

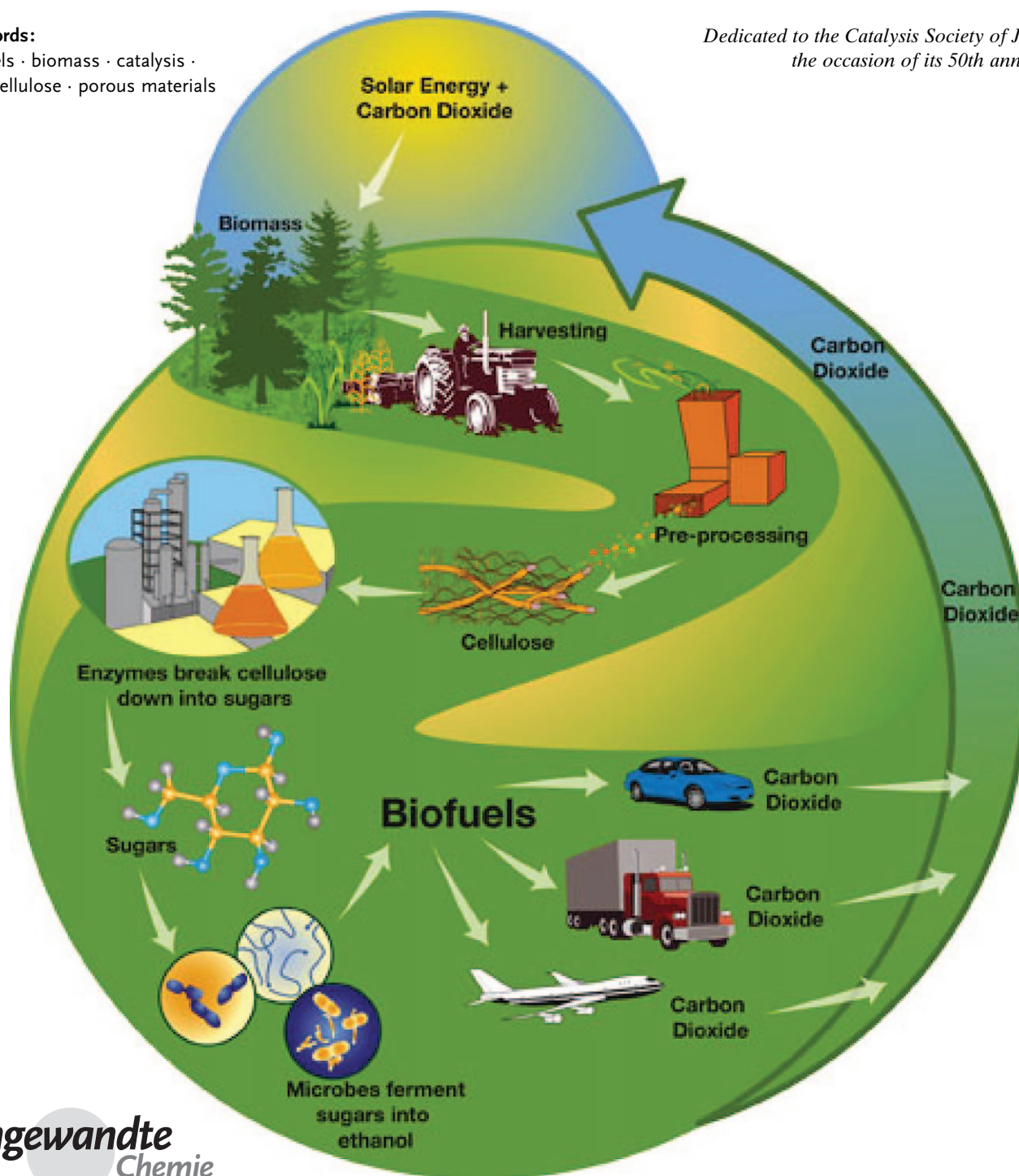
Biofuels and Biomass-To-Liquid Fuels in the Biorefinery: Catalytic Conversion of Lignocellulosic Biomass using Porous Materials

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Keywords:

biofuels · biomass · catalysis ·
lignocellulose · porous materials

*Dedicated to the Catalysis Society of Japan on
the occasion of its 50th anniversary*



At a time when the focus is on global warming, CO₂ emission, secure energy supply, and less consumption of fossil-based fuels, the use of renewable energy resources is essential. Various biomass resources are discussed that can deliver fuels, chemicals, and energy products. The focus is on the catalytic conversion of biomass from wood. The challenges involved in the processing of lignocellulose-rich materials will be highlighted, along with the application of porous materials as catalysts for the biomass-to-liquids (BTL) fuels in biorefineries. The mechanistic understanding of the complex reactions that take place, the development of catalysts and processes, and the product spectrum that is envisaged will be discussed, along with a sustainable concept for biorefineries based on lignocellulose. Finally, the current situation with respect to upgrading of the process technology (pilot and commercial units) will be addressed.

1. Introduction

Currently, fossil-based energy resources, such as petroleum, coal, and natural gas, are responsible for about three-quarters of the world's primary energy consumption, each corresponding to 33, 24, and 19%, respectively. Alternatives to fossil-based energy resources are nuclear power (5%), hydropower (6%), and biomass (13%), representing currently about one quarter of the world's primary energy consumption. With decreasing crude-oil reserves, enhanced demand for fuels worldwide, increased climate concerns about the use of fossil-based energy carriers, and political commitment, the focus has recently turned towards improved utilization of renewable energy resources. Biomass is an abundant and carbon-neutral renewable energy resource for the production of biofuels and valuable chemicals.^[1–8] Energy production from biomass has the advantage of forming smaller amounts of greenhouse gases compared to the conversion of fossil fuels, as the carbon dioxide generated during the energy conversion is consumed during subsequent biomass regrowth (Figure 1).^[2]

At the beginning of the 20th century, a large number of industrial products, such as solvents, dyes, and fibers, were

manufactured from wood-based resources and crops.^[5]

After the second World War, crude-oil upgrades were used for the production of these chemicals originally based on biomass. However, the energy crisis of the 1970s turned the

focus again towards the utilization of bio-based resources for the production of fuels and valuable chemicals. This focus, however, declined during the time the oil price decreased.^[5]

Moving the world market dependence away from fossil-based energy resources to renewable alternatives, such as biomass resources, can be regarded as an important contribution towards the establishment of favorable conditions for the climate and a sustainable economy.^[5] Current production and application of first-generation biofuels, such as biodiesel and bioethanol, are steps in the right direction. However, the second generation of biofuels will be based on biomass resources processed from integrated biorefineries, covering not only the production of biofuels, heat, and electricity, but also biomaterials (Figure 1).

Multiple biomass resources are presently applied to obtain a variety of fuels, chemicals, and energy products. Resources could be from trade and industry, forestry, or agriculture (Table 1). Processing covers both biological, thermal, and/or chemical conversion, in addition to mechanical treatment to obtain solid, liquid, or gaseous fuels and/or valuable chemicals.

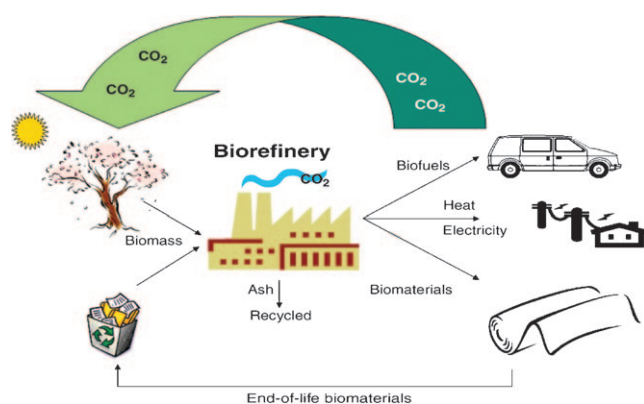


Figure 1. Sustainable technology in an integrated biorefinery. Reproduced from Ref. [5] with permission of Science.

From the Contents

| | |
|---|------|
| 1. Introduction | 9201 |
| 2. Biofuels: Definition, Political Impact, and Current Technology | 9202 |
| 3. Concepts for a Second-Generation Lignocellulose Biorefinery | 9203 |
| 4. Use of Biofuels Today | 9204 |
| 5. The Components of Lignocellulose | 9204 |
| 6. Biofuel Production from Lignocellulose | 9205 |
| 7. Catalytic Conversion of Lignocellulose-Based Biomass | 9205 |
| 8. Applications of Bio-Oil | 9210 |
| 9. Pilot Units | 9210 |
| 10. Outlook | 9210 |

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Table 1: Renewable energy versus fossil-based energy: from multiple biomass resources to fuels and energy products.

| Biomass production | Biomass processing | Biomass fuels | Biomass conversion |
|---|--|--|--|
| <i>Forestry</i> –thinning –residues | <i>Mechanical</i> –chipping –cleaving –pelleting –pressing | <i>Solid Fuels</i> –pellets –charcoal | <i>Heat</i> –single stove –central heating –heating plant |
| <i>Agriculture</i> –grain –straws –manures –energy wood –oil plants | <i>Thermal/Chemical</i> –drying –gasification –pyrolysis –esterification | <i>Gaseous Fuels</i> –biogas –wood gas –hydrogen | <i>Electricity and Heat</i> <i>Central Heating Plant (CHP) with</i> –steam turbine and/or –gas turbine –Stirling motor –combustion engine –fuel cell |
| <i>Trade and Industry</i> –sawn industry residue –wood industry residue –used wood –organic residue | <i>Biological</i> –alcohol fermentation –methane fermentation | <i>Liquid Fuels</i> –ethanol –methanol –Fischer–Tropsch liquids –oil from plants –oil from pyrolysis –esters | |

2. Biofuels: Definition, Political Impact, and Current Technology

Biofuels are liquids or gases for transport purposes that are produced from biomass. The CO₂ emission is not larger than the quantity consumed by photosynthesis (Figure 2). This carbon cycle (Figure 3) is the reason why biofuels are not included in the CO₂ balance of the Kyoto protocol from the United Nation's climate panel.

To secure the future energy supply and to handle the global warming arising from the greenhouse effect, energy from renewable sources must be increased relative to the use of fossil-based fuels. There is, in addition, a strong political focus on renewable biofuel alternatives:

1. The United Nation's climate panel aims for a reduction in greenhouse gas emissions of up to 8% by 2010 and 50–80% by 2050.



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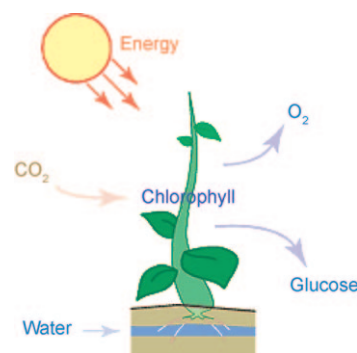


Figure 2. Photosynthesis.

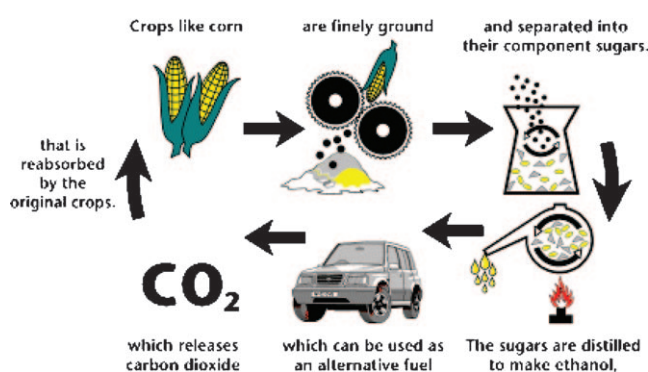


Figure 3. The carbon cycle.

and biodiesel) are also available as gaseous products, such as biogas and hydrogen. However, technologies for processing second-generation biofuels are still under development, and the focus lies on the utilization of wood-based biomass.

At present, the production of first-generation bioethanol mainly utilizes plants rich in carbohydrates (i.e., sugar, starch), such as maize, sugar cane, wheat, barley, potato,

wood, corn, or sugar beet. The production of bioethanol by hydrolysis and fermentation is an energy-intensive and complex process. No commercial wood-based process is available to date. In contrast, the first-generation biodiesel (FAME, fatty acid methyl ester) production uses a very simple process: transesterification of vegetable oils, for example rape seed to rape seed methyl ester (RME), soya bean, sunflower seed, and palm oil, or animal fats, such as slaughterhouse waste or fish oil.^[9]

3. Concepts for a Second-Generation Lignocellulose Biorefinery

Whereas the first generation of biofuels is based on well-established technologies, the development of processes related to the production of second-generation biofuels utilizing wood biomass is still in the early stages of research and development.

Technologies have been developed for the gasification of biomass to synthesis gas (syngas, containing carbon monoxide and hydrogen). Syngas, which is also available by pyrolysis of wood-based biomass, can be used to produce biomethanol or Fischer–Tropsch biomass-to-liquids (BTL) by applying well-known technologies (Figure 4).

Lignocellulosic biomass can be converted into bio-oil by fast pyrolysis. The bio-oil can then be gasified to give syngas, or can be separated to give phenolic compounds and/or

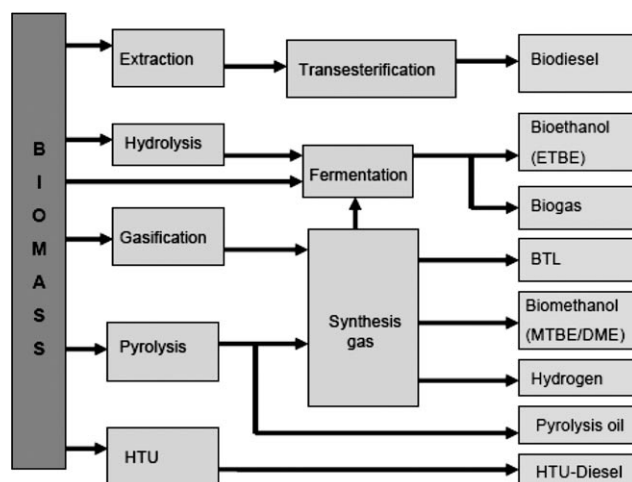


Figure 4. Simplified process flow in a lignocellulosic biorefinery.

carbohydrate fractions. The syngas can be further processed to Fischer–Tropsch products or, for example, methanol, with subsequent production of olefins and/or gasoline. The phenolic compounds can be used for the production of phenolic resins, and the carbohydrate fractions are catalytically transformed to hydrogen (Figure 5).^[6]

An overview of a modern biorefinery based on wood biomass, including the first-generation biofuels based on

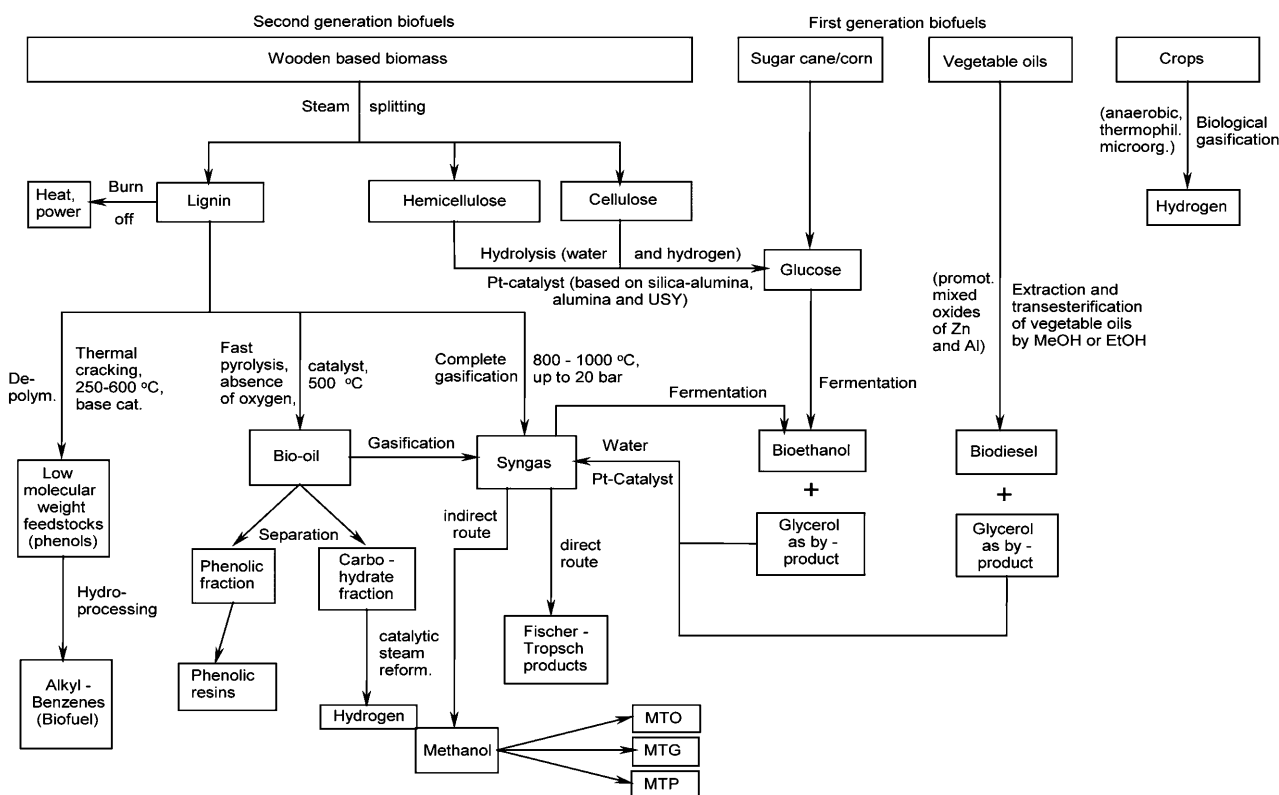


Figure 5. Process flow in a modern wood-based biomass biorefinery. MTO: conversion of methanol into olefins, MTG: production of gasoline from methanol, MTP: formation of propene from methanol.

vegetable oils and sugar cane or corn, is given in Figure 5. The relationship between the first- and second-generation biofuels is also shown. Cellulose and hemicellulose can, for example, be used to produce bioethanol, and lignin offers a broad spectrum of conversion (thermal cracking, fast pyrolysis, and complete gasification) to arrive at valuable chemicals and transportation fuels.

In general, a modern lignocellulosic biorefinery attempts to parallel the workings of a crude-oil refinery. An abundant raw material, consisting mainly of renewable lignin, cellulose, and hemicellulose, enters the biorefinery. This raw material is converted through a number of different processes into a mixture of products, including biofuels, valuable chemicals, heat, and electricity. However, the logistic problems involved in the running of a modern biorefinery should not be underestimated, especially regarding the gathering of sufficient biomass, for example, to operate a Fischer–Tropsch unit economically.

Expensive chiral catalysts or advanced synthetic routes are normally required for the targeted stereoselective introduction of functional groups. However, carbohydrates obtained from biomass are viable for the production of regio- and stereochemically pure esters, carboxylic acids, and alcohols.^[5]

4. Use of Biofuels Today

Fuels with small amounts of admixed biofuel (up to 5 vol.%; E5 Europe) are permitted in common gasoline or diesel engines, and can be used in common vehicles without any form of adaptation.

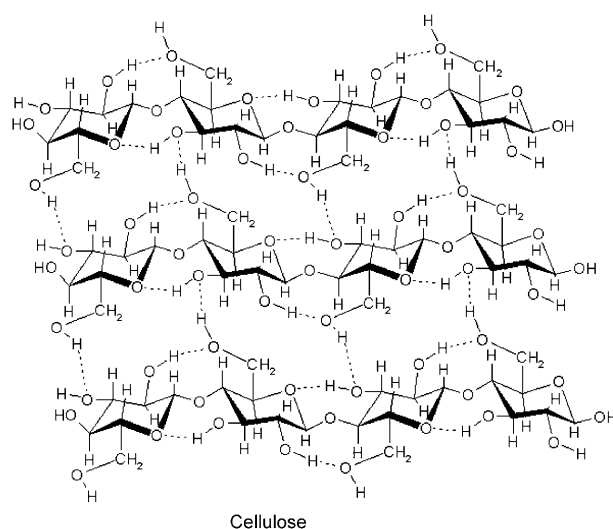
Fuels with higher levels of biofuel (more than 5 vol.%) are currently available in Brazil (gasoline, up to 25% ethanol, E25), USA (10% ethanol/90% gasoline, E10), and Sweden (85% ethanol/15% gasoline, E85). Diesel containing 5–30 vol. % FAME (B5, B10, and B30) are common, as is E95 for diesel engines. However, vehicles using this type of fuel must be adapted.

Biobutanol may be a more suitable gasoline-range biofuel than bioethanol, as it has the same energy density as bioethanol, but would increase the octane number in the gasoline pool. In addition, biobutanol has a lower vapor pressure and a lower water solubility, which simplifies handling procedures and the infrastructure.^[9]

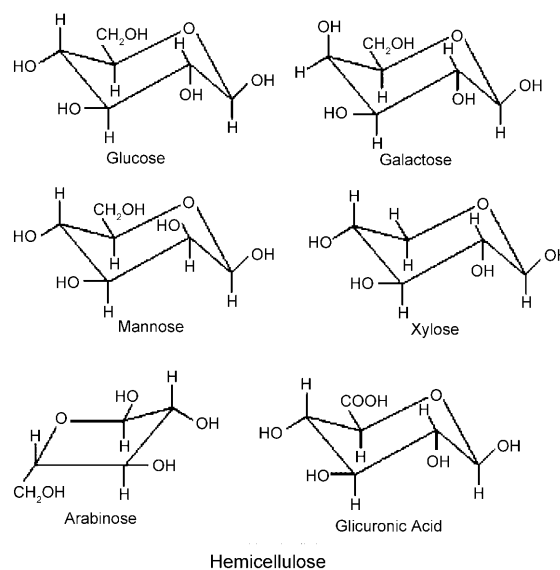
5. The Components of Lignocellulose

Wood-based biomass is available in large quantities and is cheap. It consists of three major components:

Cellulose: Linear polysaccharides in the cell walls of wood fibers, consisting of D-glucose molecules bound together by β -1,4-glycoside linkages (comprises about 41%).

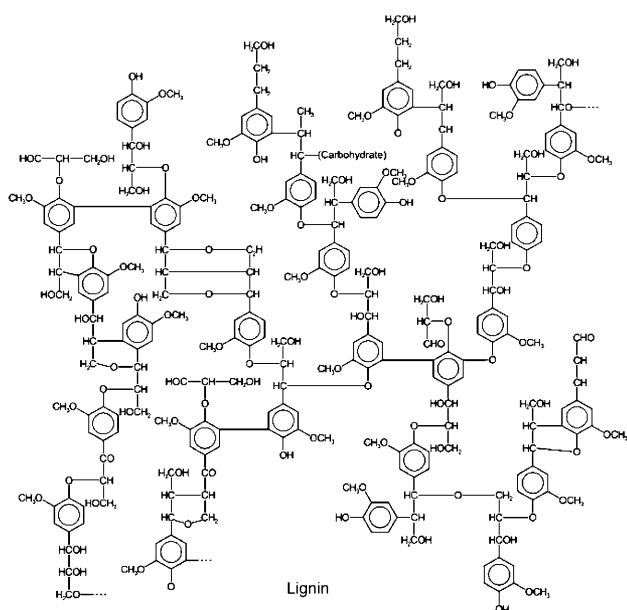


Hemicellulose: An amorphous and heterogeneous group of branched polysaccharides (copolymer of any of the monomers glucose, galactose, mannose, xylose, arabinose, and glucuronic acid); hemicellulose surrounds the cellulose fibers and is a linkage between cellulose and lignin (about 28%).



Lignin: a highly complex three-dimensional polymer of different phenylpropane units bound together by ether and carbon–carbon bonds. Lignin is concentrated between the outer layers of the fibers, leading to structural rigidity and holding the fibers of polysaccharides together (about 27%).

In addition, small amounts of extraneous organic compounds are found in lignocellulosic materials (about 4%).



6. Biofuel Production from Lignocellulose

Whereas bioethanol production from cellulose and hemicellulose is based on known technology (Figure 5), the generation of biofuels from lignin is new technology, and is abbreviated as BTL (biomass to liquids).

The direct use of lignocellulose as a chemical feedstock is difficult owing to the complex structure. In a biorefinery, separation technology that differs from a crude-oil refinery must be used. In a petroleum refinery, distillation is the main separation operation, as volatile compounds are involved. However, most biomass components are nonvolatile, and thus solvent-based extraction, chromatography, or membrane separation are the main choices for valuable chemicals derived from lignocellulose.

Cellulose, hemicellulose, and lignin pyrolyze or degrade at different rates and by different mechanisms. Therefore, before pyrolysis, the three major components of wood must be separated by steam splitting.

The pyrolysis of cellulose begins at quite low temperatures (around 50°C); however, thermal degradation proceeds by two types of reaction: a gradual decomposition at low temperatures, and a rapid volatilization at higher temperatures. The initial decomposition reactions cover both hydrolysis, oxidation, de-polymerization, dehydration, and decarboxylation.^[10]

The thermal decomposition of hemicellulose occurs more readily than that of cellulose. The pyrolysis starts at 100°C during heating for 48 h, and hemicellulose is depolymerized by steaming at high temperatures for a short time. Hemicelluloses contain more moisture than lignin, however, and thermally decompose at lower temperatures.^[10]

To make a biorefinery viable, the lignin component of wood must be addressed. Lignin decomposes over a wider temperature range than cellulose and hemicellulose. Currently, residual lignin from paper pulping is burned off to generate heat and electricity. However, it has been demon-

strated that lignin pyrolysis at temperatures between 250 and 600°C has the potential of delivering valuable low-molecular-weight feedstocks. These results suggest that the application of shape-selective cracking catalysts would allow the process to be run at lower temperatures, and at the same time providing an improved product distribution pattern. For example, lignin has been depolymerized by base-catalyzed treatment into a bio-oil consisting of low-molecular-weight phenolic compounds.^[11] The phenols form from the cracking of the phenylpropane units of the macromolecular lattice of lignin. The phenolic fraction can then be separated to arrive at phenolic resins. Alternatively, the bio-oil can be subjected to hydroprocessing to yield a mixture of alkylbenzenes useful as a potential liquid biofuel.^[5,19]

Figure 6 illustrates bio-oil production from lignin. Apart from upgrading bio-oil by separation and harvesting both phenolics and motor fuel components, the carbohydrate

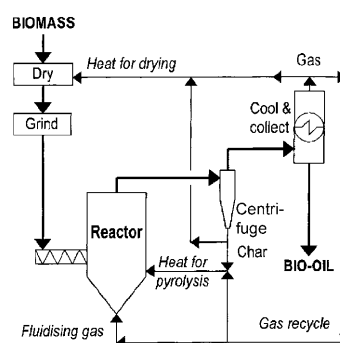


Figure 6. Flow chart showing the production of bio-oil from lignin.

fraction can be converted into hydrogen by catalytic steam reforming. In addition, the gasification of bio-oil to syngas opens the entire route to Fischer–Tropsch processing and over the indirect pathway via methanol to olefins and gasoline. The liquid fraction of the pyrolysis consists of an aqueous phase containing a wide variety of low-molecular-weight organo-oxygen compounds, and a non-aqueous phase containing insoluble organic compounds (mainly aromatics) of high molecular weight. This phase is called bio-oil, and is the product of greatest interest.^[10]

7. Catalytic Conversion of Lignocellulose-Based Biomass

7.1. Background and Current Technology

The conversion of biomass into first-generation biofuels uses only a small part of the biomass available for processing, and thus the reduction in greenhouse gas emissions is only small. However, the application of wood-based biomass in the production of second-generation biofuels is more expensive, as considerable investment costs are required.

The conversion of wood to produce biofuels by heterogeneous catalysis has received strong attention in recent

years. Of the various thermochemical processes available, pyrolysis is the preferred conversion method.^[12–14] Pyrolysis is an appropriate process for the conversion of large amounts of wood into bio-oil, from which biofuels and chemicals can be produced (Figure 5). However, some important bio-oil characteristics are disadvantageous, such as high water and oxygen content, corrosiveness, lower stability, immiscibility with crude-oil-based fuels, high acidity, high viscosity, and low calorific value. Therefore, improvement of the bio-oil quality is a prerequisite before upgrading to biofuels can be envisaged.^[15] A number of processes have been introduced for the thermochemical conversion of wood-based biomass to biofuels and/or chemicals; however, the quality of the bio-oil produced is too low for processing to valuable products.

Three alternatives are currently of interest for the conversion of wood-based biomass into biofuels:

1. BTL fuels, with subsequent refining of the bio-oil obtained.
2. Gasification of biomass, followed by catalytic upgrading of the products.
3. Separation of sugars with subsequent catalytic conversion.

In reports in the literature on higher quality bio-oil production, disadvantageous additional coke and water formation has to be taken into account. In addition, lower quantities of organic phase are produced.^[16,17]

Four main approaches to improve the quality of bio-oil:

- a) Fluidized catalytic cracking (FCC): $C_6H_8O_4 \rightarrow C_{4.5}H_6 + H_2O + 1.5CO_2$
- b) Decarboxylation (DCO): $C_6H_8O_4 \rightarrow C_4H_8 + 2CO_2$
- c) Hydrodeoxygenation (HDO): $C_6H_8O_4 + 4H_2 \rightarrow C_6H_8 + 4H_2O$
- d) Hydrotreating (HT): $C_6H_8O_4 + 7H_2 \rightarrow C_6H_{14} + 4H_2O$

$C_6H_8O_4$ refers here to the conceptual stoichiometric composition of bio-oil. The preferred catalysts for FCC are based on ZSM-5 (structure code: MFI) and zeolite Y (structure code: FAU),^[18–27] with the microactivity test (MAT) as reactor equipment.^[15,19] To date, upgrading of bio-oil by FCC has been investigated only using fixed-bed equipment within the temperature range of 340–500 °C.

State-of-the-art hydrodeoxygenation (HDO) is based on hydrotreating (HT) using sulfur-containing NiMo and CoMo catalysts processed at about 400 °C and under hydrogen at high pressures.^[3] However, owing to the questionable availability of hydrogen in refineries, processing of bio-oil by HDO may not be viable.

Complete decarboxylation (DCO) may be the best upgrading route for bio-oil, as hydrocarbons are produced and hydrogen is not required.^[3] ZSM-5 and USY zeolites have been used for this process. Decarboxylation of the organic acids leads to an improved bio-oil that is low in acids, less corrosive, more stable, and has a higher energy content. However, large quantities of coke are formed during this process. New catalysts are thus required for more intensive decarboxylation of bio-oil to make this technology economically viable. To date, most bio-oils have been obtained by thermal conversion. Using improved catalysts, the problems discussed above should be overcome.

7.2. Approaches to Obtain High-Quality Bio-Oil

Improving the quality of bio-oil using heterogeneous catalysis should be given high priority to allow the production of improved bio-oil for use within modern refinery streams. The overriding aim should be that pure bio-oils could be coprocessed with hydrocarbon fractions, such as vacuum gas oils, in a conventional refinery, giving the bio-oil the role of feedstocks or cofeedstocks in petroleum streams.

To meet these challenges, mono- and bifunctional catalysts should be investigated, such as zeolites, mesoporous materials with uniform pore size distribution (MCM-41, MSU, SBA-15), micro/mesoporous hybrid materials doped with noble and transition metals, and base catalysts. These catalysts should be able selectively favor the decarboxylation reactions, producing high-quality bio-oil with low amounts of oxygen and water. A lower degree of formation of undesirable oxygenated compounds, such as alcohols, ketones, acids, and carbonyl compounds, is envisaged, as these compounds are known to be detrimental for the direct use or further coprocessing of bio-oil. The application of catalysts doped with noble metals would promote reactions of bio-oil involving oxygen removal and ring-opening, and at the same time minimize the consumption of hydrogen.

The hydrothermal stability of the catalysts must also be improved, and this can be studied by successive addition of water to the dry feedstock. Resistance to deactivation and catalyst behavior upon regeneration must be investigated to optimize new catalysts. This optimization also includes the controlled formation of appropriate catalyst particles and tailoring the porosity, acidity, basicity, and metal-support interactions of the catalysts.

In a crude-oil refinery, liquid or vapor phases are usually in contact with the solid catalysts. In contrast, for catalytic pyrolysis, the solid biomass is in direct contact with the solid catalyst, and the bio-oil formed in the pyrolysis reactor is worked up in-situ. Thus the properties of the catalyst have to be tuned to this new system.

The improved-quality bio-oil could then be blended with conventionally formed hydrocarbon fractions and further refined by FCC and/or HT processes. Both the new catalysts and those that are already commercially available should be investigated for their suitability to the direct processing of high-quality bio-oil and mixtures with fossil-based hydrocarbon fractions.

7.3. Micro- and Mesoporous Materials as Catalysts for the Conversion of Lignocellulosic Biomass

7.3.1. Microporous Materials

The pyrolysis of wood-based biomass in the presence of H-ZSM-5 (a zeolite with the structure code MFI, Figure 7) has been studied.^[28] The 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 by-products. The regeneration of

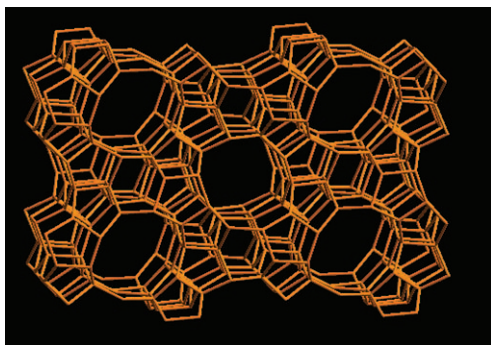


Figure 7. Structure of H-ZSM-5 (structure code: MFI), showing the three-dimensional channel system with 10-membered rings. Pore size: $5.1 \times 5.6 \text{ \AA}^2$.

the deactivated catalyst by coke burn-off at 500°C in air reduced the effectiveness of the zeolite in the catalytic conversion of lignocellulosic biomass into bio-oil and the further processing to aromatic products. H-ZSM-5 that is activated at 500°C has predominantly Brønsted acid sites; however, at higher temperatures, Lewis acid sites form, resulting in dehydroxylation reactions. The best-quality bio-oil using this catalyst was obtained at 450°C .^[28] Fast pyrolysis of vegetable biomass in a fluidized bed reactor was successfully performed using Ni-H-ZSM-5 as catalyst.^[29]

7.3.2. Mesoporous Materials

Recent focus of the development of catalysts for the conversion of lignocellulosic materials has been concentrated on mesoporous materials with a uniform pore size distribution, such as MCM-41 (Mobil Composition of Matter) or MSU (Michigan State University). The pore diameter of these materials can be tailored within the range of 2–10 nm, allowing the processing of large organic molecules, such as those present in wood-based biomass feedstocks (Figure 8).

The use of mesoporous materials for the catalytic conversion of biomass has been adapted from fluidized catalytic cracking (FCC), in which the large molecules in the residue are first cracked to gas-oil components in the macro- and mesopores, before gasoline or propylene (LPG) are formed during cracking performed in the micropores of

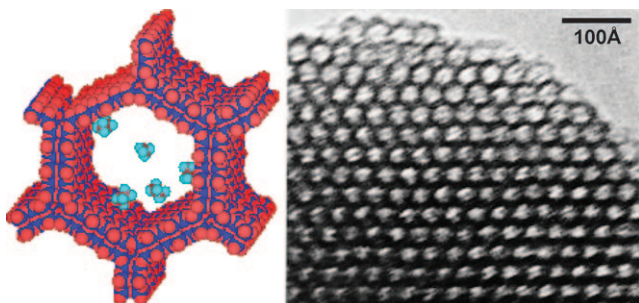


Figure 8. Left: structure of aluminosilicate MCM-41. Small molecules are shown schematically in the pores. Right: two-dimensional array of hexagonal units of MCM-41 from high-resolution transmission electron microscopy.

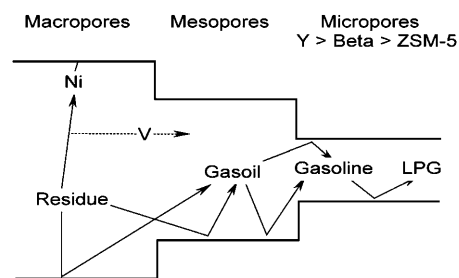


Figure 9. Conceptual pore architecture design of a FCC catalyst. LPG = liquid petroleum gas. Reproduced from Ref. [30] with permission of Elsevier.

zeolite Y or ZSM-5, respectively (Figure 9). The very large pores of mesoporous materials are able to process large lignocellulosic macromolecules, even though the chemistry is different, as the conversion involves carbohydrates rather than the hydrocarbons in conventional FCC.

The mesoporous materials can be applied as such; however, attempts have been made to improve the hydrothermal stability of these catalysts by steam treatment, as these systems must tolerate certain amounts of water, or by introduction of noble and/or transition metals to enhance the oxygen removal capacity and/or promote decarboxylation reactions.^[16,17,31–34]

Testing was performed using a fixed-bed reactor unit (Figure 10). The catalyst is always placed in the reactor and the biomass is placed in the piston cylinder. The reactor and piston cylinder are connected and placed into an oven. As soon as the reaction temperature of 500°C is achieved, biomass enters the reactor and the experiment can start.

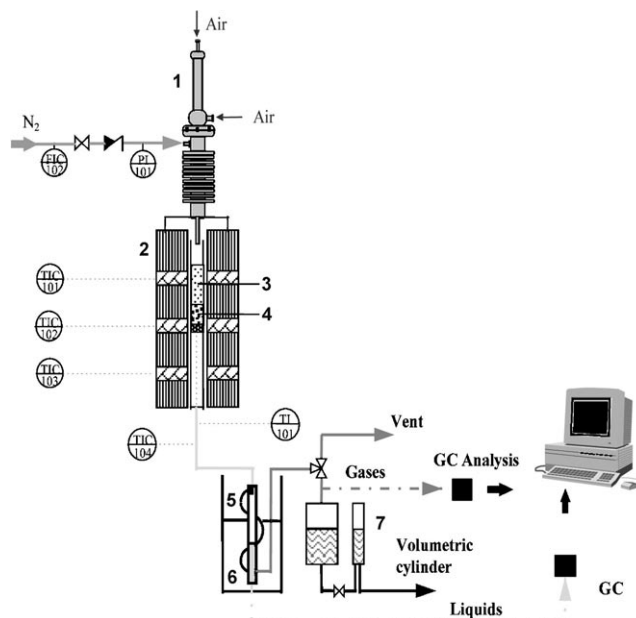


Figure 10. Fixed-bed unit for the catalytic conversion of wood-based biomass. 1: embol (entrance unit), 2: reactor furnace, 3: biomass bed, 4: catalyst bed, 5: cold liquid bath, 6: liquid product receiver, 7: gas collection system. Reproduced from Ref. [32] with permission of Elsevier.

Two different feedstocks were used for the investigation of the mesoporous materials: lignocel (LIG, originated from beech wood) and miscanthus (MIS, an energy crop). Samples of Al-MCM-41 materials have been tested with different Si/Al ratios, namely Si/Al = 20 (MCM-1), Si/Al = 40 (MCM-2), and Si/Al = 60 (MCM-3), and three metal-containing mesoporous samples, Cu-Al-MCM-41 (Cu-MCM), Fe-Al-MCM-41 (Fe-MCM), and Zn-Al-MCM-41 (Zn-MCM). The results are summarized in Figure 11.^[32]

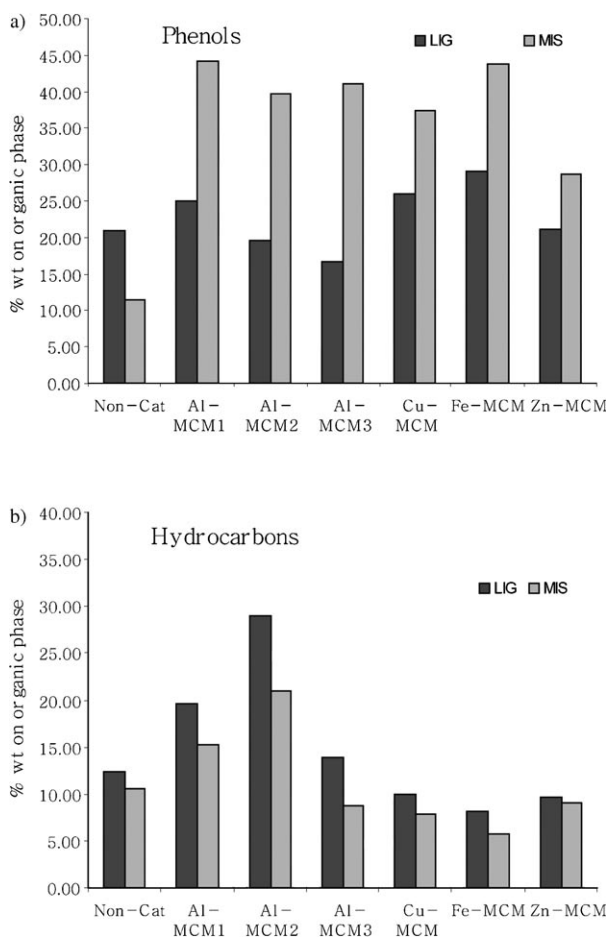


Figure 11. Phenols (a) and hydrocarbons (b) produced from lignocel (LIG) and miscanthus (MIS) feedstocks using mesoporous MCM-41 materials with different Si/Al ratios and transition-metal content. Reproduced from Ref. [32] with permission of Elsevier.

Compared to conventional non-catalytic pyrolysis, the presence of MCM-41 alters the quality of the pyrolysis products significantly. All the catalysts increased the amount of phenolic compounds, which are very important in the adhesives industry. A low Si/Al ratio of MCM-41 was found to have a positive effect on phenol yields and composition. Fe-Al-MCM-41 and Cu-Al-MCM-41 are the best transition-metal-containing catalysts for the production of phenols. The presence of the Al-MCM-41 material also decreased the fraction of undesirable oxygenated compounds in the bio-oil produced, which is an indication that the obtained bio-oil is more stable.^[32]

The proportion of liquids produced is lower relative to the non-catalytic runs, and the formation of gaseous compounds is comparable or lower; however, the production of coke is higher. The most important finding in the gaseous pyrolysis products is the increased concentration of the hydrogen in the presence of transition metals, especially when applying Cu-Al-MCM-41. Lignocel produced higher levels of hydrocarbons and miscanthus higher levels of phenols for all the catalysts investigated.^[32]

Comparisons were made with microporous materials (ZSM-5) as well, and in Figure 12 it can be seen that mesoporous MCM-41 was most favorable regarding the formation of phenols and hydrocarbons.

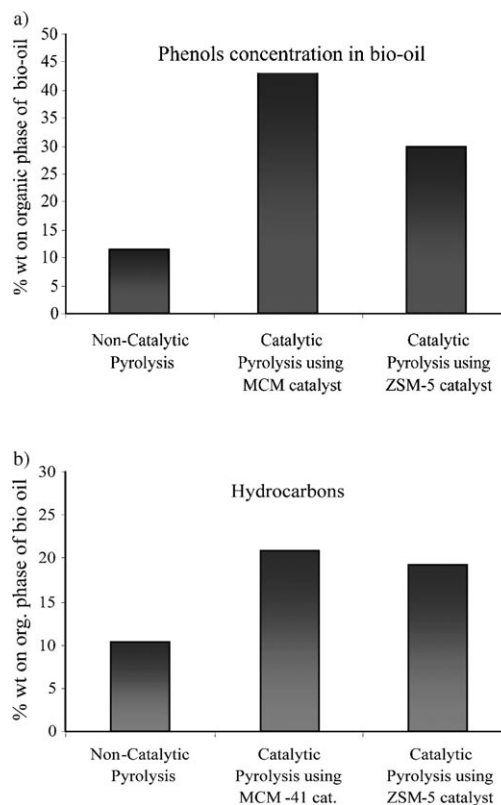


Figure 12. Comparison of the production of a) phenols and b) hydrocarbons using mesoporous MCM-41 material (MCM) and microporous ZSM-5 catalysts compared with non-catalytic pyrolysis.

The effect of steam treatment and the acidity of mesoporous Al-MCM-41 (Si/Al ratios of 50 and 30) in comparison to pure siliceous MCM-41 and to non-catalytic pyrolysis on the in-situ upgrading of lignocel biomass has been investigated by Iliopoulou et al.^[17] All the MCM-41 materials significantly affected the product yield and quality of the obtained bio-oil. This behavior was mainly attributed to the one-dimensional mesopores (pore diameter ca. 2–3 nm) in combination with the large surface area of the MCM-41 materials (about 1000 m² g⁻¹), and their mild acidity. All these factors provide the desired environment for a controlled conversion of the high-molecular-weight lignocellulosic molecules. The major improvement in the quality of the bio-oil

using Al-MCM-41 materials was an increase in the concentration of phenols and a lower concentration of corrosive acids. Moderate steaming of the Al-MCM-41 samples at 550 and 750 °C (20% steam partial pressure) resulted in active catalytic materials having a different product selectivity owing to the relatively low surface area and number of acid sites compared to the parent samples (Figure 13).^[17]

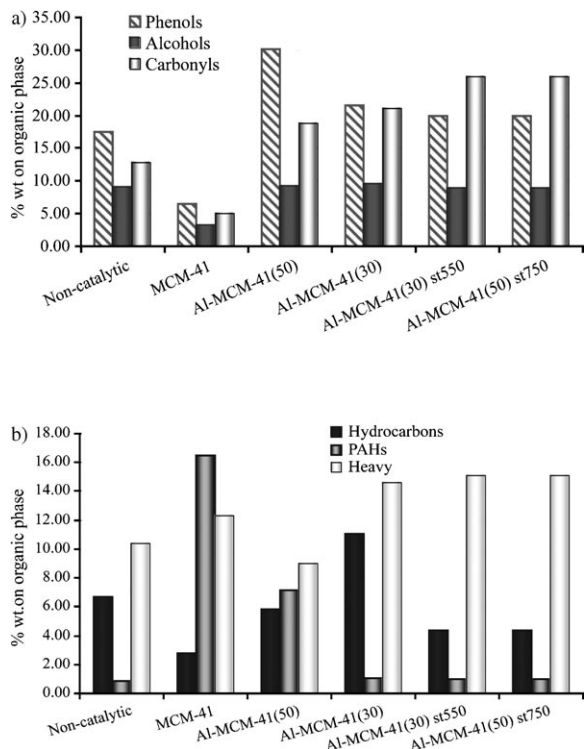


Figure 13. Concentrations of phenols, alcohols, and carbonyls (a) and hydrocarbons, PAHs (polycyclic aromatic hydrocarbons), and heavier compounds (b) in the organic phase of the bio-oil produced by the pyrolysis of lignocel with different mesoporous MCM-41 materials. Numbers in parentheses correspond to the Si/Al ratios; st 550 and st 750 correspond to steam treatment at 550 and 750 °C, respectively. Reproduced from Ref. [17] with permission of Elsevier.

The application of Al-MCM-41 materials as catalysts for the pyrolysis of wood-based biomass is promising, especially regarding the improvement of the quality of the obtained bio-oil by increased formation of phenols. Even the siliceous MCM-41 material was active in biomass pyrolysis, producing high amounts of total liquid products by the enhanced thermal cracking of lignocellulosic biomass, owing to the high surface area of the mesopores. Fine-tuning the acidity and porosity of the MCM-41-based materials seems to be a prerequisite for improving the bio-oil quality and the product selectivity.^[17]

Triantafyllidis et al. investigated the catalytic conversion of lignocel with two mesoporous aluminosilicate materials from the MSU family: MSU-S/H with hexagonal mesopores, and MSU-S/W with a wormhole-like structure and high textural porosity.^[16] The MSU-S catalysts led to a significantly lower quantity of organic phase in the obtained bio-oil, but

higher coke and char yields compared to Al-MCM-41 and non-catalytic pyrolysis. The MSU-S catalysts were quite selective towards polycyclic aromatic hydrocarbons (PAHs) and heavy fractions, whereas they produced only small amounts of acids, alcohols, carbonyls, and phenols. The MSU-S type materials appeared to possess stronger acid sites than Al-MCM-41, resulting in enhanced yields of aromatics, PAHs, and coke, along with propene in the pyrolysis gases (Figure 14).^[16]

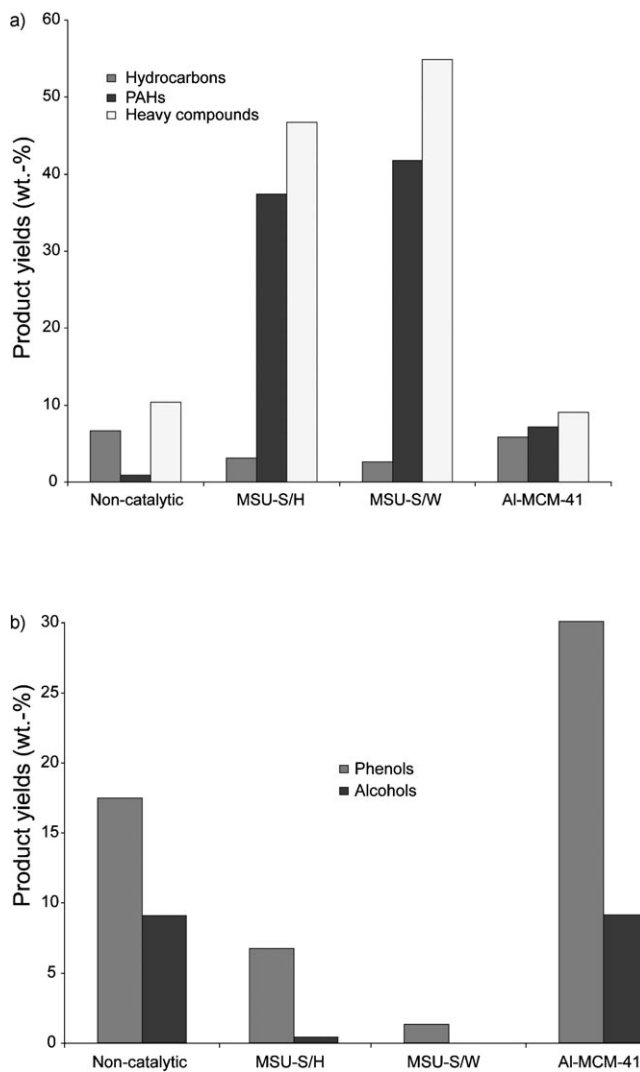


Figure 14. Hydrocarbons, PAHs, and heavier compounds (a), and phenols and alcohols (b) in the organic phase of the bio-oil produced from the pyrolysis of lignocel (originating from beech wood) with MSU-S and Al-MCM-41 type mesoporous catalysts. Reproduced from Ref. [16] with permission of Elsevier.

Future studies need to focus on the acidic properties of the mesoporous materials (type, strength, and number of acid sites) and on the pore architecture to gain information about the structure–property relationships of mesoporous materials as catalysts in the conversion of lignocellulosic biomass.^[16]

The results of using MCM-41 as catalyst for the conversion of wood-based biomass has been confirmed by Park

et al.^[35] They investigated the catalytic upgrading of bio-oil obtained pyrolytically from Japanese larch using MCM-41 systems. Oil with enhanced stability was produced applying these mesoporous materials by transfer of oxygen, which is known as the main cause for the instability of bio-oil, into water, carbon monoxide, and carbon dioxide. Furthermore, the MCM-41 catalysts produced larger amounts of phenolics in the bio-oil obtained. The catalytic activity of Al-MCM-41 for bio-oil upgrading was higher than that of siliceous MCM-41 because of the larger number of acid sites. Finally, improved reforming results were obtained when the pyrolytic bio-oil vapor passed through a catalytic layer rather than if wood from Japanese larch was mixed with the catalyst directly.^[35]

8. Applications of Bio-Oil

High-quality bio-oil can be used to obtain biofuels and/or valuable chemicals (Figure 5). Gasification of bio-oil to syngas opens routes to Fischer–Tropsch products and methanol. From methanol, olefins and gasoline can then be obtained. Separation of bio-oil leads to phenolics and to hydrogen from the carbohydrate fractions. However, the bio-oil can also be used to produce heat and electricity (Figure 15).

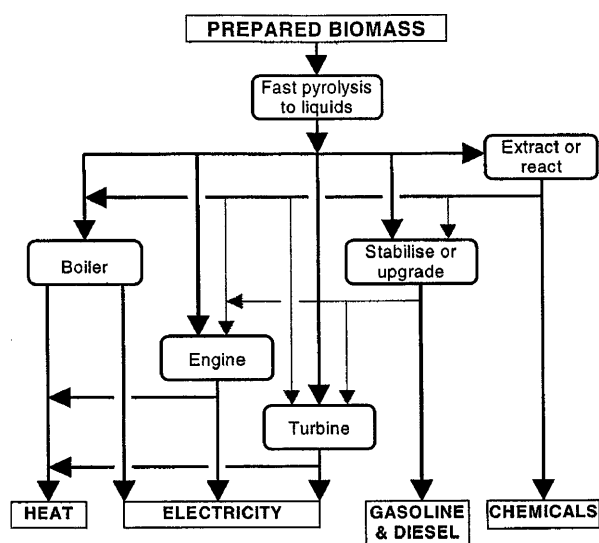


Figure 15. Applications of bio-oil.

The improved-quality bio-oil can be upgraded by FCC and/or hydrotreating (HT), which means that the catalytically produced bio-oil can be used as a blend in FCC and/or HT. The direct processing of high-quality bio-oil and the use of bio-oil as cofeedstock with hydrocarbon fractions will contribute to a decreased use of fossil-based energy sources. The overriding aim should be that pure bio-oils could be coprocessed with hydrocarbon fractions, such as vacuum gas oils, in a conventional refinery, giving bio-oil the role of feedstocks or cofeedstocks in petroleum streams.^[3]

9. Pilot Units

BTL processes for the production of bio-fuels are under development, and several pilot units are under construction or already running.^[36,37] The most advanced unit is probably the pilot plant from Choren Industries in Freiberg (Germany) in cooperation with Shell. For the years 2007/2008, Choren Industries announced the production of 15 000 t a⁻¹ of “Sun-Fuel” obtained from 68 000 t a⁻¹ biomass by pyrolysis. An increase in production to 200 000 t a⁻¹ “SunFuel” by using 1 000 000 t a⁻¹ biomass is scheduled for the next years. Choren Industries is using the Fischer–Tropsch technology to produce fuels.^[7]

A two-stage pilot unit for the production of biofuels from biomass is under construction at the Forschungszentrum Karlsruhe (bioliq).^[38] This center is cooperating with Lurgi AG in this development, and this approach may produce biofuels by the (indirect) methanol route and MTSynfuel technology.^[7]

Other BTL pilot units are under construction in Güssing (Austria) and Värnamo (Sweden).

10. Outlook

The use of carbon dioxide neutral and renewable biomass for the production of fuels is a vital alternative to fossil-based energy resources. However, there are a number of major obstacles to an economically feasible production of biofuels by the BTL process. These are:

- High investment costs
- Low volumetric energy density of biomass
- Lack of infrastructure
- Limitations to the productivity of photosynthesis
- Availability of cultivable land areas for the production of bioenergy plants, which are in competition with food production.

The low energy density of wood-based biomass in particular, which is the cheapest and most abundant biomass, makes it difficult to convert this source into biofuels. The pyrolysis of lignocellulosic biomass into high-quality bio-oil by using suited catalysts is still the main challenge to the concept of a modern lignocellulosic biorefinery. Once high-quality bio-oil is achieved, the subsequent use as direct feedstock or as cofeedstock in conventional refinery processes, such as FCC or HT, can be envisaged to produce diesel and/or gasoline. Hydrotreating requires high-pressure hydrogen; however, it might be feasible that this hydrogen demand can be satisfied from biomass conversion as well (catalytic steam reforming of the carbohydrate fraction, see Figure 5). There are a number of alternatives available for the utilization of biomass-derived feedstocks in a crude-oil refinery, and the development of technology for the production of biofuels will allow a move towards a sustainable economy.^[1,7]

In a time in which the focus is on global warming, carbon dioxide emission, a secure energy supply, and lower consumption of fossil-based fuels, the use of renewable energy

resources is essential. Biomass is one of these renewable resources!

Challenges related to the catalytic conversion of wood-based biomass remain and have to be addressed in the future research:

1. Understanding the mechanism of the catalytic conversion of lignocellulosic biomass into bio-oil, including structure–property relationships and product distribution.
2. Catalyst development, regarding porosity, acidity, basicity, metal–support interactions, controlled formation of appropriate catalyst particles, improved hydrothermal stability, and resistance to catalyst deactivation.
3. Process conditions and large-scale production.

The biorefinery approach using wood-based biomass does not compete with traditional crude-oil refining, rather it is complementary to petroleum refining.

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