Catalysis for Renewables (Centi)

Chapter 6

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6
Options for Catalysis in the Thermochemical Conversion of Biomass into Fuels

Sascha R. A. Kersten, Wim P. M. van Swaaij, Leon Lefferts, and Kulathuiyer Seshan ▌AQ1▌

6.1
Introduction

Progress towards a sustainable energy supply is without doubt one of the biggest challenges that mankind has ever faced. Energy scenarios [1–3] project that the world's annual energy consumption will increase steeply from the current 500 Exa (10^{18}) joules (EJ) per annum to 1000–1500 EJ by 2050. At least for the coming 50 years, sustainable energy sources alone will not be able to fulfill the world's energy demand. Fossil fuels will continue to dominate, and CO_2 emission abatement will become more and more important. It is forecasted that in 2050 ca. 400 EJ of energy per annum has to originate from sustainable sources to fulfill the needs of that generation. To achieve this, non-fossil energy systems such as solar (thermal, photovoltaic), indirect solar (biomass, water, wind, thermal gradients) and nuclear (fusion, fission, and geothermal) will be developed, optimized and implemented. At this point in time, it cannot be said unequivocally which ''source-technology-product'' combination(s) will dominate under the prevalent economical, social and environmental systems of 2050. It is recognized, however, by governmental bodies [4–6] and large industries [7] that biomass is a relevant sustainable candidate for the replacement of fossil sources, especially when it comes to the production of fuels for (non)stationary applications [e.g., gasoline, diesel, kerosene, oxygenates, heavy fuel oil, (S)NG, H_2]. These fuels are essential for our present society and it is of paramount importance for the world's economy and stability that a fuel supply is guaranteed in the future.

The present chapter discusses the options for application of catalytic technology in the thermochemical conversion of lignocellulosic biomass into fuels. It is envisaged that catalysis will play an important role in the production of biofuels, just as catalysis plays a major role in the conversion from fossil feeds into fuels currently. The development of catalytic cracking, isomerization and hydro-treating technologies have been key expertise for shaping the mineral-oil-refining industries during the 20th century into its present position, exploiting

all fractions of mineral oil for producing fuels and chemicals. Thus, application of the knowledge and technology currently available is essential for a smooth and economical transition. Adaptation of biomass as a feedstock in (a) the current processes for chemicals and fuels or (b) new conversion processes is by no means automatic and poses new challenges in catalyst design. Importantly, the use of lignocellulosic waste material (not digestible by humans) or energy crops as feedstock prevents competition with the food chain. Next to thermochemical routes, biochemical conversions also show promise for the production of bio-fuels. Investigations into these routes are dominated by expertise in the areas of biochemistry, biotechnology, microbiology etc., and are outside the scope of this chapter. Most likely, both thermochemical and biochemical conversions processes will contribute in an integrated manner to the concept of the bio-refinery to produce fuels and chemicals.

Recently, Corma and coworkers [8] published an exhaustive descriptive review on the synthesis routes of transportation fuels from biomass, and Ragauskas et al. [9] sketched their vision on the path forward for bio-fuels and biomaterials. Furthermore, a review by Lange et al. [10] appears in this book.

The present chapter discusses aspects, known by the authors, of (a) biomass as feedstock, (b) the concept of bio-refinery, (c) thermochemical routes from lignocellulosic biomass to fuels, and (d) the contribution of catalytic technology. The main focus will be on the catalytic conversion of fast pyrolysis oil into fuels with regard to problems encountered currently and the challenges for future research and development.

6.2
Biomass as Feedstock for Fuels

Biomass, via its photosynthesis, has provided energy for life for the longest period of its existence. Industrial processes that take-in biomass can be integrated with the natural photosynthesis/respiration cycle of vegetation. If used in this manner, biomass is a renewable energy source and, by its utilization, overall much less CO_2 is added to the atmosphere compared with the fossil fuel counterpart processes. When combined with CO_2 sequestration, biomass based processes can actually lower the CO_2 concentration in the atmosphere [11].

Ethically, only biomass that is not competing with the food chain should be used for the production of fuels, chemicals, power or heat. This competition can be avoided by first using the abundant residues from forests (e.g., leaves, timber residues) and agriculture (e.g., stems, straws, husks, bunches) and subsequently energy crops (e.g., algae, specially engineered short rotational crops) if the residues are not sufficient or are too expensive to collect or to process. Agricultural and forestry wastes are estimated to be the energy equivalent to half of the current world's oil production [12]. The potential of special energy crops is estimated to be in the range 50–250 EJ per annum [13]. Under strict conditions, such as closure of the mineral balance at the biomass production side, water balance control, and not making use of any fossil fuels and fossil-based utilities (fertilizers),

Table 6.1 Comparison of fossil and biomass derived fuel equivalents.

Fossil	Biomass alternative (100% bio-based replacement and/or blending component for fossil fuel)
Natural gas	CH_4
LPG ($C_3 + C_4$)	DME (dimethyl ether)
Gasoline (C_6–C_9)	Butanol Ethanol Methanol MTHF (methyltetrahydrofuran) MTBE (methyl tertiary-butyl ether) Deoxygenated and refined primary bioliquids
Diesel (C_{14}–C_{16})	Fatty acid esters (methyl = FAME, ethyl = FAEE) Levulinic acid esters (methyl, ethyl) DME Ethanol Fischer–Tropsch diesel (from bio-based synthesis gas) Deoxygenated and refined primary bioliquids
Kerosene (C_{10}–C_{14})	Fischer–Tropsch wax (from bio-based synthesis gas)
Heavy fuel oil	Primary bioliquids (pyrolysis oil, hydrothermal liquefaction oil)
Coal	Solid biomass, charcoal

the use of biomass is completely sustainable. Technical and non-technical facilitators and barriers for large-scale industrial biomass use are discussed in detail by Van Swaaij et al. [11].

Biomass is built-up mainly out of the elements C, H and O, just like many of our current fuels and chemicals, although the C-H-O ratio differs significantly, as will be discussed later. The proof of principle for the conversion of biomass into single components or mixtures that can be blended with fossil fuels or that can replace fossil fuels has been delivered already. Table 6.1 lists fossil fuels that are in use today and their possible biomass derived fuel equivalents.

The list contains components that are considered as 100% bio-based replacements and/or blending components for fossil fuels. At the time of writing it is not clear if each listed component can completely replace the corresponding fossil fuel or if it is only suitable for blending.

Blends of petroleum diesel and gasoline with, respectively, bio-diesel (fatty acid esters produced by trans-esterification of vegetable oil) and bio-ethanol (from fermentation of sugar cane/corn) are already approved by the automotive industry. However, the present industrial processes for bio-ethanol and bio-diesel interfere with the food chain by consuming sugars and vegetable oils, often have a too low fuel yield per acre, and require a too high (fossil) energy input [14]. An interesting development in that respect is the cellulose-ethanol demonstration plant from

IOGEN that produces bio-ethanol from straw by a combination of thermal, chemical and biochemical techniques [15, 23; Vol. I, Chapter 7]. Synthesis gas (CO & H_2) [16] and methane-rich gas [17, 18] have been produced at demonstration scale from lignocellulosic biomass via entrained flow gasification and methanation in hot compressed water, respectively. Laboratory-scale research on thermochemical conversions has shown the possibility of converting liquid lignocellulosic biomass [19, 20] into gasoline and diesel precursors. These technologies are in an embryonic stage of development and require extensive research to identify the best routes and to develop the required catalysts and reactors.

6.3
Composition of Biomass

Biomass contains more oxygen than fossil sources (30–50 wt.%, see Fig. 6.1). In Fig. 6.1, (biomass and fossil) sources and fuels (fuel blends) are positioned in the O/C–H/C plane.
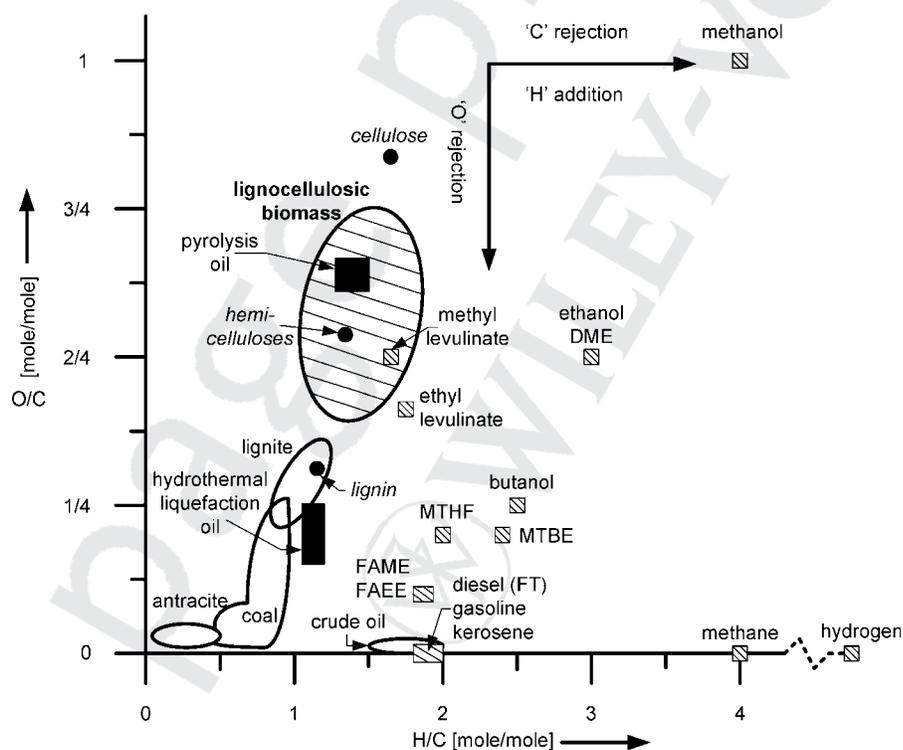
Fig. 6.1 Composition (dry basis) of fossil and biomass feed stocks and fuels derived from them. Arrows indicate current/possible upgrading routes.

Liquid hydrocarbon fuels (gasoline, diesel, kerosene, heavy fuel oil) have a typical composition of $[CH_{1.8-2}]$ and they are made from the hydrogen-deficient fossil crude $[CH_{1-1.5}]$ via two routes: (a) hydrogen addition (hydro-processing) and (b) carbon rejection (coking, FCC). Production of liquid hydrocarbon fuels from biomass requires, in addition to hydrogen addition or carbon rejection, oxygen removal (Fig. 6.1). Oxygenated fuels from lignocellulosic biomass such as DME, MTBE, esters, and alcohols need less oxygen exclusion. Hydrogen manufacturing from biomass requires, obviously, complete carbon and oxygen rejection. Bio-based methane can be produced by combined hydrogen addition and oxygen removal.

Along with carbon, hydrogen and oxygen, lignocellulosic biomass also contains hetero elements such as alkali and other metals. The amounts of these ashes vary over a broad range, from 30–50 wt.% in chicken litter to 1–3 wt.% in wood. Moisture is always present in lignocellulosic biomass and can be up to 80 wt.% in some cases. Detailed information on the composition of biomasses can be found in data bases, e.g., Phyllis [21] from the Dutch Energy Research Foundation (ECN). Table 6.2 lists the compositions of some typical biomasses.

The organic fraction of lignocellulosic biomass is built-up of cellulose, lignin, hemi-cellulose (Fig. 6.2), and extractives. Cellulose is a long-chain homo-polymer of β $[(C_6H_{10}O_5)_n, n > 3000]$. Lignin is a macromolecule with a molecular mass of higher than 1000 gram mol^{-1} and is built-up randomly from ordered aromatic substructures. Hemicellulose is a co-polymer of any of the following monomers: xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan ($n > 500$). The cell walls of plants, crops, and trees are made of insoluble cellulose fibers meshed into a matrix of hemicelluloses. Lignin fills the spaces in the cell wall between cellulose and hemicelluloses. It confers mechanical strength to the cell wall

Table 6.2 Analysis (typical values in wt.%, dry) of selected biomasses.

Component	Biomass				
	Poplar (hardwood)	Pine (softwood)	Corn stover	Rice husk	Cotton seed hulls
C	50.8	52.9	47	36	33
H	6.4	6.3	5.5	5	6
O	41.8	40.7	41	40	59
N	0.3	0.1	1.5	2	0.1
Ash	0.7	1.0	5	17	1.9
Cellulose	45	46	35	33	53
Hemicelluloses	30	20	37	29	18
Lignin	22	32	18	20	25
Extractives	2.1	2	5	1	2.1

(a) Cellulose
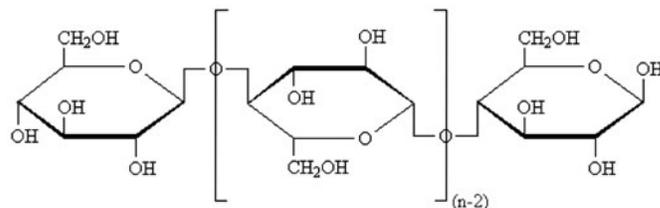
(b) Hemicelluloses
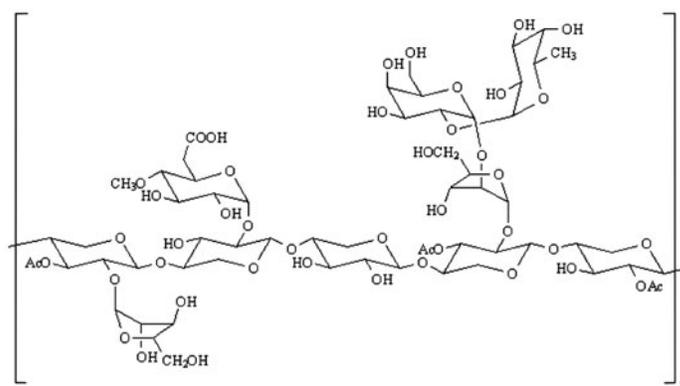
(c) Lignin
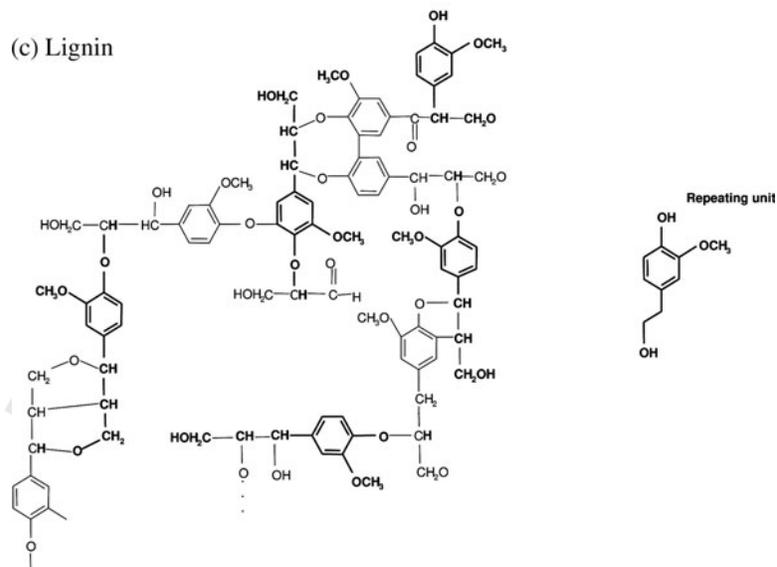
Fig. 6.2 Structural formulas of cellulose (a), example of hemicelluloses (b), and an example of lignin (c), showing a repeating unit as possible model compound.

and, therefore, the entire biomass. Extractives are non-structural components and are deposited in cell cavities or infiltrated into the cell wall structure and occur as complex mixtures of tannins, flavonoids, stilbenes, resin- and fatty-acids, waxes, sterols, and simple sugars.

6.4
Biorefinery

There are already some industrial biomass-based processes operational (e.g., bio-diesel, bio-ethanol, bio-based heat and power). However, in general these processes cannot compete economically with their fossil counterparts, because yields of target products are not maximized and by-products often have a very low or even a negative value. An integrated concept aiming at full utilization of biomass, in which different fractions of biomass are converted in large-scale plants (economy of scale) or in standardized small-scale units (economy of numbers) in an economically optimal product state is termed a "Biorefinery". A biorefinery might, for example, produce one or several "low-volume, high-value" chemical products and a "low-value, high-volume" liquid transportation fuels. The high-value products enhance profitability while the high-volume fuel helps to meet energy needs. To start-up the biorefinery concept it is essential to integrate and to partner-up with existing industries and markets. This lowers the required capital investments and offers guaranteed markets for the products. Integration can be at the level of the products only, e.g., by producing biomass-based blending components for fossil transport fuels, or by co-processing biomass in existing refineries and chemical plants. In a later stage, 100% biomass based products can gradually replace the functionality of existing fossil products or can be linked with new applications. By producing multiple products from different fractions of biomass, a biorefinery takes advantage of the differences in the constituents of biomass and of the specific characteristics of intermediate energy carriers (e.g., pyrolysis oil and charcoal). A bio-refinery may include thermal, chemical and biological conversion processes and its development requires input from various disciplines, viz. process technology, (bio-)chemistry, bio-technology, catalysis, (micro-)biology and separations. As mentioned earlier, we will discuss the challenges of the thermochemical conversion and catalytic processing of lignocellulosic biomass.

Several biorefinery schemes have been proposed during the last 5 years [9, 22, 23]. They differ in the choice of feedstock, the proposed technologies and the targeted products. The following concepts have been considered: the Lignocellulosic Feedstock Biorefinery, the Whole Crop Biorefinery, the Green Biorefinery, and the Two Platform Biorefinery [23]. At present, we do not have detailed flow schemes envisaged for the different types of proposed biorefineries, because many of the involved technologies are still in the early stages of development and the optimal product state has not yet been identified. Therefore, the description of a biorefinery must remain abstract. Figure 6.3 is our conceptual outline of a bio-refinery that takes in raw biomass from the fields, extracts food and feed from it, and uses the remaining lignocelluloses to produce fuels, chemicals, heat and power.
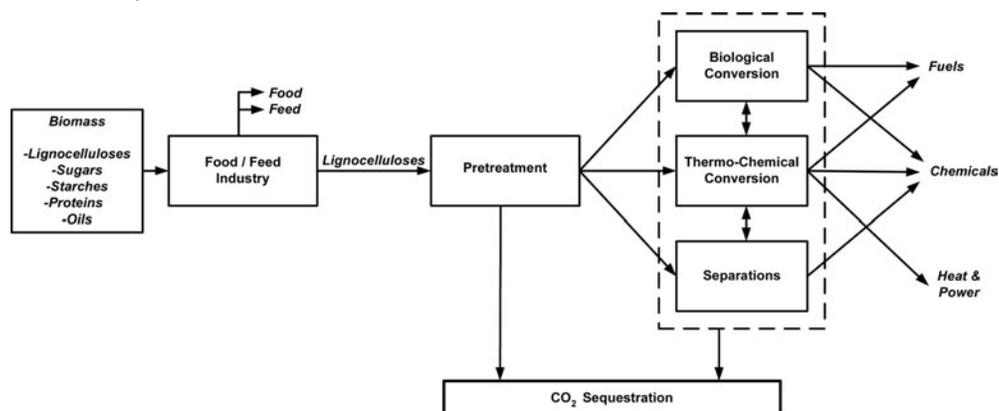
Fig. 6.3 Conceptual outline of a biorefinery.

6.5
Biomass Pretreatment

Lignocellulosic biomass needs pretreatment before it can be directed to the first process step in a series towards fuels. Drying to less (<25 wt.%) water content is required for processes such as gasification, and combustion. To simplify feeding, raw solid lignocelluloses must be homogenized by mixing, grinding, palletizing, liquefaction, or slurry preparation. Grinding becomes much cheaper when the biomass is first torrefied. Torrefaction is a roasting process that breaks down the fibrous structure of biomass, making the material more brittle. By liquefaction the volumetric energy density of biomass is increased by about a factor 5 and the produced liquid (20 MJ L^{-1}) can be more easily processed (incl. contact with catalyst) than solid biomass (4 MJ L^{-1}). Liquefaction ($T > 400$ °C) can be done at ambient pressure [24] or at elevated pressure [25, 26]. For processes at ambient pressures (pyrolysis) the feed is dry while for high pressure processes a "biomass in water slurry" is fed (hydrothermal liquefaction). Interesting results have been achieved by dissolving (liquefying) lignocelluloses in a mixture of 90 wt.% ethylene glycol and 10 wt.% ethylene carbonate at ambient pressure and 150 °C [27]. In Section 6.9 the liquefaction processes are discussed in more detail.

Fractionation is considered as starting point for the production of chemicals and fuels from lignocelluloses via the production of sugars. A good review on the fractionation techniques is given by Huber et al. [8]. Here, only two interesting developments are mentioned: (a) Organosolv pulping is a fractionation method where organic solvents (e.g., ethanol) are used to facilitate lignin extraction [28]; (b) Zhang and Lynd [29] have developed a new fractionation method based on acid treatment, solvent extraction, and Organosolv operating at very mild temperatures of ca. 50 °C.

6.6
Thermochemical Conversion of Lignocelluloses

Basically, there are three thermochemical routes (Fig. 6.4) for the conversion of lignocelluloses into fuels:

1. **g**asification followed by catalytic upgrading of the produced gases;
2. liquefaction of biomass followed by refining;
3. **e**xtraction of sugars and sugar derivates followed by their catalytic conversion.

Figure 6.4 also shows some integration options (dotted arrows) to achieve full utilization of the feedstock, e.g., (a) aqueous phase by-product streams of hydrolysis can be used for the production of H_2-rich gas or methane via conversion in hot compressed water and (b) lignin, separated before hydrolysis, can be gasified (entrained flow) to synthesis gas. Options for the integration of the thermochemical lignocelluloses biorefinery with other biorefinery concepts are legion. The lignocellulosic waste of other biorefinery concepts (e.g., stems from the sugar cane based bio-ethanol process) can be used as feedstock for all primary conversions in Fig. 6.4.

In Section 6.7 onwards the processes listed in Fig. 6.4 are discussed while focusing on the production and upgrading of pyrolysis oil. The route involving oxygen-blown high-temperature gasification followed by catalytic upgrading of the produced synthesis gas is not discussed here. It includes technologies that are commercially available for coal, natural gas, and heavy oil feeds. The authors expect that only minor modifications are required to adapt these technologies for biomass feedstock materials. In this way bio-based top fuels can be produced in the near future. However, there is always the question of the wisdom of first breaking up the lignocelluloses polymers to the smallest possible molecules (CO and H_2) from which then a synthesis is started again up to C_{20} components.

In thermochemical conversion of biomass, temperature is a key parameter. At lower temperatures (<300 °C) only catalytic processes (e.g., acid-catalyzed hydrolysis) are possible. Conversion into various oxygenates, such as acids (e.g., levelunic acid), ▌AQ14▐ heterocyclic hydrocarbons (furans), alcohols (phenols) via sugars with promising yields has been shown to be possible. Lignin is not or hardly decomposed in this regime. In the low temperature processes most use is made of the composition of biomass by keeping much of the functionality of the sugar building blocks intact. However, pretreatment is required to make the fibers accessible (e.g., by steam explosion), because native lignocelluloses is inert for hydrolysis at these temperatures. In addition, the reactions are slow and require often homogeneous catalysts. In the mid-temperature range ($300 < T < 700$ °C) complete conversion of lignocellulosic biomass is possible. Temperature, contact time and use of catalysts, and water dilution level determine the type of products and their aggregation state. Liquefaction processes (pyrolysis and hydrothermal liquefaction) yield a multicomponent liquid product containing oxygenates, some permanent gases, and a solid that consists of the remainders of the fiber structure of the feedstock. Applying catalysis in aqueous environment
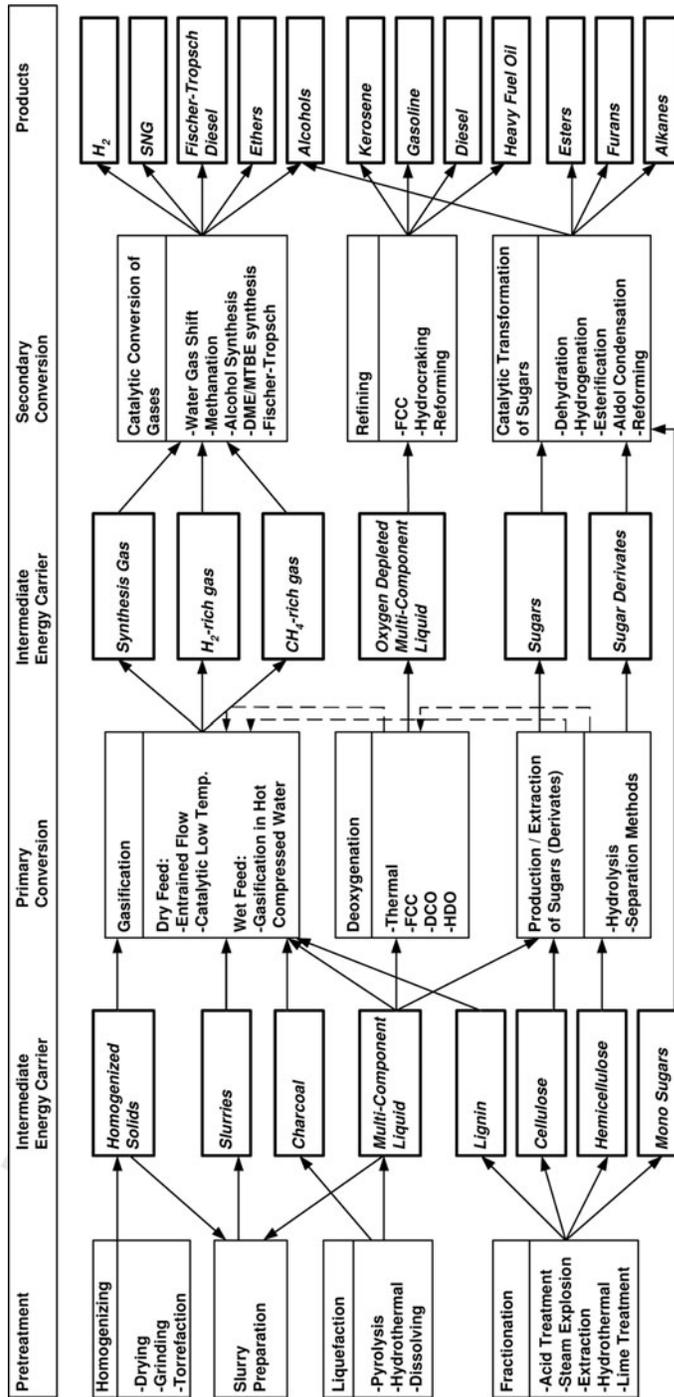
Fig. 6.4 Routes for the production of fuels from lignocellulosic biomass.

can give only gaseous products (H_2 and CH_4). At high temperature ($T > 700\ °C$) gasification is also possible for dry biomass. Gasification is uncontrolled and in the absence of a catalyst, up to $1300\ °C$, methane is always produced. The product gas reaches equilibrium above $1300\ °C$.

6.7
Biomass Gasification

6.7.1
Gasification of Dry Biomass

Gasification was the first technology to be considered for industrial biomass conversion. Complete and good reviews on biomass gasification are available [30–34]. Non-catalytic biomass gasifiers ($T < 950\ °C$) typically produce a fuel gas (CO, CO_2, CH_4, C_{2+}, H_2, H_2O, tars, N_2) that requires extensive upgrading before it can be used in sophisticated down-stream technology applications such as turbines and catalytic conversions. Entrained flow non-catalytic biomass gasification ($T > 1300\ °C$) has been demonstrated for both liquid (G16) and solid feeds (G17). These processes are currently being used on a large-scale for fossil-derived synthesis gas and can be put into service for bio-based synthesis gas with no or minor modifications (especially for co-feeding applications). Synthesis gas can be converted into hydrogen (water-gas shift, over supported Cu-catalysts and Fe catalysts in two stages), alcohols (Cu-Zn catalysts), DME (CuO), MTBE (zeolites), and synthetic diesel (Fischer–Tropsch, over Co or Fe catalysts) by catalytic processes. Producing CH_4 from synthesis gas is thermodynamically not favorable, because a low temperature exothermic process (methanation) needs to be coupled with a high temperature endothermic process (gasification). SNG (synthetic natural gas) from methanation of bio-based fuel gas is an interesting route to make domestic and industrial heating more sustainable. Intermediate gasification temperatures ($950 < T < 1300\ °C$) are extremely unfavorable because the ash becomes partly molten, a situation that is almost impossible to handle in a reactor. One escape from this forbidden temperature region is using ultralow ash containing bioliquids as feedstock [35].

6.7.2
Catalytic Gasification of Pyrolysis Oil

Czernick and coworkers [36, 37] have shown that the fraction of pyrolysis oil that dissolves in water (cellulose and hemicelluloses derivates) can be gasified with a nickel catalyst to hydrogen-rich gas at around $800\ °C$. The steam over carbon ratio used [10–20] was, however, unrealistically high. Recently, Van Rossum et al. [38] introduced a new catalytic reactor concept using a commercial nickel-based pre-reforming and reforming catalyst. In a continuous bench scale unit of $0.5\ kg\ h^{-1}$ pyrolysis oil (whole oil) intake, they produced hydrogen-rich gas ($H_2 = 63$ vol.%,

CO = 25 vol.%, CO_2 = 12 vol.%) not containing any hydrocarbons and a low tar (200 mg Nm^{-3}) content at 800 °C and S/C (steam over carbon ratio) = 1.5. Problems associated with pyrolysis oil gasification are similar to those of biomass gasification. Gasification of the tar fraction and conversion of methane formed are important challenges. Both require highly active and stable steam/autothermal reforming catalysts. ▮AQ15▮

6.7.3
Chemistry and Catalysis of Gasification

Ideal stoichiometric reaction equations for, respectively, synthesis gas, hydrogen-rich gas and methane-rich gas production by gasification are given by Reactions (1) to (3):

$$C_6H_8O_4 + 2H_2O \rightarrow 6CO + 6H_2 \tag{1}$$

$$C_6H_8O_4 + 8H_2O \rightarrow 6CO_2 + 12H_2 \tag{2}$$

$$C_6H_8O_4 + 2H_2O \rightarrow 3CO_2 + 3CH_4 \tag{3}$$

The application of catalysts would lower the operation temperature as compared with the entrained flow process. Lower operation temperatures would not only decrease capital cost, but would also increase the thermal efficiency. Such processes require catalysis. Ross et al. [39] elaborate the criteria for an effective biomass gasification catalyst to be (a) effective to gasify/remove tars, (b) capable of reforming methane, (c) resistant to deactivation by coke/oligomer deposition and sintering, (d) easy to regenerate, (e) robust (mechanically strong) and, most importantly, (f) cheap. Dedicated efforts to develop catalysts for biomass gasification are in their infancy, and the strategy till now has been to use catalysts (a) off the shelf, commercial, not so cheap, methane steam reforming catalysts, (b) cheaper materials, dolomite-based clays, alkali salts (Na, K, chlorides). For solid feed stocks some success has been achieved with natural (dolomite & olivine) and nickel catalysts, although operational problems remain and the tars and hydrocarbons can be removed only partly [31, 32, 39, 40]. It is possible to remove tars and hydrocarbons from fuel gas with down-stream processes, i.e., catalytic wet (steam) and dry (CO_2) reforming [41]. Supported Ni catalysts form the best option but catalyst stability still remains a major set back due to coking. Further, with conventional steam reforming catalysts (Ni, Pt based) hydrogen or syngas selectivity is not an issue; however, the catalyst activity is the limiting factor and require higher temperatures of operation [42]. These catalysts also require high steam/carbon ratios [10–20] to operate even for short times on stream. High steam usage makes the process energy intensive and inefficient. For comparison, the steam/C ratio for commercial steam reforming of methane is <3 [43]. If syngas or hydrogen is the targeted product, consecutive conversion of methane formed requires high temperatures, despite the presence of a catalyst. Impurities contain-

Acetic acid conversion
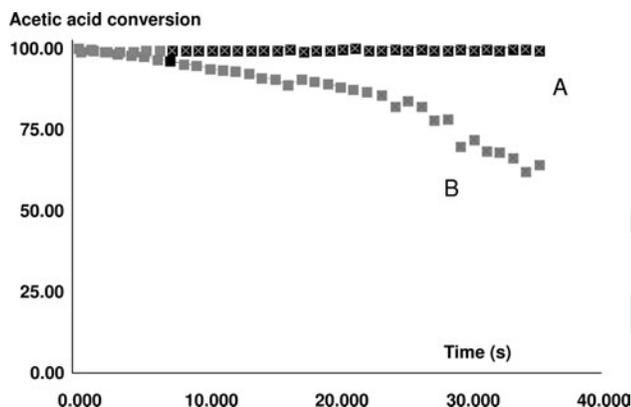
Fig. 6.5 Influence of the presence of traces of oxygen on the stability of the catalyst for steam reforming of acetic acid over Pt/ZrO_2 catalyst (300 °C, SV 14000 h^{-1}). (a) 500 ppm oxygen in the feed and (b) no oxygen present.

ing N, S, Cl and alkalis in the feed stock can also affect both catalyst performance and product quality.

The design of stable catalysts for the efficient gasification of biomass should take into account the ability of the catalysts to depolymerize deposits because suppressing oligomerization is nearly impossible as it occurs almost on any surface. One possibility is to remove the coke/deposits that deactivate the catalysts, via gasification with steam. For this, high activity reforming catalysts need to be developed, the idea being that the coke-forming precursors are also gasified and catalyst stability is improved. The rate-limiting step in steam reforming is normally the activation of water [44]. Thus, new catalyst (metal/support) combinations to maximize the availability of activated water on the catalyst, and to help gasification of coke oligomers as well, are essential. Another option is to carry out gasification in the presence of steam and/or oxygen just as with typical autothermal reforming. The role of oxygen in this case is to help to combust coke/oligomer and keep the catalytic sites clean. However, the catalyst should selectively combust coke and not CO or H_2. This is certainly both a catalyst and reactor design issue. Preliminary experiments show that at low concentrations of oxygen selective combustion of coke can be achieved (Fig. 6.5) [45].

6.7.4
Gasification in Hot Compressed Water

The high moisture content of the wet biomass streams (e.g., slurries of grass or algae, aqueous by-products of biochemical biomass conversions) makes conventional thermochemical technologies inefficient due to the high-energy requirement for water removal. Reforming (gasification) in hot compressed water

($P = 150$–250 bar, $T = 250$–600 °C) is considered as a promising technique to convert such wet streams into a gas that is rich in either hydrogen or methane (see Section 6.7.3 for reaction equations), depending on the operating conditions and applied catalysts [17, 18, 46–48]. Feed stocks are either homogeneous liquids or slurries.

In hot compressed water ($P > 200$ bar), the heat effect associated with water evaporation is marginal compared with that at ambient conditions. Therefore, by practicing counter-current heat exchange between the feed stream and the reactor effluent, high thermal efficiencies can be reached despite the low dry matter content of the feedstock [48]. The process is still in the research phase, although some pilot plants [46] are already operational to start the process development. At laboratory- and demo-scale, methane-rich gas has been produced by using Raney nickel [18] and Ru/TiO$_2$ [17, 49] and hydrogen-rich gas has been produced with activated charcoal [47] and with Raney Ni-Sn [50]. The potential of heterogeneous catalysis is clearly demonstrated for reforming of biomass in hot compressed water. Hot compressed water, especially when supercritical, is acidic and a good solvent for most organic chemicals. The latter characteristic is especially useful to dissolve coke/coke precursors and keep the catalyst surface clean and extend life time. However, this also often leads to leaching of the catalytic active phase. Other challenges that are ahead are instable performance, ignorance of deactivation phenomena and chemical instability of support materials [50]. In addition, fundamental knowledge of the catalytic mechanism and reliable structure–performance relationships are missing.

6.8
Liquefaction of Biomass

6.8.1
Non-catalytic Pyrolysis

Fast pyrolysis is a high temperature (ca. 500 °C) process in which biomass is rapidly converted into vapors, gases and charcoal, in the absence of oxygen. After cooling and condensation, a dark brown organic liquid is formed from the vapors. Short contact times (<0.5 s) maximizes liquid yield. Such a fast pyrolysis process produces a liquid intermediate energy carrier (often called bio-oil or fast pyrolysis oil) at a scale that matches the local logistics of biomass transportation and storage (1–5 tons h^{-1}). Fast pyrolysis oil can be stored and transported over long distances using existing, or slightly modified, fossil oil infrastructure. The latter feature allows the decoupling of the locations where biomass is available and where the bio-based products are needed and produced at large scale. Owing to the relatively low process temperature (~500 °C), minerals and metals remain mostly in the charcoal and can thus be recovered at the biomass production site and returned to the soil. As a result, pyrolysis oil contains significantly less mineral and metal components than the solid biomass feedstock it is produced from.
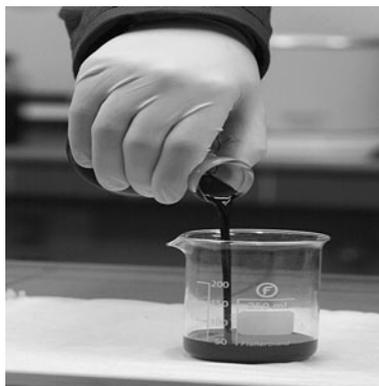
Fig. 6.6 Fast-pyrolysis oil poured out of a flask.

The literature on biomass fast pyrolysis is quite extensive and excellent research and technology reviews are available [51–55]. For an optimal fast pyrolysis process in terms of organic liquid yield the temperature is around 500 °C; the biomass particle size should be small (≤5 mm).

Kinetic parameters of fast pyrolysis were derived while assuming a single process for the decomposition of wood, including three parallel first-order decay reactions for the formation of the product classes. This is the so-called ''Shafizadeh'' scheme [56]. The three lumped product classes are: permanent gas, liquids (bio-oil, tar), and char; a classification that has become standard over the years. The produced vapors are subject to further degradation to gases, water and refractory tars. Charcoal, which is also being formed, catalyzes this reaction and therefore needs to be removed quickly [57].

Fast pyrolysis oil is an acidic viscous dark brown liquid (Fig. 6.6) containing oxygenated hydrocarbons, water and small carbonaceous particles including some minerals.

The organic phase includes aliphatic as well as aromatic acids, alcohols, esters, ethers, sugars and extractives (Table 6.3). Approximately 70 wt.% of the oil has been identified. The molecular weight of the individual components ranges from 18 up to 2000 gram mol^{-1}. At a microscopic level the oil is an emulsion [58].

Fast pyrolysis oil has almost the same elemental composition as the biomass itself; hence it can be seen as a kind of liquid wood. It can be transported, can be pressurized and processed more easily than solid biomass. One of the major difficulties in the catalytic conversion of solid biomass is achieving efficient contact between the heterogeneous catalyst (which is most of the times a solid) and the biomass itself. In this context, bio-oil provides more options for easier catalytic conversion. However, pyrolysis is a very complex and the oil is a difficult to handle chemical mixture. Complete vaporization, for instance, is not possible because part of the components start to decompose and polymerize upon heating

Table 6.3 Composition of typical bio-oil.

Component	wt.%
Acetic acid	1–32
Formic acid	1–20
Hydroxyacetaldehyde	1–13
Furfural alcohol (2-hydroxymethylfuran)	1–5
Acetol (1-hydroxy-2-propanone)	2–8
Syringol (2,6-dimethoxyphenol)	1–5
Phenol	0–4
Methanol	1–3
Tars (polycyclic aromatics)	2–7

Table 6.4 Physical characteristics and elemental composition of bio- and fossil-oils [53].

Characteristic	Pyrolysis oil	Heavy fuel oil
Water content (wt.%)	15–35	0.1
C (wt.%, dry)	50–64	85
H (wt.%, dry)	5.2–7	11.1
O (wt.%, dry)	35–40	1.0
N (wt.%, dry)	0.05–0.4	0.3
S (wt.%, dry)	0.05–0.3	2.3
Heating value (MJ kg^{-1})	16.5–19	40
Viscosity (cp at 50 °C)	40–150	180
pH	2.4	–

before having a chance to evaporate. Table 6.4 lists typical properties of a bio-oil and petroleum crude oil.

The key problems in application of bio-oil as a fuel are related to the oxygen content. First, the heating value decreases due to the presence of oxygenates. Second, organic acids and phenols cause the oil to be corrosive. Third, too many oxygenates would prevent miscibility with hydrocarbons and, fourth, reactive oxygenates tend to oligomerize, causing chemical instability.

6.8.2
Catalytic Pyrolysis

Biomass pyrolysis in the presence of a catalyst, *in situ*, is considered as one of the options to overcome the problem characteristics of bio-oil mentioned above. Selective removal, by decarboxylation, of carboxylic acids (formic, acetic acids) will

decrease the acidity of bio-oil. Selective deoxygenation of organic fractions (aldehydes, unsaturates, etc.) that undergo easy condensation/oligomerization reactions can help in the stabilization of the oil.

Several researchers have shown that alkali present in the feedstock influences the yields and compositions of the pyrolysis products [56, 59]. An interesting result was reported by Brown and coworkers [60] who found that addition of $(NH_4)_2SO_4$ as catalyst to the pyrolysis of dematerialized (alkali free) corn stover resulted in a pyrolysis oil that contained 23 wt.% levoglucosan (normally 1–3 wt.% levoglucosan is present in pyrolysis oil). Levoglucosan is a component from which various fuel blends and chemicals can be produced.

Deoxygenation reactions are catalyzed by acids and the most studied are solid acids such as zeolites and clays. Atutxa et al. [61] used a conical spouted bed reactor containing HZSM-5 and Lapas et al. [62] used ZSM-5 and USY zeolites in a circulating fluid bed to study catalytic pyrolysis (400–500 °C). They both observed excessive coke formation on the catalyst, and, compared with non-catalytic pyrolysis, a substantial increase in gaseous products (mainly CO_2 and CO) and water and a corresponding decrease in the organic liquid and char yield. The obtained liquid product was less corrosive and more stable than pyrolysis oil.

Factors that have to be taken into account while designing catalysts are (a) the bulky nature of organic molecules (large molecules up to 2000 g mol^{-1}) that escape from the biomass matrix, (b) the need to control the extent of pyrolysis/cracking and (c) selective scission of bonds, i.e., C–C > C–O > C–H to help maximize oxygen removal as CO_2. Thus, texture (pore size, geometry etc.) and acidity (strength, concentration of acid sites) are the two important parameters for design. Large-pore zeolites (Fuajasites) whose acidity can be manipulated by easy ion exchange with alkalis (Na, K) and weaker acids such as amorphous silica–aluminas are possible candidates for *in situ* catalytic pyrolysis [63].

Most importantly, biomass pyrolysis will be carried out at remote locations, and in distributed manner. Thus, the catalysts should be cheap and simple to use. Acidic clays, silica aluminas and H-FAU type zeolites are relatively cheap and robust materials, can be mixed easily with heat carriers, and used for pyrolysis. Efficient contact between the solids (catalyst and biomass) to maximize catalytic action is one of the challenges that need to be overcome.

6.8.3
Hydrothermal Liquefaction

Liquefaction of wet biomass streams is done by hydrothermal processes at elevated pressures. The feed stocks for these high pressure liquefaction processes are slurries of biomass particles and water. Feeding these slurries into the high pressure equipment, at reasonable costs, is an important hurdle in the process development. For example, the reported operating conditions for high pressure liquefaction are in the range 280–360 °C and 90–250 bar [25, 25]. ▊AQ3▊ Under these conditions, biomass is converted, in a complex sequence of chemical reactions, into various compounds. Upon cooling, the reactor effluent consists of

three different phases: a water phase, a hydrophobic phase and a gas phase. By extraction the hydrophobic reaction product can further be separated into a solvent (e.g., acetone) soluble and a solvent insoluble part. The hydrophobic phase is considered the main reaction product and has considerably lower oxygen content than the feedstock (typically 10–20 vs. 45 wt.% of the feed). It is reported that the solvent-soluble hydrophobic product can be upgraded into diesel/gasoline range fuels by means of catalytic hydrocracking more easily than pyrolysis oil [64].

6.9
Upgrading Pyrolysis Oil to Fuels

Reviews on the status of pyrolysis oil upgrading until 1996 are those by Bridgwater [65, 66]. The goal of the early research on deoxygenation of pyrolysis oil was to produce fractions that could be blended directly to the gasoline and diesel pool. It soon became clear that, although diesel and gasoline range products were produced, the paraffins, olefins, naphthenes, aromatics ratio was not of the required specification, as a result of which further refining was required [67]. Nowadays the goal is to produce a liquid fuel precursor that can be refined. In the near future, co-feeding of these products at strategic points (e.g., FCC, hydrocracking, reforming) in a mineral oil refinery seems the most feasible option.

Deoxygenation can be done by decarboxylation, cracking, hydrodeoxygenation. The conceptual stoichiometric equations of these processes are:

$$\text{Decarboxylation (DCO): } C_6H_8O_4 \rightarrow C_4H_8 + 2CO_2 \tag{4}$$

$$\text{Hydrodeoxygenation (HDO): } C_6H_8O_4 + 4H_2 \rightarrow C_6H_8 + 4H_2O \tag{5}$$

$$\text{Cracking (CRA): } C_6H_8O_4 \rightarrow C_{4.5}H_6 + H_2O + 1.5CO_2 \tag{6}$$
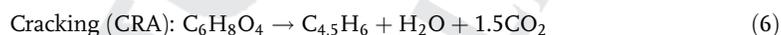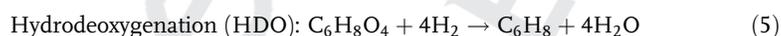
Only full decarboxylation (Reaction 4) produces a paraffin-like product (H/C = 2), all the other methods produce more aromatic fuel precursors and need full hydrogenation (Reaction 7) if paraffins are aimed for.

$$\text{Hydrogenation (HYG): } C_6H_8O_4 + 7H_2 \rightarrow C_6H_{14} + 4H_2O \tag{7}$$

6.9.1
Decarboxylation (DCO)

Deoxygenation by full decarboxylation is the best route to make fuel precursors from bio-oil, because paraffin is produced and expensive hydrogen is not required. Decarboxylation of bio-oil has been tried over zeolites, yielding an aromatic product with a too low yield and excessive coke formation (Section 6.9.3). Selective decarboxylation of organic acids makes the bio-oil less acidic and corrosive. If acids can be removed selectively as CO_2, it would also improve the energy

content of the resultant bio-oil. Removal of oxygen as CO_2, as against water, retains hydrogen content and hence the higher energy content of the bio-oil. Using an H-Y zeolite results in complete removal of formic acid, *in situ*, during pyrolysis [68]. Preliminary studies show that it is also possible to achieve selective deoxygenation as CO_2 by choosing proper catalysts. The actual oxygen removal by only decarboxylation of the acids is, however, not sufficient. New catalytic processes for deeper decarboxylation of pyrolysis oil are required to make the production of liquid fuel precursors from pyrolysis oil economically feasible. Some work on decarboxylation of model compounds has been reported [69–71].

6.9.2
Hydrodeoxygenation (HDO)

At the start of the bio-liquid upgrading research in the late 1970s, hydroprocessing was considered an obvious choice because of the existing knowledge on hetero atom (S, N, O) removal from petroleum products. Hydrotreating (standard commercial process based on Ni-Mo or Co-Mo based catalysts are available) can completely de-oxygenate pyrolysis oils to yield gasoline and diesel range hydrocarbons.

However, the cost of hydrogen required for this makes the route currently unattractive. One ton of biomass would require stoichiometrically 62 kg of hydrogen [65] and the products found until now still need to be refined before they can be added to the diesel or gasoline pool. Otherwise, commercial catalyst and process experience is available for developing a process and promising results have been obtained with pyrolysis oil as feedstock [64–67, 72, 73]. In our opinion, complete HDO of pyrolysis oil is a dead end, especially with the hydrogen shortage in refineries and the demand for hydrogen in fuel cell applications in the future. HDO might still be interesting as the last step in a series of deoxygenation processes (e.g., DCO followed by HDO) for production of a bio-liquid that can be refined (co-fed in a petroleum refinery or as such). A challenge for catalysis is the design of a catalyst that combines DCO and HDO actions with a minimum of hydrogen consumption. This would imply minimizing hydrogenolysis and formation of gaseous alkanes. Extensive commercial knowledge and experience is available at the moment (hydrotreating is one of the largest commercial catalytic processes currently) in the design of suitable catalysts, typical examples are bimetallic Pt-Pd supported on zeolites.

6.9.3
Cracking over Zeolites (FCC)

Since the early 1980s, zeolites have been considered for the upgrading of biomass-derived fluids into aromatic fuels [74, 75]. Researchers of the Univerité Laval (Québec, Canada) performed pioneering work on model compounds (phenols and furans) [76, 77]. A recent study investigating the transformation of alco-

hols, phenols, aldehydes, ketones, and acids on a HZSM-5 zeolite has been reported by Gayubo et al. [78–80]. The general conclusion of the work on model compounds is that the individual components in biomass derived liquids show great differences with respect to reactivity and coke formation, which can be severe. For upgrading of fast pyrolysis oils by zeolites two concepts have been applied at laboratory scale, viz. (a) downstream cracking of the pyrolysis vapors [81] and (b) cracking of the liquid pyrolysis product [82, 83].

Up to now, zeolite cracking of pyrolysis oil has been studied only by passing it over fixed beds [74, 82, 83]. Temperatures in the range 340–500 °C were used. All researchers found large amounts of carbonaceous deposits (10–30 wt.% of the feed) on top of the fixed bed. It was reasoned that these deposits were formed out of the heaviest compounds (lignin derivates) of the feed [1], which cannot be evaporated. Using a reactor concept with a mobile catalyst phase and an advanced atomization system may reduce the amount of these deposits considerably. In addition to the carbonaceous deposits on top of the fixed bed, coke formation on the catalyst was also observed (5–15 wt.% of the feed) and large amounts of water and gases were produced (mainly CO, CO_2, ethylene, propylene and butane). About 15–20 wt.% of the feed was converted into organic liquid products that consisted of 70–90 wt.% aromatic hydrocarbons, 0–5 wt.% aliphatic hydrocarbons, and 5–30 wt.% oxygenates. Hence, the organic liquid product needs further refining to produce conventional transportation fuels. Owing to catalyst deactivation the fraction of oxygenates increased at longer run (space) times [81, 84]. It was proven for HZSM-5 that deactivation by coking is reversible, but that dealumination by water causes irreversible deterioration of the acidity and hence activity. Except for less formation of carbonaceous deposits, work on pyrolysis vapors [81] afforded the same insights as the work on pyrolysis oil.

In conclusion, the development of upgrading technology for biomass derived liquids using zeolites is still in an embryonic stage. The main challenges for catalyst development are to avoid (a) deep cracking and formation of gas, which reduces liquid yields; (b) deep deoxygenation yields an aromatic product; and (c) severe catalyst deactivation due to oligomer/coke formation. Previous work has shown that the use of commercially available zeolites leads to a low liquid product yield. Deep cracking and the formation of gas may be controlled by manipulating the strength and concentration of acid sites in zeolites. Modification of acidity of H-Y zeolites with Na shows indeed that liquid yields can be affected [85]. The formation of aromatics cannot be avoided, as it arises from the low hydrogen content of biomass/bio-oil. Thus, suitability of this product as an additive to gasoline will depend on legislation. From this point of view, a selective deoxygenation, which leaves behind part of the oxygen in the bio-oil, may be a more attractive option. The resulting mixture should be made suitable for blending with hydrocarbon fuels by further processing. Formation of coke and catalyst deactivation is not a major problem. An FCC type operation, where continuous regeneration of the catalyst generates the energy required to run the endothermic cracking process, can be easily adopted as long as not too much coke is formed (otherwise enhanced gasification of coke is required).

**6.10
Hydrolysis**

Native cellulose is resistant to catalytic hydrolysis because it is protected by a matrix of lignin and hemicelluloses. Consequently, pretreatment is required to make the cellulose accessible and to extract the lignin (Section 6.5). Hydrolysis is the depolymerization of cellulose and hemicelluloses into mono sugars via the reaction with water using acid catalysis at 40–250 °C ([23], Vol. I, Chapter 6 and [86]). ▌AQ4▌ C_6 (Glucose, mannose etc.) and C_5 (xylose, arabinose etc.) sugars are the primary products, which are subject to further degradation. The rate of the sugar (monomer, oligomer, and polymer) degradation depends on the temperature, acid concentration and type of acid. For cellulose the idealized stoichiometric reaction transformation is given by:

$$Cellulose \rightarrow Glucose \rightarrow 5\text{-}HMF + H_2O \rightarrow Levulinic\ acid + Formic\ acid$$

The development of economically viable hydrolysis processes for lignocelluloses has just started. Production of mono C5 and C6 sugars from lignocelluloses paves the way for development of sophisticated chemical process for the manufacture of, for example, *n*-alkanes (see below). An example of a hydrolysis process that integrates the primary conversion to mono sugars with the further conversion of these mono sugars into target components is the Biofine process. In this process, methyl-tetrahydrofuran is produced from levulinic acid made from acid hydrolysis of lignocelluloses ([23], Vol. I, Chapter 7). Catalysis may help in increasing the reaction rate and optimizing the yields of target products. The development of heterogeneous catalysts would be beneficial, because the homogeneous acid used in the present process is very corrosive, requiring expensive acid recovery units. Similar developments in catalysis of hydrocarbon alkylation point to large-pore zeolites (H-FAU, H-BEA) as possible starting catalysts [87].

Recently a very comprehensive report on the pathways from sugars to chemicals and fuels has been issued by the US department of energy [88]. The report identifies the twelve most promising building blocks (Table 6.5) that can be produced from sugars via biological and chemical conversions. These building blocks can be subsequently converted into several chemicals and fuels.

Another interesting example of a sugar route is the conversion of (a) sorbitol into hexane by acid-catalyzed dehydration to tetrahydrofuran followed by (b) aldol condensation over a solid base catalyst and (c) hydro-conversion over Pd, Pt on $SiO_2\text{-}Al_2O_3$ acid supports to give diesel range hydrocarbons, as recently reported by Dumesic et al. [89]. The development of the routes from sugars to alkenes is very promising and the proof of principle has been delivered. However, much more research is required to develop feasible processes. Conversion of cellulose into butanol, an additive to gasoline, is commercially targeted. Efforts in the USA aim to develop efficient cellulose conversion technology by 2012. Developments in these areas will help in the futuristic process of direct conversion of lignocellu-

Table 6.5 Top twelve building blocks from sugars according to the US department of energy [88].

1,4 succinic, fumaric and malic acids
2,5 furan dicarboxylic acid
3 hydroxy propionic acid
aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol/arabinitol

lose via cellulose into fuels and chemicals. Another chapter of this book discusses in more detail the routes via sugars [90]. █AQ2█

6.11
Underlying Approach for Catalyst Design

Currently, there is a debate going in the scientific community regarding the choice of methodology in catalyst development. In reality, research activities at the moment fall into three categories: (a) catalytic biomass related conversions using off the shelf commercial catalysts and the complex feed; (b) use of catalysts that are suitable for similar, though not identical, conversions in fossil oil upgrading; and (c) the use of model organic compounds with well-defined catalysts. Obviously, short term results are best obtained with approach (a) and it should be stressed that this type of research has been done over the last decade; the results have not been sufficient so far, as discussed earlier. The response to this situation can be twofold. Either rapid testing of many catalysts can be envisaged (high-throughput testing) but it is obvious that the type of experiments are even more difficult to mimic in high-throughput mode than for ''standard'' heterogeneous catalysis. Or, catalysts are to be improved based on a thorough knowledge of the fundamental processes on the catalyst. This approach should be inspired according to methodology (b) and requires the acceptance of methodology (c). Based on the history of the development of catalytic technology for refining of mineral oil, it is fair to state that a mix of these approaches will be indispensable to move forward rapidly, by involving the expertise available in both companies and academia.

Well-defined reaction and catalytic systems enable the development of fundamental knowledge that helps in with long term and more exhaustive problem

solving possibilities. Thus the debate is not whether studies on model compounds are useful or not, but the choice of model compounds themselves. These should represent the nature and characteristic of the biomass fraction that one is studying. Not surprisingly, efforts to identify representative model compounds are gaining attention. 4-Hydroxyphenylpropane derivatives such as coniferyl, coumaryl or sinapyl alcohols can be representative for lignin, as the latter is made by the dehydrogenative polymerization of these compounds (Fig. 6.2c). Similar studies are now appearing [91]. Model systems that represent the full complexity of the cellular structure of lignocellulosic biomass are not available. They are, however, necessary for catalysis research on pretreatment and primary conversions as it is already known that superposition of cellulose, hemicelluloses and lignin behavior does not mimic lignocelluloses [92].

6.12
Summary

A smooth transition, from the current fuel/energy scenario to a future dominated by the demand for sustainability, is essential to guarantee World's future economy and stability. Proper and timely development of technology to achieve this is therefore of paramount importance. Catalyst and reactor technology to convert fossil oil into the fuels needed by society today are mature. However, the transition from fossil to lignocellulosic biomass based feedstocks brings in new challenges both for catalyst and reactor engineering developments. To meet these demands, it is essential to adapt the knowledge available for making fossil fuels to lignocelluloses based fuels. Additionally, development of efficient processes will also demand new concepts for catalysts and reactor technologies. The focus of catalysis development should be on pretreatment (e.g., fractionation) and primary conversion processes (e.g., pyrolysis) of lignocelluloses. These processes require cheap and robust catalysts that can cope with the fouling conditions caused by the complex feedstock materials. Secondary conversions processes take in much simpler feeds (e.g., sugars) and can, accordingly, make use of dedicated complex catalysts. Most importantly, teaming up of catalysis, reactor engineering and process engineering at an early stage is needed for the development of biomass-based processes for the generation of fuels.

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