solid phase (Perry and Green 1984). In circulating fluid-bed gasifiers the fluidizing velocity in the circulating fluid bed is high enough to entrain large amounts of solids with the product gas (▶Fig. 13.3). These systems were developed so that the entrained material is recycled back to the fluid bed to improve the carbon conversion efficiency compared with the single fluid-bed design.

Although minerals (Ca, S, Cl, K, Na) positively catalyze reactions of combustion and gasification (Risnes et al. 2003; Nordin 1994), agricultural residues and energy plants

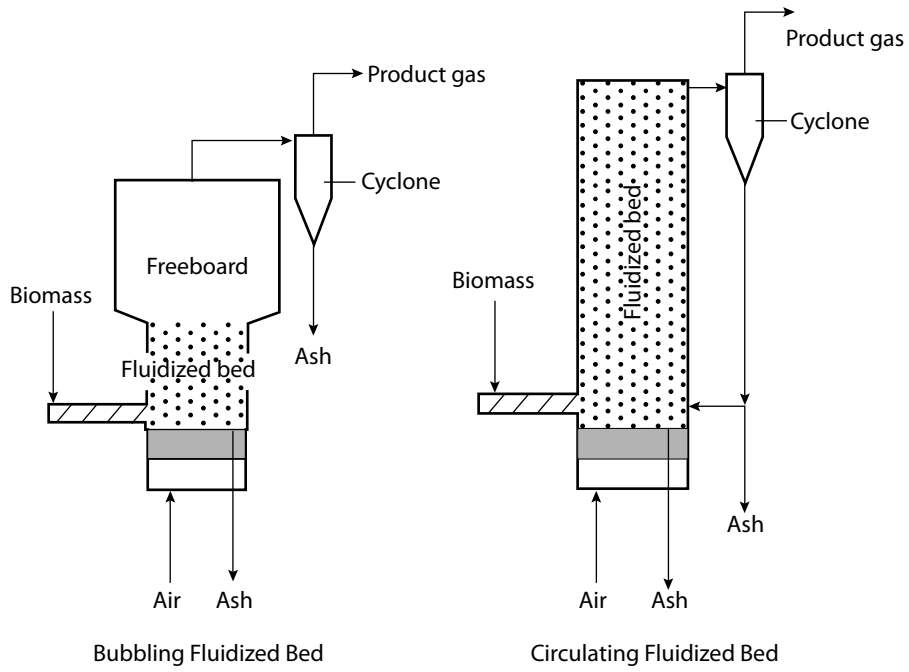


Fig. 13.3: Principle of bubbling and circulating fluidized bed (Bridgewater 1995).

tend to cause serious erosion and depositions of ashes at higher temperatures (Gupta, Wall, and Baxter 1997; Michelsen et al. 1998; Riedl and Obernberger 1996) associated with high levels of chlorine and alkalis. The alkalis are generally volatile, and at elevated temperatures react toward chlorides (Nordin et al. 1995), which cause corrosion on heat-transfer surfaces. Erosion can be caused by molten salts (Kofstad 1988), alkali chloride, or so-called active corrosion by chlorine (chlorine-induced active corrosion) (Vaughan, Krause, and Boyd 1977; Grabke, Reese, and Spiegel 1995; McKee, Shores, and Luthra 1978).

In the temperature range of fluidized-bed gasification reactors, the ash-derived alkali metals create operational problems due to the formation of molten salts and oxides (rust), namely (1) their reaction toward alkali silicates that melt at temperatures even below 700°C, depending on their composition (Dayton, French, and Milne 1995), and (2) the reaction Ca/K and S to sulfates and sulfides. Increased proportions of melt cause agglomeration of particles and finally loss of fluidization. This results in shut downs of the gasifier.

13.2 Thermodynamics of biomass gasification

To better understand the process of biomass gasification, simulation processes are commonly based on the principles of chemical thermodynamics. The thermodynamic models are flexible since they can be used to predict the composition of product gas regardless of the gasifier design under study, but they diverge from reality due to the assumption that the system reaches chemical equilibrium, which in fact is generally not the case. Examples of thermodynamic models are described in the works of Schuster et al. (2001), Li et al. (2001), and Mathieu and Dubuisson (2002).

The overall process of gasification can be divided into three stages performed sequentially (Slesser and Lewis 1979): the first is the direct drying that occurs up to 280˚C, followed by the second step, pyrolysis between 280–500˚C where the thermal degradation of biomass results in volatiles, tars, and char. This pyrolysis step proceeds rapidly at high temperatures and increased heat-transfer rates of a fluidized bed. In the third stage, the pyrolysis gas and tars react according to the main reactions of gasification with the char in the so-called heterogeneous reactions (►Tab. 13.3). From these reactions, only four independent reactions are sufficient for a complete description of the system (Karl 2004).

It is common to consider char as graphite ($C_{(s)}$), which has clearly defined thermophysical properties (Prins, Ptasinski, and Janssen 2003). Given enough oxidant, gasification would result in the complete conversion of the pyrolysis products (tar) in gases. The conversion rate, however, depends on the type of reactor and chemical limitations of the reactions, and the final product also contains products of the pyrolysis step. In oxygen or air gasification the required heat for carrying out the endothermal reactions is provided by the exothermal reactions and the system is autothermal. This is not the case with steam gasification in which only endothermal reactions occur and heat has to be provided externally, usually in the form of hot-bed inventory from a combustion fluidized bed.

The condition of chemical equilibrium for a given stoichiometry, temperature, and pressure is solved easily by applying the principle of minimization of Gibbs free energy for the mix of potential gases in the product; for example, using multipliers Lagrange and considering the Gibbs function of the reactants and products as a function of moles, with restrictions based on the atom balance. ►Fig. 13.4 shows the limit of carbon

Tab. 13.3: Gasification reactions.

Exothermal reactions		
$C_{(s)} + O_2 \leftrightarrow CO_2$	$\Delta H_R = -393$ kJ/mol	Oxidation
$C_{(s)} + 1/2O_2 \leftrightarrow CO$	$\Delta H_R = -110$ kJ/mol	
$H_2 + 1/2O_2 \leftrightarrow H_2O$	$\Delta H_R = -242$ kJ/mol	
$CO + 1/2O_2 \leftrightarrow CO_2$	$\Delta H_R = -283$ kJ/mol	
$C_{(s)} + 2H_2 \leftrightarrow CH_4$	$\Delta H_R = -75$ kJ/mol	Methane formation
Endothermal reactions		
$C_{(s)} + CO_2 \leftrightarrow 2CO$	$\Delta H_R = +173$ kJ/mol	Boudouard
$C_{(s)} + H_2O \leftrightarrow CO + H_2$	$\Delta H_R = +132$ kJ/mol	Steam char reaction
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	$\Delta H_R = +206$ kJ/mol	Methane reforming

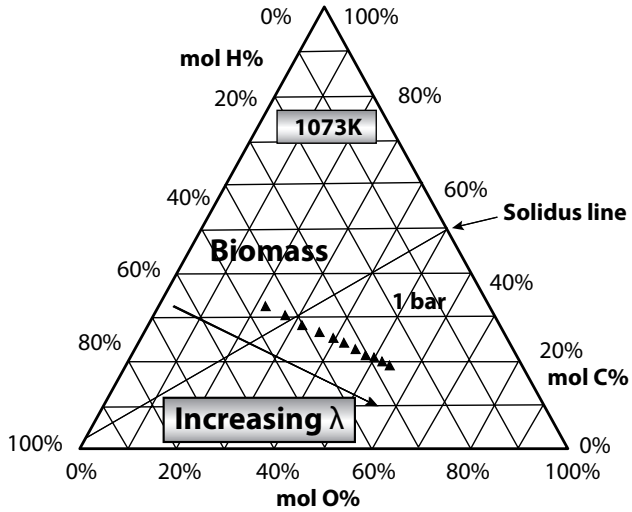


Fig. 13.4: Carbon solidus line in a C-H-O for biomass.

in a triangular phase diagram C-H-O, which was calculated on the operating parameters temperature gasification T_{gas} = 800°C and gasification pressure P_{gas} = 1 bar. Above the line of solid carbon limit, the solid carbon is thermodynamically stable; that is, incomplete gasification is expected.

The composition of the syngas actually contains some unreacted char, methane from the pyrolysis step, and other hydrocarbons. So, to take into account this fact, the thermodynamic model needs to be corrected based on experimental findings. In the gas phase results presented in ▶Fig. 13.5, we assumed that 15% of the biomass carbon is found in the remaining char, the CH_4 content in the dry gas product is 5% v/v, while

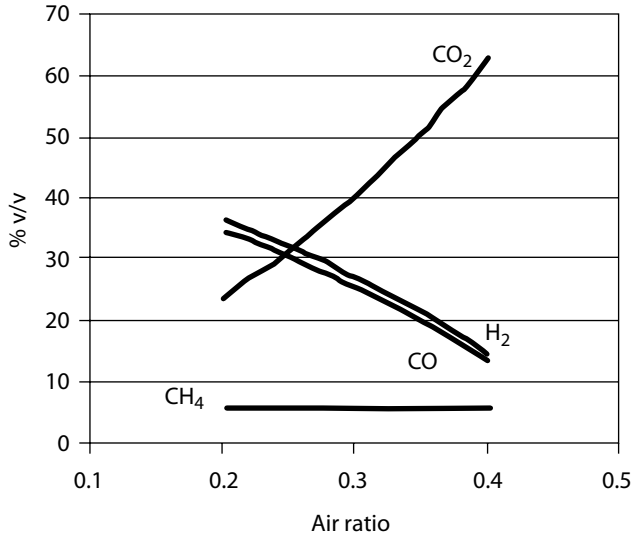


Fig. 13.5: Dry and nitrogen-free product gas composition (% v/v) prediction for air gasification vs. air ratio, based on thermodynamics with an assumption of 15% carbon in the char, 5% v/v CH_4, and 5 gr Nm^{-3} of tars.

5 gr/Nm^3 of tars escape with the product gas (Devi et al. 2005). Tars in this study are represented only by the naphthalene, which is an essential ingredient of their composition (Nordgreen, Liliedahl, and Sjöström 2006; Iaquaniello and Mangiapane 2005).

13.3 Syngas quality for CHP systems

For larger power plant biomass (i.e. >20 MWe), the technology of IGCC can yield electricity efficiencies of up to 50% (Bridgwater 2002; Maniatis and Millich 1998; Spliethoff 2001). In this case the gas turbine fuel specifications have to be met. In smaller systems, gasification can be combined with any power generation technology using gaseous fuel: internal combustion engines, gas micro-turbines, and high-temperature fuel cells. In those cases electrical efficiencies are lower (20%–30% on the lower heating capacity of biomass gasified). Again, fuel specification of these prime engine movers has to be met accordingly (BioHPR 2002).

The major contaminants of the produced gas are tars, which are condensable heavy hydrocarbons of oxygenated organic nature, produced mainly during the pyrolysis of biomass. According to a generally accepted definition, they are the set of organic molecules with molecular weights greater than that of benzene (Milne, Abatzoglou, and Evans 1998). The formation of tars is complex and depends directly on the conditions in which gasification takes place, especially temperature, residence time, and the stoichiometry applied as well as the properties of the fuel that is used. Tar-related problems occur when it is condensed into cold surfaces, resulting in deposits and clogging of pipes, surfaces, and equipment. Condensed tars form persistent aerosols that are very difficult to break.

Tab. 13.4: Concentration limits for safe operation of tar per application (Stevens 2001).

Application	Maximum Tar Levels
Internal combustion engines	<100 mg/Nm^3
Gas turbines	<0.5 mg/Nm^3
Compressors	50–500 mg/Nm^3
	<0.2% v/v (olephins C_2-C_6)
Molten carbonate fuel cells (MCFC)	<0.5% κ. o. (aromatics)
	<0.5% κ. o. (polycyclic)
Solid oxide fuel cells (SOFC)	Equivalent to MCFC for higher HCs
Phosphoric acid fuel cells (PAFC)	<0.5% (olephins C_2-C_6)

Removal of tar from the gas before its use can be achieved by scrubbers, electrostatic separators, and by chemical or catalytic decomposition of tar to form other gases, inside the reactor gasification as well as downstream (Devi et al. 2005). ▶Tab. 13.4 presents estimates for the concentration of tar in the gasification gas by type of end applications, which are indicative limits of safety for normal function (Stevens 2001).

13.4 Syngas quality of chemical syntheses

Some basic impurities that can prove detrimental to the main chemical products syntheses in the EuroBioRef project are summarized in ▶Tab. 13.5. These include particulates, tars, sulfur, halogen, nitrogen, and alkali species, as well as metal traces.

There is no optimum process for the removal of one or all the contaminant species listed in ▶Tab. 13.5 and in most of the cases, different processes and combinations accomplish the optimum gas cleaning system that accounts for the desired limits for the downstream equipment. A detailed performance and cost analysis is required in every case.

13.4.1 Gas cleaning systems for biomass syngas impurities

The diagram in ▶Fig. 13.6 summarizes the gas cleaning steps that will be analyzed in the following sections.

13.4.1.1 Removal of particulates

The initial gas clean-up step includes the removal of particles. Particulates derive from the gasifier's bed material, unconverted biomass (char), and the mineral matter of biomass feedstock (fly ash). According to the size and the type of the gasifier cyclonic, rotating particle separators, barrier or electrostatic filters, as well as wet scrubbers can be used for the removal of particulates (Rezaiyan and Cheremisinoff 2005; Stevens 2001; Peukert 2001).

Cyclones are commonly employed in gasification systems due to their effective and relatively easy and inexpensive operation as well as due to their advantage of operating in high temperatures, preventing a sensible heat loss.

Tab. 13.5: Impurity level for several catalytic processes.

	H_2O_2		Higher Alcohols		MeSH	
	AQ process	Direct process	Cu-based catalysts	MoS_2- based catalysts	CH_3OH process	H_2/CO process
Temp. (°C)	0–45	40–60	250–350	250–350	<400°C	<400°C
Pressure (bar)	3–6	10–300	30–80	30–80	<25 bars	<50 bars
Desired ratio	H_2 > 99.8%	H_2 > 99.8%	H_2/CO: 1*	H_2/CO: 1*	H_2S:CH_3OH <15 H_2 = S (mol/mol)	H_2/CO ≥ 2 H_2S/CO ≥ 1 (mol/mol)
Tars	No tars	No tars	<0.1 mg nm^{-3} **	<0.1 mg nm^{-3} **	<10 ppm	<10 ppm
Sulfur species	H_2S <1 ppm	H_2S <1 ppm	H_2S: 0.1 ppmv-60 ppb COS <9 ppm***	H_2S: 100 ppmv COS:<9 ppm***	–	–
Halogen species	Cl_2 < 1 ppm NaCl < 60 ppm	–	<1 ppb+	<1 ppb+	Cl <0.5 ppm	Cl <0.5 ppm
HCN	Possible poison: <1 ppm	Possible poison: <1 ppm	<10 ppb++	<10 ppb++	No data	No data
NH_3	<10 ppm	<10 ppm	<10 ppm*	<10 ppm*	<10 ppm	<1 ppm
As, Se, Hg	<0.01 ppm	<0.01 ppm	ppb levels+++	ppb levels+++	<0.5 ppm	<0.5 ppm
Alkali species	NaCl <60 ppm	No data	No data	No data	<0.5 ppm	<0.5 ppm

* (Houben 2004; NREL Report 2006)
** (Xu, Donald, and Ohtsuka 2010)
*** (Spath and Dayton 2003)
+ (Twigg and Spencer 2001)
++ (Turk et al. 2001)
+++ (Subramani and Gangwal 2008)
– no poison effect

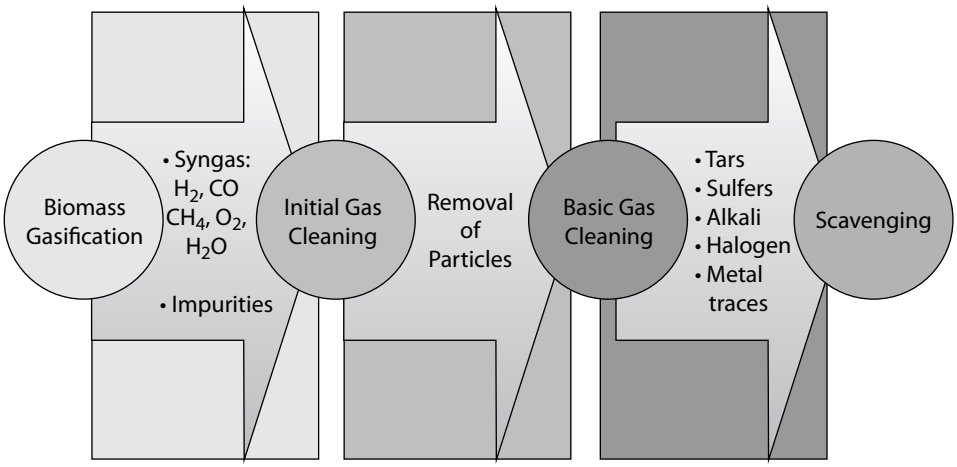


Fig. 13.6: Basic scheme of gasification and gas cleaning.

Cyclones can remove >90% of particulates above 5 microns at minimal pressure drops of 0.01atm (Rezaiyan and Cheremisinoff 2005). The design of the cyclone is basically driven by the specified limit imposed by the pressure drop and the required efficiency of the particulate matter removal. In most cases, more cyclones are used in parallel to remove the particulates, whereas stricter control is achieved with fabric filters and electrostatic precipitators. Cyclonic particle removal is a commercially mature technology that has found many applications. Especially in biomass gasification it is used as the initial gas cleaning system for the removal of particulates and offers flexibility in operating temperatures.

Barrier filters can be designed to remove any particulate even in the submicron range. The reasons that they have not been widely used are the economic and technical constraints (tar clinging) in large-scale gasification plants. Barrier filters include candle or cross-flow filters (metallic or ceramic), bag filters, and packed bed filters (Stevens 2001). Electrostatic filters have great potential in particle removal, but their use is restricted to large-scale applications due to economic impediments. Wet scrubbers are mainly used for the removal of tars in cold gas cleaning systems but they can successfully remove particles over 1μm with a pressure drop of 2.5 ÷ 25kPa (Stevens 2001). ▶Tab. 13.6 summarizes the basic particle removal technologies according to operating temperature and efficiency.

13.4.1.2 Categories of gas cleaning systems according to operating temperatures

The temperature at which gas cleaning takes place is determined by the appropriate solvents/sorbents and regimes, as well as by the conditioning and requirements of the application. Conventional cold gas cleaning methods take place at low temperatures (<200°C) – at those temperatures the system can be categorized as wet or cold gas cleaning according to the water condensation. Although wet gas cleaning is a mature technology, high energetic losses occur due to the water condensation after syngas cooling and the overall system efficiency decreases. The synthesis of higher alcohols and

Tab. 13.6: Particle removal technologies.

	Efficiency	Temperature	Characterization
Cyclones	Up to 5 microns	Flexible	Mature technology, initial removal
Barrier: ceramic candle filters	Designed according to required efficiency. Limits of pressure drop.	700°C	Fragile, thermal stress limits, life duration
Electrostatic filters		500°C	Only for large-scale applications
Barrier: metallic candle filters	Designed according to required efficiency. Pressure drop limitations.	350°C	Susceptible to corrosion, metal sintering, life duration
Barrier: bag filters		<300°C	Cooling of product gas prior to filter, tar clogging
Wet scrubbers		<100°C	

MeSH require temperatures ranging from 250°C to 350°C (as reported in ▶Tab. 13.5) while the synthesis of H_2O_2, depending on the process followed, requires temperatures of 0–45°C for the anthraquionone process and 40–60°C for the direct process. Based on these specifications, the gas cleaning system should be adjustable to the operating conditions of the gasifier and of the downstream requirements. The different operating temperatures and pressures require different treatments: for example, the state-of-the-art Rectisol™ process (Leibold, Hornung, and Seifert 2008) involves the cryogenic process in a methanol scrubber at −70°C up to room temperature; thus, reheating the product gas for higher alcohol syntheses brings inevitable high exergetic losses. In scrubbing gas cleaning systems, regeneration processes should also be taken into consideration in order to assure that a large amount of solvent is not wasted. Some gas cleaning processes or even downstream applications require a certain amount of steam for higher efficiencies and for eliminating the risk of carbon deposition on catalysts. If the water content has been removed in previous gas cleaning steps, it should be regenerated and added to the product gas steam leading inevitably to efficiency decrease. The high energetic losses caused by the syngas cooling, scrubbing, and compression and the complexity of such systems are the main obstacle for cold gas cleaning. Especially in air-blown gasifiers where energy density is lower due to nitrogen (N_2) content, a large amount of sensible heat is transferred to cool down the product gas volume.

On the other hand, gas cleaning at high temperatures – also reported as dry gas cleaning methods (over 300°C) – overwhelms the drawbacks from the vapor condensation, which occurs in cold-wet gas cleaning and increases the system efficiency. From a thermodynamic viewpoint, hot gas cleaning could favor the synthesis of higher alcohols, H_2O_2, MeSH, and any other syngas application (FT, SNG, GT, ICE). However, hot gas cleaning techniques have not been fully commercially applied due to technical and economical drawbacks. At high temperatures, the removal of particles is accomplished by candle filters, while sorption and catalytic processes are involved for the

other impurities. Candle filters can operate at high temperatures with high efficiency but the life duration of those filters is decreasing according to the operating temperature. In Martin et al. (2002) and Scheibner (2002), candle filters have been reported in IGCC applications to have sufficient removal efficiency durability at 400°C for 2,700 hours and at 285°C for 15,000 hours, respectively.

Comparison between the two main categories of gas cleaning methods, the compromise of warm gas cleaning in the range of 200–500°C seems to be the most promising technology. Warm gas cleaning avoids the great loss of useful heat due to vapor condensation and product gas sensible heat loss during excessive cooling. The dry processes minimize water effluents and there is a high potential for meeting ultra-clean gas cleaning demands. The objective of this conceptual evaluation is to generate a comparison of performance of the state-of-the-art, conventional gas cleaning technology and a novel gas cleaning process that utilizes activated carbon as adsorbents that can operate in warm conditions.

13.4.1.3 Gas cleaning according to syngas impurities

The state-of-the-art gas cleaning systems for the removal of syngas impurities are described in detail in the following section. A summary of the methods is given in ▶Tab. 13.7.

If alkali species are not condensed down and removed with conventional filters, bag filters, or wet scrubbers, in order to avoid sensible heat loss, aluminosilicates like kaolin, bauxite, and clay are excellent sorbents for alkalis at temperatures below 1,000°C (Turn et al. 1998; Punjak and Shadman 1998; Turn et al. 1999).

Biomass feedstock contains small amount of sulfur (▶Tab. 13.1). During gasification it is mainly released in the form of hydrogen sulfide and to a lesser extent carbonyl sulfide and secondary in small amounts as organic sulfur (mercaptanes and thiophenes) (Zwart 2009). For the removal of sulfur species, the conventional flue-gas desulfurization systems used in coal combustion have prohibiting costs for biomass gasification where the sulfur content is lower (Zwart 2009). The most commonly used desulfurization methods are chemical absorption in an alkaline-water solution or in alkanolamines or physical solvents (Rectisol™, Selexol™), catalytic conversion, and solid sorption. Physical absorption such as the Rectisol™ process has high efficiencies when the operation is performed above the pressures of 6–7 bar (Leibold, Hornung, and Seifert 2008). As COS is not present in temperatures above 200°C, it is removed along with secondary sulfur species after the conversion into H_2S with the hydrodesulfurization process using Al-Co-Mo and Al-Ni-Mo catalysts (Stevens 2001; Verelst 1999).

Corrosive chlorine compounds have to be removed because they can react with alkali species or ammonia and form solid salts at low temperatures that result in aerosol formation. Scrubbing is one of the wet gas gleaning methods for removing HCl. Water or alkali solution scrubbers can be used. Water scrubbers can remove up to 500 ppmw. Alkali solution scrubbers are used to effectively remove not only HCl but also sulfur species and CO_2 (Stevens 2001). Oxide and carbonate sorbents belong to dry gas gleaning technologies and can also effectively remove HCl. Sodium carbonate, potassium carbonate, and calcium oxide have been used in many commercial applications. Sodium carbonate is preferred over the others because it does not react and remove CO_2 and has the lowest vapor pressure, similar to NaCl.

Tab. 13.7: Summary of operating conditions of syngas purification technologies.

	Particles Removal	Akali Species	Sulfur Species	Halogen species	Tars	Nitrogen species
HOT	Cyclones, barrier (ceramic candle filters)	Aluminosilicates (kaolin, Bauxite, and clay)	Solid sorbents (Zn, Ce, Co,Fe)		Particle removal techniques, thermal cracking Catalysts (Ni-Fe-dolomite)	Catalysts (Ni-Fe-dolomite)
WARM	Electrostatic filters Barrier-Metallic Candle Filters	Particle removal techniques	Catalysts (Al-Co-Mo, etc.)	Ca, Na, K carbonate based sorbents	Particle removal techniques Activated Carbon	
COLD	Wet scrubbers	Wet scrubbers	Chemical absorption (alkaline/water or alkaloamines)	CRI catalyst dioxine reduction	Particle removal techniques	Wet scrubbers (water)
		Particles removal technique	Physical absorption (Rectisol, Selexol)	Wet scrubbers (water/alkali solution/ OLGA)	Wet scrubbers (water/oil) Activated carbon	Activated carbon

Tar reduction systems can be classified as (1) physical or mechanical tar removal and (2) tar cracking and reforming.

Physical tar removal

Physical methods for tar reduction are combined with the methods for particle removal and involve the use of cyclonic, rotating particle separators; barrier or electrostatic filters; as well as wet scrubbers. Cyclone is not a very efficient technology for tar removal, although tars condense on the particle's surface and hence are removed, sticky tars deposit as well on cyclones' surfaces.

The operating temperature of cyclones also plays a significant role because in high temperatures tars may still exist in vapor phase and, in addition, tar aerosols with small diameters (<1μm) exceed the cyclone's removal capacity. Rotating particle separators (RSP) as reported in Stevens (2001) could not remove tar compounds when they were operated at temperatures above dew points. Electrostatic precipitators (ESPs) can also be categorized in wet tar removal systems because they can efficiently remove only condensate tars. Although they can operate at higher temperatures for particle removal, they can migrate and collect more effectively ionized liquid droplets of tars than vapors. Barrier filters such as bag filters, as described previously, face serious plugging problems due to the high viscous tars, thus a granular packed bed is the most appropriate and widely used method for tar removal.

Activated carbon, sand, and lignite coke can be used to purify the gas stream from tars and particles in different operating temperatures. Wet scrubbers with water and oil have been widely used for the removal of tars and particles from other compounds. Water scrubbers produce a high amount of waste water and require extra water cleaning systems with additional costs and complexity. In oil scrubbers, the treatment of oil and regeneration processes also have a high importance. The OLGA process (Bergman, van Paasen, and Boerrigter 2002) has a significant advantage over rapeseed methyl ester (RME) scrubbers due to the regeneration of the tar-laden oil and the flexibility on the removal of various tar loads. The gasification conditions as well as appropriate modifications in the mechanical design of the gasifier could also be included in physical tar reduction and removal methods (Devi, Ptasinski, and Janssen 2003).

Tar removal by thermal cracking and reforming

Thermal cracking involves the decomposition of tars to lighter gases and oxygenated and refractory tars (Fjellerup et al. 2005). The main drawbacks of thermal cracking are the decrease of the product gas heating value as well as the decrease in the cold gas efficiency of the gasifier system (Stevens 2001). Partial oxidation of tars involves the cracking with oxygen, or, most commonly, air, as an oxidizing agent and employs a catalyst to have a certain selectivity on the tar components (Fjellerup et al. 2005; Milne, Abatzoglou, and Evans 1998). Dolomite, limestone, and olivine sand have been the most known and efficient among the nonmetallic oxides catalytic bed materials (Dayton 2002). Complete dolomite calcination occurs at 800–900°C, therefore, the effective use of this catalyst is restricted at relatively high temperatures and in pressurized gasification due to loss of catalytic activity, but has found use in secondary catalyst beds.

Olivine has shown high catalytic activity and high attrition resistance (Devi et al. 2005). Olivine has similar tar conversion activity to that of calcined dolomite, can

be applied as a primary catalyst, and appears to be an appropriate bed material for fluidized-bed gasifiers regardless of other hot gas conditioning methods (Dayton 2002). Both calcined rocks and olivine sand can be considered disposable and cheap materials, which is the main reason for their wide use.

Among the metal-based catalysts, nickel-based steam reforming catalysts are the most commonly used and have been most effectively applied as secondary catalysts in separate fixed-bed reactors downstream from the gasifier. The main drawbacks of these catalysts are the coke formation and attrition, which leads to the loss of catalytic activity (deactivation) and limited life duration. Sulfur, chlorine, and alkali metals can also poison these catalysts, therefore, it is suggested that they be used as secondary catalysts downstream of primary catalysts. Regeneration processes for the removal of coke formation are applicable in high temperatures and can lead to sintering, phase transformations, and volatilization of nickel. Repeated disposal of spent nickel catalysts is not economical and poses an environmental hazard because of the toxicity of nickel (Dayton 2002). Other metal blends (Co, Mo) and supports such as alumina, zeolites, and mineral olivine are being investigated in order to overcome the life duration barrier due to catalyst poisoning and sintering.

Among the carbon-based catalysts, activated carbon has shown high affinity and adsorption selectivity to hydrocarbons. Efficiencies of activated carbon have been superior to those of dolomite and olivine, reaching the complete conversion of 90g/Nm^3 of naphthalene at 900°C (Abu El-Rub, Bramer, and Brem 2008). These materials are promising because they can be produced from biomass sources; that is, in the biorefinery complex.

▶Tab. 13.8 presents the categorized tar removal methods.

During the processes of gasification and pyrolysis, the major nitrogen species can occur mainly in the form of NH_3, N_2, and some HCN, HNCO, and NOx species. Most of the nitrogen species found in feedstock are converted to NH_3 and N_2 depending on the gasification temperature, while HCN and NO_x species are present at low concentrations (Zhou et al. 2000). The concentration of HCN in biomass syngas can be in the level of a few ppmv (Stevens 2001). HCN can contribute to the deactivation of catalysts or the formation of NOx in the case of combustion; thus, it should be removed in water or caustic wash. The presence of NH_3 in biomass syngas can reach the level of thousands of ppmv (Zhou et al. 2000; Stevens 2001) and it has to be reduced as well: the removal techniques for ammonia can be categorized in either catalytic decomposition (hot gas cleaning) or wet scrubbing (cold gas cleaning). Ammonia removal by wet scrubbers, because it is soluble in water, can be done either in one step simultaneously

Tab. 13.8: Tar removal methods.

Physical Methods	Thermal and Catalytic Cracking Methods
• Cyclones	• Thermal cracking with agents
• RPS	• Plasma-enhanced thermal cracking
• ESPs	• Nickel-based catalysts
• Barrier filters	• Carbon-based catalysts (activated carbon)
• Wet scrubbers	• Iron-based catalysts (olivine)
• Gasification design and operation	• Dolomite catalysts
• Activated carbon (packed barrier filters)	

with the tar removal or in two steps downstream of tar removal. Similar catalysts for the catalytic tar cracking are used for the removal of NH_3 with efficiencies reaching >99% (Stevens 2001). Steam or dry catalytic decomposition of ammonia to form N_2 and H_2 is performed in dolomite, olivine, and nickel-based and carbon-supported catalysts (Xu, Donald, and Ohtsuka 2010).

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14 From Syngas to fuels and chemicals: chemical and biotechnological routes

Marco Ricci and Carlo Perego

14.1 Introduction

Western economy, society, and culture are largely founded on the availability of extremely huge amounts of cheap energy, mostly produced by burning fossil fuels: coal, oil, and gas. It is unlikely that this situation will radically change within a few decades.

Nevertheless, we can not avoid a transition from a fossil fuel–based economy to another one based on different energy sources. Basically, there are two major reasons for this transition:

- the increasing concern about the observed global warming, widely held as a consequence of the increase of atmospheric CO_2 concentration due to fossil-fuel combustion
- the awareness that fossil-fuel reserves are large but not unlimited

In the long term, only the Sun can provide enough energy to satisfy humankind's increasing need for energy. Unfortunately, however, most of the technologies for the exploitation of its energy are still not economical, nor can they be scaled up to the necessary size. Further, to take advantage of solar energy, we still need major technological innovations. In the meantime, a relatively simple (although not so efficient) way to exploit the Sun is the use of fuels derived from biomass. By this approach, we rely on plant photosynthesis for using solar energy to produce organics, including fuels or raw material for them, by reduction of atmospheric CO_2.

The primary products of photosynthesis are carbohydrates, which can be easily converted to ethanol with a technology that was basically already known in protohistoric ages (ca. 2000 BC) as witnessed, for example, by the Bible (Gen. 9:20–24) and the *Odyssey* (Book IX). Many centuries later, Henry Ford proved that ethanol is a valuable fuel for cars, largely used today as a gasoline component, either as such or as its ethyl *ter*-butyl ether (ETBE) derivative.

Plants are also very good at transforming carbohydrates into all the other molecules they need, including, for example, lipids and oils. Oils, in their turn, are very good feed for diesel motors, as was already recognized by Rudolf Diesel himself who, at the Paris Expo of 1900, showed an engine running on peanut oil.

A large part of a plant's biomass, however, is not suitable as a feed for motors or turbines, and in order to take advantage of its energy content, you can just burn it in your fireplace. Alternatively, this "poor" biomass can be broken down thermally to a mixture of very simple molecules that, according to well-known chemistry, can then be reassembled to build molecules of significant interest. Such a mixture, mainly formed by hydrogen and carbon monoxide, is usually referred to as synthesis gas (syngas).

Historically, the availability of syngas played an extremely important role in the development of the chemical industry, which was originally based on coal until well into

the 20th century when oil-based materials became its main feedstocks. Several chemicals, such as aromatics, were accessible by destructive coal distillation. Others were built starting from carbon monoxide and/or hydrogen that, in their turn, were prepared as the syngas mixture by the reaction of coal with steam:

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H_{298\,K} = 131 \text{ kJ/mol} \tag{1}$$

The reaction is endothermic and the needed heat was provided by burning part of the feed. Since different applications usually require a different CO-to-H_2 ratio, the latter can be adjusted by exploiting the water gas shift reaction (WGSR), discovered in 1780 by the Italian chemist Felice Fontana:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298\,K} = -41 \text{ kJ/mol} \tag{2}$$

As already stated, today the chemical industry is firmly based on oil-derived feedstocks. Nevertheless, syngas still retains its importance even if most of it is no longer prepared from coal but through the steam reforming of natural gas over nickel-based catalysts, a mature and most established process:

$$CH_4 + H_2O \leftrightarrow CO + 3\ H_2 \qquad \Delta H_{298\,K} = 206 \text{ kJ/mol} \tag{3}$$

Syngas can also be prepared from biomass, including organic wastes, by so-called gasification, which is basically a careful partial oxidation; that is, a high-temperature reaction with less oxygen, or air, than is needed for complete combustion. Syngas produced by biomass gasification is sometimes referred to as *biosyngas* and, besides carbon dioxide, water, and some methane, also contains characteristic impurities such as HCN, NH_3, H_2S, COS, and HCl, deriving from biomass heteroatoms.

In the following sections, chemical and energy uses of syngas will be briefly reviewed, paying particular attention to biosyngas.

14.2 Uses of syngas

Current uses of syngas can be arranged into three main classes:

- as a chemical feedstock for producing a number of chemical intermediates
- as a fuel by itself (and as a biofuel if biosyngas is concerned)
- as an intermediate for the production of other fuels or biofuels

Main current processes for the production of both chemicals and fuels starting from syngas are summarized in ▶Fig. 14.1 (Wender 1996).

14.2.1 Syngas as a chemical feedstock

Syngas is the obvious key intermediate in the industrial production of hydrogen. Other major chemical applications include methanol and ammonia synthesis and the Fischer-Tropsch reaction. Several other uses of syngas or carbon monoxide can be found in intermediate production and in fine chemistry. The following paragraphs discuss a few of these applications. The Fischer-Tropsch reaction will be discussed later in deeper detail.

Hydrogen production. Hydrogen is one of the most important industrial chemicals. Not only does it find wide application in the production of methanol and ammonia (see the following two paragraphs), but it also turns out to be essential in the hydrotreatment

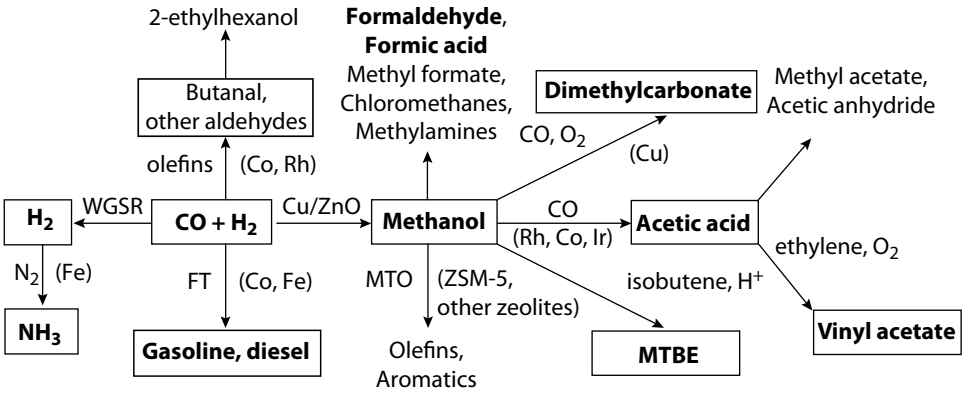


Fig. 14.1: Main current processes for producing chemicals and fuels from syngas.

processes used in refineries, or even in future biorefineries, for the production of high-quality fuels with low environmental impact (e.g. desulfurization and dearomatization) and for the conversion of heavy crude oil and byproducts into middle distillates.

More than 95% of hydrogen production occurs via the steam reforming of methane (Eq. 3), oil, or coal (Eq. 1), all affording syngas that then undergoes the WGSR (Eq. 2). The use of methane, oil, and coal as raw materials account, respectively, for almost 50%, 30%, and nearly 20% of the global hydrogen production.

Methanol and dimethyl ether production. Methanol is another major product of the chemical industry with a global production capacity of 64 Mt/year in 2008. It is largely used in refrigeration systems or as an antifreeze, an inhibitor of hydrates formation in natural gas pipelines, an absorption agent in gas scrubbers, and, to a lesser extent, as a solvent. However, about 70% of its production is used as a raw material for the synthesis of intermediates. The most relevant of them, in order of decreasing importance, are:

- Formaldehyde. It accounts for more than 34% of the world methanol demand and is mainly used in the construction industry to produce adhesives for the manufacture of various construction board
- Methyl *ter*-butyl ether (MTBE). Produced by an acid catalyzed addition of methanol to isobutene. Heterogeneous catalysts are used, for example, acid rains resins. MTBE production accounts for 13% of the global methanol demand. MTBE is largely used as a gasoline additive
- Acetic acid and anhydride. Acetic acid is mainly obtained by methanol carbonylation; that is, by the reaction of methanol with CO. The reaction is catalyzed by salts or carbonyl complexes of cobalt, rhodium, or iridium. Acetic acid production consumes about 10% of the world methanol market. Acetic acid is mainly required for the manufacturing of vinyl acetate monomer or as a solvent for terephthalic acid production
- Methyl methacrylate
- Dimethyl terephthalate

Methanol is produced from syngas by catalytic hydrogenation of carbon monoxide over a zinc/copper-based catalyst:

$$CO + 2\ H_2 \leftrightarrow CH_3OH \qquad \Delta H_{300\,K} = -91\ \text{kJ/mol} \tag{4}$$

Methanol synthesis is exothermic and equilibrium limited, favored by low temperature and high pressure. Commercially, fixed-bed reactors are used, operating at 230–270°C and 50–100 atm.

The stoichiometry requires 2 mole of hydrogen per mol of CO. So, when syngas is prepared, as usual, by steam reforming of natural gas (Eq. 3), some excess of hydrogen is available with respect to Equation 4. In this case, it can be useful to co-feed some CO_2, the reduction of which is still an exothermic reaction, although to a lesser extent compared to that of carbon monoxide:

$$CO_2 + 3\ H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{300\,K} = -49\ \text{kJ/mol} \tag{5}$$

Interestingly, from a mechanistic point of view, it is increasingly accepted that methanol forms almost exclusively by hydrogenation of the CO_2 contained in the syngas or formed upon the WGSR. In fact, it has been shown that the reaction on a conventional methanol catalyst of a CO/H_2 mixture carefully purified from both CO_2 and water affords no or very little methanol (Olah, Goeppert, and Prakash 2009).

Could methanol be produced in sufficient amounts from biomass, the increasing availability of the methanol-to-olefins processes may in principle allow us to re-found on renewable raw materials most of the current chemical industry, which is largely based on olefins (mostly, ethylene and propylene) obtained by the cracking of naphtha.

Finally, it should be remembered that methanol can be dehydrated to dimethyl ether (DME), a chemical with a good potential as a fuel that can be used in power generation and as a blending or substitute of LPG or diesel, due to its very high cetane properties. Moreover, a boiling point of –25°C provides fast fuel/air mixing, reduced ignition delay, and excellent cold starting properties.

Ammonia production. Ammonia is another major product of industrial chemistry. About 1.6% of the world consumption of fossil energy goes into the production of ammonia, which is only exceeded by those of sulfuric acid, ethylene, lime, and phosphoric acid. In 2005 ammonia production was about 119 Mt/year. The most relevant use of ammonia is in the production of fertilizers. In addition, every single nitrogen atom of the industrially produced chemicals comes, directly or indirectly, from ammonia, which is a fundamental building block for the production of intermediates, plastics, fibers, and explosives.

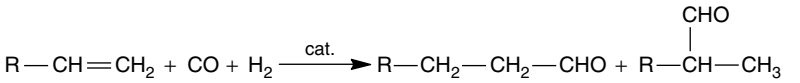
By far the most important method for manufacturing ammonia is synthesis from the elements, which accounts for over 90% of the global production and is still basically run according to the Haber-Bosch process, first industrialized in 1913. Hydrogen and nitrogen in a stoichiometric 3:1 molar ratio are reacted at high pressure (100–250 bar) and temperature (between 350 and 550°C), usually over iron-based catalysts:

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3 \qquad \Delta H_{298\,K} = -46\ \text{kJ/mol} \tag{6}$$

The once-trough conversion is low (20%–30%) and a substantial part of the unconverted gas is recirculated to enhance the total conversion.

The hydroformylation of olefins. Olefins react with syngas in the presence of homogeneous catalysts to afford aldehydes with one more carbon atom. The reaction, discovered in 1938 by the German chemist Otto Roelen at Ruhrchemie, is usually referred to as hydroformylation or oxosynthesis. Cobalt carbonyl or rhodium complexes

are most often used as catalysts. Alpha-olefins can afford two isomeric aldehydes – linear and branched:



(7)

Important oxo products are C_3-C_{14} aldehydes and the most significant among them are, by far, butyraldehydes (butanals), manufactured by propene hydroformylation. Linear butyraldehyde is mostly subjected to aldol condensation on the way to preparing 2-ethylhexanol. Mixtures of aldehydes with 12–15 carbon atoms are used as intermediates in the production of surfactants for detergency. At the end of the 1990s, the total worldwide oxo production capacity for aldehydes and the corresponding alcohols was 6.5 Mt/year.

14.2.2 Syngas as a fuel

Syngas has approximately half of the energy density of natural gas and can be used in steam cycles, gas engines, fuel cells, or turbines to generate power with the co-production of heat.

Syngas, including biosyngas, was also used as a car fuel in Italy during the sanctions that followed the Ethiopia invasion (1935–1936). At that time, many cars were equipped with the *gasogeno*, a cumbersome device in which wood (or coal) was burnt in an O_2-poor atmosphere to provide a mixture of CO, CO_2, N_2, and H_2. This mixture was a cheap fuel that, despite its low energy content, could be used instead of gasoline. Both the power and mileage of modified cars were very poor, and frequent stops were needed to recharge the wood, since 2.5 kg of it provided the energy of just 1 liter of gasoline.

14.2.3 Diesel fuels from syngas: the Fischer-Tropsch process

As already seen, methanol is obtained by the heterogeneously catalyzed hydrogenation of CO. Different catalysts and conditions dramatically change the reaction output: substantial formation of the carbon-carbon bond occurs and linear alkenes and alkanes are the main products:

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \qquad \Delta H_{298} = ca.\ -150\ \text{kJ/mol}_{CO} \tag{8}$$

along with methane formed by CO hydrogenation:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H_{298} = -206\ \text{kJ/mol} \tag{9}$$

The reaction is usually referred to as Fischer-Tropsch (FT), after the names of Franz Fischer and Hans Tropsch, who discovered it in 1923 at the Kaiser Wilhelm Institute (Germany). So far, the process has found only limited commercial application: only particular geopolitical situations favored the realization of industrial plants to produce synthetic fuels and chemicals starting from syngas obtained, in turn, from coal. This was the case of various German companies during World War II and of Sasol in South Africa during the period of the embargo.

The core of any FT process is the catalyst. Few metals show activity in the FT synthesis.

The FT reaction is a sort of polymerization, with an initial adsorption step followed by a chain initiation, chain propagation, and finally chain growth termination. The FT reaction starts with the adsorption of CO on the catalyst surface. Two main classes of mechanisms have been proposed for the following steps: those in which the C-O

bond of carbon monoxide is first cleaved and those in which some hydrogenation by adsorbed hydrogen atoms precedes the C-O cleavage (▶Fig. 14.2).

Most mechanisms, however, converge on the formation of a surface-bound methylene species that would be responsible for the chain growth. It is also generally agreed that the chain propagation is terminated by transfer of a surface hydride to the alkenyl (i.e., by a reductive elimination) with the formation of alkenes that would be the primary products of the reaction, largely produced under kinetic control. According to this scheme, paraffins would result from consecutive hydrogenation reactions (Maitlis and Zanotti 2009).

In this framework, a good catalyst should adsorb both CO, possibly in a dissociative manner, and H_2. Furthermore, since metal oxide formation is always possible under FT conditions, either by dissociative CO absorption or by metal reaction with co-produced water, the metal oxide should be easily reduced. With this respect, transition metals of the third, fourth, fifth, and sixth group are not good FT catalysts because, despite their favorable CO adsorption, they form very stable oxides that are not reduced under FT conditions. Iridium, platinum, and palladium adsorb CO in a nondissociative manner, while metals of groups 11 and 12 hardly adsorb it – none of them is an effective FT catalyst. Nickel, in its turn, has a too high hydrogenation activity and its selectivity to methane is too high for FT purposes. So, the best FT catalysts are based on iron, cobalt, ruthenium, and osmium, with rhenium and rhodium behaving in the middle.

Ruthenium is actually the most active catalyst. However, a single FT plant requires huge amounts of catalysts, and both ruthenium and osmium, not to mention rhodium and rhenium, are too rare and expensive to be used. As a matter of fact, cobalt and iron are the only metals of choice for industrial applications. Iron is economic, but has low selectivity to long-chain paraffins and produces high amounts of olefins and oxygenates. Cobalt is more expensive than iron, but it has a very good selectivity to long-chain paraffins, with limited production of olefins and oxygenates.

To select between cobalt and iron, an important parameter is the carbon feedstock. Iron has a high water-gas shift activity, and for this reason is particularly suitable for hydrogen-poor feedstocks, such as those obtained from coal or biomasses. Cobalt performs better with an almost stoichiometric ratio of hydrogen and carbon monoxide, so it is preferred when the carbon feedstock is natural gas.

A key aspect of a FT process is syngas cleanup. Syngas impurities depend on the carbon source used for its production (natural gas, coal, biomass, or waste) and on the reforming or gasification process. Contaminants include hydrogen sulphide, COS,

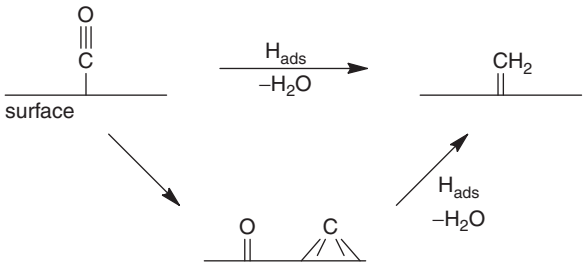


Fig. 14.2: Possible initial steps in FT catalysts.

nitrogen compounds (mainly ammonia and hydrogen cyanide), hydrogen chloride, tars, and particulate. ▶Tab. 14.1 summarizes the typical impurities of a biosyngas.

Possible catalysts involved in an FT process show very different tolerances to these impurities and any FT process fed with biosyngas requires a complex sequence of gas-cleaning steps.

At first, the biosyngas is cooled and filtered to remove particulate and tars in order to avoid obstruction of pipelines and catalytic beds.

Chlorine compounds present in the biomass afford hydrogen chloride upon the gasification. This acid must be removed to a very low level since it can cause both catalyst poisoning and reactor corrosion. It is possible to use water scrubbing or a solid adsorbent in a packed bed with marginal effect on the investment cost. Water scrubbing also removes ammonia and hydrogen cyanide.

Sulphur compounds are the most critical to control since both hydrogen sulphide and COS are strong poisons not only for any FT catalyst but also for the catalyst of the reforming unit, which can be included to convert the methane and light hydrocarbons into CO and H_2, which are always present in the biosyngas and represent a significant part of its heating value. Cobalt or iron catalysts used in the FT section and nickel-reforming catalyst are all quickly poisoned by H_2S or COS, due to the formation of catalytically inactive metal sulphides. ▶Tab. 14.2 shows typical impurity tolerances for FT catalysts.

The activity of cobalt catalysts is almost completely compromised when 2,000 ppm of sulfur have been adsorbed, while iron catalysts resist up to 20,000 ppm.

▶Tab. 14.3 shows the lifetimes of typical Co/Al_2O_3 and precipitated iron catalysts exposed to a syngas with 0.1 ppm of sulfur, as well as the maximum hydrogen sulphide concentration for a catalyst life of 1 year.

Ideally the sulfur content in the syngas must be equal to zero, but gas cleaning is very expensive, so there is some trade-off among the catalyst cost and the investment and operating cost of the gas-cleaning facility. Usually for FT cobalt catalysts a very efficient sulfur removal is justified by their cost and sensitivity to sulfur poisoning. Nevertheless, this is not the only element to consider. For instance, the interaction between sulfur and

Tab. 14.1: Typical impurities of a biosyngas.

H_2S (ppm)	COS (ppm)	NH_3 + HCN (ppm)	HCl (ppm)	Tars (g/Nm^3)
180–350	20–40	2,100–3,000	130–250	2–5

Tab. 14.2: Impurity tolerances of FT catalysts.

Impurity	Tolerance
Sulphur	<4 ppb for Co catalyst; <1 ppm for Fe catalyst
Halides	<10 ppb
Nitrogen (NH_3, NO_x, HCN)	<1 ppm
Particulate	Absent

Tab. 14.3: FT catalysts lifetime.

	Lifetime with 0.1 ppm of H_2S (days)	Maximum H_2S concentration for 1 year catalyst lifetime
Co/Al_2O_3	83	0.02 ppm
Precipitated Fe	830	0.2 ppm

catalyst is also related to the FT reactor fluidodynamics: in a slurry bubble column reactor (SBCR) sulfur is deposited on all the catalyst particles, while in a fixed-bed reactor sulfur is mainly adsorbed on the catalyst at the reactor entrance: the first section of the catalyst bed can therefore behave as a guard bed.

Desulfurization of biosyngas may be obtained by chemical or physical adsorption, or by some combination of the two.

In chemical adsorption, a base reacts with the acid gases to form some complexes that, changing pressure and temperature, can in turn dissociate to release the acid gases. The most-used bases are alkanolamines, particularly ethanolamines. Monoethanolamine (MEA) has been extensively used in the past, but now methyl-diethanolamine (MDEA) is preferred because it has a high H_2S/CO_2 selectivity and is very stable and less corrosive compared to primary and secondary amines.

Processes based on physical adsorption use a solvent to adsorb acid gases by dissolution, typically at subzero temperatures. Acid gases can then be released from the solvent by pressure reduction or temperature change. Physical processes require more electrical energy (for refrigeration) than chemical ones, but the solvents are more stable than ethanolamines, still retaining high selectivity for H_2S and COS over CO_2.

Selexol™ and Rectisol™ are the most widely used physical processes. The former is licensed by UOP (formerly known as Universal Oil Products) while the latter was independently developed by Linde and Lurgi, which use common patents and trade marks.

The solvent used in the Selexol™ process is the dimethyl ether of polyethylene glycol (DMPEG), while Rectisol™ uses methanol, with obvious cost advantages: about 75% of the world's syngas produced from oil residue, coal, and waste is purified by the Rectisol™ process. Solubilities of hydrogen sulphide and COS in methanol, under process conditions, allow a sulfur removal below 0.1 ppmv. Carbon dioxide is also removed under the process conditions.

Carbon dioxide and sulfur compounds can then be selectively desorbed and collected in separate fractions, resulting in a pure CO_2 product (for possible sequestration or use, for example, in urea production) and an H_2S/COS-enriched fraction to be sent to a Claus unit for the recovery of elemental sulfur. Methanol is eventually regenerated by flashing the clean fuel gas at the methanol boiling point.

►Tab. 14.4 compares several processes for the chemical or physical removal of sulfur impurities from a biosyngas.

In the following paragraphs, some considerations will be developed about the possibility to exploit biomass for feeding a gasification/FT plant in order to produce biofuels. First, however, an introduction about the limit of biomass production is appropriate.

Plants build up their biomass through photosynthesis, which is basically a chemical factory based on water splitting, where oxygen is liberated and reduced coenzymes are formed, which eventually reduce CO_2 to carbohydrates. This process, energetically

Tab. 14.4: Comparison of different processes for removing sulfur impurities from biosyngas.

	MDEA	Rectisol™	Selexol™
Solvent	Methyldiethanolamine	Methanol	PEG dimethyl ether
Pressure	Moderate	20 atm	Moderate
Temperature	43°C	–40 ÷ –60°C	–50 °C
H_2S–CO_2 selectivity	Good	High	High
H_2S removal limit	4 ppm	<0.1 ppm	4 ppm
Hydrocarbon adsorption	Low	High	High
Main advantages	• CO_2 removal also possible.	• Very low H_2S removal limit. • Effective for both COS and CS_2 removal.	• Effective for both COS and CS_2 removal.
Main disadvantages	• Limited removal selectivity.	• Higher capital investment. • Higher power request.	• Higher capital investment. • Higher power request.

uphill, exploits sunlight for carbohydrate synthesis, and no energy other than sunlight is required to do the job. Thus, independent from the selected crop, the amount of produced biomass is necessarily limited by the available solar energy.

To start the calculation of this limit, we need to know how much solar energy is available on the Earth's surface: under the best conditions, sunlight provides, as a daily average, not more than 250 watt *per* square meter, or something less than 8,000 mega joule per square meter per year. This sunlight, however, consists of wavelengths spanning from ultraviolet to infrared, whereas green plants are able to exploit only wavelengths in the visible range, especially in the red and blue regions. Estimates of this useful part of the solar radiation (photosynthetically active radiation [PAR]) span from 43% to 50% of the total solar energy reaching the Earth's surface. In the following, the most favorable number of 50% will be adopted.

The energy of 1 mole of photons (1 einstein) at the blue end of the spectrum (400 nm) is 71.5 kcal. The same number for red photons (700 nm) is 40.8 kcal. A mean energy value associated with the PAR of 56 kcal/mol of photons, or 0.235 MJ/mol, can be reasonably assumed.

Thus, the photons within the PAR (i.e. the photons useful for photosynthesis) are, under the best conditions, 16.8 kmol per square meter per year.

To reduce carbon in CO_2 to the oxidation state of formaldehyde, which is the oxidation state of carbon in carbohydrates, 4 electrons are needed. According to the mechanism currently accepted for photosynthesis, 2 photons are needed for each electron, so at least 8 photons are needed for the reduction of a CO_2 molecule.

Thus, the maximum amount of CO_2 that can be fixed is 2.1 kmol per square meter per year, or 92.4 kg per square meter per year.

Since most of the biomass produced by CO_2 fixation is in the form of glucose polymers such as cellulose and starch:

$$CO_2 + 6\ H_2O \rightarrow -(C_6H_{10}O_5)- + 6\ O_2 + H_2O \tag{10}$$

six moles of CO_2 (264 g) can only afford 1 mole of glucose (162 g, if we take into account the loss of a water molecule in the polymerization process) and the upper limit for the biomass production can be put at around 57 kg per square meter per year, or 570 tons per hectare per year.

Actual yields, however, are much lower for several reasons:

- 250 watts per square meter are only available at the tropical belts, where the desert climate prevents the growth of any crop due to water shortage. Furthermore, the number assumes that every day is a sunny day, without taking into account the occurrence of cloudy weather. For most locations, a maximum value of around 200 watts per square meter is probably more safe.
- The PAR is probably closer to 45% of total solar radiation, rather than the 50% value used in the calculation.
- The number of photons needed to reduce a CO_2 molecule is not exactly known: it is not less than 8, but the right number could be 10, rather than 8.
- Last but not least, plants do not synthesize carbohydrates so we can make biofuels for our cars. Plants produce carbohydrates to fuel their own life processes via respiration. Therefore, a substantial quantity of photosynthesized carbohydrate is metabolized by the plants to support their own life.

So, what about actual biomass productions?

On our planet, the most productive photosynthetic organisms are microscopic unicellular algae. Our knowledge about the algal growth in high-density systems is rapidly increasing and dry-matter productivities of 100–150 t/ha per y^{-1} have been already relatively well established. Unfortunately, such high productivity of microalgae and the hope to exploit them as an energy source fuelled enthusiasms that, in several cases, went far beyond any reasonable limit and meaningless figures up to 1,200–1,800 tons of dry matter per hectare per year have been repeatedly claimed. Furthermore, algae exploitation still presents a number of major problems: growing them is still quite expensive and harvesting and processing are both difficult and, again, expensive. Therefore, the following discussion will focus on more traditional crops.

Current productivities of these traditional crops are, by far, lower than those of algae; actually one or even two orders of magnitude lower than the thermodynamic limit. One of the most productive crops, possibly the best one, is the sugarcane that, in Brazil, can produce up to 80–81 tons of dry biomass per hectare per year. Under Mediterranean climates, the champion appears to be the giant reed with up to 40–50 t/ha per year, while other good performers are sorghum, miscanthus, and switchgrass, all with productivities ranging from 15 to 40 t/ha per year.

14.3 The exploitation of the Fischer-Tropsch reaction in a biorefinery

The possibility to produce syngas starting from biomass and the availability of FT technologies for transforming biosyngas into hydrocarbons makes possible the production of fuels, or rather biofuels, with very good properties that are essentially not different from those of diesel and gasoline obtained by oil refining. Processes able to run the whole transformation of biomass into syngas and of the latter into hydrocarbon fuels are usually referred to as BtL (biomass to liquids) processes. Typically, they are able to transform biomass into fuel with an energy efficiency (i.e. fuel heat value/feed heat value) of about 30%.

When evaluating the possibility of building up BtL plants, it should be stressed that FT plants are quite expensive. Integrated BtL plants will be obviously even more expensive, since they also require the gasifier and a complex purification train for the syngas. Significant savings, however, can be obtained by realizing rather huge plants. Commonly used estimates agree on figures of 15–30,000 bpd (barrels per day) as the best choice for a BtL plant or, in more traditional units, 750–1,500 kt/year.

We can now evaluate a possible scenario for the application of the BtL technology, referring to the exploitation of giant reed (*Arundo donax*) farming. A production area with a radius of 20 km has been assumed.

Input data:

Radius of production area: 20 km

Exploited area: 1,257 km^2 = 125,700 ha

Dry biomass productivity: 40 t/ha per year

Harvesting efficiency: 0.8

Dry biomass heat value: 17.4 GJ/t

Energy efficiency of the process: 0.3
Diesel fuel heat value: 37.8 GJ/t

In this case, the biomass production in the exploited area will be 5.03 Mt/year. 4.02 Mt/year could be recovered, corresponding to an energy content of 70×10^{15} J/year, so that we can expect to produce liquids with an energy content of 21×10^{15} J/year, or 556 kt/year, or, finally, about 11,100 bpd. This value is not so different from the low value accepted as economically appealing. In fact, a slightly longer 25 km radius would allow us to produce 873 kt/year, or about 17,500 bpd.

CO_2 can be a significant component of the gas fed to FT plants, particularly when the syngas is obtained by biomass gasification. Any FT-like reaction fed with CO_2 instead of CO (Eq. 11) may provide a route to recycle the CO_2 produced in a number of anthropogenic processes:

$$nCO_2 + 3nH_2 \rightarrow C_nH_{2n} + 2nH_2O \qquad \Delta H_{298} = ca.\ -100\ \text{kJ/mol}_{CO2} \tag{11}$$

Due to the increasing concern about the role of CO_2 in environmental pollution and global warming, considerable effort has been devoted to the study of these FT-like reactions of CO_2.

From the thermodynamic point of view, a CO_2-FT is less favorable than the classical FT process but, nevertheless, is still favorable since additional water is formed, thus providing the chemical energy for the conversion of the very stable CO_2 molecule.

Not surprisingly, CO_2-FT reactions have been mostly studied on cobalt- and iron-based catalysts.

Cobalt catalysts are not satisfactory, since they mostly catalyze the CO_2 hydrogenation (Sabatier reaction) and methane accounts for up to 95% of the organic products:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H_{298} = -165\ \text{kJ/mol} \tag{12}$$

The output of the CO_2-FT reaction is completely different over iron catalysts. At 250°C the product distribution is basically unaffected with respect to that of a classical FT process. Particularly, the selectivity to methane remains relatively low (less than 15%). Activity tests on different iron catalysts showed that, for CO_2 transformation, Al_2O_3 is a better support than TiO_2 or SiO_2 and that alkali (potassium) are essential promoters to speed up both direct and reverse water gas shift reactions (i.e. CO formation if the reactor is fed with CO_2: vide infra) and greatly inhibit the methane formation.

From the mechanism point of view, CO_2 conversion under FT conditions can be, in principle, achieved either through its direct hydrogenation or through a reverse WGSR (Eq. 13) followed by conventional FT conversion of CO.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{13}$$

The latter pathway is supported by increasing evidence provided, for instance, by isotopic experiments (Krishnamoorthy, Li, and Iglesia 2002).

From the process point of view, it has already been remarked that Equation 11 requires more hydrogen than the classical FT process and is therefore less attractive, unless: (1) a cheap source of hydrogen will be available, possibly not involving CO_2 co-production, for example, by splitting of water promoted by sunlight or by hydroelectric, wind, or nuclear power; or (2) the reverse WGSR (Eq. 13) is substituted for a thermal dissociation

of CO_2 to CO at high temperatures (for instance, by a thermochemical solar approach), followed by a standard FT process.

On the other hand, compared to the classical FT process, Equation 11 is less exothermic, thus making easier the temperature control of the reactor, even if CO_2 transformation will likely require high temperatures that favor the reverse WGSR (Eq. 13).

A challenging possibility to improve the performances of CO_2-FT reactions is the use of membranes able to selectively remove water from the reaction medium, thus forcing the reverse WGSR (Eq. 13) and, consequently, the whole process.

In conclusion, an industrial FT-type process fed with CO_2 appears technically feasible. Some iron-based catalyst will probably be the catalyst of choice for such a process. Much optimization, however, is still to be done on issues including, for example, reaction conditions (particularly temperature), catalyst composition, and reactor configuration.

14.4 Can syngas undergo fermentation?

Yes, it can. Although it may appear surprising, syngas can be exploited by few bacterial strains to grow autotrophically on mixtures of H_2 and CO_2 or CO, affording mostly ethanol as the result of the fermentation, although acetic acid (or acetate anion, according to the fermentation conditions) is also co-produced. Work on syngas fermentation started in the late 1980s at the University of Kansas. The microorganisms are obligate anaerobes and the best known among them is a *Clostridium* (*C. ljungdahlii*). The overall transformations are as follows.

Ethanol production:

$$6CO + 3H_2O \rightarrow C_2H_5OH + 4CO_2 \quad (14)$$

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \quad (15)$$

Acetic acid production:

$$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2 \quad (16)$$

$$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O \quad (17)$$

Carbon monoxide is a preferred substrate with respect to the CO_2/H_2 mixture: typical CO conversions for lab scale fermentations are about 90%, while hydrogen conversions are around 70%.

The ratio of ethanol to acetic acid depends on the strain and the fermentation conditions. The microorganisms are inhibited by low pH and high concentrations of acetate ion. When acetic acid is formed, the pH drops and the acetate concentration rises. So, the microorganisms switch to ethanol production to alleviate further stress. Typically, pH is kept at around 4.5 in ethanol production.

Many of the microorganisms are mesophiles or even termophiles, with temperature optimums in the range between room temperature and 90°C. A fairly rich medium is required, with possible contamination problems. However, contamination risks are greatly reduced by the harsh fermentation conditions: high temperatures, low nutrient

levels, and low pH. Furthermore, the high level of carbon monoxide inhibits the growth of methanogenic bacteria.

Syngas purity could not be critical, since some tolerance is expected to sulfur compounds, tars, and other impurities. Published work on this issue, however, is still too sparse for any conclusion to be drawn.

Simple gas-sparged tank reactors, operating either in batch or in continuous mode, can be used. Such an arrangement, however, suffers from low volume productivity, affording dilute ethanol solutions (2% or less). Improvements have been suggested, including a two-stage fermentation: in the first stage, conditions are selected in order to speed up cell growth, while in the second stage they are chosen to maximize ethanol production. Mass transfer between the gas and the liquid phase can limit the reactor performance. Few press releases suggest that ethanol productivities quite close to those of standard alcoholic fermentation (about 10%) have already been attained.

Despite its low concentration, ethanol can be recovered using procedures close to those already in use in the corn ethanol industry; for example, the ethanol/water azeotropic mixture can be distilled overhead, and then water can be removed by an adsorption unit.

The energy efficiency (heat of combustion of products/ heat of combustion of feed) is 0.80–0.81 for Equations 14 and 15 and 0.77 for Equations 16 and 17. These figures are rather low for an anaerobic fermentation: by comparison, the ratio for the glucose fermentation affording ethanol is 0.98.

Although syngas fermentation raised little interest until recently, in the past few years several companies have tried to develop it and few of them (e.g. LanzaTech and Coskata) have started pilot plant productions since 2008 and 2009, respectively. Particularly, the pilot plant built by LanzaTech at BlueScope Steel in Glenbrook, New Zealand, has a 400 liter fermentor with a production capacity of 45 t/y (15,000 gallons) of ethanol, using real waste gas to grow the microorganisms.

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15 Conversion of biomass to fuels and chemicals via thermochemical processes

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15.1 Introduction to biomass thermochemical conversion processes

An approximate 50% increase above the 2002 level is expected in world energy demand, which is currently mainly fulfilled through conventional energy resources such as coal, petroleum, and natural gas. However, all these sources are on the verge of extinction, with an estimated tentative depletion of oil sources in 2050. The global energy crisis, including depleting deposits and the consequent increasing prices of petroleum oil, combined with environmental problems and concerns strongly motivated our society to search for alternative, renewable energy sources and, specifically, liquid transportation fuels. In this respect, biomass is an abundant, inexpensive, renewable energy source expected to play a substantial role in the future global energy balance, leading through its better utilization of the production of renewable fuels and commodity chemicals (Goyal, Seal, and Saxena 2008; Lin and Huber 2009; Huber, Iborra and Corma 2006). Currently, biomass is the fourth largest source of energy in the world after coal, petroleum, and natural gas. It provides about 14% of the world's energy (Saxena, Adhikari, and Goyal 2009) and it is the only renewable source of carbon, which can be converted to solid, liquid, and gaseous products through various processes (Demirbas 2008).

Biomass can provide energy through direct combustion, physical processes, and conversion processes. Physical processes include grinding, drying, filtration, pressing, extraction, and briquetting (Demirbas and Yazıcı 2000). Direct combustion of biomass is known and has been applied for ages, but it is not favored because of a too high moisture content to perform stable combustion. On the other hand, biomass energy density is lower than that of coal, leading to important economic limitations in transportation (Balat 2008a). Biomass conversion may be conducted with two broad approaches: chemical decomposition and biological digestion. The latter approach refers to biological processes and, essentially, microbic digestion and fermentation. The former (thermo)chemical approach for biomass conversion has received special attention because it can lead to useful products and simultaneously contribute to solving the pollution problems that arise from biomass accumulation (Rocha et al. 1999; Witold et al. 2011). Thermochemical conversion of biomass includes gasification, biocarbonization, liquefaction, and thermal decomposition (pyrolysis) processes. In this introduction we will present a short description of the first three processes, since some of them are covered in other chapters of this book. Pyrolysis will be described more extensively in the second section of this chapter.

15.1.1 Gasification

Biomass gasification is a thermochemical process that results in a high proportion of gaseous products and small quantities of char (solid product) and ash (Lappas and

Heracleous 2009). Gasification is widely recognized at present because its end-product gas can find flexible applications by industries or by home users, particularly in decentralized energy production coupled with micro turbine/gas, turbine/engine, boilers, and even fuel cells (Chen et al. 2004). Biomass gasification technologies have historically been based on partial oxidation or partial combustion principles, resulting in the production of a hot, dirty, low Btu gas that must be directly ducted into boilers or dryers. In addition to limiting applications and often compounding environmental problems, these technologies are an inefficient source of usable energy (Balat 2008a). On the other hand, gasification may be defined as that regime in which biomass is degraded by thermal reactions in the presence of controlled amounts of oxidizing agents to provide a simple gaseous phase comprising hydrogen and CO (referred to as syngas), water, CO_2, methane, small or trace amounts of other components, and residues from contained inorganic matter. As compared to the pyrolysis process, gasification in normally carried out at a higher temperature region. An additional difference is that (Maschio, Lucchesi, and Stoppato 1994) in pyrolysis the products of interest are the char and liquids, which as a result of the incomplete nature of the process retain much of the structure, complexity, and signature of the raw material undergoing pyrolysis. The main operating parameters for the gasification process are compared with pyrolysis conditions in ▶Tab. 15.1 (Maschio, Lucchesi, and Stoppato 1994; Balat, Kirtay, and Balat 2009).

Many technologies are available for syngas production (Lappas and Heracleous 2009; Balat, Kirtay, and Balat 2009), while biomass gasifiers can be classified as air-blown, oxygen-blown, or steam-blown; as atmospheric or pressurized; as slagging or non-slagging; as fixed-bed updraft/downdraft; fluidized-bed or entrained flow; and as allothermal (indirect heating) or autothermal (direct heating by combustion of part of the feedstock). Fixed-bed gasifiers have a relatively low throughput and, therefore, they are considered unsuitable for large-scale applications with very strict requirements concerning the purity of the syngas (Wang et al. 2008). On the basis of throughput, complexity, cost, and efficiency issues, circulating fluidized beds (CFB) (Wang et al. 2008; Hamelinck et al. 2004; Tijmensen et al. 2002) and entrained flow gasifiers (Van der Drift et al. 2004) are very suitable for large-scale syngas production. Examples of CFB gasifiers employed for the gasification of biomass that have reached a certain degree of commercialization are the Lurgi CFB process, the Foster Wheeler gasifier, the VVBGC gasifier (constructed under the EU-funded project Chrisgas), and the UCG (Ultra Clean Gas), programmed by VTT, and so on (Higman and van der Burgt 2008). Slagging entrained-flow gasifier manufacturers are Shell, Texaco, Krupp-Uhde, Future-Energy (formerly Babcock Borsig Power and Noell), E-gas (formerly Destec and Dow),

Tab. 15.1: Range of the main operating parameters for the gasification process (Maschio, Lucchesi, and Stoppato 1994).

Parameter	Pyrolysis	Fast Pyrolysis	Steam Gasification
Temperature (K)	675–875	975–1,225	975–1,225
Heating rate (K/s)	0.1–1	250–300	300–500
Solid residence time (s)	600–200	0.1–3	0.5–2
Water/biomass ratio	0.1–2	0.2–0.6	0.8–2

MHI (Mitsubishi Heavy Industries), Hitachi, and CHOREN (formerly UET) (Van der Drift et al. 2004).

Tar formation is one of the major problems that arises during biomass gasification (Pfeifer, Rauch, and Hofbauer 2004). The use of an active bed material as a primary catalyst is the best solution in contrast to the more expensive use of a secondary downstream catalytic reactor. The choice of an appropriate in-bed catalyst is then crucial for the optimization of gasification technology (Pfeifer et al. 2004). Among them, iron- and nickel-based catalysts exhibited the highest initial catalytic activity, but lost their activity well before the char completely reacted (Demirbas 2000). Ni-olivine catalyst has been developed (Courson et al. 2000) to enhance olivine performances in steam biomass gasification by methane and tar reforming, leading to hydrogen production and gas upgrading. The main advantage of Ni-olivine catalyst is its attrition resistance due to strong metal support interactions, permitting its direct use in a fluidized-bed reactor. The main drawback of Ni catalyst's use for hot gas conditioning of biomass gasification product gases is its sensitivity to deactivation, which seriously limits the catalyst's lifetime. Ni catalyst's deactivation is caused by several reasons; for example, sulfur, chlorine, and alkali metals present in gasification product gases act as catalyst poisons. Coke formation on the catalyst surface can be substantial when tar levels in product gases are high. Loss of catalyst activity is apparently due to fouling by carbon accumulation, which blocks access to the catalyst pores (Pfeifer et al. 2004). Ni-based catalysts have proven to be very effective for hot conditioning of biomass gasification product gases above 1,023 K (Pfeifer, Rauch, and Hofbauer 2004).

Syngas production, cleaning, and use were detailed in Chapter 14.

15.1.2 Biocarbonization

Because of the big cubature and small specific gravity, the transport of biomass across far distances is unprofitable; thus, energy plantations and other biomass sources must be placed in a radius of about 100 km from an energy adaptive plant. A solution to this problem is the conversion of biomass into biocarbon, which is pure charcoal and has a considerably greater energy density than biomass. Biocarbon, just as charcoal, is received during biomass warming in the absence of air. It is possible to carry out this process in closed reactors with overcoat heating: $(CH_2O)n \rightarrow nC + nH_2O$. Additional advantages of biocarbon as a fuel are the capability of incinerating it in a traditional carbon boiler without the necessity of modernization, the lack of sulfur in it, and a possibility of obtaining a green energy certificate and the additional profit from increment emissions trading (according to a CO_2 limitation emission program) (Witold et al. 2011).

15.1.3 Liquefaction

Liquefaction is the thermochemical conversion of biomass in the liquid phase at low temperatures (523–623 K) and high pressures (100–200 bar), usually with a high hydrogen partial pressure and catalysts to enhance the rate of reaction and/or to improve the selectivity of the process. The main goal is to reach maximum liquid yields with higher quality than from the pyrolysis process; that is, the product fuel has a higher heating value and lower oxygen content. The lower oxygen content makes the fuel chemically more stable and requires less upgrading to obtain a hydrocarbon product.

During liquefaction the macromolecule compounds in biomass are degraded into small molecules with or without a catalyst in an aqueous medium or using an organic solvent. Thus, obtained small molecules are unstable and reactive and can repolymerize into oily products with a wide range of molecular weight distribution. In the liquefaction process, the micellar-like, broken-down fragments produced by hydrolysis are degraded to smaller compounds by dehydration, dehydrogenation, deoxygenation, and decarboxylation. These compounds, once produced, rearrange through condensation, cyclization, and polymerization reactions, leading to new compounds (Balat 2008b). Liquefaction was initially developed for coal liquefaction. Recently, liquefaction has been used to describe any thermochemical conversion process that primarily yields a liquid tar/oil product.

Pyrolysis and liquefaction processes are sometimes confused with each other, and a simplified comparison of the two follows. Both are thermochemical processes in which feedstock organic compounds are converted into liquid products. In the case of liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds with appropriate molecular weights. With pyrolysis, on the other hand, a catalyst is usually unnecessary, and the light decomposed fragments are converted to oily compounds through homogeneous reactions in the gas phase. The differences in operating conditions for liquefaction and pyrolysis are shown in ▶Tab. 15.2 (Demirbas 2001). The commercial interest in liquefaction is relatively low because the reactors and fuel feeding systems are more complex and more expensive than those used for pyrolysis processes (Demirbas 2000, 2001).

15.2 Pyrolysis

15.2.1 Process overview

As mentioned in Section 15.1, the final products of the biomass thermochemical processes are made up of a volatile fraction, consisting of gases, vapors, and tar components, and a carbon-rich solid residue (Yaman 2004). In contrast to gasification, in which all structural identity is lost in the formation of simple gaseous molecules, pyrolysis potentially offers high yields of liquid products (Sensöz and Can 2002), thus thermochemically converting organic materials into usable fuels. Pyrolysis produces energy fuels with high fuel-to-feed ratios, making it the most efficient process for biomass conversion and the method most capable of competing and eventually replacing nonrenewable fossil fuel resources. Pyrolysis is the technique of applying high heat to

Tab. 15.2: Comparison of liquefaction and pyrolysis (Demirbas 2001).

Process	Temperature (K)	Pressure (MPa)	Drying
Liquefaction	525–600	5–20	Unnecessary
Pyrolysis	650–800	0.1–0.5	Necessary

lignocellulosic materials in the absence of air or in reduced air. The process can produce charcoal, condensable organic liquids (pyrolytic fuel oil or bio-oil), noncondensable gases, acetic acid, acetone, and methanol (Demirbas and Güllü 1998). As a result, the pyrolysis method has been used for commercial production of a wide range of fuels, solvents, chemicals, and other products from biomass feedstocks (Yaman 2004), while a large number of research projects in the field of biomass pyrolysis have been carried out (Balat 2008c).

Pyrolysis lies at the heart of all thermochemical fuel conversion processes and is assumed to become an avenue to petroleum-type products from biomass resources. Pyrolytic oil may be used directly as a liquid fuel, added to petroleum-refinery feedstocks, or catalytically upgraded to transport-grade fuels (Balat 2008c; Demirbas 2003a, 2003b, 2003c). Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: slow pyrolysis (carbonization), fast pyrolysis, and flash pyrolysis. The range of the main operating parameters for pyrolysis processes is given in ▶Tab. 15.3 (Demirbas and Arın 2002). It seems that the currently preferred technology is fast or flash pyrolysis at high temperatures with very short residence times (Balat 2008c).

In slow pyrolysis the use of a slow heating rate permits the production of solid, liquid, and gaseous products in significant portions. The first stage of biomass decomposition, which occurs between 395 and 475 K, can be called pre-pyrolysis. During this stage, some internal rearrangement, such as water elimination, bond breakage, appearance of free radicals, and formation of carbonyl, carboxyl, and hydroperoxide groups, takes place (Demirbas and Arın 2002; Shafizadeh 1982). However, if the aim is the production of mainly liquid and/or gaseous products, a fast pyrolysis is recommended. Typically, fast pyrolysis processes produce about 70 wt. % of liquid bio-oil, about 20 wt. % of solid char, and about 10 wt. % of gases. Flash pyrolysis is an improved version of fast pyrolysis, with extremely high heating rates and reaction times of a few to several seconds.

Since biomass is a mixture of structural constituents (hemicelluloses, cellulose, and lignin) and minor amounts of extractives, each of these components pyrolyze at different rates and by different reaction mechanisms and pathways. It is believed that, as the reaction progresses, the carbon becomes less reactive and forms stable chemical structures; consequently, the activation energy increases as the conversion level of biomass increases (Balat 2008c). Lignin decomposes over a wider temperature range as compared to cellulose and hemicelluloses, which rapidly degrade over narrower temperature ranges, hence the apparent thermal stability of lignin during pyrolysis. Thermal

Tab. 15.3: Range of the main operating parameters for pyrolysis processes (Demirbas and Arın 2002).

	Slow Pyrolysis	Fast Pyrolysis	Flash Pyrolysis
Pyrolysis temperature (K)	550–950	850–1,250	1,050–1,300
Heating rate (K/s)	0.1–1	10–200	>1,000
Particle size (mm)	5–50	<1	<0.2
Solid residence time (s)	450–550	0.5–10	<0.5

degradation properties of hemicelluloses, cellulose, and lignin can be summarized as follows (Demirbas 2000, 2001):

Thermal degradation of hemicelluloses > of cellulose > of lignin

As already mentioned, if the purpose is to maximize the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, short gas residence time process would be required. On the contrary, for a high char production, a low temperature, low heating rate process would be chosen. If the purpose is to maximize the yield of fuel gas resulting from pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred (Demirbas 2006).

15.2.2 Pyrolysis reactors

At present, reactors for flash pyrolysis include different technologies. Traditionally, fixed-bed reactors were used for the production of charcoal. Poor and slow heat transfer resulted in very low liquid yields (Bridgwater 2003). These reactors do not have very high heating rates and are therefore unsuitable for liquid biofuels production. On the contrary, bubbling fluidized beds have many more advantages and they have been widely used in the literature. In bubbling fluidized beds, biomass particles are introduced into a bed of hot sand, fluidized by an inert gas, possibly a recirculated product gas. The high heat transfer rates from fluidized sand cause rapid heating of biomass particles, while some ablation by attrition with the sand particles occurs. The bubbling fluidized-bed pyrolyzer is characterized by simple construction and operation and is a well understood technology (Scott, Piskorz, and Radmanesh 1997; Scott et al. 1999). Bubbling fluidized beds have good temperature control and provide very efficient heat transfer to biomass particles due to high solid density. This process proved to be very efficient for maximum bio-oil yield and for this reason it has been scaled up by companies such as Dynamotive. As we will discuss in Section 15.3, this technology, although suitable for the conventional biomass technology, is very difficult to apply to the biomass catalytic pyrolysis. The reason is that catalyst deactivation usually takes place during catalytic pyrolysis, which makes the catalyst inactive within a very short time. In circulating fluidized bed (CFB) reactors, biomass particles are introduced into a circulating fluidized bed of hot sand. The high heat transfer rates from sand ensure rapid heating of biomass particles, which along with rapid quenching of the pyrolysis vapors results in the maximization of the liquid products. The CFB reactor is quite similar to the bubbling fluidized bed, however, it allows an even better temperature control, it eliminates plugging problems due to excessive coking because of the continuous recirculation of fresh regenerated sand, and it is very suitable for in situ catalytic upgrading of the pyrolysis vapors. The rotating cone reactor is also based in the general CFB concept although very little carrier gas is needed. This technology achieves high heating rates and short residence times (Wagenaar et al. 1994), resulting in small char formation and high liquid yields up to 70 wt. %. BTG in the Netherlands and the University of Twente operate pilot plants based on this design (Prins and Wagenaar 1997; Wagenaar et al. 2001).

Entrained-flow fast pyrolysis is, in principle, a simple technology. However, poor heat transfer between the hot gas and solid particles limits the success of the technology. In the vacuum furnace reactor, the biomass is thermally decomposed under a vacuum.

The vapors produced are quickly removed from the vacuum, and are recovered as bio-oil by quenching. This pyrolysis reactor is characterized by longer residence time of solids and short vapor residence times (Bridgwater, Czernik, and Piskorz 2001; Bridgwater and Peacocke 2000). The main advantages of this technology are the ability to process larger particles than most fast pyrolysis reactors and there is no requirement for carrier gas, a feature that allows for the better use of the gas products. Liquid yields are, however, much lower (30–50 wt. %) as compared to other technologies. The ablative reactor technology is based on impacting biomass particles on a hot reactor surface. NREL (Diebold and Scahill 1988) and Aston (Peacocke and Bridgwater 1994) use this technology. The ablative biomass pyrolysis technology presents several advantages over conventional fluidized-bed reactors (Diebold and Scahill 1988; Peacocke and Bridgwater 1994, 1996), including the fact that no milling of the biomass is required, they have a compact design due to their good heat transfer, and no carrier gases are necessary for the process. Finally, in the screw/augur reactor, hot sand and biomass particles are mixed inside a screw feeder. The screw mixes the sand and biomass and conveys them along. Alternating rpms of the screw feeder allow good control of the reaction temperature and of the solids residence time.

The Chemical Process Engineering Research Institute (CPERI) has developed a pilot plant unit based on the CFB technology. The flow diagram of the unit is shown in ▶Fig. 15.1 (Lappas et al. 2008).

The entire process scheme is divided into five sections: biomass feed, catalyst regeneration, reactor/mixing zone, product stripper – solid/vapor separation, and liquid product recovery. The biomass is loaded at ambient temperature into a feed hopper (D-61) that can be subsequently pressurized. Then the biomass is fed from the feed hopper to the hot reaction section using a screw feeder (SF-61). The solid heat carrier (sand or catalyst) is loaded into the heat carrier vessel or regenerator (D-100). The regenerator is a fluid-bed reactor aiming to burn off the coke that is deposited on the sand and provide the required heat for the cracking of biomass. The sand in this vessel is fluidized with air. A sample flow is continuously taken from the flue gas stream and passed through a CO/CO_2 analyzer to measure in real time the coke deposited on the heat carrier. Solids from the heat carrier vessel pass through a standpipe and slide valve (SV-101), which controls the flow of the hot catalyst toward the reactor. The reactor usually consists of a mixing zone vessel (D-201) and the riser. The mixing zone should be designed to promote intimate contact of hot catalyst, hot fluidizing gas, and biomass in order to have very high heating rates of the biomass particles. Once mixed, the combination is transported out of the mixing zone into the riser (D-202), where the pyrolysis reactions continue to take place. The mixture of biomass pyrolysis vapors and solid heat carrier then enters the cyclonic head of the stripper tangentially where the solids are separated from the pyrolysis vapors. The solids are recirculated in the regenerator, where the coke is burned off the heat carrier, while the pyrolysis vapors go to the final section of the unit, the product recovery system, which encompasses a number of vessels and heat exchangers along with a stabilizer that recovers the produced bio-oil. Finally, the process gases are passed through special devices for the online measurement of the flow of the cracked gases.

The factors of this technology leading to an optimum bio-oil yield include (besides the type of catalyst) the design of the mixing zone to assure the very rapid mixing of biomass particles with the hot sand particles that come from the regenerator, the

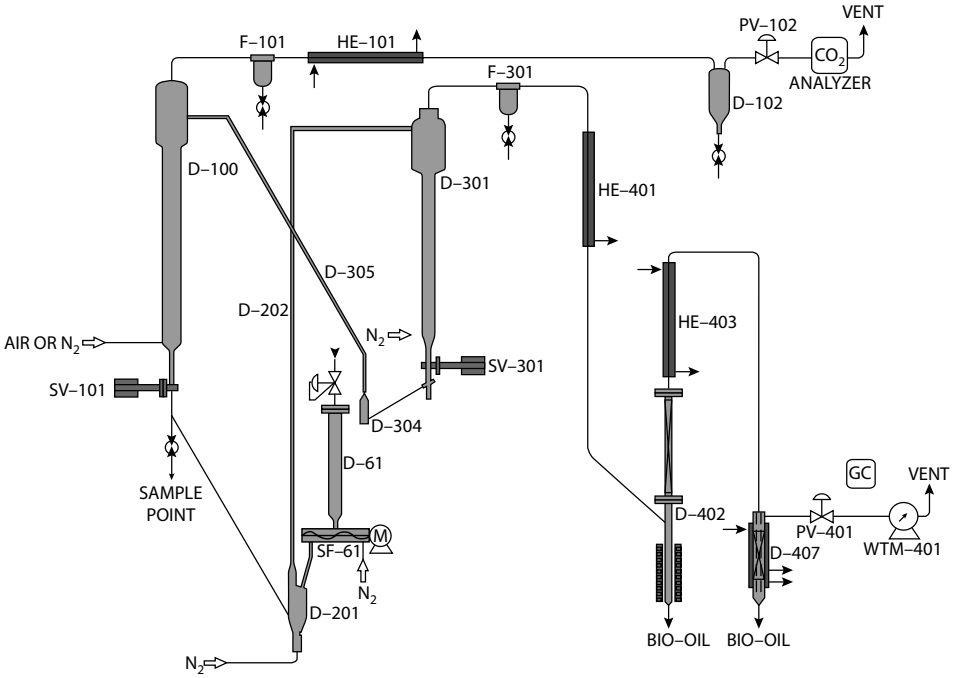


Fig. 15.1: Schematic flow diagram of the CPERI biomass pyrolysis pilot plant unit, depicted in the recirculation of the heat carrier configuration. The following sections of the BIOCAT unit are presented: Heat carrier vessel or regenerator (D-100), biomass feed hopper (D-61), mixing zone (D-201), reactor/riser (D-202), stripper (D-301), lift line injector (D-304), lift line (D-305), bio-oil recovery vessels (D-402, D-407), heat exchangers (HE-101, HE-401, HE-403).

residence time of the vapor in the riser that should be low (<2 s) to avoid overcracking of the vapors, the fast separation of the solid and the vapors in the cyclone-type stripper, and the fast quenching of the produced vapors in the heat exchangers that also favor a high liquid yield. Ensyn and CPERI have developed technology for CFB pyrolysis.

15.2.3 Drawbacks of thermal bio-oil

Bio-oils are dark brown, free-flowing liquids with an acrid or smoky odor. They are complex mixtures of compounds that are derived from the depolymerization of cellulose, hemicellulose, and lignin. Chemically, they comprise of quite a lot of water, more or less solid particles, and hundreds of organic compounds such as acids, alcohols, ketones, aldehydes, phenols, others, esters, sugars, furans, nitrogen compounds, and multifunctional compounds (Milne et al. 1997). Bio-oils are low-grade liquid fuels when compared with petroleum fuels. The poor fuel properties include the complex multiphase structures; high contents of oxygen, water, solids, and ash; low heating values; high viscosity and surface tension; chemical and thermal instability; low pH values; and poor ignition and combustion properties. Specifically, bio-oils appear homogeneous, however, they are multiphase systems that tend to separate into different

phases with time. They are comprised of highly polar compounds such as acids ketones and aldehydes; less polar compounds such ethers, esters, and phenolics; and nonpolar compounds such as hydrocarbons (Lu, Li, and Zhu 2009).

Bio-oils retain most of the original oxygen in the feedstocks. Their oxygen contents vary in the range of 35–60 wt. % (wet basis). Oxygen is present in almost all organic compounds in bio-oils and is considered the main reason for the differences between bio-oils and petroleum fuels. These oxygenated compounds make bio-oils polar, immiscible with nonpolar petroleum fuels, and are responsible for the low heating value, corrosiveness, and instability of bio-oils. Specifically, the lower heating value of bio-oils is around 14–18 MJ/kg, which is much lower than that of petroleum fuels (41–43 MJ/kg). Bio-oils tend to react during storage. Oasmaa and Kuoppala (2003) concluded that the instability of bio-oils can be described as (1) a slow increase in viscosity during storage, (2) a fast increase in viscosity by heating, and (3) an evaporation of volatile components and oxidation in air. The main chemical change is the increase in high molecular lignin materials, with a decrease in aldehydes, ketones, and lignin monomers. The physical changes include the increase in viscosity, density, flash point, and pour point and the decrease in heating value. At elevated temperatures, ageing reactions such as those described previously are accelerated. Bio-oils usually contain about 7–12 wt% acids, and have a pH of 2–4 and a TAN (total acid number) of 50–100. It has been reported that bio-oils are very corrosive to aluminum, mild steel, and nickel-based materials (Aubin and Roy 1990).

Despite these poor fuel properties, bio-oils also have some promising properties. The main reason for the drawbacks of the bio-oils and what separates them from hydrocarbon fuels is the high oxygen content. This is why research on bio-oil production focuses mostly on deoxygenation of the bio-oils in an efficient and low-cost manner.

15.3 Biomass catalytic pyrolysis

15.3.1 Overview of the biomass catalytic pyrolysis process

In biomass catalytic pyrolysis processes, a heterogeneous catalyst is used as a heat carrier in the pyrolysis reactor for the in-situ upgrading of the quality of the bio-oil by minimizing its undesirable properties discussed in the previous paragraphs (high viscosity, corrosivity, instability, low heating value, etc.). Heterogeneous catalysis are widely used in the petrochemical industry for the conversion of heavy oil fractions into lighter fuels and chemicals. This concept is transferred to the biomass pyrolysis process where, ideally, the heavy oxygenated volatiles from the decomposition of biomass are deoxygenated and converted to lighter fuels and chemicals by coming in contact with a suitable catalyst. Ultimately, the goal of the process is to produce a liquid with improved properties that is suitable for combustion in thermal engines or, alternatively, produce a liquid (biocrude) that can be used as a feedstock in modern refineries, much like crude oil. As will be discussed in Section 15.4, there is a research trend today to use bio-oils as feedstocks or co-feedstocks in petroleum streams, co-processing them with hydrocarbon fractions, such as vacuum gas oils, in the fluid catalytic cracking (FCC) and/or hydrotreating (HT) processes of a conventional refinery (Stocker 2008).

An ideal catalyst for the biomass pyrolysis process should produce a high-quality yield of bio-oil with low amounts of oxygen and water, should minimize the undesirable compounds present in the bio-oil, and should exhibit both resistance to deactivation and thermal stability. The reduction of oxygenated species increases the bio-oil's heating value and results in a product with improved physical and chemical properties. Research on development and optimization of new catalysts includes controlled formation of appropriate catalyst particles and tailoring the porosity, acidity, basicity, and metal-support interactions in the candidate catalytic materials (Stocker 2008; Triantafyllidis et al. 2007; Iliopoulou et al. 2007).

Among the various pyrolysis reactors discussed in Section 15.2, the most appropriate technology for catalytic pyrolysis is the circulating fluid-bed technology that includes a regeneration step for the continuous catalyst regeneration. In all other types of reactors, replacing the heat carrier with the catalyst leads to a very fast deactivation of the catalyst. With the CFB technology, the catalyst is mixed with the biomass particles in an always active state. The technology is similar to the FCC process that is the biggest conversion unit of heavy hydrocarbons to lighter fuels in a refinery and is described in ▶Fig. 15.1 (Lappas et al. 2008). The factors of this technology for optimum bio-oil yield are, besides the catalyst type, the design of the mixing zone (which assures the very rapid mixing of biomass particles with the heat carrier particles that come from the regenerator), the residence time of the vapors in the riser (which should be low (<2 s) in order to avoid overcracking), the fast separation of the solid and the vapors in the cyclone-type stripper, and the fast quenching of the produced vapors in the heat exchangers. Ensyn and CPERI have developed technology for CFB pyrolysis. The rotating cone technology developed by BTG also works in circulating mode and thus can be used for catalytic pyrolysis as well.

15.3.2 Catalyst effects on bio-oil yield and quality

Several groups have studied the catalytic pyrolysis of biomass over acidic zeolite catalysts, such as zeolites Y and ZSM-5. These zeolites are both very acidic, the latter being also very shape-selective due to its two-dimensional channel-like pore system. Studying the pyrolysis of wood-based biomass in the presence of H-ZSM-5 suggested that all deoxygenation, decarboxylation, and decarbonylation reactions of the bio-oil components, cracking, alkylation, isomerization, cyclization, oligomerization, and aromatization are catalyzed by acidic sites of the zeolite by a carbonium ion mechanism. However, tar and coke were also formed as undesirable byproducts (Vitolo et al. 2001). In general, zeolite ZSM-5 has been mainly investigated as a catalyst for biomass pyrolysis and is found to dramatically change the composition of the bio-oils by both reducing the amounts of oxygenated compounds in bio-oil via deoxygenation reactions and simultaneously increasing the aromatic species, producing a premium-grade gasoline-type fuel, while also decreasing the bio-oil molecular weight.

Horne and Williams (1994, 1995; Williams and Horne 1995) used a combined fluidized-bed pyrolysis unit in which a fixed catalyst bed was packed on the freeboard of the fluid bed. The pyrolysis oil was highly oxygenated, with a single liquid phase and a significant aqueous content. After catalysis, oil gas and aqueous phases increased at the expense of oil yield, while oil and aqueous were present as two separate phases. The presence of zeolite catalyst reduced the oxygen content in bio-oil from 33% to

13%. Oxygen removal was found to take place as H_2O at lower temperatures and as CO and CO_2 at higher temperatures (Horne and Williams 1994; Williams and Horne 1995). The influence of ZSM-5 catalyst deactivation due to coke formation on the upgraded pyrolysis product was also examined (Horne and Williams 1995). Coke formation was reported to be extremely high during the initial catalytic stages, resulting in catalyst deactivation and, thus, reduced activity and selectivity of catalytic process and also reactor plugging problems. All these results confirm that the circulating fluid-bed technology is the best for catalytic biomass pyrolysis.

Atutxa et al. (2005) studied the catalytic pyrolysis of pine biomass over HZSM-5 zeolite in a spouted bed reactor. They observed that by increasing the amounts of acid sites in the reactor, gas yield increased, while the oil yield decreased, keeping the char yield fairly constant but lower than the one formed in the absence of any catalyst. Catalyst use drastically changed bio-oil composition, as heavy organic fraction was transformed to aqueous fraction via cracking, whereas aqueous liquid fraction underwent dehydration, decarboxylation, and decarbonylation reactions. The application of HZSM-5 was successful in the deoxygenation of the bio-oil.

In another study (Aho et al. 2007), catalytic pyrolysis of pine biomass was successfully carried out in a fluidized-bed reactor using H-beta zeolites. Presence of the H-beta zeolite catalysts decreased the yield of the organic oil (from about 27% to 12%–17% depending on the silica-to-alumina ratio of the H-beta zeolite structure) and increased the percentage of char (from about 15% to more than 20%) as a result of catalyst coking. More water was formed (water yield increased from about 5% to about 13% in most cases) during the catalytic pyrolysis of biomass than in the noncatalytic. The increase of the water content was probably a result of the formation of polyaromatic hydrocarbons. The gas yield was fairly constant in both the catalytic and noncatalytic experiments. The same group reported in a subsequent study the influence of several zeolite structures – Beta, Y, ZSM-5, and Mordenite – on the yields and the chemical composition of the bio-oil from the catalytic pyrolysis of biomass. HZSM-5 zeolite gave the highest liquid yield, while noncatalytic pyrolysis produced roughly the same percentage of oil, but with lower water content. The formation of acids and alcohols over ZSM-5 was lower, while the formation of ketones was higher than that over the other tested zeolites. It was possible to successfully regenerate the spent zeolites without changing their zeolitic structure (Aho et al. 2008).

The significant increase in the production of water and gases at the expense of the organics yield, the formation of undesired PAHs, and the rapid catalyst deactivation by coke deposition are serious drawbacks of the zeolitic material. To overcome these problems, catalysts with a larger pore size than that of ZSM-5 have recently attracted much attention, as they are expected to allow the larger molecules of the pyrolysis products, particularly lignin-derived compounds, to enter, reformulate, and exit the catalyst matrix with less chances of coke deposition and blocking of pores (Pattiya, Titiloye, and Bridgwater 2008). Mesoporous siliceous materials MCM-41, MSU, SBA-15, as well as aluminosilicates Al-MCM-41, Al-MSU, and Al-SBA-15 have been studied by several groups (Triantafyllidis et al. 2007; Iliopoulou et al. 2007; Pattiya, Titiloye, and Bridgwater 2008; Samolada, Papafotica, and Vasalos 2000; Adam et al. 2005, 2006; Antonakou et al. 2006; Nilsen et al. 2007; Lu et al. 2009a, 2009b; Jackson, Compton, and Boateng 2009). Samolada, Papafotica, and Vasalos (2000) used an Al-MCM-41 catalyst for the catalytic pyrolysis of biomass and found that it was characterized by poor hydrothermal

stability and suggested that further optimization of this material is required for the process. Iliopoulou et al. (2007) studied the steam stability of Al-MCM-41 catalysts and observed that moderate steaming resulted in 40%–60% reduction in the catalyst surface area. Al-MCM-41 has been found by several groups to increase the phenol, hydrocarbon, and PAH content of the bio-oil, while they decrease the acid, furan, carbonyl, and heavier compound content (Adam et al. 2005, 2006; Antonakou et al. 2006; Nilsen et al. 2007). Synthesized mesoporous zeolites have been studied as well (Lee et al. 2008; Park et al. 2010). MSU-S materials were studied by Triantafyllidis et al. (2007) and were found to significantly lower the organic fraction of the bio-oil and promote coke formation. They were also very selective toward PAHs and heavier compounds, but produced negligible amounts of acids, alcohols, carbonyls, and a few phenols.

Synthesized mesoporous zeolites have been tested for the catalytic pyrolysis of biomass as well (Lee et al. 2008; Park et al. 2010). Lee et al. (2008) synthesized ordered mesoporous aluminosilicates (MMZ) using commercially available beta and ZSM-5 zeolites. The mesoporous zeolites exhibited excellent hydrothermal stability as compared to Al-MCM-41. In consideration of both their selectivity toward phenolics and organic fraction yield and the reduction of undesirable compounds such as oxygenates, the synthesized catalysts were found to be promising catalysts for the upgrading of bio-oil. Park et al. (2010) synthesized a mesoporous MFI zeolite and compared its catalytic activity to those of conventional HZSM-5 and mesoporous material from HZSM-5 (MMZ_{HZSM-5}). The mesoporous MFI zeolite exhibited the best activity in terms of deoxygenation and aromatization. In particular, high selectivity toward valuable BTX hydrocarbons was observed but organic fraction yield was decreased. Incorporation of gallium into the mesoporous MFI zeolite resulted in less cracking of the pyrolytic vapors, as well as an increase in the organic fraction of bio-oil and resistance to coke deposition.

While solid acid catalysts are the predominately tested materials in the effort to convert biomass to oils using pyrolysis, basic metal oxides have also been studied as catalysts by several groups (Nokkosmaki et al. 2000; Fabbri, Torri, and Baravelli 2007; Lu et al. 2010a, 2010b; Wang et al. 2010; Torri et al. 2010; Chen et al. 2008; Babich, van der Hulst, and Lefferts 2011). ZnO was found to be a mild catalyst that only slightly decreased the bio-oil yield, while it reduced the proportion of the heavy fraction and significantly improved bio-oil stability (Nokkosmaki et al. 2000; Lu et al. 2010a; Torri et al. 2010). CaO was studied by Lu et al. (2010a) and Wang et al. (2010) and was found to be extremely effective in the reduction of acids, while it also promoted the formation of hydrocarbons. Fe_2O_3 promoted the formation of hydrocarbons as well (Lu et al. 2010a). Lu et al. (2010b) also investigated the catalytic effect of TiO_2 Rutile, TiO_2 Anatase, ZrO_2/TiO_2, and their modified with Ce, Ru, and Pd counterparts in a Py-GC/MS system. TiO_2 Rutile, and especially the Pd incorporated counterpart, exhibited very promising effect to convert the lignin-derived oligomers to monomeric phenols and favored the reduction of aldehydes and sugars while increasing the ketones, acids, and cyclopentanones. The ZrO_2/TiO_2 catalysts reduced the phenol and acid yields remarkably, eliminated sugars, and, meanwhile, increased hydrocarbons, light linear ketones, and cyclopentanones. Inorganic additives with different basicity were applied in the pyrolysis of pinewood sawdust by Babich et al. (2011). Strongly basic zeolites have been synthesized from the reaction of zeolites with ammonia at elevated temperatures, providing unique activity and selectivity for base catalyzed reactions (Ernst, Hartmann, and Sauerbeck 2000). Such basic zeolites (e.g. amine-substituted ZSM-5) are suggested

as promising candidate catalysts for biomass conversion to hydrocarbons via catalytic pyrolysis (Carlson et al. 2009). Peralta et al. (2009) investigated the deoxygenation of benzaldehyde on basic CsNaX and NaX zeolites and observed that the direct decarbonylation of benzaldehyde to benzene can be readily promoted over highly basic catalysts containing excess Cs.

A very systematic and comprehensive study regarding the effect of zeolitic catalysts in biomass pyrolysis was performed in CPERI. Most of this work is summarized by Lappas, Iliopoulou, and Kalogiannis (2010), where work even in a pilot plant was carried out. From this study it was concluded that the raw total liquid yield produced from the silica sand was the highest, reaching around 74% wt. The use of catalytic materials does not favor the production of the liquid (bio-oil). The more active the catalyst (higher surface area), the less liquid is produced. Thus, with the less-active catalyst (with TSA around 30 m^2/g) there is a significant drop of 17 wt. % on the liquid yield (from 74 wt. % to 57 wt. %). Catalysts with higher activity (higher TSA) decrease the bio-oil yield but to a lesser extent compared to the lower-activity catalysts. Even with the more active catalyst (TSA = 180 m^2/gr) the liquid yield was dropped from 57 wt. % to 50 wt. %. These experimental results show that the effect of catalyst surface area (or catalyst acidity) on bio-oil yield seems to be exponential. This effect is a general one, since it was found to be valid in all other conditions (temperature, solid/biomass ratio, type of biomass, etc.) tested in CPERI. From the previous CPERI results it can be concluded that the zeolite catalysts cause secondary reactions to the primary pyrolysis products, leading to lighter products and coke. These secondary reactions crack the bio-oil vapor compounds to lighter ones, producing gases, coke, and water. The bio-oil produced from the test with the silica sand contained mainly phenolic and carbonylic compounds (5.8 wt. % and 4.0 wt. %, respectively). Furans, acids, and hydrocarbons were about 2.5 wt. % each. Moreover, the heavy oxygenates and the unidentified compounds were present in significant amounts (14.7 wt. % and 9.7 wt. %, respectively). The catalyst's presence causes a significant change to the bio-oil's composition. By increasing the catalyst surface area, the hydrocarbon concentration increases. With the most active catalyst this concentration is almost double, as compared to that from the nonactive material. Carbonylic compounds were also decreased. However, the most important effect of catalysts is on the heavy compounds, which are drastically decreased. It seems that by using a high-activity catalyst we can minimize these undesirable compounds.

A systematic catalytic pyrolysis study was recently performed at CPERI. In this study 15 catalysts were evaluated using a biomass feed in a small-scale pyrolyzer. The catalytic materials that were used were: an Ecat FCC catalyst (TSA = 176 m^2/g), three commercial ZSM-5 catalysts (TSA = 61, 90, and 138 m^2/g), two MgO materials (TSA = 40 and 52 m^2/g), a NiO catalyst (TSA = 30 m^2/g), four alumina catalysts (TSA = 93, 160, 193, and 205 m^2/g), a zirconia/titania catalyst (TSA = 85 m^2/g), a tetragonal zirconia catalyst (TSA = 120 m^2/g), and a titania (TSA = 8 m^2/g) catalyst and a silica alumina catalyst (TSA = 203 m^2/g). All pyrolysis experiments were performed at 500°C at a bench-scale fixed-bed reactor. The bio-oil produced from each catalyst was fully characterized for its physical and chemical properties.

The water, organic, gas, and solid product yields (wt. % based on biomass) obtained by the in situ catalytic upgrading of lignocellulosic biomass pyrolysis products are given in ▶Tab. 15.4. It is obvious that each catalytic material seems to affect the product yields to a different extent. The highest liquid (58.76 wt. %) and organics (37.37 wt. %) yield

was achieved in the noncatalytic runs (with silica sand). The use of catalysts led to a decrease in the liquid and organic product yields with a simultaneous increase in water yield. Depending on the catalytic material, the liquid yield ranged from 57.19 wt. % to 37.39 wt. % on biomass and the organic yield from 33.21 wt. % to 5.46 wt. % on biomass. The solid products (coke + char) yield also increased, ranging from 22.89 wt. % for the noncatalytic run to 33.85 wt. % on biomass, when using the alumina with the highest surface area. Gas products (mainly CO_2 and CO) increased in the presence of all catalytic materials as compared to the noncatalytic runs.

NiO, zirconia/titania, and MgO (TSA = 52 m^2/g) led to a considerable increase in CO_2 yield from 10.02 wt. % in the noncatalytic runs to 16.15, 15.33, and 14.79 wt. % on biomass, respectively. Catalytic runs led to an increase in CO and other gases as well. Oxygen is removed from the pyrolysis vapors in the form of CO_2 (most preferable), CO, and H_2O. Oxygen removal by formation of CO_2 or CO is in turn more preferable than H_2O formation in order to preserve the hydrogen molecules for hydrocarbon forming reactions (Williams and Horne 1995). It can be observed that the increase of total gas yield for acidic materials (FCC, ZSM-5, alumina, silica alumina) is mainly due to the increase in the production of CO (decarbonylation reactions), while the increase in CO_2 production is relatively low. Basic materials (MgO, NiO, titania, zirconia) on the other hand tend to favor CO_2 production. This is especially noticeable for NiO, zirconia/titania, and MgO and it is attributed to the conversion of acids in the pyrolysis vapors to ketones via ketonization reactions, which release CO_2. NiO was the

Tab. 15.4: Product yield distribution for noncatalytic and catalytic experimental runs (wt. % on biomass).

Catalyst	Organic	H_2O	Total Gas	CO_2	CO	Solid
Silica sand	37.37	21.38	18.35	10.02	6.54	22.89
ZSM-5 (61)	28.40	25.11	20.11	9.55	8.81	26.38
ZSM-5 (90)	27.59	24.95	19.76	9.50	8.56	27.70
ZSM-5 (138)	20.82	27.70	25.86	11.10	11.43	25.70
FCC	23.48	25.89	22.21	10.19	9.59	28.42
Silica alumina	16.53	28.86	25.03	11.49	10.54	29.62
Alumina (93)	16.62	29.08	24.76	11.18	10.17	29.55
Alumina (160)	7.28	32.81	27.90	12.39	10.95	32.05
Alumina (193)	8.46	31.51	26.69	12.72	10.49	33.34
Alumina (215)	5.46	32.47	28.23	12.93	11.12	33.85
MgO (40)	26.77	24.48	22.83	12.64	8.12	25.91
MgO (52)	15.02	29.22	28.30	14.79	9.64	27.50
NiO	22.65	24.81	27.73	16.15	8.87	24.84
Titania	33.21	23.98	18.10	9.63	6.97	24.71
Tetragonal zirconia	29.86	26.25	20.32	11.07	7.53	23.52
Zirconia/titania	13.98	28.25	29.61	15.33	10.10	28.17

most selective catalyst toward CO_2 production, suggesting its incorporation in to other support materials and evaluation of the derived Ni-based catalysts in biomass pyrolysis.

Detailed results of the catalysts' effects on the chemical composition of the bio-oil are presented in Stefanidis et al. (2011). Here we present the catalysts effects into the desirable and undesirable compounds. Aromatic hydrocarbons, aliphatic hydrocarbons, phenols, furans, and alcohols were classified as desirable, while acids, aldehydes, ketones, PAHs, and heavy compounds were classified as undesirable, as previously explained. In addition nitrogen, compounds are classified as undesirable as the presence of nitrogen is unwanted if the bio-oil is to be introduced in a refinery for further processing. As shown in ▶Fig. 15.2, half of the identified compounds in the organic fraction of the thermal pyrolysis bio-oil are desirable and the other half are undesirable. Most catalytic materials managed to reduce the concentration of undesirable compounds and increase the concentration of desirables. Titania and silica alumina were the only materials that showed no significant effect as compared to the noncatalytic run. The bio-oil with the most desirable products was produced with zirconia/titania and the bio-oil with the least undesirable products was produced with alumina (TSA = 215 m^2/g).

The oxygen was removed from the pyrolysis vapors in the form of CO_2, CO, and H_2O, as previously mentioned, which resulted in a subsequent reduction of the total liquid and organic fraction yields due to the transfer of carbon in the gas products, the formation of water, and the formation of coke deposits on the catalyst surface. It is therefore expected that as more oxygen is removed from the liquid organic fraction, less liquid

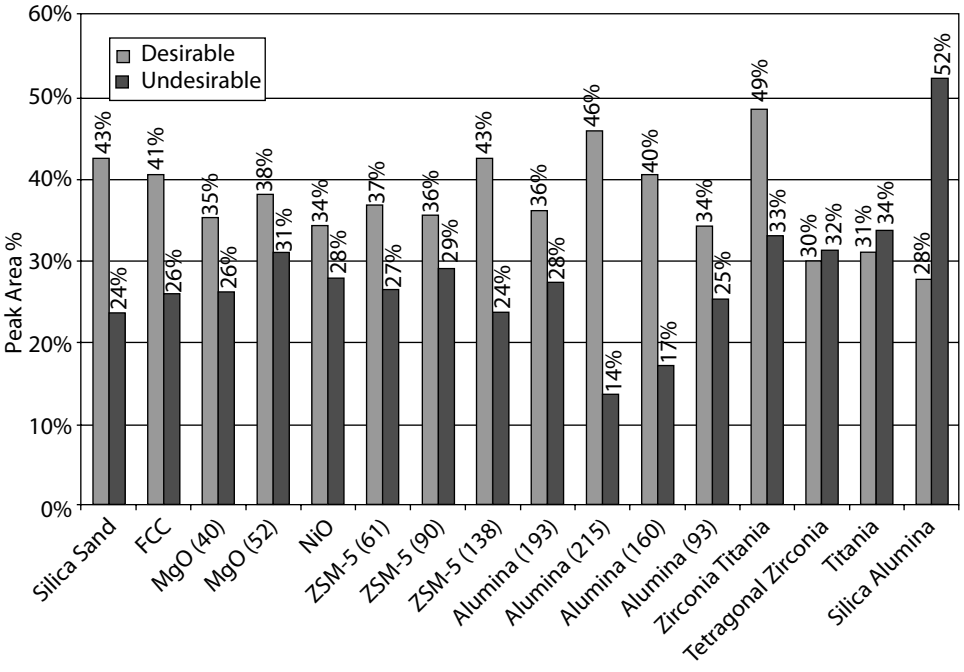


Fig. 15.2: Distribution of desirable and undesirable compounds in the organic fraction of the bio-oil produced with different catalysts.

organic products will be collected. This correlation is shown in ▶Fig. 15.3, which plots the organic fraction yield versus the oxygen content in the liquid organic products. The materials MgO (TSA = 52 m^2/g), zirconia/titania, and alumina (TSA = 93 m^2/g), which produced the most deoxygenated bio-oil, simultaneously yielded the lowest liquid organic products. However, despite this trend, some materials clearly perform much better than others, leading to a simultaneously low oxygen content and an adequate organic yield. For instance, the FCC, ZSM-5 (TSA = 138 m^2/g), and NiO materials all produce about the same amount of organic products, but the FCC's organic fraction is much more oxygenated. Similarly, silica alumina yields much more oxygenated organics than alumina (TSA = 193 m^2/g) and MgO (TSA = 52 m^2/g) despite the fact that their organic fraction yields are about the same. A plot such as Figure 15.3 allows for a quick visual evaluation of the under study candidate catalytic materials in terms of deoxygenation and organic fraction yield; that is, quality and quantity. Materials that rank on the lower right end of the plot are superior to those that rank on the upper left end.

The overall conclusion of this study is that each one of the catalysts tested had different effects on the quality and quantity of the produced bio-oil. The most interesting catalysts were zirconia/titania and the ZSM-5 formulation with the highest surface area. The zirconia/titania material displayed good selectivity toward hydrocarbons and

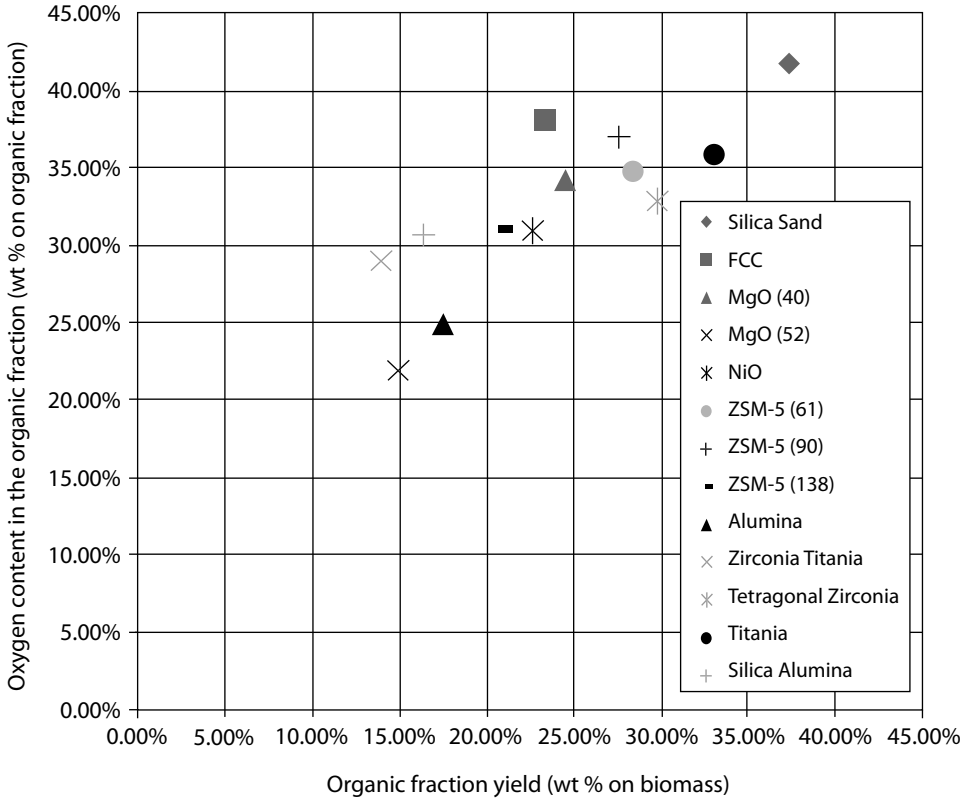


Fig. 15.3: Organic fraction yield versus oxygen content in the organic fraction.

bio-oil deoxygenation, with good selectivity toward phenols, and reduced most of the undesirable compounds. The ZSM-5 material, on the other hand, displayed a significant selectivity toward hydrocarbon production while achieving further reduction of the undesirable compounds. The organic fraction yield was higher than zirconia/titania, although its oxygen content was higher. NiO performed just as well at deoxygenating the pyrolysis vapors, lowering the oxygen content to 30.89 wt. %, while at the same time maintaining a moderately high organic liquid yield (22.65 wt. %). However, NiO displayed no selectivity toward hydrocarbons. The high selectivity of NiO toward CO_2 production renders its incorporation in to other materials an interesting option. Alumina materials with high surface areas exhibited the highest selectivity toward hydrocarbons but suffered greatly from extremely low organic liquid yields.

15.4 Recent developments in bio-oil upgrading for fuels production

A very attractive option for affordable biofuels production that requires little capital cost investment is the use of various, low-cost bio-based liquids into the existing petroleum-refining infrastructure. In this section we will review and discuss recent developments in the upgrading of bio-oil, which is produced in high yields by the biomass fast pyrolysis process. Bio-oils produced by pyrolysis of lignocellulosic biomass (Yaman 2004; Bridgwater 2003) are composed of a complex mixture of more than 400 oxygen-containing compounds and large amounts of water. Bio-oil has been used in boilers and furnaces, and sometimes in diesel engines, for the production of heat or electricity (Bridgwater and Peacocke 2000; Chiaramonti, Oasmaa, and Solantausta 2007) and it is also a very important source of renewable chemicals. However, it cannot be used directly as a transportation fuel due to its high oxygen (40%–50%) and water (15%–30%) content, limited stability, high acidity, and immiscibility with hydrocarbons (Chiaramonti, Oasmaa, and Solantausta 2007; Oasmaa and Czernik 1999). For these reasons, a prior upgrading step is necessary. This upgrading to hydrocarbon transportation fuels requires oxygen removal and molecular weight reduction (Elliott 2007). In this section we review two catalytic methods for this upgrading: catalytic hydrodeoxygenation (HDO) with hydrogen under high pressures and catalytic cracking under atmospheric pressure without hydrogen.

HDO includes reactions such as hydrotreating, hydroprocessing, and hydrocracking, where hydrogen is used to transform the bio-oils. Other reactions also take place during this process, such as decarboxylation, decarbonylation, dehydration, condensation, oligomerization, polymerization, char formation, and so on (Furimsky 2000). The complete deoxygenation of bio-oil by HDO is very costly, since it requires high hydrogen consumptions and high pressures (Samolada, Baldauf, and Vasalos 1998). However, as we will discuss later, partial HDO of bio-oil is a promising route, since the produced bio-oil could be used as a co-feed in the petroleum industry.

The literature for the HDO of bio-oil is extended (see Huber, Iborra, and Corma 2006; Furimsky 1983, 2000; Samolada, Baldauf, and Vasalos 1998; Wildschnt 2009; Zhang et al. 2007; Demirbas 2007, 2009; Bridgwater 1994; Elliott et al. 1991; Bulushev and Ross 2011). In early research studies the researchers applied classical HDS process conditions and catalysts for the HDO of bio-oil. Commercially available refinery HT catalysts were used (sulfided CoMo or NiMo supported on γ-alumina), while

the process was generally performed in two stages: the first in a low temperature range (around 100–200°C) and the second in a high temperature range (350–450°C). The aim of this approach was to reduce the chance of polymerization and thermal decomposition, which forms coke and plugs the reactor (Huber, Iborra, and Corma 2006; Furimsky 2000). The chemical instability of bio-oil is attributed to unsaturated double bonds (olefins, aldehydes, and ketones), which react through condensation reactions and create coke. The reaction was also performed at high H_2 pressure (100–200 bar) to achieve the required level of deoxygenation. Another disadvantage of the process is that it requires a sulfiding agent for retaining the activity of catalysts that contaminates the produced deoxygenated bio-oil. Moreover, poisoning effects of the water on the catalyst supports have also been identified. A lot of work on the HDO of bio-oil has been done in the FP6 Project "BIOCOUP," which was related to "co-processing of upgraded bio-liquids in standard refinery units" (Fogassy et al. 2010). The project demonstrated that HDO of thermal bio-oil is unattractive, since it requires vast amounts of hydrogen and high pressures. It was also shown that a two-stage HDO process is necessary. Taking into account the previously described problems with the classical HT catalysts, a lot of work has been done during the past few years focusing on more stable, selective, and active catalysts (e.g. supported noble metal or bimetallic noble metal catalysts) and on new supports. With these catalysts the focus was on a one-step HDO process at lower pressures and temperatures (Bulushev and Ross 2011).

The upgrading of bio-oil to transportation fuels by using a hydrotreating technology was studied in CPERI/CERTH in collaboration with Veba Oil. This technology was applied in two different modes: a catalytic one using conventional hydrotreating catalysts and a thermal one without any catalyst. The detailed results from this study are presented in Samolada, Baldauf, and Vasalos (1998) and Lappas, Bezergianni, and Vasalos (2009) and concluded, in agreement with the literature, that the catalytic hydrogenation of bio-oil has many operating problems due to plugging of the catalyst bed, although high deoxygenation (>85 wt. %) is achieved. On the contrary, the thermal hydrogenation of bio-oil was feasible without operational problems. The thermal hydrogenation achieved up to 85 wt. % deoxygenation conversion, producing a bio-oil with an oxygen content of about 6.5 wt. %. The yield of the hydtrotreated bio-oil was about 42 wt. % (based on the nonhydrotreated bio-oil). Due to the low oxygen content of the thermally hydrotreated bio-oil (6.5 wt. %), it was possible to separate the product by distillation in a light (LBFPL) and a heavy (HBFPL) fraction with the characteristics presented in ▶Tab. 15.5. From the distillation data of ▶Tab. 15.5 it seems that the light fraction comprised of components mainly in the gasoline and diesel range, and, thus, it could be blended directly with the corresponding petroleum fractions. The HBFPL has characteristics similar to conventional vacuum gas oils (VGOs). As we discuss later, this heavy fraction was used as co-feed with VGOs in the FCC process. The bio-oil co-processing technology proposed by CPERI is presented schematically in ▶Fig. 15.4.

In order to explore the processing of bio-oil via catalytic cracking (using a fluid catalytic cracking unit [FCCU] process), several studies have been carried out in the relevant literature. In some of them, model compounds either in pure form or in a mixture with a VGO were processed in a fixed- or fluid-bed reactor. In others, partially HDO bio-oil was used in mixtures with VGO. The catalysts used in these studies were mainly zeolitic. An excellent review on the catalysts used for this type of upgrading is presented in Bulushev and Ross (2011).

Tab. 15.5: Properties of the two fractions produced after thermally hydrotreated the bio-oil.

Property	Light Fraction	Heavy Fraction
Elemental analysis (%wt)		
C	82.2	84.4
H	10.7	9.4
S	0.01	0.01
N	1.15	0.42
O	6.4	4.9
H2O, %wt	0.99	–
Density, gr/cc (15°C)	0.942	1.036
Distillation (°C, %wt)		
<200	27	
200–350	55.3	23
350–500	17.8	66
>500		11

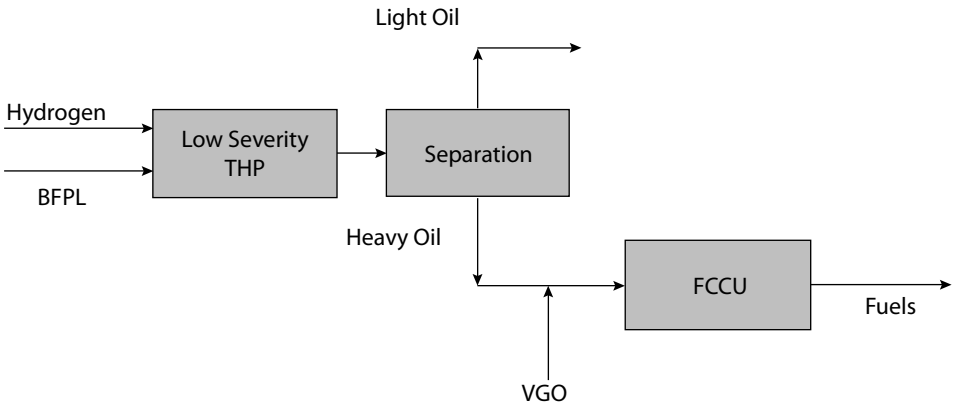


Fig. 15.4: Bio-oil co-processing technology investigated in CPERI. The heavy oil from the low severity hydrotreating process of the bio-oil is introduced to the FCC after mixing with conventional VGO.

In Sharma and Bakhsi (1993) the bio-oil was first separated to remove the nonphenolic fraction (NPF). This was done via extraction with ethyl acetate (EA). The EA-insoluble phase was carefully separated and was termed NPF. This fraction was then processed in a dual reactor system (two fixed-bed reactors in series) with a ZSM-5 catalyst. The temperature in the first reactor was in the range of 340–400°C and in the second was in the range of 350–450°C. The feed was a two-phase mixture with tetralin in a 1:1 weight ratio. It was found that up to 400°C tetralin goes through the reactor without cracking. The results from this study showed that the yield of the desired distillate fraction is

higher with a two-stage system than with one stage only, while the ZSM-5 restricts the formation of polycyclic compounds, responsible for coke formation.

In Gayubo et al. (2004) various model compounds (1-propanol, 2-propanol, 1-butanol, 2-butanol, phenol, and 2-methoxyphenol) were studied with an HZSM-5 catalyst, in a fixed-bed reactor, over a temperature range of from 200°C to 450°C. It was found that for 1- and 2-propanol, at low temperatures (about 250°C), the main reaction is dehydration to propene, which is the primary product. Above 400°C, the amount of C_{5+} paraffins and aromatics increase considerably and a high amount of ethane is also formed. For 1- and 2-butanol at 230°C there is complete dehydration to butenes. Above 300°C, butenes are transformed into higher olefins. Phenol conversion is low even at 450°C. Because phenol was processed with water, coke deposition was low. Methoxyphenol run in a 10% dilution in toluene was found to generate high coke yields (up to 50%) on the acid sites, and this leads to attenuation of the kinetics of coke evolution on the acid sites. Thus it was concluded that moderate acid sites are required for the dehydration of alcohols, while stronger acid sites are required for the reaction steps needed for heavier products. Moreover, it was shown that separation of phenolic products from bio-oil is highly recommended before any processing, since phenolics are the main precursors leading to thermal coking.

In Graca et al. (2009) an experimental study was carried out in a fluid-bed unit, using as catalyst a mixture of 90% Ecat with 10% steam-deactivated ZSM-5. A variety of different feeds were used, such as VGO, VGO + 10 wt. % phenol, VGO + 6.6 wt. % acetic acid, and VGO + 8 wt. % hydroacetone. The VGO contains 1,307 ppm basic and 3,250 ppm total nitrogen. The results when using the Ecat showed that, contrary to the expectations, the coke yield with addition of oxygenated compounds was reduced. It is conjectured that, due to the feed's high nitrogen content, the oxygen-containing species are not preferentially adsorbed because, due to competitive adsorption, nitrogen compounds are attached to the acid sites. Phenol is partially converted to benzene, indicating low phenol reactivity. Depending on the C/O ratio, 50%–80% of phenol was converted. The converted phenol is dehydrated to benzene. Hence, co-processing of phenol might be critical due to benzene content in the gasoline. Acetic acid is converted to methane and CO_2. Hydroacetone mixed with VGO results in a slight increase in fuel gas, LPG, and gasoline yields. The runs with Ecat + ZSM-5 showed that the increase in olefins is less pronounced when oxygenated compounds are present in the VGO. Phenol alkylation and dehydration takes place. ZSM-5 results in a lower increase in coke yield as compared to Ecat with the acetic and hydroacetone mixtures. The opposite is true with phenol-containing mixtures.

In Adjaye and Bakhsi (1995) a bio-oil (with 47.2 wt. % O_2) was catalytically cracked in a fixed-bed reactor at two space velocities (WHSV = 1.8 and 3.6 h^{-1}) and a temperature range of 290–410°C, with a variety of different catalysts. For each run the following products were measured: char, coke, gas, tar, residue, water, and an organic distillate fraction (ODF). With the ZSM-5 catalyst, the conversion of bio-oil to ODF increased to a maximum 29.5 wt. % (WHSV = 1.8) and 33.6 wt. % (WHSV = 3.6) at 370°C. At temperatures above 370°C, ODF consisted mostly of aromatic hydrocarbons and a few phenols. At these temperatures, ZSM-5 was effective in converting oxygenated compounds to mostly aromatic hydrocarbons. With H-mordenite catalyst, a maximum yield of 19.9 wt. % of ODF was obtained at 290°C and at WHSV = 3.6. The analysis of ODF showed that the aliphatic and aromatic hydrocarbons were 10.5 and 11.6 wt. %

on liquid product, respectively. The remaining components were oxygen-containing compounds. At 370°C and WHSV = 1.8 the ODF yield was 11.7 wt. % on bio-oil. The composition of the ODF was 11.5% aliphatics and 46.6% aromatic hydrocarbons with the balance distributed in oxygenated compounds. With silicalite catalyst, the optimum yields of ODF were 8.8% at 330°C and 10.8 wt. % at 370°C (for WHSV = 1.8 and 3.6, respectively). These low yields make silicalite undesirable for bio-oil upgrading. With H-Y catalyst, a maximum yield of 25.5 wt. % ODF on bio-oil was obtained at 290°C and WHSV = 1.8 and 28.4 wt% at 330°C at WHSV = 3.6, respectively. The composition of the ODF in aliphatics was 62.4 wt. % and 41.3 wt. % and in aromatics 6.5 wt. % and 8.4 wt. %, with the balance being various oxygen-containing compounds. The corresponding amounts of char and coke were 27.3%/28.1% and 8.8%/9.4%. This may be due to the catalyst acidity and larger pore size of the H-Y catalyst. With the silica-alumina catalyst, the optimum ODF yields were obtained at 330°C and were 16.9 and 25.2 wt. % at the low and high WHSV, respectively. The reason for the low ODF yields was the high char, coke, and tar formation. The ODF contained mostly aliphatic hydrocarbons (45.1 wt. % and 47.6 wt. % on ODF in the optimum yields), while the aromatics (5.3 wt. % and 7.5 wt. %) and oxygenated compounds make the balance. The overall conclusion from this work was that by changing the type of catalyst it is possible to alter the composition of the desired distillate fraction. The optimum yield of ODF was with HZSM-5, at 3.6 WHSV and 370°C. Under these conditions, approximately 33 wt. % of the bio-oil is converted to an ODF, which contains almost 80% aromatic hydrocarbons.

In a recent study (Wilson and Williams 2003), sulfated zirconia was used as a potential low-temperature catalyst for upgrading biomass pyrolysis oil and was claimed to avoid problems with the polymerization of the biomass oils. On the contrary, sulfated zirconia resulted in both high product yield and low hydrocarbon distribution of upgraded biomass oil.

From all of these studies it becomes clear that, depending on the catalyst used and the type of model compound, there is an optimum operating envelope for producing useful products. Outside this operating envelope there are secondary reactions, which lead to the formation of coke, gases, and secondary products. This operating envelope depends strongly on the type of catalyst. Regarding bio-oil processing with catalysts of varying acidity and pore structure, it has been found that as soon as bio-oil enters the reaction zone, char is formed. The remaining bio-oil is vaporized and it flows to the catalyst surface where additional catalytic coke is formed. The product selectivity depends on the type of catalyst. Maximum hydrocarbon selectivity and deoxygenation is achieved with ZSM-5 catalyst. However, the product is highly aromatic. Silica alumina catalysts result in high coke yields, but the product is made mostly of aliphatic hydrocarbons. From all studies, it becomes evident that phenol compounds are mainly responsible for the large coke formation.

From the work carried out for the BIOCOUP project, the catalytic cracking upgrading of an HDO oil was studied in two recent publications from CNRS and the University of Twente (Fogassy et al. 2010; Mercader et al. 2010). In the CNRS work (Fogassy et al. 2010) an HDO oil (with 21 wt. % O_2) was used as co-feed with VGO (at a 20/80 ratio) in a fixed-bed reactor, simulating FCC conditions and using a commercial FCC Ecat. The results were very promising, since the co-processing of 20% HDO oil with VGO gave gasoline yields comparable to that of the pure VGO. Most of the oxygen in HDO oil was removed as CO_2 and H_2O by means of decarboxylation and dehydration

reactions. However, during co-processing, oxygen removal from HDO-oil oxygenates consumes hydrogen coming from hydrocracking, whereas cracking results in more coke and in more aromatics and olefins in the final products. The results for the University of Twente were consistent with those from CNRS. In this study (Mercader et al. 2010) the HDO oil (with O_2 up to 28 wt. %) was co-processed with long residue at the same ratio (20/80). About 45 wt. % gasoline and 24 wt. % light cycle oil (LCO) was produced with this mixture, without an excessive increase in coke and dry gases. Near oxygenate-free biohydrocarbons were obtained, probably via hydrogen transfer from the long residue.

In CPERI, the co-feeding approach was studied using the thermally hydrotreated heavy bio-oil fraction of ▶Tab. 15.5 as co-feed with conventional VGO in the FCC unit. The experiments were performed in an FCC pilot plant unit using as feedstock a blend of the above heavy hydroteated fraction with conventional VGO. In order to overcome plugging problems, the HBFPL was diluted in LCO in a portion 15/75 by weight, and the mixture was finally blended with a conventional FCC feed (VGO). The total mixture of the LCO + HBFPL was 15 wt. %. For a direct comparison of the effect of bio-oil in the FCC unit, base case tests were initially performed using as feed VGO + 15% LCO and tests with the mixture of VGO + 15% (LCO + HBFPL). All cracking experiments were carried out at 520°C and the main variable of the unit was the C/O ratio, by changing the feed preheat in order to achieve different conversion levels. The catalyst used was a commercial Ecat with a TSA of 158 m^2/g. The pilot plant performance during the tests was satisfactory and without any operating problems (nozzle plugging) during the injection of the bio-oil into the unit. Full experimental results from this study are given in Lappas, Bezergianni, and Vasalos (2009). The study showed that the VGO/HBFPL co-feed produces about 1 wt. % more gasoline (▶Fig. 15.5), which contains more aromatics and less parafins and olefins, as compared to the gasoline produced from pure VGO. Coke is higher (about 0.5 wt. %) when co-feeding (▶Fig. 15.6), as compared with the pure VGO. The experimental results also showed that the presence of bio-oil in VGO reduces the crackability of the feedstock and, thus, at the same C/O ratio the conversion was reduced about 1 wt. % when the HBFPL was present. The previously described tests showed that the suggested option of co-feeding a petroleum VGO with a thermally hydrotreated bio-oil (HBFPL) is technically viable for FCC units running with good quality feedstocks (and thus having excess coke-burning capacity). Certainly, further investigation is needed for this option, regarding mainly the effect of bio-oil concentration (used as co-feed) on the FCC product yields and selectivities.

15.5 Conclusions

The conversion of biomass to fuels and chemicals from thermochemical processes is today technically feasible. The main routes include biomass gasification, following F-T synthesis and biomass pyrolysis. Today, both of these processes are in the demonstration phase. In this chapter we mainly reviewed the biomass pyrolysis process. This is an old technology producing a fuel (bio-oil) that has many drawbacks. This is the reason that it has not yet been commercialized. However, the use of heterogeneous catalysis (biomass catalytic pyrolysis) can assist in the production of a better quality

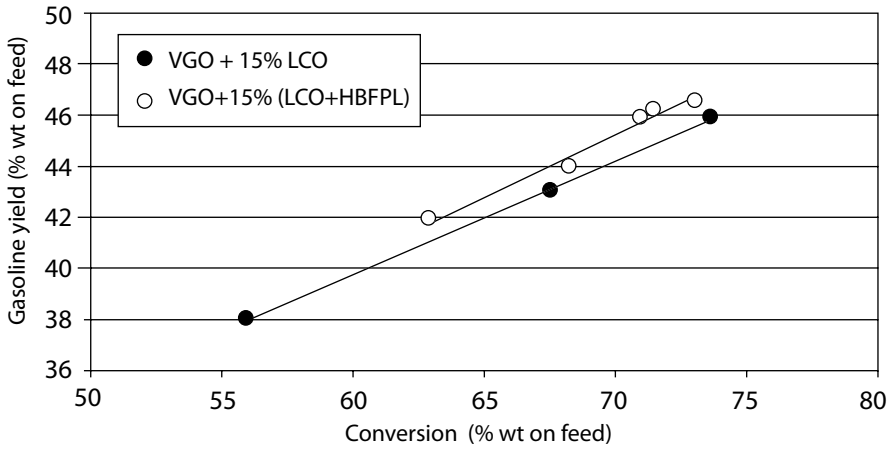


Fig. 15.5: Gasoline yield from co-processing hydrotreated bio-oil (HBFPL) with VGO in the FCC pilot plant.

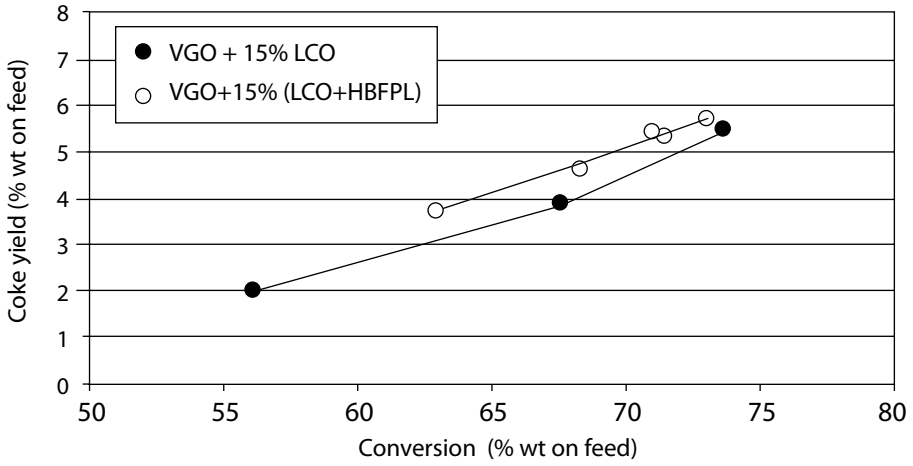


Fig. 15.6: Coke yield from co-processing hydrotreating bio-oil (HBFPL) with VGO in the FCC pilot plant.

bio-oil. Catalytic biomass pyrolysis has recently gained a lot of attention in the literature focusing on new, tailored catalysts. CPERI has developed technology on this process using a circulating fluid-bed reactor. The main conclusion from the research work up to today is that the catalysts affect the primary heavy pyrolysis products by cracking them toward coke and gases. Thus, we can achieve lower yields of bio-oil, but with a better quality, since it contains less heavy oxygenates. Different types of catalysts have already been investigated, both mesoporous and microporous. It seems that the ZSM-5 catalyst is a promising catalyst. Bio-oil upgrading has also been investigated

using hydrodeoxygenation and catalytic cracking processes. For the deoxygenation, the research challenge is to design novel catalysts with enhanced activity and selectivity and, especially, better stability to deactivation. The partially deoxygenated bio-oil is probably the best solution, since it can be further upgraded by co-processing. For the catalytic cracking process the challenge is to design catalysts with less coke selectivity or to use bio-oil with less phenolic compounds.

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16 Cellulosic ethanol production in northern Sweden – a case study of economic performance and GHG emissions

Raphael Slade

16.1 Introduction

The development of ethanol as an alternative transport fuel has been actively promoted in Sweden since 1980. Cellulosic ethanol is a fundamental part of a political vision to increase domestic production of transport fuels and is seen as a natural extension to Sweden's existing forest industries, as a mechanism to support regional development, and as a means of achieving environmental goals. Activity has been concentrated in the Västernorrland area of northern Sweden, which began promoting itself as a biofuel region in 2003. Private, not-for-profit, political, and academic organizations have all played a role in the development of the technology. Most notably, lab-scale development has been led by the Universities of Umeå, Luleå, and Lund, and industrial development and commercial evaluation has been led by a private company: Sekab E-technology.[1]

The focus of Sekab's technical work has been a softwood-to-ethanol pilot plant located in Örnsköldsvik, a coastal town in the Västernorrland region. This plant is a large-scale experimental facility, unique in Europe, and likely to be highly influential if the scale-up of ethanol production from lignocellulosic feedstocks is to be achieved. Nevertheless, in order to take advantage of economies of scale and produce ethanol that is cost competitive with gasoline, a plant that is 100 to 1,000 times larger than the pilot plant will be necessary. One of the key considerations affecting the feasibility and location of such a plant is the availability of biomass feedstocks. Sekab has investigated a number of locations where such a plant could be built, and consider one of the most promising to be another coastal town, Skellefteå, approximately 200 km north of Örnsköldsvik.

The case study presented here briefly summarizes the development of lignocellulosic ethanol technology in Sweden, it outlines the structure of the Swedish forest industry sector, and describes detailed marginal cost and greenhouse gas (GHG) emission curves for feedstock supply in the Skellefteå region. These estimates are then integrated into a combined cost and GHG emission model to obtain estimates of ethanol costs and potential GHG reductions from a plant located in Skellefteå. The results obtained are contrasted with a European base-case scenario. Lastly, the implications for ethanol development in Skellefteå are discussed in the context of the limitations of the assessment.

1 Sekab is a commercial company that imports, upgrades, blends, and distributes ethanol to serve the Swedish transport market. Sekab E-technology is its research and development arm.

16.2 The pursuit of cellulosic ethanol in Sweden

Research into alternative transport fuels in Sweden began following the 1970's oil shocks. At this time the principal motivation was to increase the security of Sweden's fuel supply. Since then, unlike many other countries, government funding for research into alternative transport fuels has been continuous (Zacchi and Lars 2001). When oil prices declined, increasing environmental awareness in Sweden provided sufficient justification for continued investment: initially, concerns about air quality and acidification provided the rationale and, more recently, concerns about the contribution of CO_2 emissions to global warming have come to the fore (Grahn 2004).

Between 1975 and 1985 the research emphasis was on gasification and methanol production, and research into ethanol production from lignocellulosic feedstocks did not start until 1980. During the 1990s research began to concentrate on ethanol: the Swedish ethanol program was established in 1993 and the level of governmental funding was increased. A further increase in funding came in 1998 when the government invested about US$4 million per year for seven years to lower the production cost of lignocellulosic ethanol and to verify the production process at a large scale. Throughout the course of the ethanol program, three different processes were evaluated and categorized according to the hydrolysis process they employed: *concentrated hydrochloric acid hydrolysis* (CHAP), *dilute acid hydrolysis*, and *enzymatic hydrolysis*. Life-cycle analyses were conducted and work on the CHAP process was discontinued because the energy consumption was high and it was considered the least environmentally friendly option. Laboratory-scale investigation of the dilute acid and enzymatic processes continued, most notably at the University of Lund, to the point where it was agreed that research in a larger scale facility – a pilot plant – was necessary to continue the validation of the technology.

In 2002 the construction of a pilot plant began in Örnsköldsvik. The pilot plant was designed to produce ethanol from softwood using the dilute acid process and had a design capacity of two dry tones of woodchips per day; subsequent modifications have extended the facility to permit it to switch between dilute acid and enzymatic hydrolysis operation. The initial investment for the plant was about US$20 million and was funded mainly by the Swedish Energy Council (US$15 million). The facility is owned by the universities of Umeå and Luleå, and Sekab E-technology is responsible for its operation and continued industrial development.

The ethanol pilot plant is a complete, integrated facility, but what made it unique is that it can be run continuously on the same basis as an industrial plant with operators on location 24 hours a day, 365 days per year. (All in all there are about 12 operators, 10 research and development engineers, and 2 operating engineers working with the pilot plant.) Whereas lab-scale experiments are sufficient to investigate discrete process elements and validate flow sheeting models, a continuously operating plant was considered necessary to investigate the stability of the process over time and to predict the process economy of a full-scale plant. For example, stoppages – which are of critical importance to the financial viability of any future production plant – may be caused by problems such as deposits, clogging, and wear and tear. These problems could only be identified during long-term operation, and may be mitigated by improved design and operational control. Scale-up decisions can also be informed by research conducted at the pilot plant, including choice of construction materials, detailed

process design, and operational strategies. During the first two years of the plant's operation the research focus was on accessibility, operational safety, and process monitoring. A large number of process refinements were also made, especially in regard to the hydrolysis reactors.

The ethanol pilot plant has also received a great deal of attention internationally and Sekab regularly gives guided tours of the facility.

Skellefteå is an industrial town on the north coast of Sweden, known for its mining and sawmilling activities. These two industrial branches have given the town its marketing nicknames: *the wood town* and *the gold town*. The location of Skellefteå is shown in ▶Fig. 16.1. The municipal area includes several medium-sized sawmills. There is also a large district heating plant that uses combined heat and power (CHP) technology, and incorporates a wood-pelleting facility, located just outside the town. Despite its heavy industry, there are no pulp or paper mills in the municipality. The nearest are located 70 km to the north in the town of Piteå, which has two plants: Smurfit Kappa Kraft Liner (Europe's largest Kraft liner[2] mill with an output of ~700 ktpa), and SCA Munksund[3] (a medium-sized Kraft liner mill; ~340 ktpa). To the south, it is 140 km to the next pulp

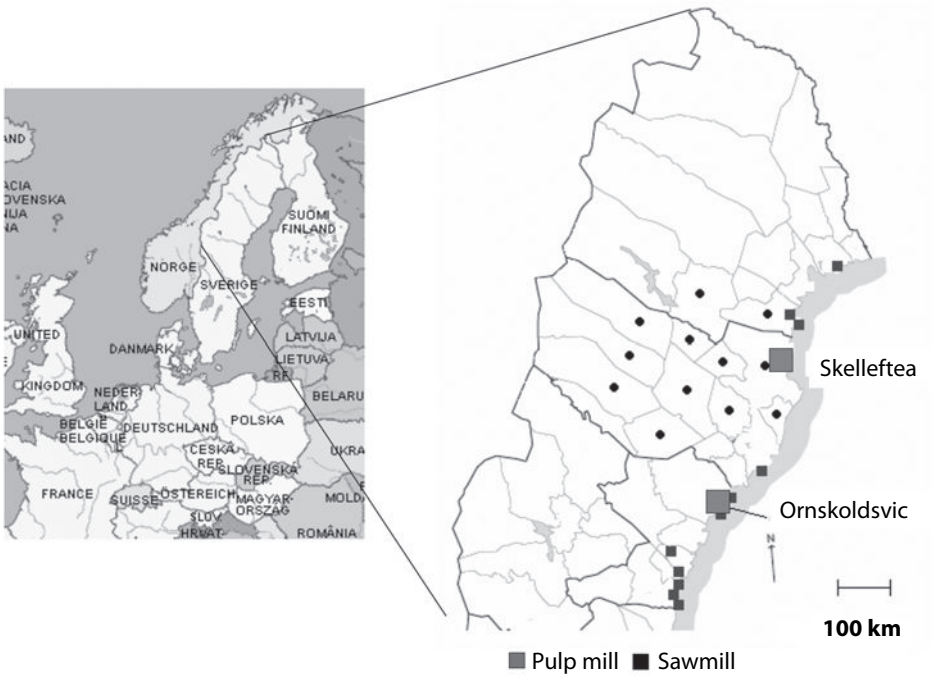


Fig. 16.1: The location of Skellefteå.

2 Kraftliner is a base paper made principally from fresh fibres and used for the manufacture of high quality corrugated packaging. See www.smurfitkappa-kraftliner.com.

3 See www.scacontainerboard.com.

and paper mill: SCA Obbola. This is also a medium-sized mill producing Kraft liner from virgin (~243 ktpa) and recycled (~300 ktpa) fiber.

From the feedstock supply perspective, Sekab considers that Skellefteå is well suited for an ethanol plant. Some competition for feedstocks is inevitable, but integrating ethanol production with the district heating plant could potentially reduce capital and operating costs. Skellefteå also makes sense for political reasons: it is an area targeted for regeneration and is the home of Skellefteå kraft AB, a large municipal utility company that is one of Sekab's principal shareholders.

16.4 Modeling the conversion process

The cost model used here is described in detail in Slade, Shah, and Bauen (2009a, 2009b), and was based on process data for enzymatic and dilute acid conversion developed by Sassner, Galbe, and Zacchi (2008). These conversion processes both use softwood as a feedstock and produce ethanol and lignin. Cost results are described in terms of the *net present value* (NPV) of an ethanol production facility and also the *levelized cost* of ethanol production. The levelized cost of ethanol is defined as the minimum ethanol selling price required to give an NPV of zero. All costs are quoted in 2005 U.S. dollars. Greenhouse gas emissions are quoted in terms of carbon dioxide equivalents.

16.5 The Swedish market for forest products

Sweden has an active forest industry and the market structure reflects this maturity and diversity. In total, there are some 23 million hectares of productive forest land (Skogforsk 2007). These areas hold around 3,050 Mm^3 standing volume; annual growth is about 100–110 Mm^3, of which about 85 Mm^3 is harvested annually (Skogforsk 2006). Forests are typically managed as even-age stands, grown and harvested on a 60–100 year rotation. The main forest industries are sawmills, where saw-logs are processed to sawn wood and byproducts, and the pulp and paper industry, where wood and sawmill residues (chips) are processed to pulp, paper, and other products. The energy sector also uses a large quantity of forest products, principally for CHP and district heating. The general flow of forest materials and products is illustrated in ►Fig. 16.2.

The forest industries are interdependent. Harvesting or thinning a forest stand yields sawlogs, pulplogs, and forest residues, each destined for different process industries. The industries themselves also generate tradable products. For example, processing 100 m^3 of sawlogs will yield about 45–50 m^3 sawn wood, about 35 m^3 wood chips for pulp and paper production, and about 10–15 m^3 sawdust and bark for bioenergy purposes. It is possible, therefore, that the sawmill industry might become a major supplier of biomass to the future ethanol industry but that this may divert biomass from existing industries or energy products. It should also be borne in mind that because sawmill waste is co-produced with timber, the price elasticity of supply will be almost zero, meaning

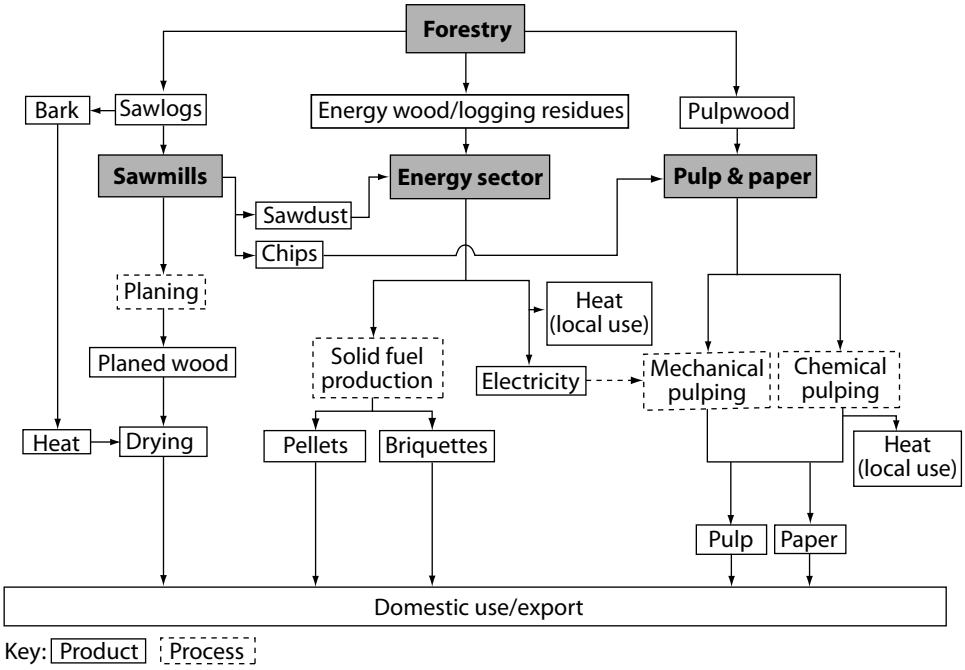


Fig. 16.2: Material flows in the Swedish forest sector.

that the supplied quantities will not increase with increased prices (Grahn 2006; Tilton 1992).

16.5.1 Quantifying feedstock availability

There are no specific studies that investigate feedstock availability for ethanol production, but there are several that analyze feedstock supply for the pulp and sawmill industries. The general conclusion that may be drawn from these studies is that wood is a scarce resource but that it might be possible to increase supply if prices were to increase (Brännlund 1988; Aronsson 1990; Bergman 1991; Brännlund et al. 2004; Ankarhem 2005; Samakovlis 2001; Eriksson 2002; Lundmark and Söderholm 2004). The majority of these assessments are conducted at the national level, and the results cannot necessarily be considered representative of the local situation at Skellefteå. Nevertheless, the general determinants of feedstock supply are expected to be the same at the regional level as at the national level. These determinants are: (1) the cost of logging, (2) transport costs, (3) the forest inventory (i.e. standing volume), and (4) existing demand. Each may be further characterized as follows.

- Logging costs arise from three areas:
  - Harvester cost. This machine fells, de-branches, and cuts the trees into transportable logs. Cost is a function of time, and, because moving the machine and its crane is the most time-consuming factor, productivity is principally a function of

stem size. The larger the stems, the greater the volume of wood produced per unit time. Harvester costs are estimated to be about US$124.h^{-1}.
  - Forwarder cost. The forwarder transports the logs to the closest forest road. Like the harvester, cost is a function of time. Forwarder costs are estimated to be about US$100.h^{-1}.
  - Establishment cost. This is the cost of setting up a new harvesting site and is estimated to be about US$670.discrete harvest area^{-1}.
- Transport costs are principally a function of the time taken to transport each load. This is determined by transport distance, which depends on stand location.
- The forest inventory is a key determinant because it sets the limit of supply as well as the level of economic scarcity. The inventory is a function of average stem size and location.
- Existing demand is essentially determined by existing forest industries, and to a lesser extent, imports.

To estimate the availability of feedstocks in the Skellefteå area, data on stand location and forest inventory were collected from the Swedish National Forest Inventory and databases held by the Swedish University of Agricultural Sciences (SUAS) – Department of Forest Resource Management and Geomatics for the time period 1998–2002. Inventory data was in the form of sample plot information representing 2,327 locations within a 100 km radius of Skellefteå. The maximum sustainable yield (MSY) that could be harvested without violating the standing stock and reducing future growth was obtained from the same source. Production costs and fuel consumption were assumed to be in line with the national average, and estimates from Skogforsk[4] and Eliasson (1999) were used. Using these estimates, marginal cost functions were constructed for the delivery of pulpwood and softwood to a single site in Skellefteå from thinning and final-felling activities. The consumption of fossil fuel was also estimated as a function of the volume of feedstock required.

16.5.2 The marginal cost of feedstocks at Skellefteå

Marginal cost functions for the production and transport of sawlogs and pulplogs are shown in ▶Fig. 16.3. The vertical black lines show the current annual harvest, and the vertical dashed lines show the MSY on a long-term basis.

It can be seen that current harvest levels are already approaching the MSY from both final felling (87% of MSY) and thinning (66% of MSY). In the case of final felling, the cost of meeting additional demand starts at about US$117.odt^{-1} (oven dry tones), rising to about US$144.odt^{-1}, and a total of 187 kodt are available. In the case of thinning, the cost of meeting additional demand starts at about US$57.odt^{-1}, rising rapidly to US$150.odt^{-1}, and a total of 183 kodt are available. The slope of the cost curve for thinning rises more rapidly than for final felling because thinning is associated with longer forwarding distances and smaller stem sizes. The fact that thinning initially yields wood at a lower cost than final felling reflects the relatively high level of competition for feedstocks in

4 Skogforsk (the Forestry Research Institute of Sweden) is the central research body for the Swedish forestry sector: www.skogforsk.se.

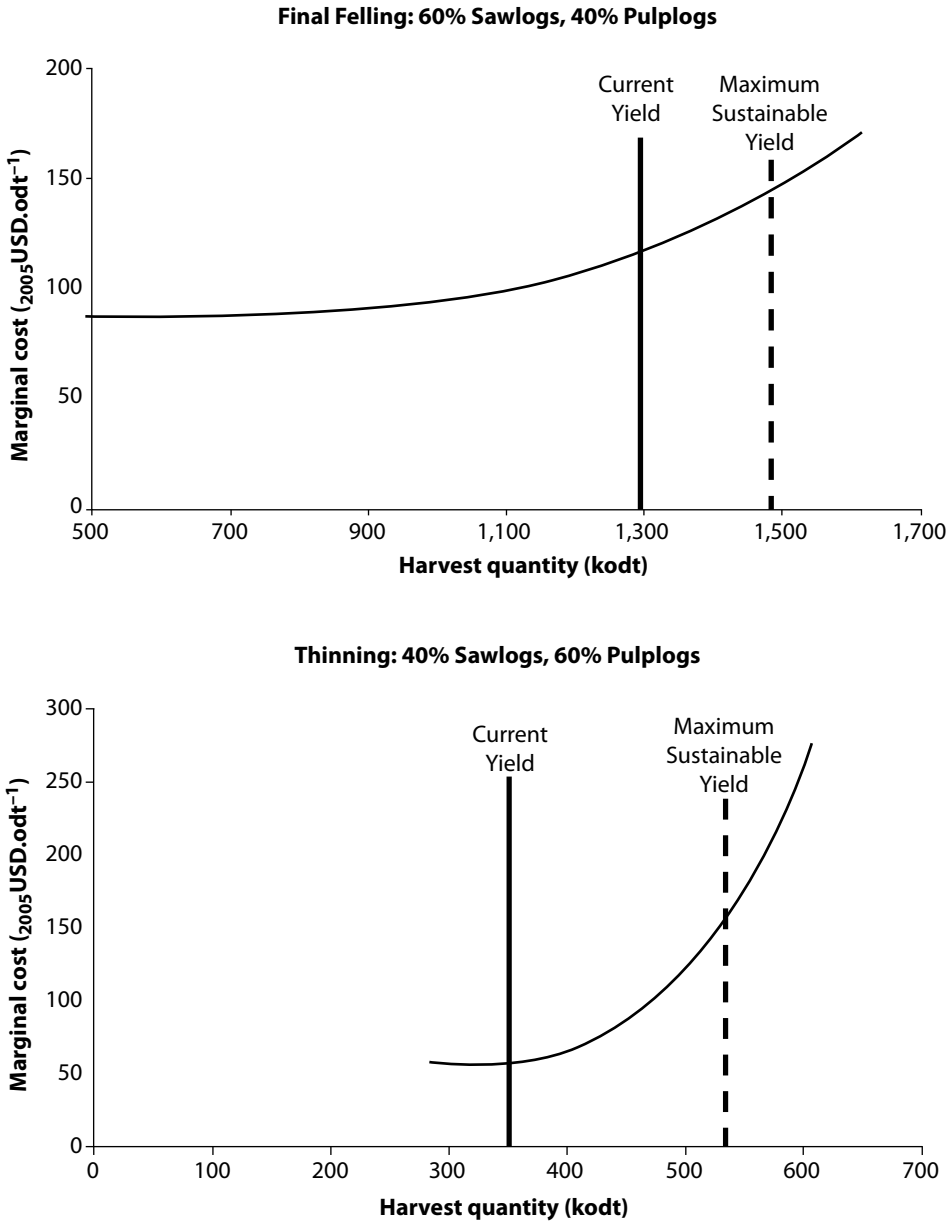


Fig. 16.3: Marginal cost of feedstock supply – final felling and thinning.

the Skellefteå area. Despite the initial cost of production being lower, thinning is less profitable than final felling because fewer sawlogs are produced.

Average diesel consumption and corresponding GHG emissions are shown as a function of additional demand in ▶Fig. 16.4. In the case of final felling, average emissions from fuel consumption vary from about 94kgCO_2e.odt^{-1} at the current level of demand,

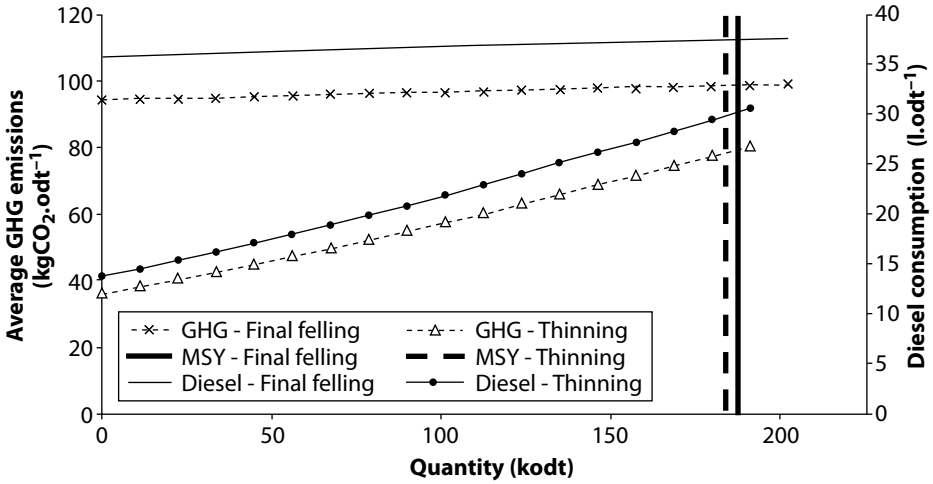


Fig. 16.4: Average GHG emissions and diesel consumption from final felling and thinning as a function of additional demand.

to about 98kgCO_2e.odt^{-1} at the maximum sustainable yield. In the case of thinning, average emissions start at about 36kgCO_2e.odt^{-1}, rising to about 78kgCO_2e.odt^{-1} at the MSY. The lower embodied GHG emissions associated with thinning relative to final felling reflects the situation on the ground: there are more stands that may be thinned than felled and they are closer to the proposed plant.

16.5.4 Integrating Skellefteå feedstock data into the cost and GHG models

A cellulosic ethanol plant located in Skellefteå would compete with existing forest industries for wood; consequently, in the long term, the average price for all industries might be expected to increase. To integrate Skellefteå feedstock costs into the cost model, however, it was assumed that the cost of additional supply would be borne by the ethanol plant alone. This is a worst-case scenario, but it is also representative of the local situation where incumbent industries have long-term contracts for feedstock supply. A further assumption was that the ethanol plant would use both the pulplogs and sawlogs from additional felling and thinning activities; this increases the total volume of feedstocks available but does not change the cost of production for any given quantity. Because feedstocks from thinning cost less to produce, it was assumed that thinning would be carried out up to the MSY prior to additional final felling being undertaken.

The same assumptions were applied when estimating the GHG emissions; that is, GHG emissions attributable to increased feedstock supply were borne by the ethanol plant alone. To complete a GHG estimation, however, it is also necessary to apportion the fossil GHG emissions between the two principal products: ethanol and solid fuel. The method used here was to apportion the fossil GHG emissions between the ethanol and the residual solid fuel in proportion to energy content (although it should be noted that a range of alternative allocation methodologies could be justified).

The results for the Skellefteå case study are contrasted with the results obtained from a base-case scenario that uses European average data. The differences in the underlying

Tab. 16.1: Skellefteå case-study and base-case assumptions.

	Skellefteå	Base-case
Processes considered	Dilute acid (DA)/enzymatic hydrolysis (EH)	Dilute acid (DA)/enzymatic hydrolysis (EH)
Finance	*N*th plant (discount rate = 6%)	*N*th plant (discount rate = 6%)
Feedstock price	Skellefteå-specific: varies as a function of quantity	EU average – mid-range estimate (US$74.odt^{-1})
Feedstock – embodied GHG	Skellefteå-specific: varies as a function of quantity	EU – average (46kgCO_2.MWh^{-1})
Purchased electricity – embodied GHG	Sweden average (44kgCO_2.MWh^{-1})	EU average (340kgCO_2.MWh^{-1})

assumptions are listed in ▶Tab. 16.1. For both cases the same capital costs and process yield assumptions are used, based on the assumption of a stand-alone plant. It has already been noted, however, that ethanol production at Skellefteå could potentially be integrated with the existing CHP plant and that this could reduce capital and operating costs. The extent to which integration could reduce costs is an interesting area for further investigation. A brief and qualitative discussion of the opportunities for integration is presented further on.

16.6 Results

▶Fig. 16.5 shows how the levelized cost of ethanol changes with plant capacity for both the dilute acid and enzymatic processes and for the base-case and Skellefteå scenarios. The levelized cost of ethanol produced in the base-case scenario falls as capacity increases for both process types. In contrast, the levelized cost of ethanol produced at Skellefteå reaches a minimum of US$0.80.l^{-1} for the enzymatic process, and US$00.95.l^{-1} for the dilute acid process, at a plant capacity of about 24odt.h^{-1}; this optimum capacity corresponds to the use of all available feedstocks from thinning.

From these results, it is clear that feedstock constraints are a genuine limitation on plant size in Skellefteå. It is also apparent that if the market value of ethanol remained constant at US$0.65.l^{-1},[5] then even at the optimum size, a stand-alone plant would require additional subsidy, or cost reduction through technical improvement, in order to compete with gasoline. The market value ethanol in 2008, however, was considerably higher than in 2005, and, if the existing subsidy for ethanol were maintained, an oil price of US$90.barrel^{-1} would correspond to a market value of ethanol of about US$0.81.l^{-1}. At this price a stand-alone ethanol plant using the enzymatic process would be borderline profitable. This is illustrated graphically in ▶Fig. 16.6.

5 Its estimated value in 2005 based on an average wholesale price of gasoline of US$0.43.l^{-1} and an average subsidy for ethanol in the EU of US$0.22.l^{-1}.

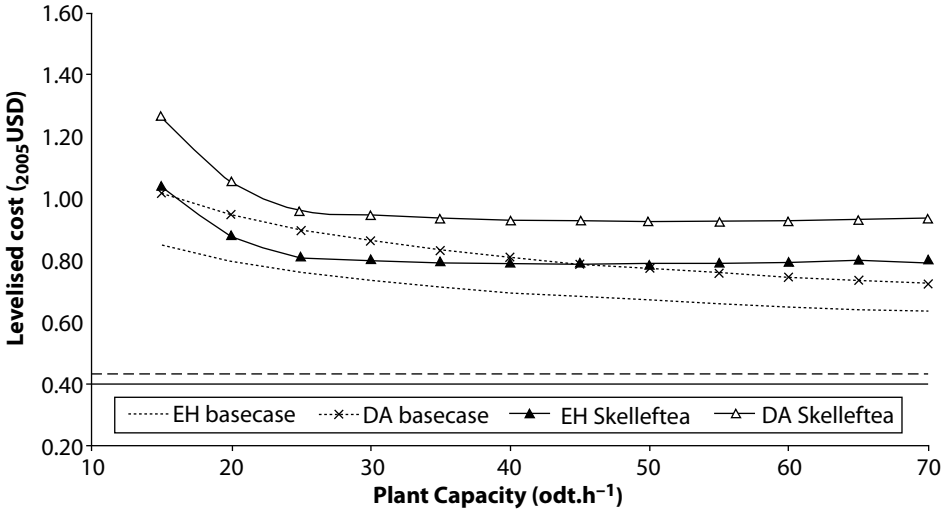
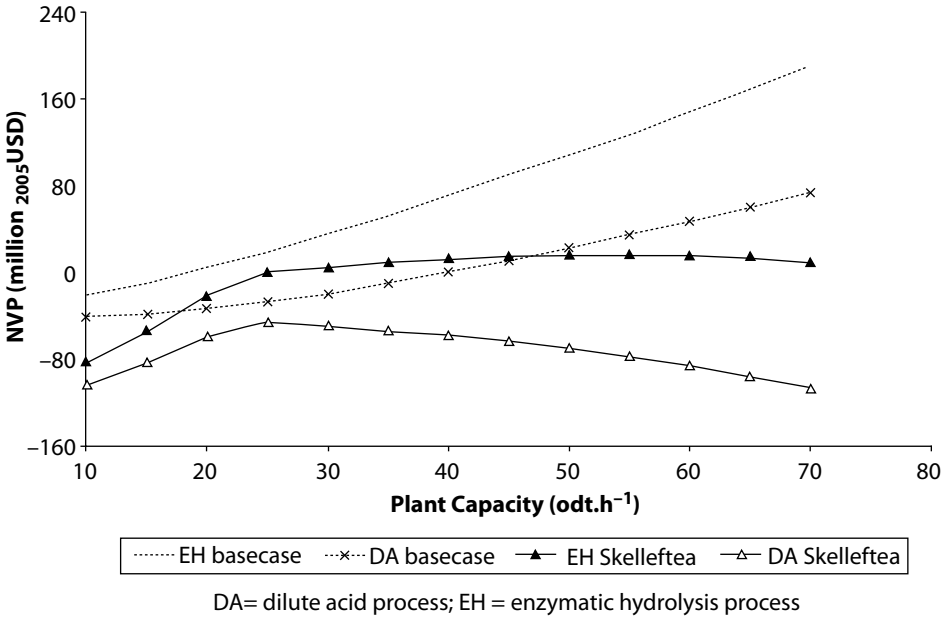


Fig. 16.5: Variation in levelized cost with plant capacity: EU base-case and Skellefteå.



DA= dilute acid process; EH = enzymatic hydrolysis process

Fig. 16.6: Variation in NPV with plant capacity for base-case and Skellefteå plants. The market price of ethanol was assumed to be US$0.81.l^{-1}, which corresponds to an oil price of US$90.barrel^{-1}.

GHG emissions per gigajoule (GJ) ethanol arising from fossil-fuel use throughout the supply chain are shown in ▶Fig. 16.7, for a 25odt.h^{-1} plant. It can be seen that despite feedstock GHG emissions at Skellefteå being higher than base-case emissions, because the emissions from electricity in Sweden are so much lower than the European average

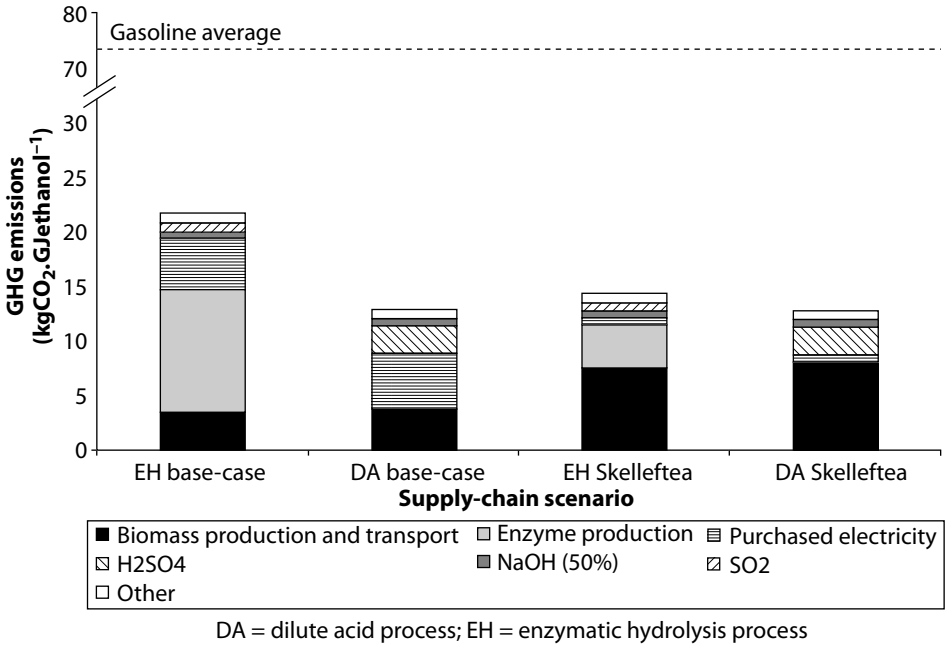


Fig. 16.7: GHG emissions from fossil-fuel use per GJ ethanol. The example shown is for a 25odt.h^{-1} capacity plant. Fossil GHG emissions are apportioned between ethanol and solid fuel on the basis of energy content.

the overall GHG impact for the Skellefteå scenarios and the DA base case are similar: about 15kgCO_2.GJethanol^{-1}.

A large plant requires feedstocks to be gathered from a larger area, thereby entailing greater transport costs and emissions compared to a small plant. The effect of increasing plant capacity on GHG emissions is shown in ▶Fig. 16.8. It can be seen that the difference between emissions for a small (5odt.h^{-1}) plant and a large (50odt.h^{-1}) plant is only about 5%–6%. So, while there is a trade-off between minimizing transport emissions and obtaining economies of scale, the environmental consequences of this trade-off are minimal.

The GHG emissions associated with gasoline are about 74kgCO_{2e}.GJ^{-1} (Defra 2007), compared with about 15kgCO_2.GJ for ethanol produced at Skellefteå. On the basis of GHG emissions, therefore, ethanol produced at Skellefteå would be environmentally beneficial, reducing overall emissions by about 80%. This is equivalent to a savings of about 1.8kgCO_{2e}.l^{-1}. At an oil price of US$90.barrel^{-1}, and with the current subsidy for ethanol, a stand-alone plant in Skellefteå would also be a commercially viable, although risky, investment. If the subsidy for ethanol (~US$0.22.l^{-1}) were justified solely on the basis of the carbon saving, this would imply a cost of carbon of about US$122.tone$CO_2^{-1}$. If, however, the oil price were to increase to about US$130.barrel^{-1}, no subsidy would be required, and the effective cost of carbon would be zero.

The results presented here describe the commercial and environmental performance of a hypothetical, stand-alone plant in Skellefteå. As presented, however, the results

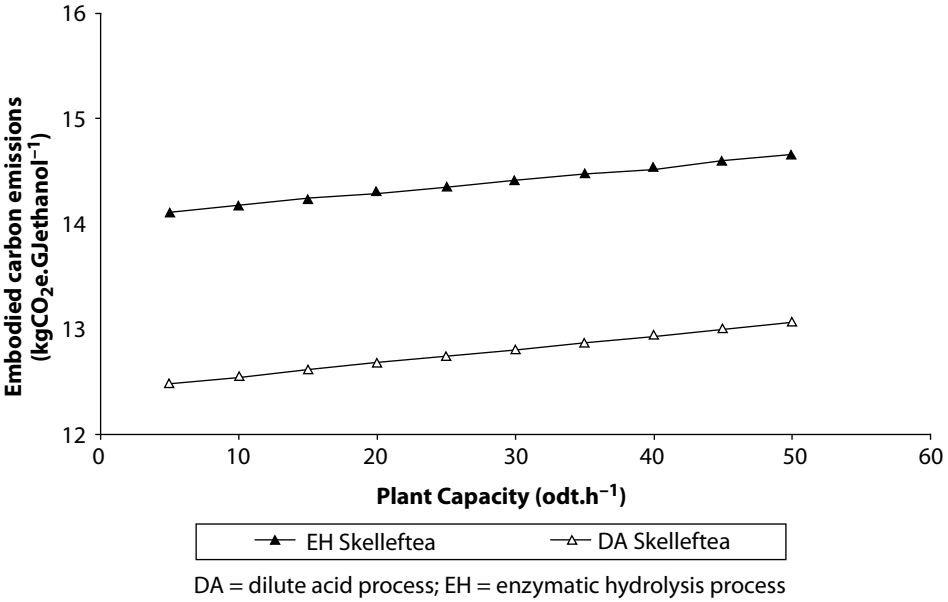


Fig. 16.8: Variation in GHG emissions with plant capacity for a cellulosic ethanol plant in Skellefteå. The example shown is for a 25odt.h^{-1} capacity plant. Fossil GHG emissions are apportioned between ethanol and solid fuel on the basis of energy content.

do not show the proposed plant at Skellefteå in the best possible light: the ethanol plant is assumed to bear all the costs and all the fossil GHG emissions associated with increased feedstock supply. Possibly the greatest simplification, however, is the limited assessment of integration with other facilities. Although the detailed design of the plant has not been finalized, Sekab considers that integrating ethanol production with operations that add value to the side streams (solid residue and biogas) will be of critical importance (Fransson 2008). Many integration options have been proposed, but the principal ones considered by Sekab are integration with pellet production, with CHP, with first-generation ethanol production, and, in the longer term, with biorefineries.

The integration of ethanol production with pellet production and/or CHP is the concept closest to commercial reality in Sweden. With current technology, approximately 30% of the energy, input as wood, is output as a solid residue side stream. This residue contains lignin and nonhydrolyzed cellulose; it has a low alkali content and a high energy value, approximately 15% greater than wood (22.3GJ.odt^{-1}). First attempts, at the Bioenergy Technology Centre (BTC) in Umeå, to make pellets from the solid residue after two stage dilute acid hydrolysis have been reported to be very positive. The low alkali content of the residue also makes it suitable as a feedstock for CHP, for gas turbines, and as an incineration additive. The solid residue could also be the starting material for a range of novel chemistries and products. Lignin in particular has a very wide range of potential applications. This is the basis of the biorefinery concept and new routes to green products based on renewable feedstocks are currently being investigated. One example of activity in this area is the Processum

Biorefinery Initiative, a consortium of companies in the Örnsköldsvik area set up to investigate new processes and products. The integration of cellulosic ethanol production with production from sugar and starch crops in a modified conventional plant could also increase overall ethanol yields. This option is attractive because it could enable increased economies of scale and has the potential to take advantage of synergies in common process steps; for example, raw materials handling, distillation, and waste water treatment.

16.7 Conclusions

The results presented here show that the area of northern Sweden around Skellefteå is a relatively high-cost location for feedstocks and that only limited volumes are available. This restricts the maximum size of a plant and limits the economies of scale that may be obtained. Nevertheless, with an oil price of US$90.barrel^{-1} and with the current subsidy regime, an ethanol plant utilizing the enzymatic process is on the verge of commercial viability and could lead to GHG reductions in the region of 70%–80% (less if co-products are not taken into account). The technology itself is still at a developmental stage, and its commercial viability could be improved given further technical advances. In particular, GHG savings may be increased by improving the thermal efficiency of the process plant, thereby maximizing the quantity of solid fuel co-product, and the availability of feedstocks could also be increased if forestry practices permitted the use of fertilization. Given, however, that feedstock limitations dictate a relatively small-capacity plant, the option most likely to provide cost reductions and a practical way forward is the integration of ethanol production with facilities such as CHP and district heating.

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17 Anaerobic fermentation: biogas from waste – the basic science

Michele Aresta

17.1 Introduction

Noncellulosic vegetal materials (the so-called fruit-vegetal-garden [FVG] residues) are characterized by a high water content that discourages their thermal treatment that results in them being economically and energetically disadvantageous. Conversely, such organic waste, as well as monomeric organics, are suitable for the generation of energy products like methane and/or other biofuels (alcohol, oil, biodiesel): such practice is expanding worldwide with steadily growing intensity. The valorization of waste (1) contributes to avoiding landfilling, which is under strict limitation in many countries; (2) reduces water and soil pollution; and (3) allows water recovery and reutilization, while producing usable energy that would otherwise be lost. The conversion of FVG could in principle take place in the presence or absence of oxygen. The two processes are referred as *aerobic* and *anaerobic* treatment, respectively.

17.1.1 The aerobic and anaerobic processes of FVGs

FVGs, industrial organic residual compounds, and sludge can be treated either by aerobic or anaerobic digestion. In the former process, the cost of which depends on the aeration frequency (Bernard and Gray 2000), the degradable fraction is converted without energy recovery. The latter technology, instead, allows the conversion of organic carbon into biogas; that is, a mixture of methane and CO_2 from which the energy-rich species methane can be separated, even if with moderate efficiency (30%–50%) due to the low biodegradability of parts of the solid fraction and the long retention times (20–30 days) (Weemaes et al. 2000). Biogas technology is being continuously improved by optimizing the process parameters and the reactor geometry (Nutek 1995) and with integration into other waste-treatment plants. Methane can be used for thermal or electric energy production.

The treatment of FVGs must take place close to the area where it has been produced for two main reasons:

- its specific volume makes transportation quite expensive
- FVGs are good substrate for bacterial growth and, therefore, are easily attacked by microorganisms with partial conversion that could occur in the containers during transport

As a matter of fact, the action of microorganisms represents the most "natural" technology for FVGs and organics treatment.

The microorganisms respiration process, occurring in aerobic environments, ultimately leads to carbon dioxide (CO_2), water (H_2O), and biomass production (bacterial

cells). An effective aerobic degradation may occur only with soluble materials and in nonconcentrated systems, with the O_2 availability being a key point, often more important than the substrate composition. For a better result and a faster process, solid materials and suspended fine particulate must be removed, either by bioflocculation or by degradation. Aerobic organisms can also partially degrade solid organic substances, but the relevant kinetics is very slow and a proper air supply is needed (Hobson, Bousfield, and Summer 1972). A partial aerobic degradation of solids typically occurs during the making of compost, when relatively dried organic solid wastes are partially converted by oxidation. The aerobic treatment, during the respiration phase, releases energy (the temperature can rise as high as 90°C, but is usually maintained around 60°C) that is lost in the form of heat. The produced compost can be used as a soil additive, which is not the case with the biomass produced in anaerobic treatments of water or solid wastes that produce sludge that cannot be directly disposed in a landfill or used because of their possibly toxic microbial content.

Anaerobic metabolism does not require oxygen and is suitable for treating FVGs or organics. The main theoretical limits to the application of an anaerobic process are:

- incomplete conversion of the substrate: often more than 50% of the organic material (the polymeric fraction) is not degraded.
- medium or long retention time.
- formation and persistence of some acids that may be polluting agents.
- bacteria may need some nutrients that are not available in the original substrate. Their growth may be slow because of the scarce energy available.
- permanence of ammonia (NH_3) and other N-compounds.

Some of these problems have already found a solution at the industrial-scale plant, others need further study and research.

FVG biomass conversion into biogas encompasses a number of phases, namely: (1) depolymerization, (2) acidogenesis, (3) acetate formation, (4) methanogenesis, and (5) methanation of CO_2, each of which requires different bacterial communities and a complex metabolic food chain (Zehnder 1978; Zeikus 1983; Schink 1983). In the whole process, H_2 and organic carboxylic acids, such as acetic acid, are key intermediates: it is important to maintain a low H_2 partial pressure as key biological reactions may occur that, for thermodynamic reasons, do not take place under high H_2 pressure (Zehnder 1978). The anaerobic digestion of fatty acids, alcohols, and organic compounds is accomplished through a syntrophy between H_2-producing and H_2-consuming methanogenic archea (Schink 1983) that favor the best use of the energy content of primary substrates (Thauer, Jungermann, and Decker 1977).

In this chapter, the fundamental science that is at the basis of methane production is discussed, while technologies for methane production are discussed in Chapter 18. In particular, the enzymes involved in the biogas production process are described here and the role of iron, nickel, and cobalt during the anaerobic digestion of a sludge is elucidated. These metals play a key role in anaerobic metabolism during the methanogenic digestion. As a matter of fact, they constitute the active center in several enzymes, each playing a specific role in the complex methanation process (▶Tab. 17.1).

In fact, nickel is the active center of the methyl-coenzyme M reductase (known as F_{430}) and several H_2-consuming hydrogenases (Walsh and Orme-Johnson 1987; Aresta,

Tab. 17.1: Metal enzymes involved in the conversion of CO_2 or H_2.

Enzyme/Coenzyme	Metal in the Active Site	Reaction Catalyzed
Conversion of CO_2		
Formatedehydrogenase	W	$CO_2 \rightarrow HCOO^-$
Tetrahydrofolate (THF)		$CO_2 \rightarrow {}^-CH_3/CH_4$
Methanofurane (MFR)		$CO_2 \rightarrow {}^-CH_3/CH_4$
Tetrahydromethanopterin (H_4-MPT) CH_3-S-CoM methyl reductase	Ni (in F-430 factor of CH_3-S-CoM)	$CO_2 \rightarrow {}^-CH_3/CH_4$
Methyl transferase (cobalamine)	Co	methyl transfer
Carbon monoxide dehydrogenase (CODH)	Ni, Fe	$CO_2 \rightarrow CO$ or CH_3COOH
Dihydrogen formation/consumption		
Hydrogenases	Fe	$H^+ \rightarrow H_2$ (and $H_2 \rightarrow H^+$)
Hydrogenases	Ni,Fe	$H_2 \rightarrow H^+$ mainly Ni
Hydrogenases	Ni,Fe,Se	

Quaranta, and Tommasi 1988) and acetate-forming enzymes (Ellefson and Wolfe 1981; Rouviere, Escalante-Semerena, and Wolfe 1985; Albracht 1994; Tommasi et al. 1998). Iron is present in several hydrogenases (H_2 uptake or evolution) and, as an Fe_4S_4 protein, in carbon monoxide dehydrogenase (CODH), which is responsible of the formation of acetic acid (Rouviere et al., 1985; Adams, 1990; Tommasi et al., 1998). Cobalt is part of cobalamin, a methyl-transfer catalyst (Hippler and Thauer 1999). Several enzymes synergistically work for the production of methane and carbon dioxide during the anaerobic digestion of FVG or sludge (Schonheit, Mool, and Thauer 1979) (▶Fig. 17.1). It is worth recalling that the anaerobic digestion is largely applied in the treatment of process or municipal water, leading to the possibility of recovering carbon and energy, with side water streams cleaning and potential reusability.

17.2 The structure of the starting waste wet biomass

In this section the components of waste fresh biomass that maybe involved in biogas production are briefly described for the follow-up of the discussion. More detailed information on the properties and behavior of materials like cellulose and lignin can be found in other chapters in this book. The structural features of the starting materials have a great importance in the process of biogas production and determine the extent to which such compounds can be metabolized by bacteria and converted into biogas, as well as the composition of the biogas. As discussed in the following sections, compounds such as cellulose, hemicellulose, and lignin may remain untouched by bacteria and fungi and will constitute the solid residue of the digestion, while proteins will produce ammonia, which needs to be somehow eliminated.

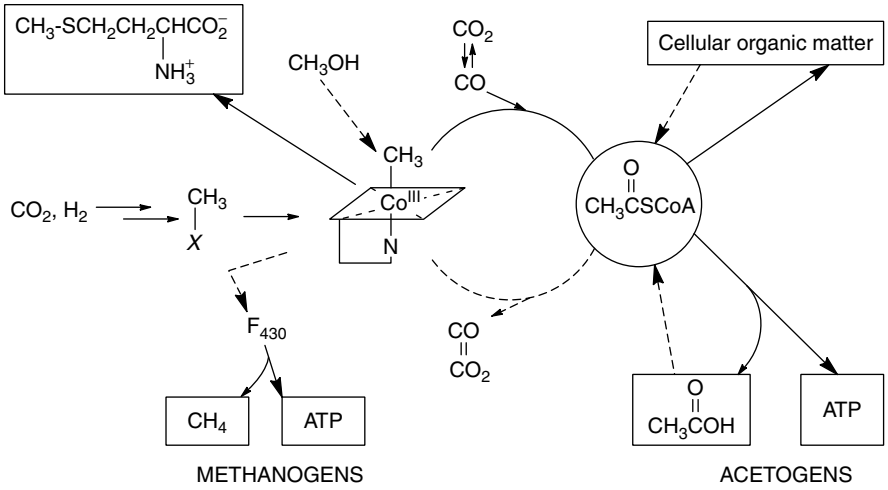


Fig. 17.1: The methanogenesis scheme.

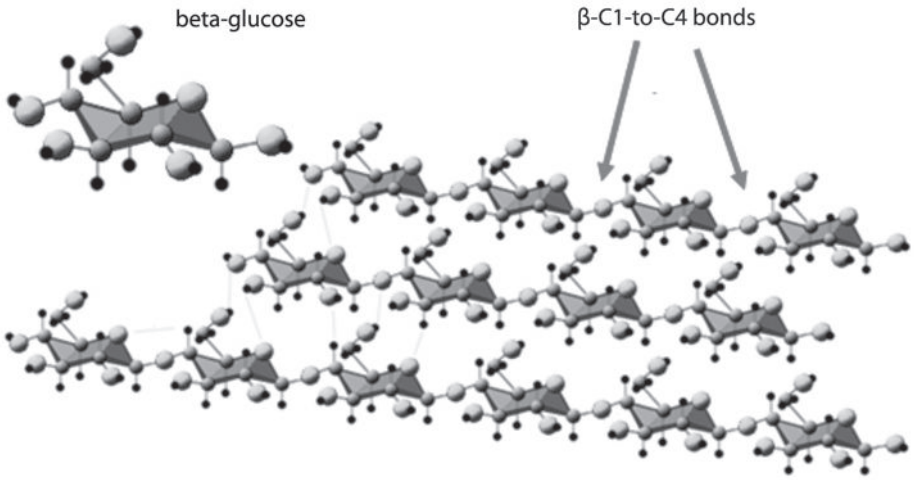


Fig. 17.2: Cellulose structure.

17.2.1 Cellulose

Cellulose is a polymer whose basic monomer is D-glucose. Different units are linked in a β-1,4 mode (▶Fig. 17.2). The cellulosic fiber resistance is due to the presence of three free hydroxyl groups in each monomer unit; these groups can form hydrogen bonds.

Extracellular or intracellular enzymes carry out cellulose hydrolytic reactions. The former perform the hydrolysis, the products of which are then transferred inside the cell where they follow the normal catabolic path. Three different cellulolytic enzyme activities can be distinguished (Fan and Lee 1983):

- *endoglucanase* attacks the internal cellulose chain. It is active on amorphous, but not on crystalline, cellulose (natural cellulose is 70% crystalline).
- *exoglucanase* attacks the terminal part of the chain.
- *β-glucosidase* hydrolyzes cellobiose and cellodextrins produced by previous reactions. The final product is glucose.

Endoglucanase is able to degrade crystalline cellulose only in combination with exoglucanase (Sleat and Math 1987). Most cellulose hydrolyzing bacteria isolated in anaerobic digesters employ carbohydrates, in particular glucose, cellobiose, and xylose, as a source of carbon (Mali 1954). But these sugars are the main energy source for many other nonmethanogenic bacteria. Therefore, cellulose hydrolysis can become either the reaction limiting the whole anaerobic digestion process or one of the reactions playing a fundamental role.

A kind of control is carried out by a feedback-like mechanism, according to which if a product of cellulose hydrolysis, for instance, cellobiose, is used at a lower rate than it is produced, causing a cellobiose accumulation, a decrease of the cellulolytic rate is observed.

17.2.2 Hemicellulose

Hemicellulose is one of the main constituents of plants. It is a polymer with short-branched chains (▶Fig. 17.3). The enzymatic functions involved in its hydrolysis are essentially extracellular (Sleat and Math 1987).

17.2.3 Lignin

Lignin is one of the vascular tissues of plants and plays an important role in building their cellular walls. It owns a complex structure that contains aromatic units like guaiacilic (I), pepperilic (II), and syringilic (III) moieties that co-polymerize (▶Fig. 17.4).

A partial solubilization of lignin is only possible by using chemicophysical treatments as high temperature and/or particular pH conditions.

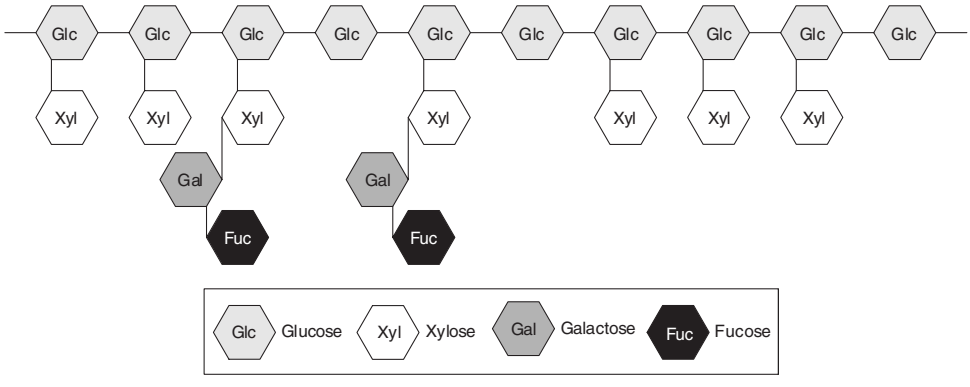


Fig. 17.3: Hemicellulose structure.

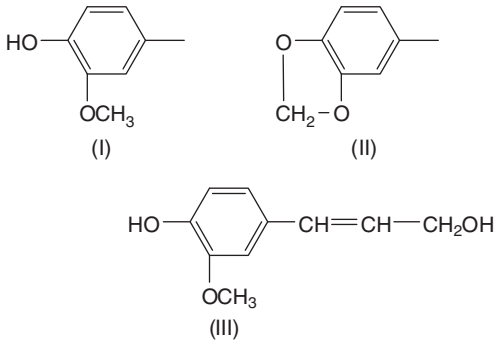


Fig. 17.4: Phenyl derivatives belonging to the lignin structure.

17.2.4 Pectin

Pectin occurs as cellular wall plant constituent and can also be found in intercellular layers. It has a linear structure with the galacturonic acid units bound through an α-1,4 bond; the carboxylic groups are methylated (▶Fig. 17.5). The enzymes leading to pectin degradation are (Sleat and Math 1987): pectinesterase, polyglycanohydrolase, and polylyase.

17.2.5 Starch

Starch is the main supply constituent for plants. It exists in two different structural forms (▶Fig. 17.6 and ▶Fig. 17.7):

- *amylose*, a linear homopolysaccharide with D-glucose units linked through an α-1,4 bond.
- *amylopectin*, similar to amylase, but bearing every 25 monomeric units (Greenwood 1970) lateral chains with α-1,6 bonds.

Four enzymatic systems are involved in starch degradation: (1) α-amylase (α-1,4 glucan glucanohydrolase), (2) β-amylase (β-1,4-glucan maltohydrolase), (3) amyloglucosidase, and (4) debranching enzymes (Hungate 1960).

17.2.6 Lipids

Lipids are derivatives of glycerol esterified in two positions with long-chain monocarboxylic acid. The third position can be either used to bind another fatty acid (triglycerides), a phosphate group (phosphatides or phospholipids), or a sugar unit (glycolipids).

Lipid hydrolysis in rumens is different from that in anaerobic digesters. While in the former, lipid degradation leads to fatty acids that are not further degraded, but directly absorbed by the intestine, in the latter the fatty acids are further degraded by means of obligate hydrogen-producing acetogens (OHPA) bacteria (Chynowethh and Mah 1971).

It is useful to recall that unsaturated fatty acids undergo a rapid hydrogenation reaction (Heuhelekian and Mueller 1958). Saturated fatty acids undergo a β-oxidation that removes two C-atoms from the carboxylic end. The products are: a fatty acid with a

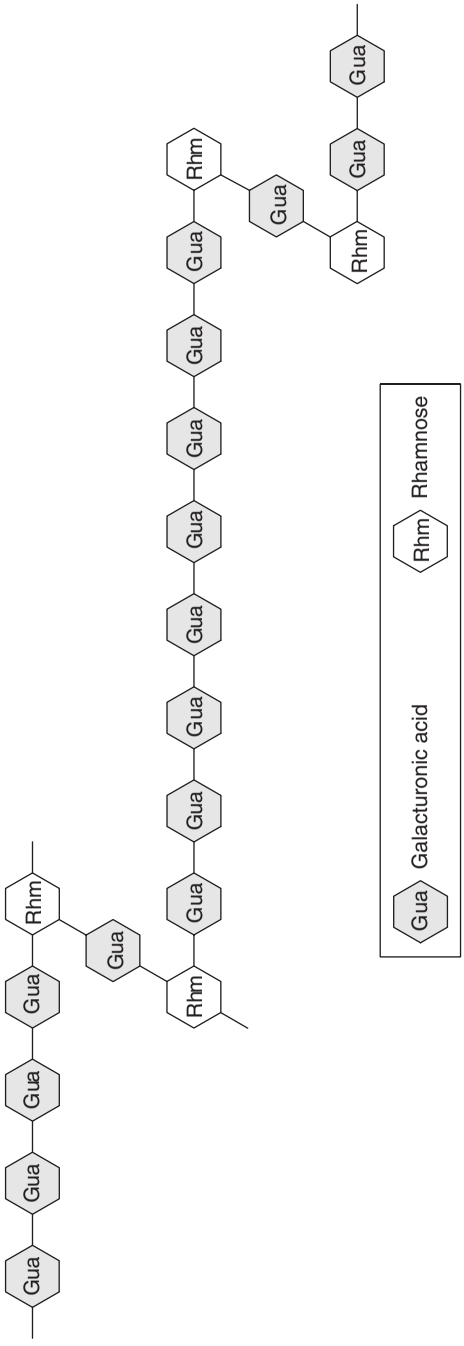


Fig. 17.5: Pectin structure.

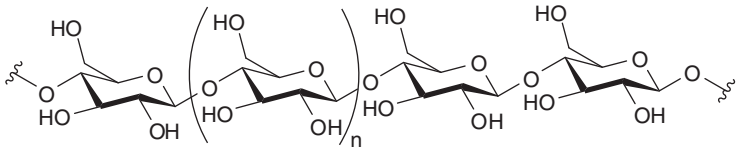


Fig. 17.6: Amilose structure.

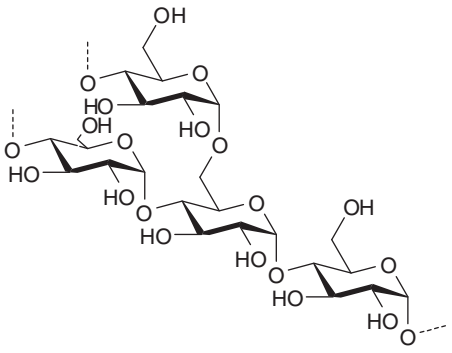


Fig. 17.7: Amylopectin structure.

C_{n-2} chain, acetic acid (as AcetilCoA), and 4H. In case the chain has an odd number of carbon atoms, propionic acid is also produced as an end product. Glycerol itself enters the glycolysis path through the glycerol-1-P-dehydrogenase enzyme.

17.2.7 Proteins

Proteins are linear sequences of amino acids characterized by peptide bonds (NH-CO) in the polymeric structure that may also bear sulfide (SH) and disulfide (S-S) moieties. They can be simple or conjugated (containing inorganic groups). Their three-dimensional structure shows different forms stabilized by hydrogen bonds and disulfide bridges. Protein degradation occurs via deamination, transamination, and decarboxylation reactions that bear the formation of free NH_3 or CO_2 and are competitive and governed by the pH value of the medium.

17.3 Biogas production

Here the complex process leading to the formation of biogas from FVGs or organics will be considered, the involved phases will be analyzed, and the active enzymes described.

17.3.1 Anaerobic digestion: natura docet

The anaerobic digestion of waste is a typical example of transfer at the industrial scale of a natural process. In fact, methanogenesis is a routine process that occurs in some

environments, such as in oceanic and lagoon sediments or in the intestines of animals (particularly in rumens).

The anaerobic digestion occurs under anaerobic or microaerobic conditions and is typical of both strict anaerobic bacteria and bacteria that grow either in anaerobic or aerobic conditions (facultative anaerobic). In this process, the organic substances are converted into methane and carbon dioxide. The whole process is driven through different steps driven by hydrolytic bacteria: the hydrolysis of polymeric organic compounds like carbohydrates, lipids, and proteins is followed by the acidogenesis, during which organic acids, alcohols, and neutral compounds are produced. The hydrolysis and acidogenesis products are then converted into acetate, hydrogen, and carbon dioxide by the OHPA bacteria. Acetate, hydrogen, and carbon dioxide are ideal substrates for the methanogenic bacteria producing methane and carbon dioxide.

Acetate, the substrate that is mostly used by methanogens, is also produced by a fourth bacterial class called homoacetogenic bacteria, which can ferment a wide spectrum of substrates. OPHA and homoacetogens are generally called *transitional* bacteria.

The methane yield of the anaerobic digestion mainly depends on the yield of the hydrolysis of the organic fraction. Lignin, for instance, under anaerobic conditions is hardly biodegraded. The difficulty is essentially due to the lack of specific hydrolytic enzymes in anaerobic bacteria, and the oxygen demand typical of hydrolytic enzymes. For this reason, it may be useful to treat the organic fraction with specific hydrolytic agents (fungi, other microorganisms) before the anaerobic digestion is started. This procedure may increase the methane yield and reduce the residual solid fraction.

Methane production also depends on the biodegradable organic fraction composition: reduced substrates (like proteins and lipids) give better methane yield than oxidized ones (sugars). Different processes regulate the methanation speed. If the substrate is rich in polymeric materials like cellulose, the rate-determining step is the hydrolysis. If the substrate is soluble, it is the methanation that determines the overall rate (Noike et al. 1985).

Several parameters are used to describe the stability and efficiency of an anaerobic process. The parameters most commonly used are:

- methane production
- methane volumetric rate (MVR)
- organic substance degradation rate (ODR)
- culture stability
- thermal efficiency

The chemicophysical changes in the biodegradation of a substrate are typical of an exoergonic process. Two levels of biodegradation are usually distinguished:

- primary, in which the reaction products are directly related to the original compounds (e.g. from cellulose to glucose)
- final, in which the substrate is converted into CH_4 and CO_2 (i.e. from cellulose to methane)

While the biodegradability of waste (e.g. the fraction that can be converted into biogas) depends on the degradation thermodynamics, the biogas daily yield depends on the kinetics of the process. A compound that is not biodegradable or requires a long induction time for biodegradation is defined as *refractory*.

17.3.2 Hydrolytic bacteria and acidogenesis

The first reaction occurring in a digester is the depolymerization of substrates with a high molecular mass, such as homopolysaccharides (cellulose, starch), heteropolysaccharides (hemicellulose), pectins, lignins, proteins, and lipids. The anaerobic degradation of these polymers requires the action of different enzymes able to attack their terminal- or internal-functional groups. ▶Tab. 17.2 lists some of the hydrolytic bacteria (Hobson, Bousfield, and Summer 1972; Sleat and Math 1987), either specific or polyvalent.

It is worth noting that none of the listed bacteria are able to hydrolyze lignin that is, as said previously, considered *nondegradable* through an anaerobic process. As cellulose, hemicellulose, and lignin are bound together to form the lignocellulose matrix, the relative percentage of lignin will make such a matrix more or less degradable (Chandler et al. 1980). Hydrolytic reactions are followed by acidogenesis, leading to the formation of soluble extracellular intermediates; that is, acetic, propionic, or butyric acid. They are produced at low concentration but with a high turnover (Boone 1982). However, the methane production is not influenced by the eventual loss of acids through the effluent. In fact, the high production rate leads to a quick reestablishment of the equilibrium conditions.

The presence of hydrolytic bacteria has been ascertained in biosystems such as the colon of humans (Orpin and Letcher 1979), caecum of rats (Montgomery and Macy 1982), intestine of horses (Davies 1964), caecum of guinea pigs (Dehority 1977), estuary sediments (Madden, Bryder, and Poole 1982), and in soil (Skinner 1960).

17.3.2.1 Transitional bacteria

It is now clear that growing bacteria on a single- or substrate (that is typical of a digester) may produce different products from both a quantitative and a qualitative point of view (Hobson 1965; Hishinuma, Kanegasaki, and Takahashi 1968).

Such variety is due to many factors, such as growth rate variation, pH value, and concentration of the substrate used as the energy source (Hobson and Summers 1967).

Tab. 17.2: Bacteria involved in the hydrolysis-acidogenesis phase (Sleat and Math 1987).

	C	H	Lg	Pc	S	Lp	Pr
Anaerovibrio						X	
Bacteroides amylophilus					X		X
Bacteroides fibrisolvens	X	X		X		X	
Bacteroides succinogens		X		X	X		X
Butyrivibrio fibrisolvens	X	X					
Clostridium multifermentans				X			X
Clostridium thermocellum	X						X
Ruminococcus albus	X	X					
Ruminococcus flavefaciens	X	X					
Succinomas amylotica					X		

C = cellulose; H = heminocellulose; Lg = lignin; Pc = pectin; S = starch; Lp = lipids; Pr = proteins.

These parameters affect the bacterial flora composition and the extracellular enzyme concentration (Henderson, Hobson, and Summers 1969; Dean 1972; Bull 1972; Demain 1972; Brown and Stanley 1972; Holme 1972; Davies and Rudd 1972).

The energy used by bacteria during anaerobic fermentation derives essentially from oxidation reactions in which molecules other than oxygen are used as electron acceptors. A narrow class of bacteria use either nitrates or sulfates as electron acceptors, but the greatest part reduces the compounds produced in the hydrolysis-acidogenesis phase, or form gaseous H_2 in combination with hydrogenase enzymes (Wolin 1982).

17.3.2.2 Acetogenesis

As reported previously, acetate, hydrogen, and carbon dioxide are the substrates mostly used by methanogenic bacteria. The hydrolysis of the original substrate provides 24% of these products (Smith and Mah 1966), whereas the remaining 76% results from further reactions occurring on the other substrates produced during the hydrolysis-acidogenesis phase (propionate, butyrate, lactate, ethanol, methanol) (Lorowitz and Bryant 1983).

The acetogenesis reactions are driven by the transitional bacteria (OHPA and homoacetogens). Acetate derives from both the hydrolysis of the original substrate and the action of transitional bacteria, in particular the OHPA ones.

There is an important functional difference between the two bacterial classes producing acetate. Whereas hydrolytic bacteria can produce acetate also in the presence of an excess of hydrogen produced by themselves, the OHPA bacteria are able to produce acetate only if H_2 is removed. If a high hydrogen concentration is reached in the liquid or gaseous phase, it originates a feedback mechanism that inhibits the OHPA bacteria with a consequent accumulation of organic acids (propionic, butyric) at the expense of acetic acid. The interaction between the H_2-producing and H_2-utilizing species is known as *H_2-transfer interspecies* (Boone and Mah 1987). The reactions involving OHPA bacteria are endoergonic if the substrates and products are in their standard state (Boone and Mah 1987). Actually, the concentration in digesters differs from the standard one. It has been shown that within a well-defined range of H_2 (1.6×10^{-6} atm $< pH_2 < 5.8 \times 10^{-5}$ atm) the reactions are exoergonic. The H_2 partial pressure plays, thus, an important role in the overall process.

17.3.2.3 Bacterial flora composition

Several OHPA bacteria have been identified, among which include *Syntrophomanas wolfei* (oxidises butyrate to acetate and hydrogen) (McInerney et al. 1981; Beaty and McInerney 1986), *Syntrophomanas wolinii* (oxidizes propionate to acetate, carbon dioxide, and hydrogen) (Boone and Bryant 1981), and *Methanobacterium thermoautrophicum* (oxidises butyrate to acetate and hydrogen) (Henson and Smith 1985).

The bacteria that produce acids different from acetic acid perform the opposite reaction carried out by OHPA bacteria. This rises an issue of energy; in fact, the two reactions (direct and reverse) can not both be exoergonic. However, it is possible to assume that if the hydrogen concentration varies with the microsystem considered, the two reactions may be both exoergonic in different microenvironments (Boone and Mah 1987). ▶Tab. 17.3 provides a list of some homoacetogenic bacteria that synthesize acetate (and other volatile organic acids) from H_2 and CO_2. In any case, the acetate produced in this way represents only 1% of the total (Smith and Mah 1966).

Tab 17.3: Homoacetogenic bacteria (Boone and Mah 1987).

Organism	Products
Acetobacterium kivui	Acetate
Acetobacterium wierinage	Acetate
Acetobacterium woodii	Acetate
Clostridium aceticum	Acetate
Clostridium formicoaceticum	Acetate
Clostridium thermoaceticum	Acetate
Desulfobulbus propionicus	Propionate
Eubacterium limosum	Acetate, butyrate
Peptostreptococcus products	Acetate, succinate

17.4 Biogas formation from waste: phases and reactions

As previously mentioned, the production of biogas (CH_4 and CO_2) from FVGs or other residual organics, such as monomeric compounds, proteins, or polysaccharides, occurs in five interconnected phases, three of which – depolymerization, acidogenesis, and methanogenesis – are directly consociated (Zehnder 1978; Zeikus 1983; Schink 1983). In the first phase, the depolymerization of complex molecular structures (starch, proteins) takes place under the action of hydrolytic bacteria or fungi. Oligomers or monomers are formed, such as sugar, amino acids, peptides, and acids. Such monomers are converted in the acidogenesis phase by fermentative bacteria into the so-called volatile fatty acids (FVAs); that is, acetic, propionic, and butyric acid, and H_2. Ammonia and CO_2 are also formed. FVAs can be converted into CO_2 and H_2. In the third step, or methanogenesis, acetic acid, CO_2, and H_2 are converted by methanogens into CH_4 and CO_2. In such a complex process, metal enzymes play a key role because they drive the key reactions, such as H_2 formation and conversion (such enzymes are called hydrogenases and indicated as H_2-ases), CO_2 reduction to CO (carbon monoxide dehydrogenase [CODH]), and the formation of acetic acid from CO, among others. ▶Tab. 17.1 lists the enzymes and the relevant active centers involved in H_2 formation. In general the H_2-ases enzymes can be classified by indicating the transition metal present in their active site. In this way, three main H_2-ases (FeFe, FeNi, FeS) are classified plus a Mo-ase that is also involved in nitrogen fixation to afford ammonia. The main H_2-ases will be described in the following sections.

17.4.1 [FeFe]H_2ase

The active site in *Clostridium pasteurianum* (▶Fig. 17.8) contains a large unit characterized by an unusual arrangement of two moieties; an Fe_4S_4 iron protein linked, through a cysteine-S, to an Fe_2 cluster in which two octahedral irons bear five – CX groups (CO or CN); one water molecule; and three bridging sulfur groups. Such "large domain" is accompanied by four "small domains" containing either the Fe_4S_4 protein or the Fe_2-nonproteic cluster.

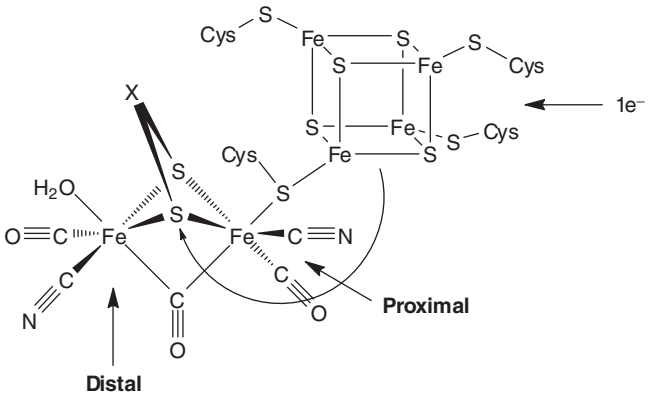


Fig. 17.8: The active center of *Clostridium pasteurianum* hydrogenase.

The two iron centers are designated as proximal and distal depending on their spatial relation to the nearby $[Fe_4S_4]$ cluster and protein backbone.

Infrared (IR)-spectroscopy (Pierik et al. 1998; Nicolet et al. 2001; De Lacey et al. 2000; Chen et al. 2002) and electron paramagnetic resonance (EPR)-spectroscopy (Adams and Mortenson 1984; Adams 1987; Zambrano et al. 1989; Bennett, Lemon, and Peters 2000) have demonstrated the existence of at least four different forms of the [FeFe]-$[Fe_4S_4]$ active site. Two S=1/2, EPR-active states have been identified, designated as H_{ox} (g=2.06) and H_{ox} (g=2.10). Two EPR-silent states, namely H_{ox} and H_{red}, have been identified using IR, the H_{ox} form corresponds to a over-oxidized species, which is not an active catalyst for H^+ reduction or H_2 oxidation. The H_{ox} form may be reactivated by either electrochemical reduction or by using a reducing agent. The active site can undergo a one-electron reduction: the electron is initially localized on the $[Fe_4S_4]$ moiety (▶Fig.17.8), generating a species designated as H_{ox} (g=2.06). The transfer of the electron from such a site to the [FeFe] cluster is performed through a conformational change of the protein superstructure. The second one-electron reduction follows, yielding a species designated as H_{red}. Models of the active site of [FeFe]H_2-ase have been built by using small molecules (Georgekaki and Darensbourg 2004).

Iron-only hydrogenases have been isolated from several microorganisms (Dance 1999; Nicolet et al. 1999) and are shown to be able both to produce and to consume dihydrogen (Eq. 1).

$$H^+ + e^- \rightleftharpoons 1/2\ H_2 \tag{1}$$

17.4.2 [FeS]H_2-ase

The iron-sulfur cluster-free H_2-ase are H_2-utilizing enzymes, which activate dihydrogen for use in catabolic processes within the cell but do not catalyze H^+ reduction or H_2 oxidation.

17.4.3 [NiFe]H_2ase and [Fe-Ni-Se]ase

Nickel-iron hydrogenases [NiFe] (▶Fig. 17.9) are present in several bacteria. Their basic metal site as demonstrated by x-ray diffraction (XRD) (Volbeda et al. 1995, 1996) is a heterodimeric unit formed by four subunits, three of which are small [Fe] and one of which contains the bimetallic active center consisting of a dimeric cluster formed by six coordinated Fe linked to a pentacoordinated Ni(III) through two cysteine-S and a third ligand whose nature changes with the oxidation state of the metals: in the reduced state it is a hydride H^-, while in the oxidized state it may be either an oxo, O^{2-}, or a sulphide, S^{2-}.

It has also been shown that in some microorganisms, such as *Desulfomicrobium baculatum*, a S-cysteine has been replaced by a Se-cysteine (Garcin et al. 1999), giving place to a trinuclear [FeNiSe] hydrogenase.

The mechanism of action has been studied by several authors (Dance 1999; Higuchi et al. 1999) and the implication of a Ni(III)/Ni(II)/Ni(0) system has been proposed. Ni and Fe enzymes apparently have a different role in H_2 production-consumption. In fact, Ni enzymes are more specifically involved in H_2 consumption, while Fe enzymes are more involved in H_2 production.

Ni and Fe are equally implied in the synthesis of the acetyl moiety from CO_2 (Hu et al. 1996; Tommasi et al. 1998; Aresta et al. 2002), while Co (as cobalamine) is well known to act as a carrier of methyl groups. Using infrared (IR) and electron paramagnetic resonance (EPR), spectroscopy works were demonstrated in at least seven different forms of the Ni-Fe center. Three S=1/2, EPR-active states designated as Ni-A, Ni-B, and Ni-C were evidentiated (Albracht 1985; Fernandez, Hatchinkian, and Cammack 1985; Cammack, Fernandez, and Schneider 1986; Fernandez et al. 1986; Maroney et al. 1995; Dole at al. 1997; Bleijlenìvens, Faber, and Albracht 2001; Vincent et al. 2005; De Lacey et al. 1997, 2002). Four EPR-silent states were shown by IR that have been designated as Ni-SU, Ni-SI_I, Ni-SI_{II}, and Ni-SR (also known as Ni-R). Still, investigation is needed for the complete elucidation of the structures of the various species, their role in the catalytic cycle, and the details of their interconversion. The Ni-A and Ni-B are not active in the catalysis for H_2 oxidation as they are over-oxidized. They can be reactivated by reduction. Ni-C and Ni-R species are believed to be intermediates in the oxidation of H_2. Species designated as Ni-SU, Ni-SI_I, and Ni-SI_{III} can be intermediates in the reactivation of the over-oxidized forms of the enzyme, while one of the Ni-SI species is supposed to play a role in the catalytic cycle (Volbeda et al. 1996; Bagley et al. 1994, 1995; Van de Spek et al. 1996; Berlier et al. 1987; Bleijlevens et al. 2004).

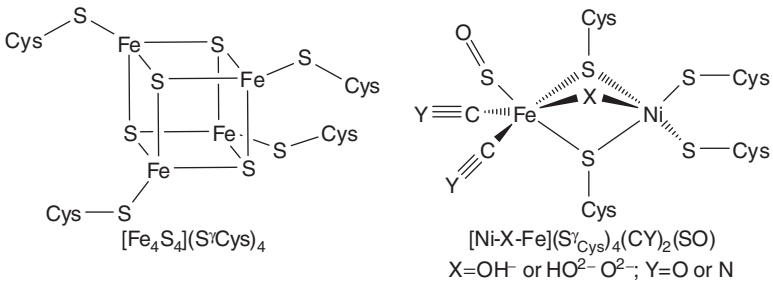


Fig. 17.9: Two different subunits present in FeNi-hydrogenases.

In the active cycle, nickel changes from EPR-active Ni^{III}, to Ni^{II}, and finally to Ni^{I}, which has not been observed because of its rapid electron transfer. The Ni^{II} forms themselves have high spin, as demonstrated by nickel L-edge soft X-ray spectroscopy and density functional theory (DFT) calculations. Ni-center is the site where the external CO binds, as demonstrated by IR e XRD studies on the CO-inhibited forms of [NiFe] H_2-ase derived from *Desulvibrio vulgaris* (Ogata et al. 2002) with unusual Ni-CO angles of 136.2° and 160.9°.

The synthesis of small-molecule models of the active site of [NiFe]H_2-ase has been attempted and has proven to be difficult (Georgekaki and Darensbourg 2004) so far. Computational studies on the [NiFe] active site (De Gioia et al. 1999a, 1999b; Bruschi et al. 2004; Niu, Thomson, and Hall 1999; Fan and Hall 2001; Li and Hall 2001; Niu and Hall 2001; Stein et al. 2001; Stein and Lubitz 2002; Foerster et al. 2003; Stein and Lubitz 2004; Van Gastel et al. 2006; Pavlov et al. 1998; Pavlov, Blomberg, and Siegbahn 1999; Siegbahn et al. 2001) and theory support high-spin nickel (Fan and Hall 2002) and suggest that terminal cysteine ligands act as bases in the heterolytic cleavage of dihydrogen through the S-atoms.

17.4.4 Molybdenum-iron-containing N_2-ase

The molybdenum-containing enzyme Mo-N_2-ase is well studied. Also known are all-iron, vanadium-containing, and tungnsten-containing enzymes. The Mo-N_2-ase enzyme is composed of two subunits, which are referred to as the iron subunit and the molybdenum-iron subunit (Kim and Rees 1992a, 1992b; Chan, Kim, and Rees 1993; Kim, Woo, and Rees 1993; Bolin et al. 1993; Peters and Mehn 2006; Peters et al. 1997; Mayer et al. 1999; Einsle et al. 2002). The iron subunit contains a single [Fe_4S_4] cluster, which mediates electron transfer to the Fe-Mo-containing subunit. The Fe-Mo subunit contains two 8Fe-7S clusters, referred to as P-cluster, and two 1Mo7Fe-9S clusters, referred to as Fe-Mo cofactors (FeMoco).

The FeMoco is the putative active site for dinitrogen and proton reduction, with the iron and molybdenum centers extensively bridged by sulfide ligands. Metal centers in FeMoco are organized in a bicapped trigonal prism, formed by six iron atoms and capped on opposite sides by an iron and a molybdenum center (▶Fig. 17.10). An interstitial N-atom occupies the center of the trigonal prism. A protein-bound cysteinate ligand binds the capping iron center to the protein. Histidine binds the molybdenum center to the protein; the molybdenum center is further coordinated by a homocitrate ligand.

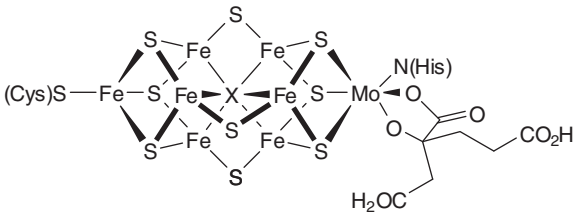


Fig. 17.10: Iron-molybdenum cofactor (FeMoco).

Tab. 17.4: Methanogenesis reactions.

(1) $4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2$
(2) $4\ HCOOH \rightarrow CH_4 + 3\ CO_2 + 2\ H_2O$
(3) $CH_3COOH \rightarrow CH_4 + CO_2$
(4) $C_2H_5COOH + 2\ H_2O \rightarrow CH_4 + 2\ CO_2 + 2\ H_2$
(5) $C_3H_7COOH + 2\ H_2O \rightarrow 2\ CH_4 + 2\ CO_2 + 2\ H_2$
(6) $C_4H_9COOH + 4\ H_2O \rightarrow 2\ CH_4 + 3\ CO_3 + 5\ H_2$

The mechanism of hydrogen production at FeMoco is still not well understood. Only recently has direct evidence of a hydride ligand bound to FeMoco become available (Igarashi et al. 2005). Alberty (2003), on the basis of thermodynamics, argues that the highly reduced state of FeMoco required for N_2 reduction leads to the incidental production of H_2. Others have suggested that the reductive elimination of H_2 is necessary to produce a more reduced form of the FeMoco (Orgo et al. 2004).

17.5 Methanogenic bacteria

Fatty acids are substrates employed by methanogens, as demonstrated by the fact that they do not accumulate in the digesters where they are produced during the hydrolysis, acidogenesis, and acetogenesis phases. ▶Tab. 17.4 shows the set of reactions that produce methane. About 70% of the methane produced derives from acetate, whereas the remaining 30% results essentially from the hydrogenation of carbon dioxide (Jeris and McCarty 1965; Smith and Mah 1966). These data allow us to estimate the biogas potential composition. Would biogas derive from acetate only (▶Tab. 17.4, Eq. 3), the composition would be 50% methane and 50% carbon dioxide. If 30% of methane derives from the direct reaction of carbon dioxide with hydrogen, the final potential composition is 65% methane and 35% carbon dioxide.

Differences in biogas real composition depend on the process control and the capacity to optimize the various reaction steps. Experiments with labeled carbon have shown that in the acetate molecule the methyl group gives rise to methane, whereas the carboxylate group produces carbon dioxide, as expected (Kim, Woo, and Rees 1993). Methanogenic bacteria may have specific nutritional needs (amino acids, fatty acids, vitamins, and heavy metals such as Co, Ni, and Mo) (Zeikus 1977).

More than one hundred methanogenic bacterial species have been isolated; some of the most important are listed in ▶Tab. 17.5 (Ferguson and Mah 1987).

Some species have been adapted both to mesophilic and thermophilic conditions. Methanogenic bacteria have been isolated in very different environments and conditions: anaerobic sediments (both fresh and sea water), pulp of trees, flooded lands, human and animal fecal excrements and digestive tracts, and hot springs with temperatures up to 85°C (Zeikus 1977; Mah et al. 1977; Stetter et al. 1981; Miller and Wolin 1983).

Tab. 17.5: Methanogenic bacteria.

Genus and Species	Substrates
Methanobacterium formicium DSM 863	H_2-CO_2 , formate
Methanobacterium thermoautrophicum	H_2-CO_2
Methanobacterium bryantii M.O.H.	H_2-CO_2
Methanobacterium wolfei DSM 2970	H_2-CO_2
Methanobrevibacter ruminantium DH1	H_2-CO_2, formate
Methanobrevibacter smithii PS	H_2-CO_2, formate
Methanotermus fervidus DSM 2088	H_2-CO_2
Methanococcus voltae PS	H_2-CO_2, formate
Methanococcus halophilus INMI Z-7982	Methanol, trimethylammine
Methanospirillum hungatei Jf1	H_2-CO_2, formate
Methanomicrobium mobile BP	H_2-CO_2, formate
Methanogenium cariaci JR1	H_2-CO_2, formate
Methanogenium thermophilicum CR1	H_2-CO_2, formate
Methanogenium aggregans MSt	H_2-CO_2, formate
Methanosarcina barkeri MS	H_2-CO_2, methanol trimethylammine, acetate
Methanosarcina thermophila TM-1	Methanol, trimethylammine
Methanoplanus limicola DSM 2279	H_2-CO_2, formate
Methanococcoides methylutens TMA-10	Methanol, trimethylammine
Methanolobus tindarius Tindari 3	Methanol, trimethylammine
Methanotrix soehngenii Opfikon	Acetate
Methanotrix concilii GP6	Acetate
Methanosphaera stadmane MCB-3	Methanol plus H_2

Methanogenic bacteria can be categorized into two groups:

- Acetoclasts (or methylotrophic), which are able to metabolize methanol, methylamine, and, above all, acetate. Only two genera belong to this group: Methanosarcina and Methanotrix.
- Hydrogenophils (or nonmethylotrophic), which employ H_2 and CO_2 as substrates for methanogenesis (some may use formate).

17.5.1 Methanogenesis

Several schemes have been proposed to explain the metabolic path leading to methane. The Barker scheme (1951, ▶Fig. 17.11) (Barker 1956) is of historical interest because it first proposed that intermediates are bound to carriers (generally marked with X). One of these carriers has been isolated by Mc Bride and Wolfe (1977) and has been shown

to be 2-mercaptoethanol sulfonic acid ($HS\text{-}CH_2CH_2SO_3^-$), named Coenzyme-M – it works during the last phase of the reactions presented in the Barker's scheme.

The methane production from the coenzyme-M adduct requires the intervention of the F_{430} coenzyme (▶Fig. 17.11), which has been proposed to have a nickel-tetrapyrrolic active center. The enzymes involved in the methane synthesis from CO_2 and H_2 are a matter of investigation by several research groups because their knowledge can add to the development of new interesting biotechnological applications. Recent studies have shown the implication of Ni (Aresta, Quaranta, and Tommasi 1988) in CO_2 reduction to CO and Fe and Ni (from a Fe-S/Ni protein) (Tommasi et al. 1998; Ragsdale and Kumar 1996) in the acetyl-moiety synthesis from CH_3 and CO.

Today it has been ascertained that the process goes through the THF and CODH cycles. In the THF cycle a molecule of CO_2 is reduced to formate via a formatedehydrogenase enzyme (W dependent), then to formaldehyde by a foarmaldehydodehydrogenase enzyme. Formaldehyde is taken by the THF enzyme (a nonmetal enzyme) and first bonded to an amino group to afford an imino moiety, N=CH, which is then reduced to a methylamino moiety, $NH\text{-}CH_3$. The methyl group is then taken by the cobalamin through a $H\text{-}CH_3$ exchange. Vitamin B12 then transfers the methyl to the Fe_4S_4-X-Ni enzyme. At the same time a second molecule of CO_2 is reduced to CO by CODH and transferred to the same Ni atom where the methyl is bonded. The two moieties, CO and CH_3, couple to afford the acetyl moiety bonded to Ni (Eq. 2).

$$Fe_4S_4\text{-X-Ni(CO)(CH}_3) \rightarrow Fe_4S_4\text{-X-Ni-C(O)-CH}_3) \quad (2)$$

At this point an acetylcoenzyme (A CoA-SH) takes the acetylgroup to afford CoAS-C(O) CH_3, which is hydrolyzed to afford back the CoASH moiety and acetic acid CH_3COOH. The latter is decomposed from methanogens into CO_2 and CH_4. However, starting with $2CO_2$ molecules and 8H (or $8H^+$ plus 8e-) one gets back a CO_2 molecule and methane plus $2H_2O$ (Eq. 3). It is also worth noting that once the methyl-cobalamin is formed (▶Fig. 17.12), methane can be released or methanol can be formed.

$$2CO_2 + 8\,[H] \rightarrow CO_2 + CH_4 + 3H_2O \quad (3)$$

Thus, the CH_4/CO_2 ratio depends on many factors. It has been demonstrated (Aresta, Narracci, and Tommasi 2003) that the concentration of metal ions such as Fe^{2+}, Ni^{2+},

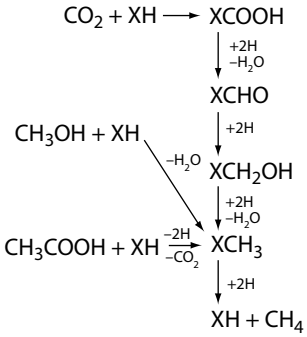


Fig. 17.11: Barker's scheme for methanogenesis.

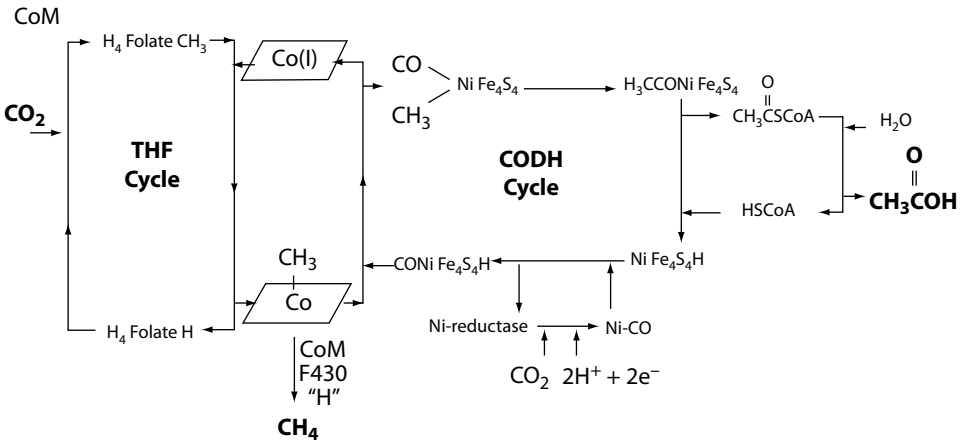


Fig. 17.12: The CODH and THF cycles implied in the formation of biogas.

and Co^{2+} can influence the rate of formation of H_2 and the ratio CH_4/CO_2, most probably through the availability of the enzymes of which they are the active centers.

The production of methane from waste organics is quite a complex process that requires several parameters to be optimized and correctly mastered for the production of methane to be effective.

17.5.2 The effect of the concentration of Ni, Fe, and Co on the production of H_2 and CH_4

The influence of the Fe, Ni, and Co concentration on the production of H_2 and on the composition of biogas was carried out by monitoring the H_2, CO_2, and CH_4 production during 8 hours after the addition of feed (acetogenesis phase) and over 5 days (methanogenesis phase). As expected, each metal produced a different effect on the basis of the role of the enzymes in which they are present. Ni(II), Fe(II), and Co(II) were added to the sludge either separately or in combination, always at a subtoxic concentration. The concentration of the metal in the solution was increased from three to four times with respect to the standard conditions (e.g. 22.4 ppm with respect to 6.5 ppm). The distribution between the liquid and solid phase was determined by elemental analysis. The metal concentration in the solution decreased from 90% of the value read soon after the addition to 70% after 2 weeks. Therefore, during the test of the 8 hours (which starts soon after the addition of metal and feeding) and 5 days, the bacteria really feel the increase in the concentration of the metal available in the solution. The response to such an increase in the metal concentration is, therefore, a real cause-and-effect process. ▶Fig. 17.13a shows that an increase of the concentration of Ni(II) in a solution causes a decrease of dihydrogen in the gas phase.

This observation agrees well with the role of nickel as part of the active site in H_2-consuming hydrogenases (Albracht 1994). Therefore, the addition of Ni(II) increases the activity of such H_2-consuming hydrogenases. Conversely, when Fe(II) was added, the increase of H_2 production in the batch reactor was observed within 2.5 hours after

feeding (▶Fig. 17.13b), in comparison with the control, which had a lower H_2 production. Also, these data agree with the role of iron in H_2-evolving hydrogenases, which promote the formation of H_2 (Adams 1990). It is noteworthy that the addition of cobalt did not cause any variation in H_2 production at any time after the start of the fermentation. Such metal-dependent effects were evident only when fresh feed was added to a not-too-aged system. ▶Fig. 17.14 shows the composition of biogas produced after the addition of Ni(II): an increase of the amount of methane in the gas phase was observed with an increase of the molar ratio CH_4:CO_2 from 3 to 4.5. However, Ni(II) caused a more effective conversion of CO_2 into methane.

The observed effects linked to an increased concentration of the metals match the role of metals in enzymes. Among the three metal ions, nickel has, thus, the most spectacular effect (Aresta, Narracci, and Tommasi 2003). These results suggest that the controlled addition of Fe, Ni, and Co could be beneficial for improving the methanation process of waste.

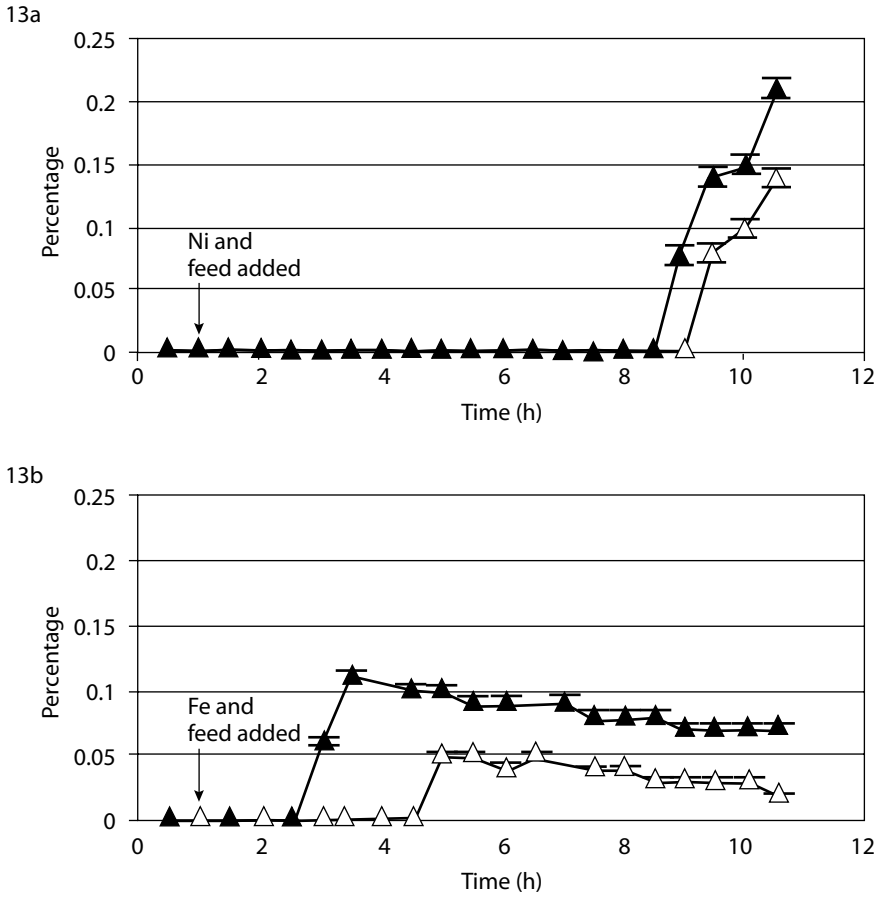


Fig. 17.13: Influence of Ni(II) and Fe(II) on the dihydrogen production during the acidogenesis phase in the anaerobic fermentation of FVG. The black triangles represent the control, the white represent the reactor where the metal is added.

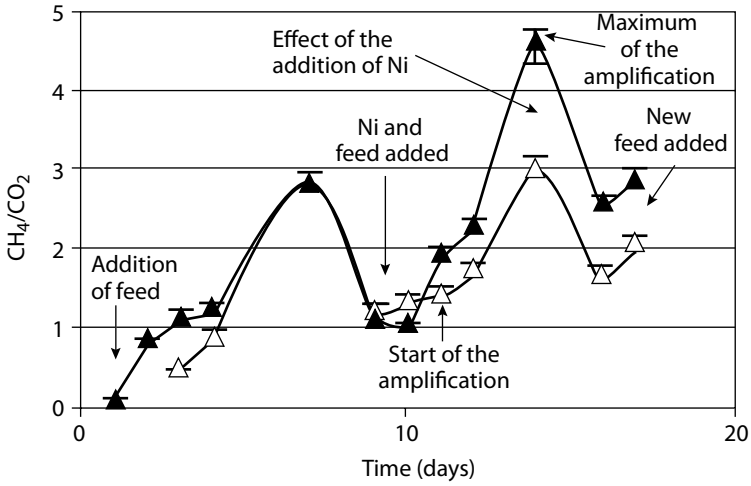


Fig. 17.14: Effect of the addition of Ni(II) on the production of biogas: an increase of the CH_4/CO_2 molar ratio (black triangles) with respect to the control (white triangles) is evident.

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18 From lab-scale to full-scale biogas plants

Roberto Farina and Alessandro Spagni

18.1 Laboratory-scale biomethane potential tests

The anaerobic digestion process is a complex biological transformation of organic matter (OM) that has, as final product, a mixture of gases mainly composed of methane and carbon dioxide. Each step during the degradation process is sustained by well-identified groups of bacteria able to conduct a specific step of the whole degradation process.

The renewed interest around anaerobic digestion during the past few years is strictly connected with the possibility of producing energy with a neutral impact on greenhouse gas emissions and with the treatment of the organics contained in the used substrates, and, consequently, the reduction of their potential pollution impact on the environment.

The other important aspect of this process is that the energetic balance is absolutely positive (at least for medium-high concentrated wastes and well-designed and managed plants), and this can generate a great advantage compared with other possible biological or nonbiological treatment technologies.

For this reason, over the past decade, several wastes (animal manure, agricultural wastes, agroindustrial wastes, organic fraction of municipal solid wastes [OFMSW]) and wastewater flows have been diverted from other possible processes (mainly aerobic biological) to anaerobic digestion. For the same reason, several crops have also been very recently cultivated for their specific use in anaerobic reactors for energy production.

From this wide range of possible substrates, the first questions we would like answered when approaching anaerobic digestion reactors are: Will they produce biogas? How much methane or biogas is it possible to recover from them? How long will this process take?

The answers to these questions strictly depend on the biodegradability of the substrates.

Biodegradability evaluation of an OM can give the first information regarding the possibility of using it for economically valuable biogas production.

Although this information seems particularly relevant, and several methods with a high grade of confidence have been developed, their harmonization has not yet solved all the problems in the comparison of the results.

In general, it is possible to divide the different methods into two main groups according to the methodological approach to the solution of the problem. The first group is based on the theoretical evaluation of the chemical compound's degradation. The second group is based on empirical laboratory tests, which can use simple or very complex analytical instruments.

The most popular approach at the evaluation of the theoretical amount of methane or biogas that it is possible to obtain from a general organic molecule has been proposed by Buswell and Boruff (1932).

In this method, the chemical composition of the OM is considered based on its elementary composition, such as carbon, hydrogen, nitrogen, and oxygen. In the Buswell equation, the growth of the microbial biomass is not considered because its influence is assumed negligible and the OM is supposed to be completely transformed to methane

and carbon dioxide. In some re-elaboration of the proposed model other elements have been included, such as sulfur. In the following example the basic demonstration is shown (Buswell and Boruff 1932).

The transformation of an organic molecule to methane and carbon dioxide during the anaerobic digestion process can be described by the following Equation 1:

$$C_aH_bO_cN_d + \alpha_1H_2O \rightarrow \alpha_2CH_4 + \alpha_3CO_2 + \alpha_4NH_3 \tag{1}$$

Where:

- a, b, c, d represent the molar composition of carbon, hydrogen, oxygen, and nitrogen, respectively, known because the compound taken in consideration is a known molecule or because an elementary analysis has been previously performed; and
- α_1, α_2, α_3, α_4 represent the stoichiometric coefficients for the chemical balancing of the equation.

The mass balance of the four elements present in the equation will give the solution for the α coefficients (Eq. 2):

$$\begin{cases} a = \alpha_2 + \alpha_3 \\ b + 2\alpha_1 = 4\alpha_2 + 3\alpha_4 \\ c + \alpha_1 = 2\alpha_3 \\ d = \alpha_4 \end{cases} \tag{2}$$

Solving this system of simple equations, we obtain the following result (Eq. 3):

$$\begin{aligned} C_aH_bO_cN_d + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4}\right)H_2O \rightarrow \left(\frac{4a + b - 2c - 3d}{8}\right)CH_4 \\ + \left(\frac{4a - b + 2c + 3d}{8}\right)CO_2 + dNH_3 \end{aligned} \tag{3}$$

Remembering that in standard conditions, one mole of gas occupies 22.415 L, and considering the atomic weight of the elements, the volume (standard conditions) of the (biogas $B_{0\text{-}biogas}$) obtained results as (Eq. 4):

$$\begin{aligned} B_{0-biogas}\left[\frac{m_n^3}{kg}\right] &= \frac{\left[\left(\frac{4a + b - 2c - 3d}{8}\right) + \left(\frac{4a - b + 2c + 3d}{8}\right)\right] \cdot 22.415}{12a + b + 16c + 14d} \\ &= \frac{22.415a}{12a + b + 16c + 14d} \end{aligned} \tag{4}$$

Since in the biogas the interest is mainly related to the energetic content that is given by the methane, it is possible to apply the same approach to the methane produced ($B_{0\text{-}methane}$) only as shown in Equation 5:

$$B_{0-methane}\left[\frac{m_n^3}{kg}\right] = \frac{\frac{4a+b-2c-3d}{8}\cdot 22.415}{12a+b+16c+14d} \tag{5}$$

From the combination of Equations 4 and 5 it is possible to define the ratio of methane in the biogas (P_{CH4}) according to Equation 6:

$$P_{CH_4}\left[\frac{m^3_{n-CH_4}}{m^3_{n-Biogas}}\right] = \frac{B_{0-methane}}{B_{0-biogas}} = \frac{4a+b-2c-3d}{8} \tag{6}$$

It is easy to understand from Equation 6 that the methane content in the biogas will increase with the increase of the H/C ratio.

It is usually convenient to manage the gas production in terms of chemical oxygen demand (COD): in this case, Equations 4 and 5 result in the following equations (Raposo et al. 2011):

$$B_{0-biogas}\left[\frac{m_n^3}{kg_{COD}}\right] = \frac{22.415a}{32\cdot\left(a+\frac{b}{4}-\frac{c}{2}-\frac{3d}{4}\right)} = 0.7\cdot\frac{a}{a+\frac{b}{4}-\frac{c}{2}-\frac{3d}{4}} \tag{7}$$

$$B_{0-methane}\left[\frac{m_n^3}{kg_{COD}}\right] = \frac{\frac{4a+b-2c-3d}{8}\cdot 22.415}{2\cdot\frac{4a+b-2c-3d}{8}\cdot 32} = 0.350 \tag{8}$$

The advantage of this approach is that it is possible to obtain the theoretical biogas or methane production by a simple analysis of the substrate; on the contrary, as in the case of COD or other chemical analysis, the limit is related to the impossibility of estimating whether the OM is really biodegradable, or whether it does not give any toxic or poisoning effect on the biomass.

To understand these other possible effects, confirm the theoretical results, and identify the possible range of work for a full-scale reactor, it is necessary to carry out some laboratory (biochemical) tests.

The theory of the biochemical methane potential (BMP) test is quite simple and the theoretical approach and procedures are similar to the well-known biological oxygen demand (BOD) analysis.

In the BMP test a well-known amount of substrate is put in contact with a known amount of biomass in a closed environment (airtight, or without the presence of oxygen) at a defined and stable temperature. The gas that will be produced is measured quantitatively and qualitatively. The measurements will continue until the gas production completely stops or its production can be considered negligible with respect to the total gas collected.

For good results the test must be conducted in optimal conditions with an acclimatized inoculum, without biological inhibitory factors, and with temperature and pH control (or using buffering substances).

The results obtained from these tests usually give a lower value than the ThBMP (theoretical BMP) because biomass growth subtracts from 5% to 10% of the substrate to the biogas production. It is of note to consider that if the substrate contains a large fraction of particulate organic matter (POM), the degradability (and therefore the BMP) should result lower than if the substrate is composed by dissolved OM (DOM) only; moreover, the kinetics for POM biodegradation are usually slower than DOM.

Several methods have been developed for the control of the anaerobic biodegradability of a substrate.

Most of them are based on the evaluation of the degradation products of the substrate (methane or biogas) while others instead are based on the evaluation of the substrate consumed during the process.

Two different and particular (but interesting) methods that are, however, still in the developing stage use the titration principle (Rozzi and Remigi 2001) or the calorimetric evaluation (Jolicoeur et al. 1988).

Several regulatory bodies have developed their own methods for anaerobic biodegradability and BMP evaluation (Müller, Frommer, and Jorg 2004). Existing methods are mostly related to the anaerobic biodegradability of substances for environmental pollution prevention. The most useful methods applicable for biomass and wastewater are reported in ▶Tab. 18.1.

General rules that can be extracted from the different available methods for the preparation of a BMP test are:

- Number of tests for substrate: all tests should be prepared at least in triplicate with the addition of a control test (inoculum without substrate in order to evaluate the amount of biogas produced by endogenous processes), a reference substance test (to evaluate the reliability of the inoculum), and an inhibition test if necessary.
- Inoculum: use of well-adapted anaerobic sludge under endogenous conditions. The final sludge concentration should be between 1 and 5 g_{TS}/L in the final test solution.
- Reactor vessel: should be any vessel able to resist to pressure of at least 2 bars and be made in glass or any other material that does not have effect on biological processes.

Tab. 18.1: Main methods for the estimation of anaerobic biodegradability.

Body/Number/Year	Title of the Regulation/Standard
DIN/38414/1985	Bestimmung des Faulverhaltens. Determination of the amenability to anaerobic digestion.
ISO/11734/1995	Water Quality – Evaluation of the ultimate anaerobic biodegradability of organic compounds in digested sludge – Method by using the biogas production.
ECETOC/28/1998	Guideline for screening of chemicals for anaerobic digestion.
ASTM/2170/2001	Standard test method for determining anaerobic biodegradation potential of organic chemicals under methanogenic conditions.
OECD/311/2006	Anaerobic biodegradability of organic compounds in digested sludge by measuring the gas production.

The vessel must have a gas-tight cap and a system for sampling and collecting the produced gas.

- Temperature: should be controlled at 35 ±2°C or 55 ±2°C for tests conducted under mesophilic or thermophilic conditions, respectively.
- pH value: must be maintained at 7.0 ±0.5 during the entire test duration.
- Quantitative gas measurement: can be carried out with very simple methods such as the water (or using a buffer solution) displacement method (▶Figs. 18.1 and 18.2). In this case, according to the pH of the buffer solution used, the biogas (if an acidic solution is used) or the methane only (if alkaline solution is used) can be measured, or by a pressure transducer (▶Fig. 18.3) able to measure the increase of the pressure in the test bottle and release the gas when a set point is reached. Moreover, very small gas counters should be able to measure even small amounts of gas produced (e.g. 1 ml), or with an eudiometer (▶Fig. 18.4).
- Gas quality: can be measured using titrimetric, gravimetric, or, more accurately, gas chromatographic methods.

According to this basic information, the substrate and the inoculum should be characterized before beginning the BMP test. The minimum analytical characterization should require the measurement of total (TS) and volatile solids (VS), COD (possibly distinguishing between dissolved and particulate), COD/VS ratio, nitrogen, and phosphorus.

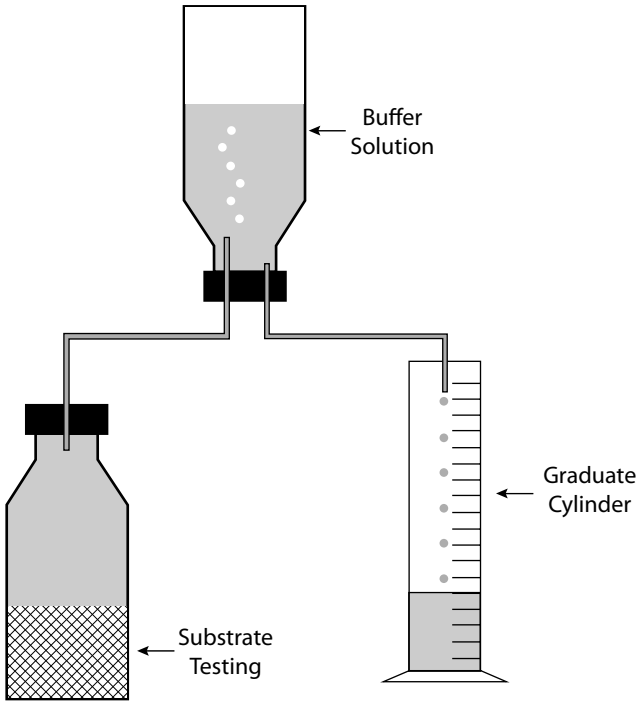


Fig. 18.1: Gas measurement system using the water displacement technique.



Fig. 18.2: BMP gas measurements in laboratory by the water displacement method.

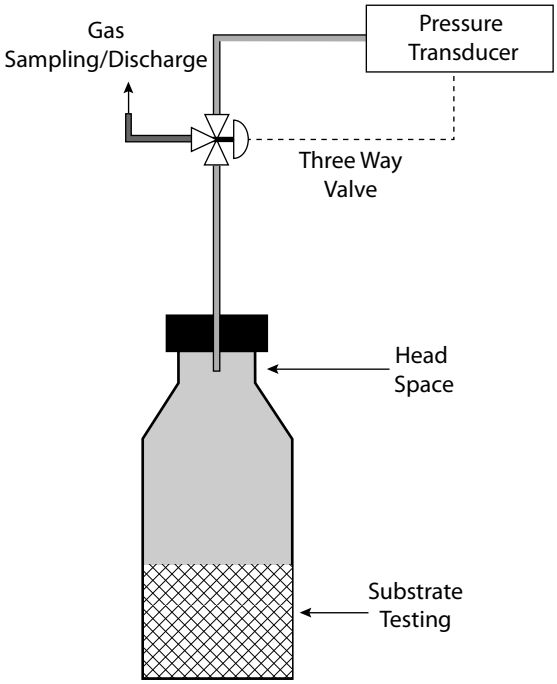


Fig. 18.3: Gas measurement using a pressure transducer device.

(Angelidaki et al. 2009). In the case of the use of wastewater, total (TSS) and volatile suspended solids (VSS) should also be performed.

Another important parameter is the substrate-inoculum (S/I) ratio. Too low values do not give enough sensitivity, whereas too high values can instead determine inhibition phenomena due to an excessive production of volatile fatty acids or a pH drop.

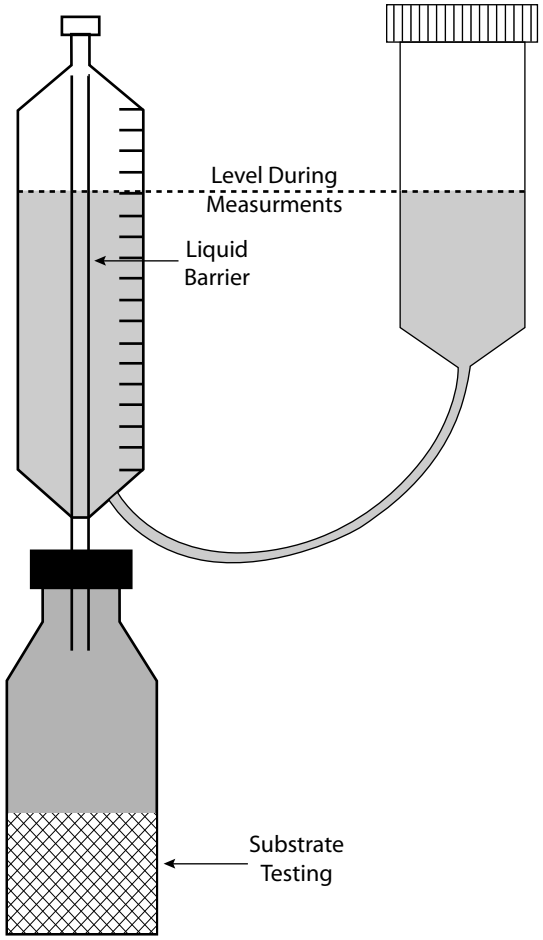


Fig. 18.4: Gas measurement using eudiometer for pressure effects abatement (as ISO 14853 2005).

For these reasons the substrate organic carbon in the mixed liquor should not exceed the value of 20–100 mg/L while the sludge concentration should range between 1 and 3 g/L.

Since a detailed measurement of organic carbon is not common, often the S/I ratio is expressed as grams of volatile solids on grams of inoculum used: in this case the ratio should range between 0.3 and 1.

If the degradation kinetic constants are known for both hydrolytic and methanogenic phases, it is possible to use one of these values to better define the S/I ratio. In this case, it is important to verify that the methanogenic growth rate is higher than the hydrolytic rate.

$$r_h\left[\frac{g_{COD}}{d}\right] = K_h\left[\frac{1}{d}\right]\cdot COD_s\left[\frac{g}{L}\right]\cdot V_s\left[L\right] \tag{9}$$

Where:

r_h: hydrolysis rate
K_h: hydrolytic kinetic constant
V_s: volume of substrate used in the test
COD_s: concentration of the organic matter in the substrate

$$r_{met}\left[\frac{g_{COD}}{d}\right] = SMA\left[\frac{g_{COD}}{g_{VS}.d}\right]\cdot VS_I\left[\frac{g_{VS}}{L}\right]\cdot V_I[L] \tag{10}$$

Where:

r_{met}: methanogenic rate
SMA: specific methanogenic activity
V_I: volume of substrate used in the test
VS_I: concentration of volatile solids in the inoculum

As stated previously, if $r_{met} > r_h$ and the COD_S/VS_I ratio (subscripts S and I stay for substrate and inoculum, respectively) is known, the S/I that should not cause inhibition problems can be easily obtained.

During the test, the biogas collected is measured and put in a graph cumulating the quantity collected with the previous samples. The test duration is usually not previously defined (although there are indications in some proposed methods) and depends on the specific substrate degradation velocity and, in the case of solid substrates (OFMSW, energy crops, manure), on substrate particle size. In the latter case, to have comparable results of the lab-scale tests with the real full-scale plants, the same substrates with the same particle size of the real case should be used.

To obtain a correct biogas production, it is important to subtract the biogas produced by sludge endogenous activity in the blank vessel test.

In ▶Fig. 18.5 it is possible to see a typical graph for a BMP test. In this case, the duration of the test could be interrupted at around day 40, because after that period no relevant changes in the gas production occur. From the cumulative BMP graphs,

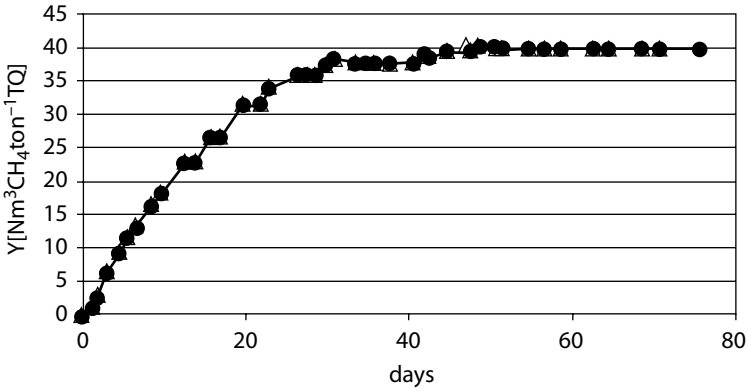


Fig. 18.5: Cumulative biogas production graph.

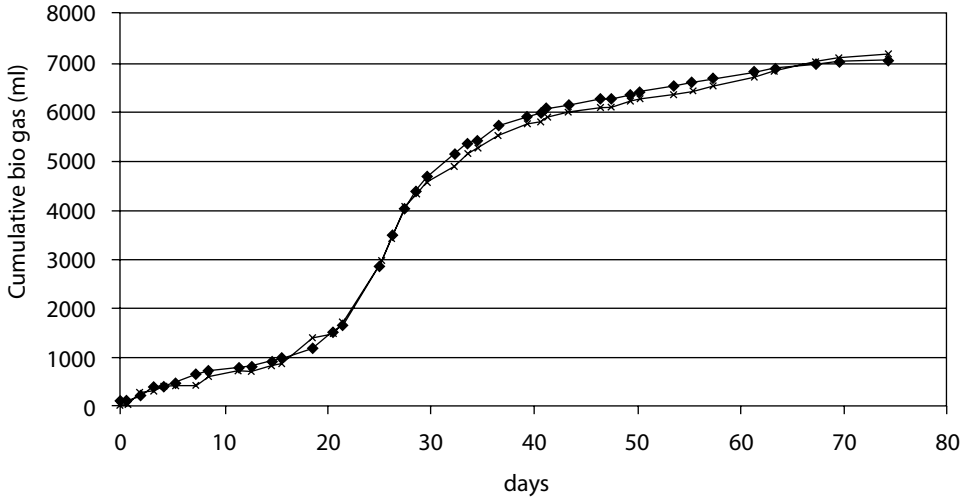


Fig. 18.6: Cumulative gas production with problems of degradation.

information on process kinetics can also be drawn, which can be used (with the S/I ratio) for the design of the HRT (and therefore the reactor volume) of the full-scale plant.

▶Fig. 18.6 shows that the substrate used in that test has some difficulties in the hydrolytic step (possibly due to acclimation) and, therefore, the biogas production takes some time before starting (lag phase): after approximately 40 days, the biogas production continues with a much lower rate for a long period of time.

The BMP can be used for the evaluation of the performances (such as $L_{CH_4}g_{VS}^{-1}$) obtained during the test.

$$BMP\left[\frac{L_{nCH_4}}{g_{VS}}\right]=\frac{\left(V_{CH_4}s-V_{CH_4}b\right)\left[L_{nCH_4}\right]}{VS\left[\frac{g_{VS}}{L}\right]\cdot Vs\,[L]} \tag{11}$$

Where:

$V_{CH4}s$ and $V_{CH4}b$ = volume produced by the sample and the blank bottles respectively
VS = volatile solids
Ln = normal (STP conditions) liter

If the methane produced during the test is put in relation with the COD/VS ratio, it is possible to calculate the biodegradability percentage of the substance tested remembering that, according to the Buswell formula, 1 kg of COD produces approximately 350L of methane.

$$BMP_{\text{degradability}}\,\%=\frac{BMP\left[\frac{L_{nCH_4}}{g_{VS}}\right]}{\frac{COD}{VS}\left[\frac{g_{COD}}{g_{VS}}\right]\cdot 0.35\left[\frac{L_{nCH_4}}{g_{COD}}\right]}\cdot 100 \tag{12}$$

The obtained results can be expressed using several units. In the case of wastewater, the most used unit is the $m^3_{CH4}kg^{-1}_{COD_{in}}$ or $m^3_{CH4}kg^{-1}_{COD_{deg}}$ (where the subscripts *in* and *deg* stand for influent and degraded, respectively), while in the case of solid or semisolid material where the analysis of the COD can be difficult or can determine incorrect evaluations, $m^3_{CH4}ton^{-1}_{WW_{in}}$ is more used (where the subscript *WW* stands for wet weight) or $m^3_{CH4}ton^{-1}_{TS_{in}}$ or $m^3_{CH4}ton^{-1}_{VS_{in}}$.

The results should be evaluated for repeatability, evaluating the differences between the duplicate/triplicate tests, which should not be higher than 10%.

Moreover, if the results obtained do not fit the expected results, it is probably because some inhibitory effect on the used sludge happened, or that the used inoculum was not adapted/acclimated. In this case, a change of the S/I ratio or a preexposition of the sludge to the substrate that will be used in the BMP test could be useful to improve the test reliability.

A second relevant test evaluation should include the check for COD and carbon mass balance. The COD balance should be carried out considering the COD of the substrate introduced in the test, the COD remaining at the end, and that derived from the produced methane. It is important to also take into account that a part or the COD has been transformed into biomass: the fraction of produced biomass from COD accounts for approximately 5%–10% of the substrate COD. Therefore, in the case of the digestion of solid wastes, as it is almost impossible to separate the biomass from the effluent, the check on the COD balance should also be carried out considering the inoculum.

For carbon mass balance, the approach should be the same, considering the contribution of the organic and inorganic carbon at the beginning and at the end of the test adding even that of the biogas.

18.2 Pretreatment of biomasses

Biomass and wastewater pretreatment is performed to enhance the productivity of the substrate and, in some cases, for sanitary reasons or for the correction of some inadequate characteristics of the material used (e.g. too high or too low pH, unbalance C/N ratio, inhibitory compounds removal, substrate size reduction).

Biogas productivity from biomasses is strictly correlated to the availability of volatile solids and their biodegradability.

In the case of energy crops, for example, the presence of lignin can strongly reduce the availability of cellulose and hemicellulose (▶Fig. 18.7) and, thus, considerably reduce the biogas production with respect to the expected values. The reason is due to the inability of the anaerobic bacteria, in a reasonable period of time (hydraulic retention time into the anaerobic reactor), to destroy the lignin and make the other compounds available to anaerobic digestion.

Several technologies can be applied for enhancing the biogas production and new applications are being studied.

Since the complexity of the organic matter used in anaerobic digestion and the different effects that pretreatments can have on the different molecules, the most relevant lignocellulosic biomass characteristics for their best pretreatment are still not completely clear.

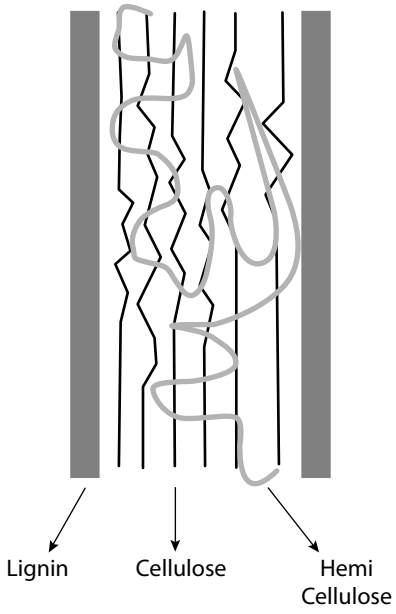


Fig. 18.7: Example of the structure of a lingocellulosic compound.

Moreover, during pretreatments (especially the thermal and chemical ones) some inhibitory compounds can be formed, which affect and reduce the microbial activity.

The last point necessary to consider is that a pretreatment is always an additional step to the digestion process and, therefore, its capital and management cost must be covered by the biogas production improvement.

Typically, pretreatments can be classified as:

- Mechanical
- Biological
- Chemical
- Thermal

Mechanical pretreatment is probably the most applied pretreatment for biomasses. Its main purpose is the reduction of the substrate particle. In this way, the soluble organic matter contained in the substrate can be more easily extracted and put in contact with bacteria, thus increasing the surface/volume ratio, making even the nonsoluble molecules more available to bacteria.

There is evidence that, for the same substrate, the size reduction improves the biogas production rate up to 60% (Delgenès, et al. 2003; Pommier, et al. 2010), whereas the biogas yield is not always improved. Therefore, mechanical pretreatment could help in the reduction of the plant size (or increase the amount of the treatable substrate), but, on the contrary, usually significantly increases the energy consumption.

The main advantage of the mechanical pretreatment is that it does not cause the production of inhibitory products: the possible disadvantage of this pretreatment is the high energy consumption that is directly correlated with the dimension size reduction.

There are several machineries able to reduce material into small particles. The choice of the machinery mainly depends on the desired final size of the substrate, the hardness of the substrate used, and the amount of the material that is daily milled. Hammer mills or knife mills are the most used, and the principle of work is quite similar for both: during the rotation of the hammers or knifes the substrate is obliged to pass between a small opening between two hammers or knifes, determining the cutting of the biomass fibrous material.

Extrusion is another mechanical pretreatment technique. In these machineries the biomass is compressed using an Archimedean screw with a larger diameter in the feeding side and a smaller diameter in the exit side. This determines an increasing of the pressure and a fraying of the material. The disadvantage of this machinery is the possibility of determining the squeezing of the material, obtaining a juice from one side and a dry panel from the other, the latter results in material difficult to mix with the material already under digestion.

Thermal pretreatments are normally used in wet conditions, with the aim of increasing the hemicellulose hydrolysis and organic acid production. These treatments are conducted at temperatures lower than 240°C to prevent the pyrolysis phenomena and reduce the energy consumption (Ramos 2003).

During thermal treatment, lignin is solubilized and some inhibitory compounds, such as phenols, may be released.

Steam explosion is one of the most interesting and promising methods, but is still very costly for large-scale application to lignocellulosic biomasses. With this technique, the biomass is closed in a chamber saturated with steam at a temperature of around 240°C and a pressure of approximately 10 bars for a short period of time (a few minutes): after this period a rapid pressure drop inside the chamber determines a rapid cooling of the biomass, determining the explosion of the cell membranes and making available the internal content of the cells.

Chemical treatment with acids or alkali is not a particularly common practice. The advantages of these pretreatments are the hydrolysis or solubilization of lignin and hemicellulose, making cellulose more available for the digestion process.

The undesired effect of chemical pretreatments is the need to readjust the pH before feeding the digesters. Moreover, the chemical should be carefully chosen, avoiding, for example, the use of sulfuric acid (to prevent the formation of hydrogen sulfide that may determine toxicity problems, corrosion, and smells), of nitric acid (which may cause the nitrogen concentration to increase in the biogas and inhibit the methanogenic activity), and of ammonia (which may cause problems for field application of the digestate).

Other possible pretreatments are related to the use of strong oxidizers to modify the molecular structure of the biomass and make the compounds more available for bacteria. The use of peracetic acid seems interesting (Teixeira, Linden, and Schroeder 1999), which is a very selective oxidant for lignin. Its use increases the hydrolysis of the cellulose contained in the biomass of about 100%. The further advantage of peracetic acid is that the final product of its reduction is acetic acid, which is a very good substrate for the methanogenic bacteria.

An important point to take into account for chemical pretreatment application is the management of the added or resulted compounds. Strong acids or alkali are dangerous

compounds that require particular attention during their use and their storage, and people who manage anaerobic digestion plants seldom have the appropriate knowledge for the safe management of these chemicals.

Biological pretreatments can also be conducted with enzymes or using selected populations of microorganisms to enhance the availability of the cellulose. Enzymes can be extracted from filamentous fungi such as *Tricoderma reesei*. There are several commercial products suggested for the treatment of lignocellulosic substrates. Normally, they contain three enzymes: endo-β-glucanase, eso-β-glucanase, and β-glucosidase.

In several cases the equalization or the mixing tank also serves for biomass pretreatment. In this case, the high loading rate applied in this tank determines the development of a microbial community particularly able to work under acidic conditions, producing organic acids that are advantageous for the subsequent methanogenic step. During this phase the fast drop of the pH to values around 4 can help the disgregation of some complex molecule yielding more available compounds for the subsequent step. During this acidification, odor could be produced, which should be controlled with specific techniques. It is of note that during this acidification phase, large quantities of hydrogen (which can reach the percentages of 20–30) could also be produced.

18.3 Design criteria

There are several possibilities to approach to the design criteria of an anaerobic digestion plant. During the planning of an anaerobic reactor design, it is important to previously collect some information regarding the material that will be treated, the possibility to change it during the life of the plant, and the possible need to separate the sludge from the digestate during or after the digestion process. This will influence the choice of the reactor type and, therefore, the applied process.

It is possible to summarize the anaerobic digestion process as a chain of four main degradation processes: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Each one of these processes is characterized by its own rate that depends on the substrate, the biomass characteristics, and the amount of available biomass. For a good conduction of the whole methane production process, it is important to maintain the rates k for the four defined phases as $k_{\text{hydrolysis}} < k_{acidogenesis} < kacetogenesis < k_{\text{methanogenesis}}$. Note that, on the contrary, the methanogenic process is usually the rate-limiting reaction for anaerobic digestion.

The reason for this necessity is because if the rate of the following step is lower than the previous one, there is an accumulation of catabolic products that can generate an unbalancing effect of the process conditions, and, in particular, the formation of long-chain fatty acids that are transformed to methane with difficulty and may determine the pH drop to values that are very inhibitory to methanogenic microorganisms.

This means that according to the Monod kinetic, the degradation rates of the process will be:

$$k_i = k_{i,\max} \frac{S_i}{S_i + K_{i,S}} \cdot X_i \tag{13}$$

Where:

k_i is the rate for the *i*-esim (where *i*, hydrolysis, acidogenesis, methanogenesis)
$k_{i,max}$ is the maximum rate of the *i*-esim process
S_i is the concentration of the substrate of the *i*-esim process
$K_{i,S}$ is the half saturation constant of the *i*-esim
X_i is the microbial biomass involved in the *i*-esim process

If this approach is taken into account for all four steps of the anaerobic process, it is possible to define which is the slowest rate and, as a consequence, which will be the maximum acceptable rate for the entire process.

Very often, in particular in anaerobic reactors fed with agricultural biomasses, the reactors are fed with different material depending on several conditions and, especially when the price of the biomass plays an important role, it is difficult to define the exact degradation rate. For this reason, it is important to take into account some safe parameters during the reactor design.

The biological process is not the only criteria that is taken into account during the plant design; for example, the working temperature is another important parameter that must be carefully considered.

Although under thermophilic conditions the degradation of several compounds is faster than under mesophilic ones, this does not give any particular advantage in terms of the total biogas production, but only in the dimension of the plant (LfU 2007) as it is possible to see in ▶Fig. 18.8.

Under thermophilic conditions the free ammonia concentration can be much higher than under mesophilic conditions. Since free ammonia is an inhibitory compound at low concentration and toxic at higher, it is important to keep in consideration that, if the

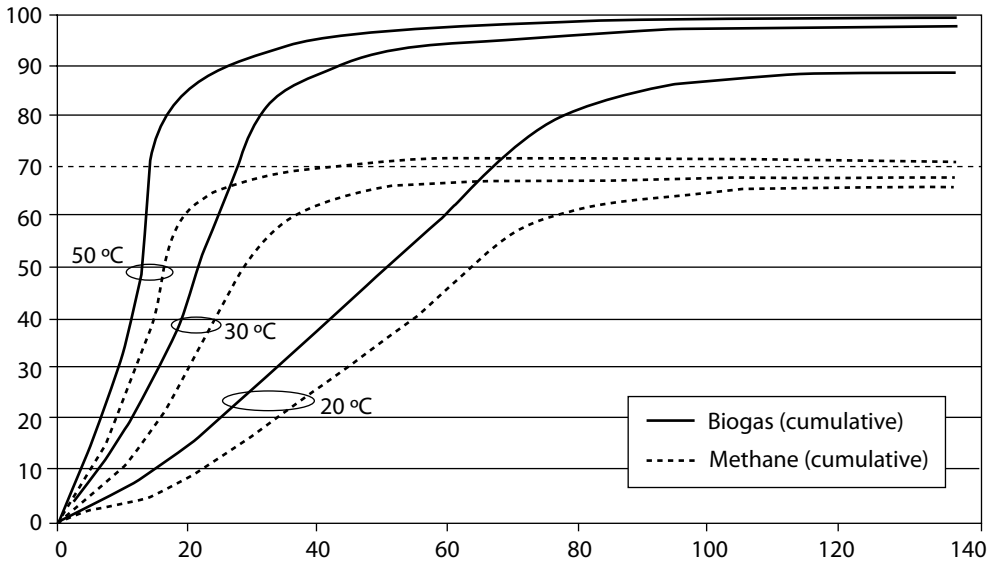


Fig. 18.8: Cumulative biogas production of methane and biogas at different temperatures.

reactor will be fed with substrates reach of proteins, it is easier to reach toxic concentrations under thermophilic conditions than under mesophilic ones. Ammonia can have an inhibitory effect (Farina et al. 1988) under mesophilic conditions from the concentration of 700 mg L^{-1}, but it is normal to operate at values as high as 1,500–2,000 mg L^{-1}, while the upper limit that should not be exceeded is 4,000 mg L^{-1} (Angelidaki and Ahring 1994).

Because the free ammonia depends on pH and temperature, the effective free ammonia concentration in the digester can be easily calculated as follows:

$$[NH_3] = \frac{[NH_3] + [NH_4^+]}{1 + \frac{[H^+]}{ka}} \tag{14}$$

Nevertheless, it is important to have a proper amount of available nitrogen for biomass protein synthesis and for the other metabolic microbial activities. This concentration can be correlated to the COD: the theoretical minimum COD/N/P ratios have been identified as 350:7:1 for highly loaded (0.8–1.2 kg_{COD} $kg_{VSS}d^{-1}$) and 1,000:7:1 for lightly loaded (<0.52 kg_{COD} $kg_{VSS}d^{-1}$) anaerobic systems (Henze and Harremoes 1983).

Under thermophilic conditions, carbon dioxide and hydrogen sulfide reduce their solubility. On the one hand, this means a lower buffer capacity of the mixed liquor in digestion with a higher problem of pH control and a release into the biogas with possible corrosion problems of the head space of the reactor or in the machineries that are in contact with the biogas. On the other hand, this can be an advantage for biological processes because the two gases are removed from the mixed liquor.

The most important advantage that is possible to obtain applying thermophilic processes is the better hygienization and, thus, the decrease of the pathogenic charge.

Normally, the higher energetic requirement needed for temperature control of the reactor does not severely affect the energetic balance of the plant because there is usually an abundance of thermal energy derived from the electricity generator.

Regarding the use of plants with one single stage or with more stages, the choice is usually related to the need to produce better conditions for the different phases of the anaerobic process. In fact, hydrolysis and acidogenesis usually require higher temperatures and lower pH than methanogenesis.

Using one-stage reactors, average conditions for all anaerobic reactions (i.e. hydrolysis, acidogenesis, acetogenesis, and methanogenesis) have to be maintained, while in multistage reactors, instead, it is possible to better control the different conditions.

However, very often in real situations, the first step (of a two-stage plant) of full-scale plants results in a hydrolytic/methanogenic reactor, and the second step is, instead, just a post reactor used to improve substrate degradation and collect the portion of the gas that otherwise would be lost with the effluent.

After these general considerations, when a reactor is designed, it is important to satisfy at least two conditions. The first condition is related to the residence time of the microflora inside the reactor (sludge age or solids retention time [SRT]), which must be longer than its duplication time (growth rate) in order to prevent the wash out of the biomass from the reactor. In reactors used for the digestion of biomasses or in continuous stirred-tank reactors (CSTRs) this time is usually equal to the hydraulic retention time

(HRT). In other reactors, mainly working on wastewaters, it is possible to separate the sludge from the water stream and in this way the SRT results much higher than the HRT.

The second condition is related to the quantity of substrate introduced in the reactor, which must always be lower than its maximum degradation capacity. If this condition is not respected (overload condition), the substrate cannot be completely utilized with loss in terms of biogas production efficiency and process failure due to the inactivation/inhibition of the anaerobic microbial community (usually due to volatile fatty acid accumulation and pH drop).

According to this introduction, the design criteria can be reduced to two: the former based on the hydraulic retention time (HRT) and the latter based on the microbial kinetics.

Because this part describes more the digestion of solid biomasses, the first approach will be described, leaving the second approach for the wastewater treatment section (Section 18.5).

The criterion based on the HRT is simpler and more often used. Nowadays, it is possible to find several data in the scientific literature for different substrates regarding the retention time required to reach good reactor performances and the maximum applicable organic loading rate (OLR).

Dealing with a substrate, we can decide the amount to be introduced to the reactor per unit of time. The ratio between the organic matter introduced per unit of reactor volume in a determined time is defined as OLR: it is normally expressed as kg m^{-3} d^{-1} of organic matter expressed as VS or COD.

If the amount of organic matter to be fed per unit of time has been defined, it is possible to simply define the volume of the reactor:

$$V = \frac{M_{om}}{OLR} \tag{15}$$

Where:

V: volume of the reactor (m^3)
M_{om}: mass of organic matter, as SV or COD, introduced in the unit of time (kg d^{-1})
OLR: mass of organic matter, as SV or COD, introduced in the unit of time (kg m^{-3} d^{-1})

Using Equation 15, it is very simple to determine the volume of the reactor and its results are obvious in that the volume has inverse proportionality with the OLR.

The HRT represents the average time that the substrate introduced into the reactor remains inside it.

If the flow of the substrate used in the reactor is known (depending on substrate availability) and the HRT has been defined (data from literature or laboratory tests), the reactor volume can be calculated as follows:

$$V' = Qs \cdot HRT \tag{16}$$

Where:

V': is the volume of the reactor (m^3)
Qs: is the flow of the substrate introduced in the reactor (m^3 d^{-1})
HRT: is the hydraulic retention time (d)

In Equation 16 the volume of the reactor is directly correlated to the considered HRT.

Usually both equations are applied, and the resulted biggest volume between V and V′ is used as the design reactor volume.

It is important to note that when the volume has been defined there is a correlation between OLR and HRT determined by the concentration of the organic matter in the substrate.

$$M_{om} = Q_s \cdot X_{om} \tag{17}$$

Where the new term X_{om} represents the organic matter concentration in the substrate expressed as kg m^{-3}.

Substituting the value of M_{om} in Equation 15 it is possible to obtain the following equation:

$$V = \frac{Q_s \cdot X_{om}}{OLR} \tag{18}$$

If from Equation 16 we obtain Q_s and we add this new value to Equation 18, we obtain the following equation:

$$V = \frac{V'}{HRT} \cdot \frac{X_{om}}{OLR} \tag{19}$$

Because V and V' should be equal, it is possible to write Equation 19 as:

$$HRT = \frac{X_{om}}{OLR} \tag{20}$$

This relationship is important not only for the design but also for the reactor management. In fact, if during the reactor working period the feeding concentration is changed, the retention time or the OLR will consequently change.

As it is possible to see from ▶Fig. 18.9, feedstocks that are normally available for biogas plants have a very large OLR range, and this must be considered.

According to Equation 20 it is possible to see that, at a stable substrate concentration, HRT depends on OLR. Because this relation can be always solved, it is important to decide which of the two values has more relevance for the process.

As a rule of thumb, in the presence of complex and slowly biodegradable substrates, it is better to give more weight to the HRT and consider the OLR as a result of the equation. Instead, in the presence of easily biodegradable substrates, especially if present at high concentrations, it is better to use the OLR as a limiting factor.

The first case is typical for agricultural manures, energy crops, and agroindustrial wastes; instead, the agroindustrial wastewaters are usually better managed using the second approach.

As stated previously, it is normal that during the life of a plant the feeding material changes, and this can affect both OLR and HRT. These changes also affect the reactor efficiency or the efficiency of the substrate transformation to biogas.

▶Fig. 18.10 shows how the maximum quantity of biogas that is possible to collect from a biomass affects the specific gas production of a reactor. It is possible to see that

Type of feedstock	Organic content	C:N ratio	DM %	VS % of DM	Biogas yield $m^3*kg^{-1}VS$	Unwanted physical impurities	Other unwanted matters
Pig slurry	Carbohydrates, proteins, lipids	3–10	3–8	70–80	0,25–0,50	Wood shavings bristles, water, sand, cords, straw	Antibiotics, disinfectants
Cattle slurry	Carbohydrates, proteins, lipids	6–20	5–12	80	0,20–0,30	Bristles, soil, water, straw, wood	Antibiotics, disinfectants, NH_4^+
Poultry slurry	Carbohydrates, proteins, lipids	3–10	10–30	80	0,35–0,60	grit, sand, feathers	Antibiotics, disinfectants, NH_4^+
Stomach/intestine content	Carbohydrates, proteins, lipids	3–5	15	80	0,40–0,68	Animal tissues	Antibiotics, disinfectants
Whey	75–80% lactose 20–25% proteins	–	8–12	90	0,35–0,80	Transportation impurities	
Concentrated whey	75–80% lactose 20–25% proteins	–	20–25	90	0,80–0,95	Transportation impurities	
Flotation sludge	65–70% proteins 30–35% lipids	–				Animal tissues	Heavy metals, disinfectants, organic pollutants
Ferment. slops	Carbohydrates,	4–10	1–5	80–95	0,35–0,78	Non-degradable fruit remains	
Straw	Carbohydrates, lipids	80–100	70–90	80–90	0,15–0,35	Sand, grit	
Garden wastes		100–150	60–70	90	0,20–0,50	Soil, cellulosic components	Pesticides
Grass		12–25	20–25	90	0,55	Grit	Pesticides
Grass silage		10–25	15–25	90	0,56	Grit	
Fruit wastes		35	15–20	75	0,25–0,50		
Fish oil	30–50% lipids	–					
Soya oil/margarine	90% vegetable oil	–					
Alcohol	40% alcohol	–					
Food remains			10	80	0,50–0,60	Bones, plastic	Disinfectants
Organic household waste						Plastic, metal, stones, wood, glass	Heavy metals, organic pollutants
Sewage sludge							Heavy metals, organic pollutants

Fig. 18.9: The characteristics of some digestible feedstock types (Al Seadi 2001).

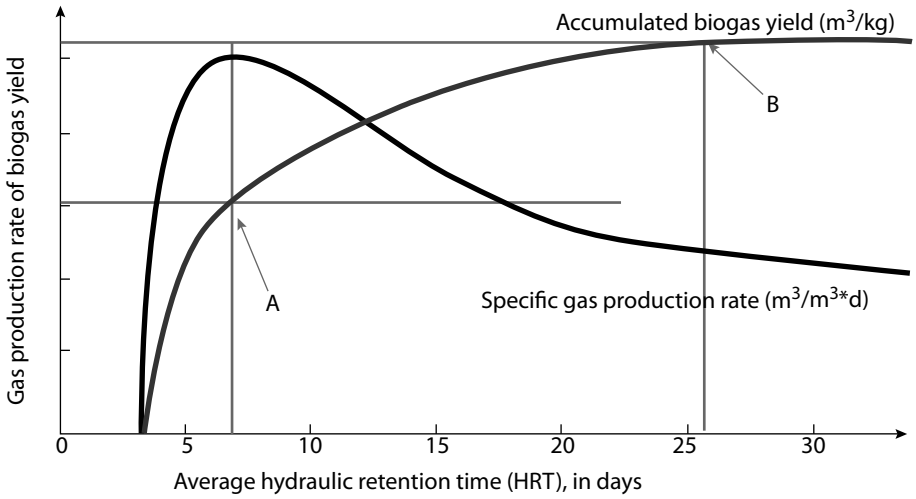


Fig. 18.10: Cumulative and specific biogas production at different HRT in batch test (LfU 2007), modified.

at the maximum value of a specific gas production per volume of reactor, only about 50% of the total biogas production can be collected in a very short period of time (HRT 4 days). Instead, the maximum gas yield, which corresponds to an HRT of 25 days, causes the drop of the specific gas production per volume of reactor (production rate or productivity).

The best conditions to set up, therefore, depend on several factors: people who manage the plant are usually more interested in the economic aspects and, thus, the costs of the raw material, the price of the produced energy, and the costs of the realization of a larger or smaller plant are all aspects that must be evaluated case by case.

In full-scale plants, the HRT can be very different according to the substrate used. In the case of very easily biodegradable organic matter and high loading-rate reactors, the HRT can drop to 6–12 hours. Instead, in the case of animal manure, the HRT must be maintained of about 15–20 days, and for cow manure this value must be increased to 40–50 days. For some energy crops these values can even reach 60–80 days.

18.4 Types of reactors and possible configurations of biogas plants

Anaerobic digestion is a process that has been used all over the world for more than one hundred years. This has permitted the development of several kinds of reactors ranging from the most simple, such as Chinese- or Indian-type reactors (Figs. 18.11 and 18.12), to very complex plants, such as those used for OFMSW treatment.

It is possible to have several classifications of reactor types. According to the average solid content in the reactor, three main categories can be defined: wet reactors, if the dry solids are lower than 15%; semiwet reactors, when the dry solids content is between 15 and 20%; and dry reactors, if the solids are higher than 20%.

According to the process temperature, three main ranges of working conditions can be identified: the fist, at a lower working temperature of approximately 20°C, is the *psychrophilic*. Reactors that work in these conditions are typically used in relatively warm

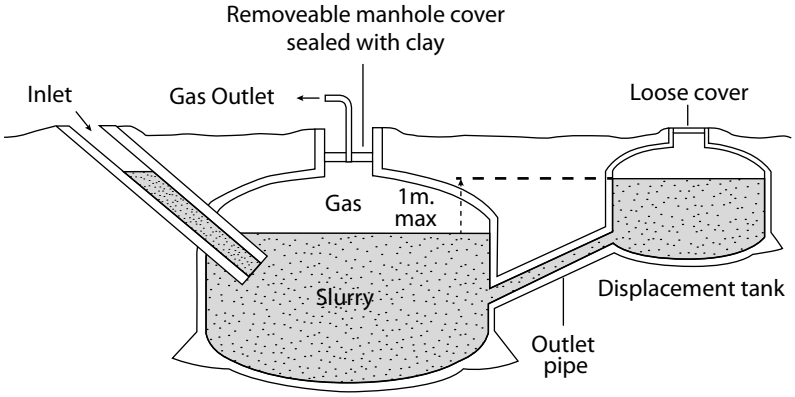


Fig. 18.11: Chinese-type reactor (Gunnerson and Stuckey 1986).

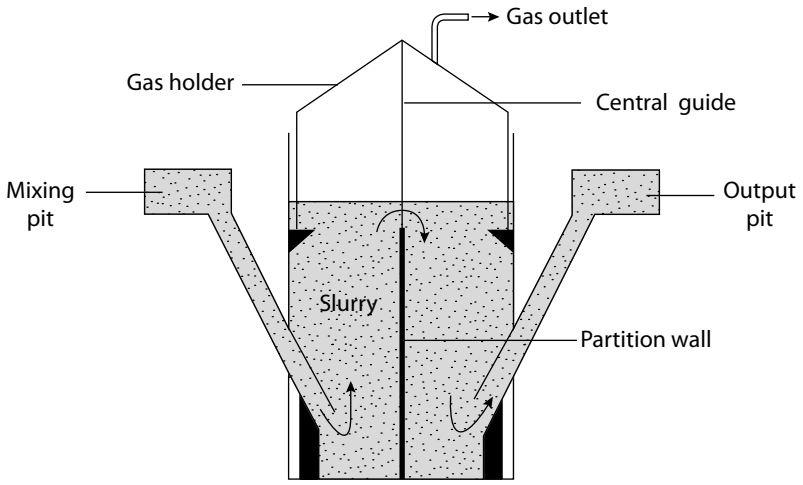


Fig. 18.12: Indian-type reactor (Gunnerson and Stuckey 1986).

climates and the main advantage is that there is not any temperature control system or any heat exchange system. The *mesophilic* conditions are the most-used working conditions because of the stability of the process and the high biogas productivity; the optimal temperature for mesophilic reactors is in the range of 35–37°C.

Thermophilic conditions require a temperature of approximately 55°C. At these conditions the efficiency of the process is higher and the process has typically faster kinetics: on the contrary, the reactor control is usually more difficult.

Another classification is based on the management of the solids and the liquid fraction of the mixed liquor that results in different or equal HRT and SRT.

Regarding the digestion technology, it is possible to distinguish the discontinuous from the continuous processes. In the first category it is possible to include batch processes and fill and draw processes (▶Fig. 18.13). In the first case the reactor is fed once and is immediately closed. The biogas production starts after the lag phase, and the collection of the gas continues until the (almost) complete degradation of the organic matter.

For this reason, it is useful to operate with a series of reactors that start at different times in order to obtain an almost continuous gas production. Another reason for using more reactors is related to the leachate characteristics: the leachate normally produced during the reactor start-up has a high content of organic acids and a low pH; at the end of the anaerobic process, instead, the leachate usually has a low content of acids and a good buffer capacity. Therefore, having several reactors, the leachate produced in a reactor can be recirculated to the other one, maintaining a proper level of humidity and pH in the fermenting mass. The use of a series of reactors has found application for the digestion of the OFMSW. In this way, the material can be fed in the reactor without the addition of water simplifying the mixing and the loading of the reactor. The advantages of these reactors are the low construction and management costs (▶Fig. 18.14).

Fill and draw reactors, instead, are used when there is no possibility of having the availability of the biomass in a short period of time. In this case, the material is

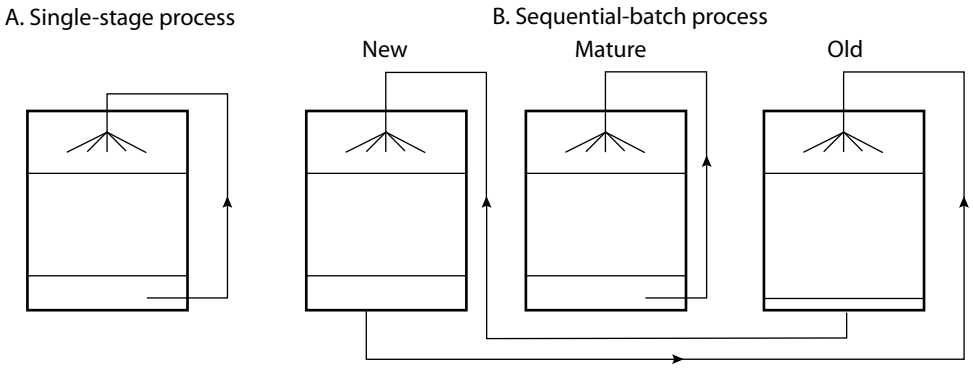


Fig. 18.13: Scheme of the management of a batch reactor in a single stage and in sequence (Wilson 2004).



Fig. 18.14: Batch reactor feeding with organic waste (http://www.kedco.com/clean-tech-energy/green-energy/).

discontinuously fed during a long period of time (3–6 months): the gas is collected continuously, but the production changes during the time period according to the OLR. This is the typical case of biogas production with simplified reactors in agriculture, where the animal manure is pumped in covered lagoons during the raining/winter period (►Fig. 18.15). Once a year the material is used as land fertilizer and the reactor is emptied. In this case the biogas production rate and quality can be very different during winter and summer seasons.

The main advantage of these reactors is the low cost of the system, while the disadvantage is related to the unstable biogas production during the year.

Continuous reactor processes are those reactors that are continuously fed and, thus, a continuously equal portion of digestate is extracted.

These reactors can have horizontal or vertical flow, up or down flow, mixing or not, one stage or more stages, one phase or more phases.

The continuous stirred-tank reactor (CSTR) is the most common reactor type used for the treatment of wastes and wastewaters in anaerobic digestion. In this reactor the



Fig. 18.15: Biogas collection system from lagoons (CRPA 2005).

biomass and the sludge are continuously (or semicontinuously) mixed. Normally, this reactor works with solid contents that range from 2% to 15% as TS; it can work under thermophilic or mesophilic conditions. In CSTR plants the mixing conditions depend on the solid contents, where, usually, the higher they are, the lower the mixing regime. This means that for substrates with high solid contents (e.g. energy crops or OFMSW), mixing is usually applied for a few minutes once or twice a day. On the contrary, for substrates with low solid contents (e.g. agroindustrial wastewaters), the mixed liquor is usually continuously mixed.

The reactors used in agriculture are usually down-flow reactors, while, when the solid concentrations are not too high, feeding is typically carried out from the bottom. The best efficiency of these reactors is obtained when they are fed with a continuous and constant flow. This is easy to obtain with diluted substrates, such as sludge and wastewater, whereas it is more difficult with high-solid content material that normally requires bigger machineries for its management. The OLR in these reactors cannot be particularly high; this is not a problem for semisolid material that is typically loaded at an OLR of 2–5 $kg_{vs}\,m^{-3}\,d^{-1}$.

The shape of these reactors is typically cylindrical with a width/height ratio from 1 to 3, but different shapes have also been designed, such as the egg-shape reactors, which have been designed to improve the mixing and, thus, to reduce possible stratification.

Mixing of CSTR is normally conducted using different types of stirrers, which can be small and fast screws distributed alongside the internal reactor wall, determining the good mixing of the material in digestion, or bigger and with a slow rotation speed, which are typically located eccentrically in the reactor. Sometimes parts of the screw blades can work over the liquid level of the reactor to break the crust that can be formed when treating fibrous material. These stirrers can work with a horizontal or vertical axis.

An uncommon way to mix the reactor at high solid concentration is the use of a pump to extract the material from the bottom of the reactor and to introduce it to the top. In this case, the recirculated mixed liquor can also be used as exchange material to heat the reactor.

CSTRs are usually used as single-phase reactors, but used in series CSTRs, the different stages or phases of the anaerobic process can be better managed. As previously described, anaerobic digestion consists of complex metabolic reactions where four main phases (hydrolysis, acidogenesis, acetogenesis, and methanogenesis) can be identified. The design of two-phase reactors tries to maintain different operating conditions, such as HRT or OLR, to stimulate the growth of specific microbial populations in the first phase and other populations in the second phase. Typically, the first phase includes the hydrolytic and the acid production processes and, because of the higher kinetic rate of the involved reactions, the first reactor has a smaller size than the second one. Moreover, the temperature of the first reactor is usually kept some degrees higher than 37°C, and the pH is maintained at a value lower than the neutrality. These conditions are realized applying HRT from 1 to 5 days, resulting in OLR usually higher than 10 $kg_{VS}\,m^{-3}\,d^{-1}$ (Ghosh et al. 2000). The second phase consists of the methane production reactor: the methanogenic reactor is usually larger than the first-phase reactor in order to decrease the OLR, and its pH is maintained at a value close to neutrality.

In several two-stage reactors, however, the biological processes are not completely separated, but both reactors are used for the hydrolytic and methanogenic processes. In this case, the first stage is still moderately smaller than the second stage. In the first stage, the easiest biodegradable products are degraded, the pH is maintained at a value of neutrality, and the temperature is typically maintained some degrees above the mesophilic condition to promote the degradation of the slowly biodegradable compounds. The second stage, which sometime is not heated, is just a finishing step of the methanogenesis and it is used to improve the biodegradation of the slowly biodegradable compounds.

Plug-flow reactors usually work with horizontal flow and either with or without small mixing. In these reactors a pumping system pushes the feeding material to one reactor side while the digestate exits from the opposite side.

These reactors are particularly advantageous as they are simple to build and easy to manage. They are typically used for animal manure digestion. They are particularly suitable for the treatment of substrates with solid contents higher than 10%, while the use of diluted substrates, because of the shape of the reactor, can determine a stratification of the material inside the reactor, reducing the working volume of the reactor.

These reactors are particularly suitable for animal manure treatment because the material results are naturally inoculated with an anaerobic microflora. It is important that the inoculum is already present at the feeding side because the biomass exchange inside the reactor is very poor: if it is not possible to use manure as inoculum, part of the digestate should be recirculated.

A particular plug-flow reactor is the well-known DRANCO process (▶Fig. 18.16). This is a dry vertical down-flow reactor developed for the digestion of organic wastes such as OFMSW, thickened sludge, and organic industrial wastes. This process can manage feeding material with solid concentration of up to 45%–50% (De Baere 2010). The raw waste is previously reduced to a size smaller than 40 mm: then, 1 ton of waste is mixed with approximately 6 tons of digestate and fed to the top of the reactor. The reactor can

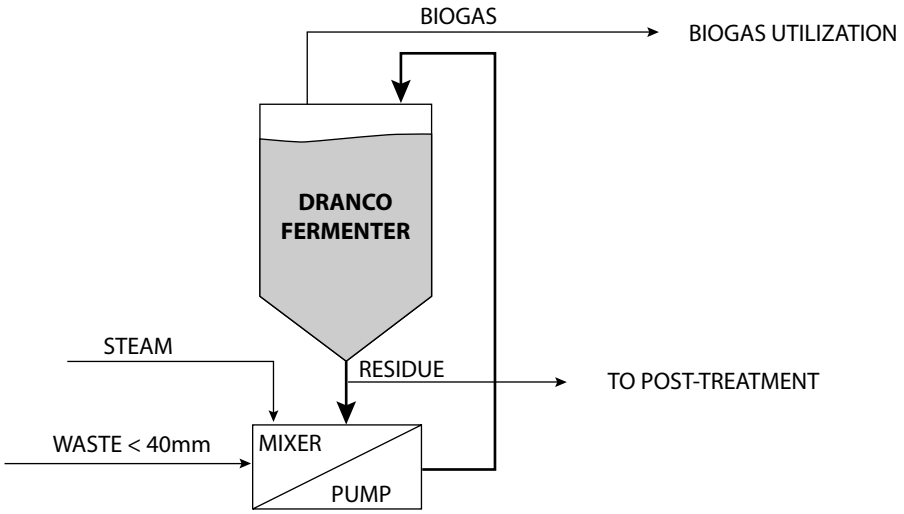


Fig. 18.16: Scheme of the DRANCO process (De Baere 2010).

operate under mesophilic or thermophilic conditions with OLR of 10–20 kg_{COD} m^{-3} d^{-1}, HRT of 15–20 days, and achieving productivity of 100–200 Nm^3 biogas per ton of waste. The low water content makes it simple and cheap to maintain the temperature even in the thermophilic range. The reactor does not use stirrers or pumps inside the reactor because the digested material moves from the top to the bottom of the reactor just due to its weight. At the reactor bottom, there is a mixing chamber that mixes the fresh waste with the digested waste, and an injection of steam increases the temperature to the appropriate value. The main advantage of this reactor is the high OLR that can be applied, the absence of foams and scum, and the easy maintenance because all the main machineries are outside of the reactor.

18.5 Biogas from wastewaters

Anaerobic processes have been largely applied for industrial wastewater treatment, although, during the past few decades, they have also become popular for agricultural and municipal wastewater because of their economic advantages deriving from biogas production and utilization.

An important factor of the anaerobic wastewater treatment reactors is the need to decouple the SRT from the HRT. As already stated, since methanogens have a slow growth rate, if the biomass discharge from the reactor is higher than the growth rate, methanogenic biomass is washed out from the reactor. Therefore, CSTRs have not been largely applied because high OLRs cannot be achieved when dealing with low- to medium-concentrated wastewaters. For that reason, during the past few decades, several strategies have been developed to separate the HRT from the SRT of the reactors.

There are several approaches to improve the biomass retention in a reactor. These are briefly described in ▶Tab. 18.2.

Tab. 18.2: Main strategies to improve biomass retention in anaerobic reactors.

Approaches Technology	Biomass Retention Mechanisms	Reactor Type
Biomass immobilization in attached growth systems	Anaerobe grow attached to a support media (e.g. plastic, gravel, sand, activated carbon, plastic foams) to form biofilm	Anaerobic filter, rotating anaerobic contactor, fluidized-bed reactor
Granulation and flock formation	Anaerobic microorganisms grow in agglomerates to form granules or flocks that settle in the bioreactor	Up-flow anaerobic sludge blanket (UASB) reactor, expanded granular sludge bed (EGSB), anaerobic sequencing batch reactor, anaerobic baffled reactor
Biomass recycling	Suspended biomass is settled in a separate settler and then recycled back to the reactor	Anaerobic contact reactor
Biomass retention	Microfiltration membrane is integrated into the anaerobic reactor to retain biomass	Anaerobic membrane bioreactor

CSTRs are exclusively used for the treatment of very high concentrated wastewater for the same reasons previously mentioned (simplicity). In these reactors, it is difficult to exceed an OLR of 5–6 $kg_{COD}\ m^{-3}\ d^{-1}$ because of management problems or biomass washout.

To dimension this type of reactor it is better to focus on the biomass growth. The methanogenic microorganisms growth rate can be described by the Monod kinetic:

$$r'_M = \mu_{max,M} \frac{S}{S + K_{S,M}} X_M - b_M X_M \tag{21}$$

Where

r'_M: is the growth rate of methanogens
$\mu_{max,M}$: is the specific maximum growth rate of methanogens
S: is the substrate concentration
$K_{S,M}$: is the half saturation constant
X_M: is the concentration of methanogens in the reactor
b_M: is the decay coefficient for methanogens

The net specific grow rate (μ'_M) for the methanogens can be obtained by dividing Equation 21 by X_M:

$$\mu'_M = \mu_{max,M} \frac{S}{S + K_{S,M}} - b_M \tag{22}$$

The mass balance of the methanogens in the digester can be written as follows:

$$\frac{dX_M}{dt}V_r = QX_0 - QX_M + r_M^{'}V_r \tag{23}$$

Where

V_r: is the volume of the reactor
Q: is the flow in the reactor
X_0: is the concentration of methanogens in the influent wastewater

It is possible to assume X_0 is equal to zero as the concentration of methanogens in wastewater is usually negligible if compared with the concentration in the reactor: for steady state, $\frac{dX_M}{dt}$ is equal to zero. With these considerations, Equation 23 becomes:

$$QX_M = r_M'V_r \tag{24}$$

Combining Equations 21 with 24, the result is:

$$\frac{Q}{V_r} = \frac{1}{\Theta_C} = \mu_{\max M}\frac{S}{S + K_{sM}} - b_M \tag{25}$$

Where Θ_C is the sludge age (i.e. SRT) and can be used to calculate the volume of the reactor. Θ_C can also be calculated, as in Equation 26.

$$\Theta_C = \frac{1}{\mu_M'} \tag{26}$$

An evolution of the CSTR reactor is the anaerobic contactor process (ACP), which is essentially a CSTR with sludge recirculation from an external settling tank. The settler can be preceded by a degassifier to enable the removal of biogas bubbles in order to improve the sludge settling. The settled biomass is recycled back to maintain longer SRT than in CSTR: the required SRT can be maintained by controlling the recycle rate, similar to an activated sludge process.

ACP is particularly useful for high-suspended solid wastewater streams.

Typical ACP biomass concentrations are 4–6 g/L, with maximum concentrations as high as 25–30 g L^{-1}, depending on the sludge settleability. The OLR ranges from minimum values of 0.5 kg $_{COD}$ m^{-3} d^{-1} (similar to CSTRs) to much higher values of 10 kg $_{COD}$ m^{-3} d^{-1}. Unfortunately, the biogas still present in the mixed liquor hinders or reduces the sludge settleability.

Anaerobic filters (AF) were the first successful attempt to have a system that retains the biomass inside the reactor preventing the wash out.

Inside an AF there is a packing material that is fixed and inert, which allows the water to flow through and the biomass to attach on (▶Fig. 18.17).

The support media should have a high surface/volume ratio to prevent possible clogging and to give the biomass a high surface where it can attach and grow; moreover,

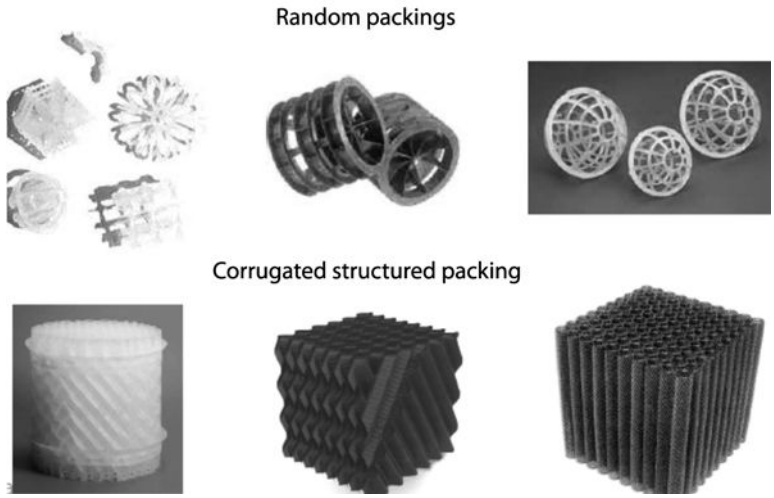


Fig. 18.17: Different types of packing material for anaerobic filters.

it should have a density slightly higher that water in order to ensure that the biofilm is always completely immersed.

AF can work as an up-flow (UAF) reactor as well as a down-flow (DAF) reactor. In both cases the packing material is positioned in a middle area of the reactor, leaving a free volume of water at the bottom and at the top for feeding and treated water collection and separation.

In the empty bottom volume of the UAF reactor, biomass develops that can aggregate in flocks or granules, while another part of the biomass develops on the support surface (▶Fig. 18.18). Supports also help the gas detachment from the flocks. With this type of reactor, very high values of SRT can be obtained and, at the same time, very short HRT, which can range from 0.5 to 4 days. In these conditions, OLRs of 5–15 $kg_{COD}\ m^{-3}\ d^{-1}$ can be achieved. Owing to the high biomass retention, maintenance should be planned in order to prevent the clogging of the packing material.

In DAF reactors, the wastewater is introduced from the top of the reactor. In this case the biomass growth in the reactor is only on the surface of the packing material and the excess is washed out from the bottom. This type of reactor is more suitable for wastewater, having a higher content of solids than the UAF. Although DAF has the biomass attached on the packing material only, and thus its total amount is usually lower than UAF of similar volume, the specific biomass activity is relatively higher and allows DAF to approximately achieve the same performance as UAF.

Furthermore, DAF is more suitable than UAF for treating sulfate-rich wastewater. The sulfate reduction can occur in the upper zone of the reactor, reducing the hydrogen sulfide in the lower zone where methanogenesis occurs.

Over the past few years several anaerobic wastewater treatment plants have been constructed. The technology that has seen the largest application is certainly the up-flow anaerobic sludge blanket (UASB) reactor (▶Fig. 18.19). It is possible to say that this reactor is a vertical plug flow with a degasing system and a settler inside. It was

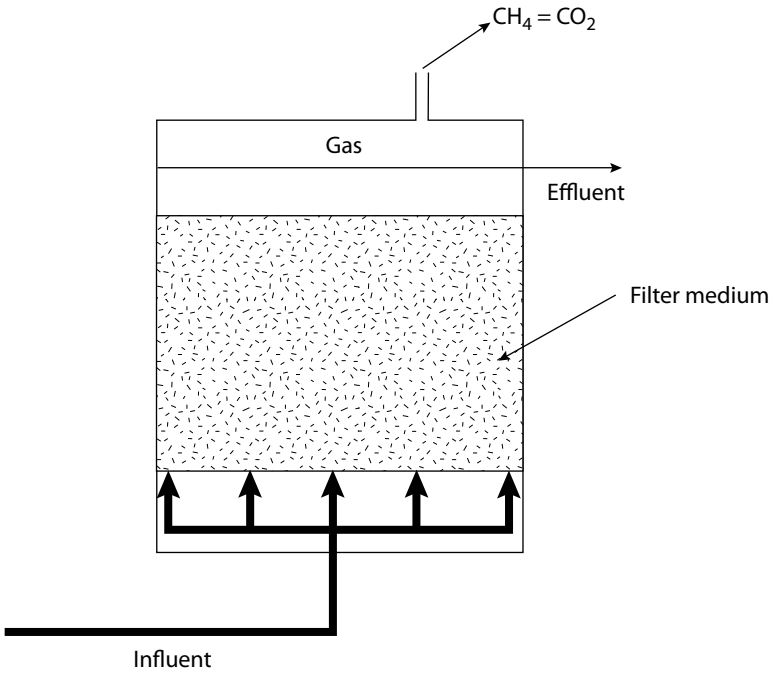


Fig. 18.18: Scheme of up-flow anaerobic filter (UAF).

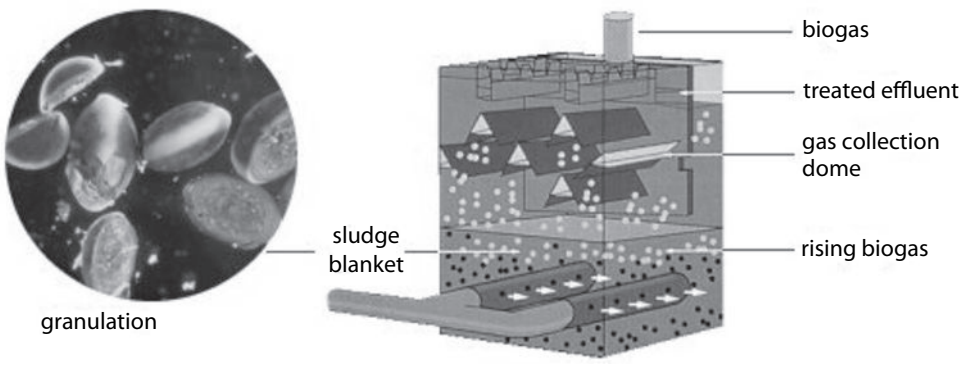


Fig. 18.19: Anaerobic granules (left side) and schematic of a UASB reactor (right side).

developed in the late 1970s for treating rich sugar wastewater (Lettinga et al. 1980). UASB reactors essentially consist of an empty tank where wastewater is distributed to the bottom and where the wastewater passes upwards (velocity not higher than 2 m h^{-1}, better is 0.5–1.5 m h^{-1}) through an anaerobic sludge bed typically composed of firm aggregates (granules) of microorganisms. These granules have a diameter from 0.5 to 2 mm and have a sedimentation velocity up to 60 m h^{-1}. In these reactors, the HRT

strictly depends on the substrate biodegradability and can be as low as 6 hours. On the contrary, the SRT can be up to 200 days. Due to this characteristic, UASB reactors can achieve very high OLR (up to 25 kg $_{COD}$ m^{-3} d^{-1}). In the upper part of the reactor there is the three-phase separator (gas-liquid-solid [GLS] separator), a specifically designed baffle that is able to retain granules, release the gas, and separate the treated water. Particular attention should be paid to the GLS separator design; in fact, it should be designed to collect as much gas as possible and to have a water velocity high enough to remove the nonaggregated biomass but not too high to wash out the granules. Specific equations for the design of GLS separators have been developed and are available in the literature.

An evolution of the UASB is the internal circulation (IC) reactor (▶Fig. 18.20). This reactor has been studied for the treatment of very high strength wastewater that cannot reach the hydraulic load of the UASB reactor to provide the correct up-flow velocity.

These reactors are divided horizontally into two parts by a first GLS system, whereas a second one is placed on the top of the reactor. After a degassing tank, the effluent is

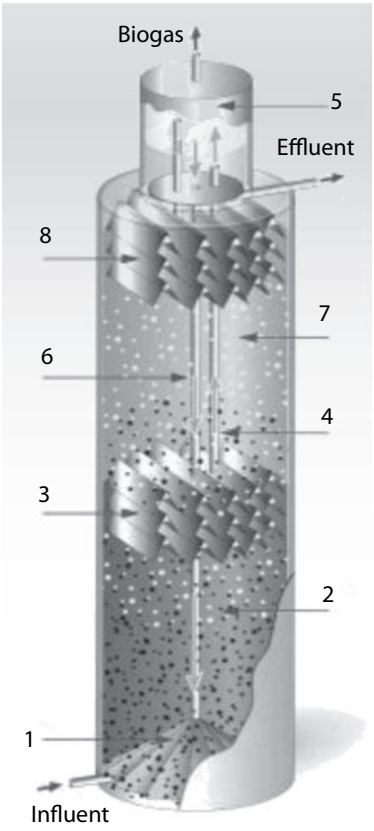


Fig. 18.20: Internal circulation reactor: 1 – distribution system; 2 – expanded bed compartment; 3 – first separator, 4 – riser; 5 – degassing tank; 6 – downer; 7 – polishing compartment; 8 – second separator.

recirculated back to the bottom of the reactor. These reactors are substantial vertical towers of 16–28 m in height and with diameters of 1.5–15 m. The OLR in these reactors can be higher than 30 kg $_{COD}$ m^{-3} d^{-1}.

Other reactors, such as the expanded granular sludge bed (EGSB) and the fluidized-bed reactor (FBR), are particular reactors that use recirculation systems to expand the sludge bed. The sludge bed can consist of granules (EGSB) or of inert support material where the biomass can grow (FBR). Performances of these reactors can be compared (or are even better) with those of the UASB reactor.

Over the past decade, according to the large development of the membrane filtration technology and its application to the activated sludge wastewater treatment plants, anaerobic membrane bioreactors (AnMBR) have been studied to improve the biomass retention and to obtain well-clarified effluents (Spagni et al. 2010; Casu et al. 2012).

The membrane can be plane or tubular and can be placed inside the reactor or externally. Although interesting performances have been obtained, the anaerobic sludge seems much less filterable than the activated sludge.

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