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Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass

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Biorefineries

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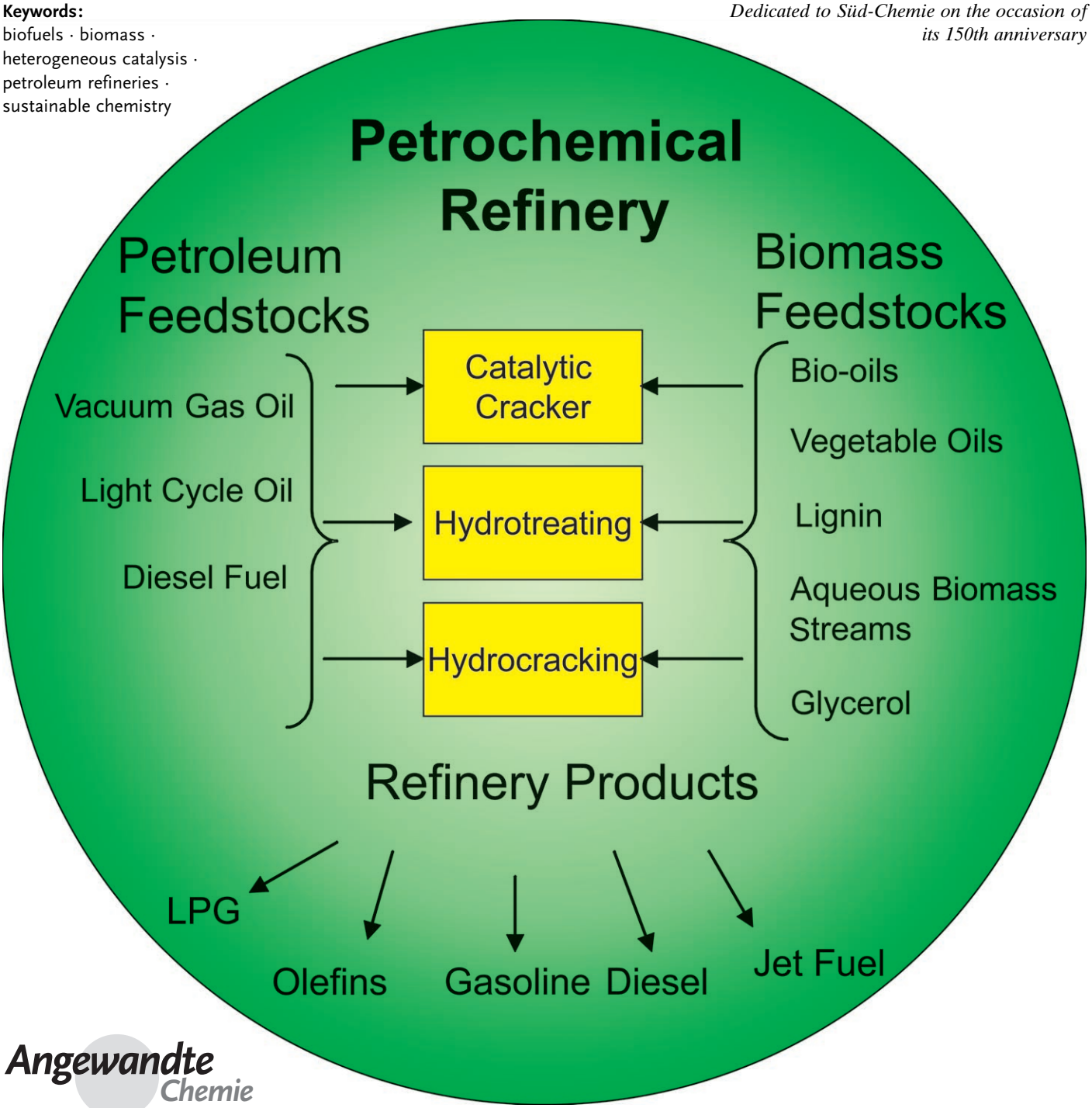

As petroleum prices continue to increase, it is likely that biofuels will play an ever-increasing role in our energy future. The processing of biomass-derived feedstocks (including cellulosic, starch- and sugar-derived biomass, and vegetable fats) by catalytic cracking and hydrotreating is a promising alternative for the future to produce biofuels, and the existing infrastructure of petroleum refineries is well-suited for the production of biofuels, allowing us to rapidly transition to a more sustainable economy without large capital investments for new reaction equipment. This Review discusses the chemistry, catalysts, and challenges involved in the production of biofuels.

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1. Introduction

Declining petroleum resources, combined with increased demand for petroleum by emerging economies, as well as political and environmental concerns about fossil fuels are driving our society to search for new sources of liquid fuels. The only current sustainable source of organic carbon is plant biomass, and biofuels—fuels derived from plant biomass—are the only current sustainable source of liquid fuels.[1–3] Biomass is an inexpensive, renewable, and abundant source of carbon. While the cost of production of biomass depends highly on regional issues, the European Biomass Association (AEBIOM) reports biomass in the European Union to cost from $11 per boe (barrel of oil energy equivalent) for solid industrial residues to $39 per boe for energy crops such as rapeseed.[4] In the US it has been estimated that the cost of cellulosic biomass is $5–15/boe.[1,5] Large amounts of biomass are present throughout the world, and the European Biomass Industry Association (EUBIA) has estimated that Europe, Africa, and Latin America could produce 8.9, 21.4, and 19.9 10^{18} J of biomass per year.[4] Biofuels give out significantly less greenhouse gas emissions than fossil fuels and can even be greenhouse gas neutral if efficient methods for production are developed.[5–8]

One promising option for the production of biofuels, that is, to use biomass-derived feedstocks in a petroleum refinery, is the focus of this Review. This process involves the co-feeding of biomass-derived feedstocks with petroleum feedstocks as shown in Figure 1. Indeed, oil companies are starting to investigate this possibility. A recent report by Universal Oil Products (UOP) Corporation discussed how biofuels can be economically produced in a petroleum refinery.[9] Neste Oil Corporation is currently building two plants at their oil refinery at Porvoo Kilpilahti, Finland, which will produce diesel fuel (3500 barrels per day) from vegetable oil by a modified hydrotreating process.[10] Petroleum refineries are already built, and use of this existing infrastructure for the production of biofuels requires little capital investment.[9] Furthermore, the infrastructure for blending fuels as well as their testing and distribution is already in place at oil refineries. Three options are available for using petroleum refineries to convert biomass-derived feedstocks into fuels and chemicals: 1) fluid catalytic cracking (FCC), 2) hydrotreating-hydrocracking, and 3) utilization of biomass-derived synthesis gas (syngas) or hydrogen. FCC gives products with a higher hydrogen content than the feed by removing carbon that remains on the catalyst and burning it off in the regenerator to produce process heat.[11] On the other hand, hydrotreating-hydrocracking produces liquid fuels with a much higher hydrogen content than the feed by hydrogenation.[12] Hydrotreating is also used in the refinery to remove sulfur, nitrogen, and oxygen from the feed. In the present Review, we discuss possibilities for converting biomass-derived feedstocks in FCC and hydrotreating refinery units. The third option, utilization of biomass-derived syngas, will not be discussed here (because of the recent emphasis on hydrogen production); however, we refer the reader to a number of other review articles that have already discussed

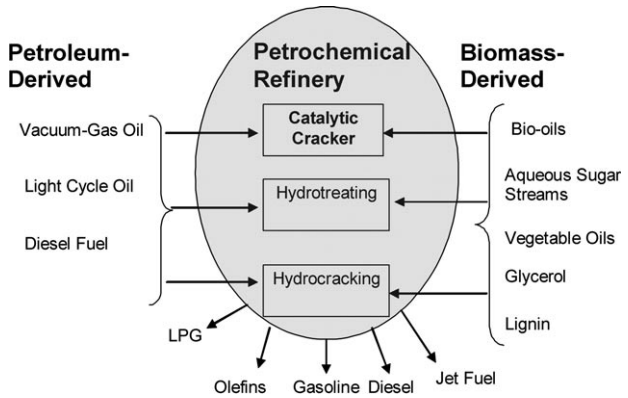

Figure 1. Conversion of petrochemical- and biomass-derived feedstocks in a petroleum refinery.

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the production of hydrogen and syngas from biomass.[13–17] The European Commission has set a goal that by 2010 5.75% of transportation fuels in the EU will be biofuels. Co-feeding biomass-derived molecules into a petroleum refinery could rapidly decrease our dependence on petroleum feedstocks. Petroleum-derived feedstocks are chemically different than biomass-derived feedstocks, therefore a new paradigm in how to operate and manage a petroleum refinery is required. Another improvement towards the production of biofuels in a petroleum refinery would be if governments were to offer tax exemptions and subsidies to all types of biofuels, and not only for selected biofuels such as ethanol and biodiesel. As the price of petroleum continues to increase, we project that refining technology will be developed to allow the co-production of bio- and petroleum-based fuels in the same (petroleum) refinery and even using the same reactors.

The transition to the carbohydrate economy will require three major shifts in approach, with respect to 1) the production of biomass, 2) the conversion of biomass into fuels, and 3) the conversion of biofuels into mechanical energy.[15] Currently, petrochemical companies operate in both the production and refining of crude oil; they have the technical expertise in both the processing and utilization of fuels. Biomass resources are currently controlled by agricultural companies and governmental institutions, which do not have the technical capabilities for fuels production. Some questions regarding the biofuels industry are: Who will control the biofuels industry? Will it be agricultural companies, who already produce biomass products but lack the technical capabilities to produce fuels? Will it be governmental institutions that manage forest lands? Or will oil companies, who have the technical capabilities in terms of production of liquid fuels but currently do not have any control over agricultural resources, control the biofuels market? A realistic practical scenario will be one in which both industries cooperate, with one producing the biofuel precursors and the other processing and converting them into valuable fuels.

2. Biomass-Derived Feedstocks

The first step in the production of biofuels is to obtain an inexpensive and abundant biomass feedstock. Biofuel feedstocks can be chosen from the following: waste materials (agricultural, wood, and urban wastes, crop residues), forest products (wood, logging residues, trees, shrubs), energy crops (starch crops such as corn, wheat, and barley, sugar crops, grasses, vegetable oils, hydrocarbon plants), or aquatic biomass (algae, water weed, water hyacinth).[15] Plant breeding, biotechnology, and genetic engineering promise to develop more efficient plant materials with faster growth rates that require less energy inputs and fertilizers. Biomass-derived feedstocks for a petroleum refinery can be classed into one of three categories according to the source: cellulosic biomass, starch- and sugar-derived biomass (or edible biomass), and triglyceride-based biomass. The cost of the biomass feedstock is dependent on regional issues, but generally increases in the order: cellulosic biomass < starch (and sugar)-based biomass < triglyceride-based biomass. The cost of the conversion technology decreases in the order: cellulosic biomass (most expensive) > starch- (and sugar)-based biomass > triglyceride-based biomass. Nevertheless, one has to consider that the cost is strongly linked to supply and demand. Consequently, finding new uses for biomass-derived products will result in an increase in their cost. This can be highly important for biomass based on waste and non-food items, and can introduce regional problems when processing food-based biomass.

2.1. Cellulose-Derived Feedstocks

Lignocellulosic or cellulosic biomass consists of three main structural units: cellulose, hemicellulose, and lignin. Cellulose (a crystalline glucose polymer) and hemicellulose (a complex amorphous polymer, whose major component is a xylose monomer unit) make up 60–90 wt% of terrestrial biomass. Lignin, a large polyaromatic compound, is the other major component of cellulosic biomass. Cellulose consists of a linear polysaccharide with β-1,4 linkages of D-glucopyranose monomers and is a crystalline material with an extended, flat, helical conformation.[18] A significant challenge in working with cellulosic biomass is overcoming the recalcitrant nature of cellulosic biomass and converting solid biomass into a liquid or gaseous product.[5,18–20] Three main technologies are used to convert cellulosic biomass directly into liquid products including hydrolysis (production of aqueous sugar solutions), fast pyrolysis (bio-oils production), and liquefaction (bio-oils production).[15] Gasification of biomass followed

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George W. Huber obtained his BS (1999) and MS (2000) degrees from Brigham Young University and completed his PhD in chemical engineering in 2005 under the guidance of J. A. Dumesic at the University of Wisconsin-Madison on the development of aqueous-phase catalytic processes for the production of biofuels. Following a postdoctoral stay with Prof. Corma at the UPV-CSIC (2005–06), he joined the University of Massachusetts-Amherst as Assistant Professor of Chemical Engineering. His research focuses include biomass conversion and heterogeneous catalysis.

by standard syngas reactions can also be used to convert biomass into liquid fuels.[15,16]

Bio-oils, produced by fast pyrolysis or liquefaction, are a complex mixture containing up to 400 different compounds.[21–24] Bio-oils contain acids (acetic, propanoic), esters (methyl formate, butyrolactone, angelica lactone), alcohols (methanol, ethylene glycol, ethanol), ketones (acetone), aldehydes (acetaldehyde, formaldehyde, ethanedial), miscellaneous oxygenates (glycolaldehyde, acetol), sugars (1,6-anhydroglucose, acetol), furans (furfural alcohol, 5-hydroxymethylfurfural, furfural), phenols (phenol, dihydroxybenzene, methyl phenol, dimethyl phenol), guaiacols (isoeugenol, eugenol, 4-methyl guaiacol), and syringols (2,6-dimethoxyphenol, syringaldehyde, propyl syringol).[25] Fast pyrolysis involves short residence times (less than 2 s), fast heating rates (500 °C s^{-1}), moderate to high temperatures (maximum 400–700 °C), and low pressures (1–5 atm). The liquids produced by pyrolysis are non-thermodynamically controlled products, and optimal residence times and temperatures are necessary to freeze the desired intermediates. Liquefaction occurs at high pressure (50–200 atm) and lower temperatures (250–325 °C) than pyrolysis. Oils produced by fast pyrolysis have a higher oxygen content, are acidic, and have a lower heating value than liquefaction oils as shown in Table 1. Pyrolysis has a lower capital cost than liquefaction, and many pyrolysis technologies are currently being used commercially. The multicomponent mixtures are derived primarily from depolymerization and fragmentation reactions of the three key building blocks of cellulosic biomass: cellulose, hemicellulose, and lignin.[15,24] The most significant problems of bio-oils as a fuel are poor volatility, high viscosity, coking, corrosiveness, and cold flow problems, which can be overcome by proper upgrading.[26] Transportation and storage problems of the still-crude bio-oils occur as a result of their polymerization and condensation with time. This process is accelerated at increasing temperatures and upon exposure to oxygen or UV light.

Table 1: Properties of fast pyrolysis bio-oil (wood-derived), liquefaction bio-oil (wood-derived), and heavy fuel oil.[26,98]

Property	Pyrolysis bio-oil	Liquefaction bio-oil	Heavy fuel oil
Elemental Composition [wt%]			
carbon	54–58	73	85
hydrogen	5.5–7.0	8	11
oxygen	35–40	16	1.0
nitrogen	0–0.2	–	0.3
ash	0–0.2	–	0.1
Moisture content [wt%]	15–30	5.1	0.1
pH	2.5	–	–
Specific gravity	1.2	1.1	0.94
Higher heating value [MJ kg^{-1}]	16–19	34	40
Viscosity [cP]	40–100[a]	15 000[b]	180[a]
Solids [wt%]	0.2–1	–	1
Distillation residue [wt%]	up to 50	–	1

[a] At 50 °C. [b] At 61 °C.

Cellulosic biomass can also be converted into sugars (which could be used for ethanol production) and solid lignin by either acid or enzymatic hydrolysis.[8,18,27] Prior to the hydrolysis step, the biomass is pretreated in a crucial step to improve the overall sugar yields. Pretreatment include physical, chemical, and thermal methods, or some combination of the three. The goal of pretreatment is to decrease the crystallinity of cellulose, increase the surface area of the biomass, remove hemicellulose, and break the lignin seal.[28]

$$(C_6H_{10}O_5)_n + n\,H_2O \rightarrow n\,C_6H_{12}O_6 \quad (1)$$

The hydrolysis reaction for the conversion of cellulose into sugars is shown in Equation (1).[18] The hydrolysis of cellulose is significantly more difficult than that of starches because cellulose is crystalline. The maximum yield of glucose obtained from the hydrolysis of cellulose with mineral acids is less than 80 %,[29] while enzymatic hydrolysis can produce yields of glucose above 95 %.[18] Organic acids have also been shown to achieve high yields of sugar.[30] Hydrolysis reactions have been optimized for fermentation reactions, and it is possible that hydrolysis reactions could be optimized for other liquid fuel reactions.

2.2. Starch- and Sugar-Based Feedstocks

Edible biomass mostly consists of starches, which are commonly found in the vegetable kingdom. Starches are a glucose polysaccharide that have α-1,4 and α-1,6 glycoside linkages, which result in an amorphous structure of the polymer.[31] Unlike cellulosic biomass and as a result of their amorphous structure, starches can easily be broken down into water-soluble sugars. Starches are commonly used as feedstock to produce ethanol by fermentation; for example, in the US, ethanol is currently produced from corn grain. Sugars can also be extracted directly from certain types of biomass, such as sugarcane.

2.3. Conversion of Cellulosic and Starch Biomass

Cellulosic biomass is more difficult to convert into a fuel than starch-based biomass as a result of its crystalline recalcitrant structure. However, starch and cellulose both have a similar elemental composition and contain large amounts of oxygen. Carbohydrates, which account for approximately 75 and 100 wt% of the composition of cellulosic and starch biomass, respectively, contain a C/O atomic ratio of 1:1. Bio-oils also contain a large amount of oxygenated molecules, with oils obtained through fast pyrolysis containing more oxygen than those produced by liquefaction.[15,24,32] The major challenge with biomass conversion strategies is how to efficiently remove the oxygen from the hydrophilic biomass-derived feedstock and convert the biomass into a product with the appropriate combustion and thermochemical properties. Oxygen can be removed as CO,

CO_2, or H_2O as shown in Equation (2). Catalytic cracking and hydrotreating are very effective at removing oxygen from the biomass-derived feedstock. However, the oxygen is not always removed by the optimal pathway, and often undesired products such as coke or acids are formed during the conversion process.

$$C_6H_{12}O_6 \rightarrow a\,C_xH_{2x+2}O_y + b\,CO_2 + c\,H_2O + d\,CO + e\,C \quad (2)$$

2.4. Triglycerides as Feedstocks

Triglycerides, or animal fats and vegetable oils, are found in the plant and animal kingdom and consist of water-insoluble, hydrophobic molecules that are made up of one glycerol unit and three fatty acids. More than 350 oil-bearing crops are known, and those with the greatest potential for fuel production, according to Peterson,[33] are sunflower, safflower, soybean, cottonseed, rapeseed, canola, corn, and peanut. Currently, vegetable oils are being used for the production of biodiesel by transesterification. A soybean plant, the principle bio-oil feedstock in the USA, contains 20 wt % triglycerides, which must be extracted from the soybean seeds. All oil-producing plants contain carbohydrates, protein, fiber, and inorganic constituents.[34]

All triglycerides can be broken into one glycerol molecule and three fatty acid molecules. The carbon chain length and number of double bonds in the fatty acids vary depending on the source of vegetable oil. A number of waste triglycerides are available, including yellow greases (waste restaurant oil) and trap grease (which is collected at wastewater treatment plants).[35] Yellow grease is used in the manufacturing of animal feed and tallow, and it contains large amounts of free fatty acids which could cause corrosion problems in chemical reactors. Trap grease has a zero or negative feedstock cost, but is contaminated with sewage components.[35] It has been estimated that biodiesel derived from yellow and trap grease could supply the US with up to 2 % diesel fuel.[15]

2.5. Conversion of Triglycerides

Triglycerides are easier to convert into liquid transportation fuels than cellulosic biomass because they are already high-energy liquids that contain less oxygen. They can even be used directly in diesel engines, however, their high viscosity and low volatility can be a disadvantage and engine problems can occur (including coking on the injectors, carbon deposits, oil ring sticking, and thickening of lubricating oils).[36,37] These problems require that vegetable oils be upgraded if they are to be used as a fuel in conventional diesel engines. The most common way of upgrading vegetable oils to a fuel is transesterification of triglycerides into alkyl fatty esters (biodiesel). Waste vegetable oils, such as frying oils, can be used as feedstocks; however, changes in the process need to be made as waste vegetable oils contain free fatty acid (FFA) and water impurities.

3. Catalytic Cracking of Biomass-Derived Feedstocks

3.1. Petroleum Technology

Fluid catalytic cracking (FCC) is the most widely used process for the conversion of the heavy fraction of crude oil (vacuum gas oil; VGO) into gasoline and other hydrocarbons in the petrochemical refinery.[11] This process consists of two main reaction zones as shown in Figure 2. In the first reactor,

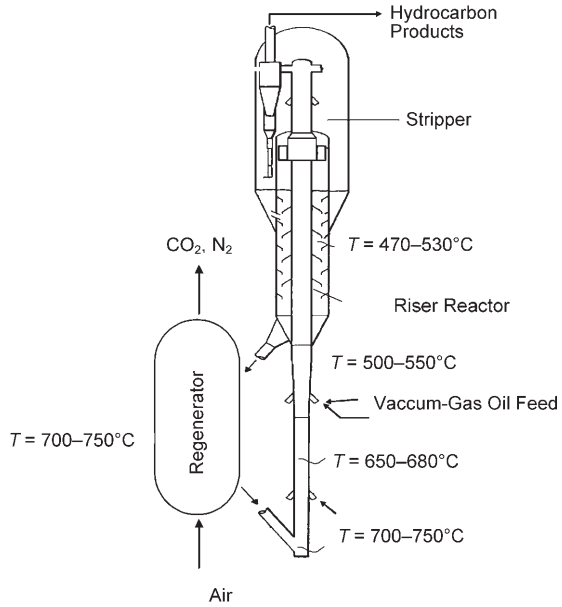


Figure 2. Flow diagram of a typical FCC process.

a hot particulate catalyst is contacted with the hydrocarbon VGO feedstock, thereby producing cracked products and the coked catalyst. After this reaction, the coked catalyst is separated from the cracked products, stripped of residual oil by steam, and then regenerated by burning the coke in a regenerator at 650–760 °C and 2 bar. The hot catalyst is then recycled to the riser reactor for additional cracking. As can be observed from Figure 2, biomass feedstocks can be injected into a number of different parts of the FCC reactor including before VGO, with VGO, after VGO, in the regenerator, or in a separate riser reactor. All of these different zones involve different temperatures and catalytic activities.

The reactions that occur in the FCC process include cracking reactions (cracking of alkanes, alkenes, napthene, and alkyl aromatics to lighter products), hydrogen transfer, isomerization, and coking reactions.[38] Catalytic cracking catalysts are solid acid catalysts (typically Y-zeolite), a binder (caolin), and alumina or silica-alumina. ZSM-5 is a common additive to FCC catalysts. Zeolites, and in general solid acids, are the most widely used industrial catalyst for oil refining, petrochemistry, and the production of fine and specialty chemicals.[39–41] Zeolites are crystalline microporous materials with well-defined pore structures generally with a diameter below 10 Å, though recently new structures with pore diameters above 10 Å have been discovered.[42,43] Zeolites

contain active sites, usually acid sites, which can be generated in the zeolite framework. The strength and concentration of the active sites can be tailored for particular applications. Zeolites have very high surface areas and adsorption capacity. Their crystallite size and adsorption properties can be controlled and varied from hydrophobic to hydrophilic materials. Zeolites can also be prepared in the form of nanocrystals[44] from hydrophobic materials.[45]

3.2. Catalytic Cracking of Cellulosic Feedstocks

Bio-oils and other cellulosic molecules can be upgraded by using catalytic cracking to reduce their oxygen content and improve their thermal stability. The advantages of catalytic cracking are that no H_2 is required, atmospheric processing reduces operating cost, and the temperatures employed are similar to those used in the production of bio-oil. This offers significant processing and economic advantages over hydrotreating.[46] However, poor yields of hydrocarbons and high yields of coke may occur with FCC of biomass-derived feedstocks. These results can be improved by operating at the proper conditions with the proper catalyst. The products from catalytic cracking of biomass-derived molecules include hydrocarbons (aromatic, aliphatic), water-soluble organics, water, oil-soluble organics, gases (CO_2, CO, light alkanes), and coke.

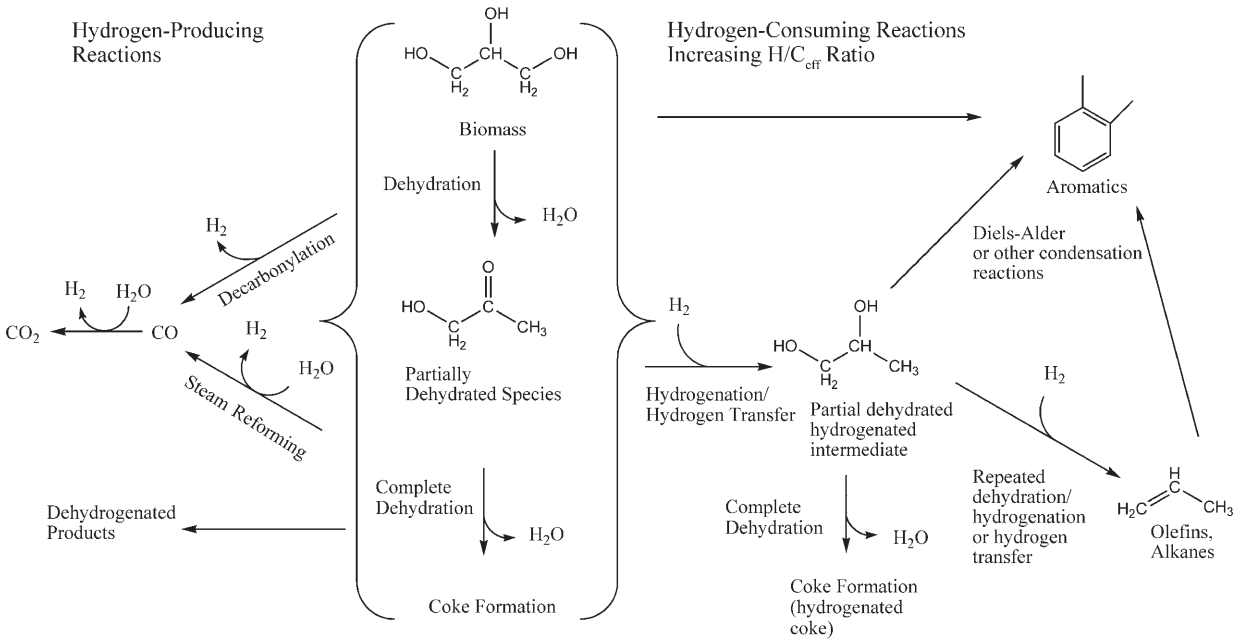
3.2.1. Chemistry of the Catalytic Cracking of Cellulosic Feedstocks

Chen et al. studied the conversion of carbohydrates over ZSM-5 catalysts in a fixed-bed reactor and observed coke, CO, hydrocarbons, and CO_2 as the major products.[47] They reported that the major challenge with biomass conversion was the removal of oxygen from the biomass and enriching the hydrogen content of the hydrocarbon product. They defined the effective hydrogen-to-carbon ratio [H/C_{eff}, Eq. (3)] to help explain the required chemistry for the conversion of biomass-derived oxygenates in catalytic cracking.

$$H/C_{eff} = \frac{H-2O-3N-2S}{C} \quad (3)$$

In Equation (3), H, C, O, N, and S correspond to the moles of hydrogen, carbon, oxygen, nitrogen, and sulfur, respectively, that are present in the feed. The H/C_{eff} ratios for glucose, sorbitol, and glycerol (all biomass-derived compounds) are 0, 1/3, and 2/3, respectively. The H/C_{eff} ratio of petroleum-derived feeds ranges from slightly over 2 (for liquid alkanes) to 1 (for benzene). Thus, the H/C_{eff} ratio of biomass-derived oxygenates is lower than that of petroleum-derived feedstocks as a result of the high oxygen content of biomass-derived molecules. In this respect, biomass can be viewed as a hydrogen-deficient molecule when compared to petroleum-based feedstocks. Hydrogen can be transferred from petroleum feedstocks to biomass feedstocks during the catalytic cracking of mixtures of biomass and petroleum-derived feedstocks.[9,48]

We have suggested that the conversion of oxygenates from biomass-derived feedstocks in the FCC occurs mainly through a series involving five different classes of reactions (Scheme 1):[48] 1) dehydration reactions, 2) cracking of large oxygenated molecules to smaller molecules (not shown in Scheme 1), 3) hydrogen-producing reactions, 4) hydrogen-consuming reactions, and 5) production of larger molecules by C–C bond-forming reactions (aldol condensation or Diels–Alder reactions). In this process, H_2 may be produced through



Scheme 1. Reaction pathways for the catalytic cracking of biomass-derived oxygenates. Note: for dehydrogenation and decarbonylation reactions, the hydrogen can be produced by hydrogen transfer to a hydrogen-deficient molecule.

steam-reforming, dehydrogenation of the carbohydrates or hydrocarbons, water gas shift, and decarbonylation of the biomass feedstock of the partially dehydrated species. These reactions produce CO, CO_2, and graphitic coke as well as hydrogen. The hydrogen produced in these reactions may be consumed in reactions that increase the H/C_{eff} ratio of the products as shown in Figure 2 and lead to olefins and alkanes. Hydrogen may be exchanged directly through hydrogen-transfer reactions between two hydrocarbon/carbohydrates chains or through consecutive dehydrogenation/hydrogenation processes. Hydrogen-transfer reactions occur on acid sites, while dehydrogenation/hydrogenation reactions are greatly accelerated by the presence of a metal. Aromatics are also produced during this process possibly by Diels–Alder reactions of partially dehydrated/hydrogenated species. To selectively produce olefins and aromatics, the dehydration, hydrogen-forming, and hydrogen-transfer reactions must be properly balanced by choosing proper catalysts and reaction conditions.

The pathway that produces the maximum amount of olefins and aromatics from biomass requires the maximum production of intermediate H_2. This maximum depends on what the carbon is converted into; the maximum yield of H_2 increases in the order $C < CO < CO_2$. For example, using glycerol as the feed, the number of moles of H_2 produced per mole of carbon feedstock decreases from 7/3 to 4/3 to 1 as CO_2, CO, and carbon, respectively, are the products of the reactions [Equations (4), (5), and (6)].

$$C_3H_8O_3 + 3\,H_2O \rightarrow 3\,CO_2 + 7\,H_2 \tag{4}$$

$$C_3H_8O_3 \rightarrow 3\,CO + 4\,H_2 \tag{5}$$

$$C_3H_8O_3 \rightarrow 3\,C + 3\,H_2O + H_2 \tag{6}$$

Decarbonylation and decarboxylation reactions are another series of reactions that afford a product that has a higher H/C_{eff} ratio. Aldehydes undergo decarbonylation reactions to produce CO and a decarbonylated product that has an increased H/C_{eff} ratio. Acids can undergo decarboxylation reactions to produce CO_2 and a decarboxylated product that has an increased H/C_{eff} ratio. Thus, these reactions can be viewed as ones that both produce and consume H_2 by internal hydrogen transfer. Decarbonylation and carbonylation reactions occur with zeolite catalysts at low temperatures.[49] Zeolite catalysts can also decarbonylate ketones, such as when acetone undergoes decarbonylation/condensation reactions to form CO and isobutene.[50,51] This last reaction pathway offers another way to produce hydrocarbon products with longer carbon chains than those in the feed, similar to the dimerization-cracking mechanism that has been identified in the cracking of paraffins to explain longer-chain products.

Hydrogenation, hydrogen transfer, and decarbonylation are the key reactions that can enrich the H/C_{eff} ratios of the products. Hydrogen-transfer reactions occur in the FCC of petroleum-derived feedstocks.[52] The typical reaction involves a hydrogen donor (e.g. a naphthene) and a hydrogen acceptor (e.g. an olefin).[11] The concentration of naphthene is low when only biomass-derived products are fed to a FCC unit, so another hydrogen source is required if products with an enriched H/C_{eff} ratio are desired. Hydrogen transfer could occur from coke species to other dehydrated species, while the coke forms a graphitic dehydrogenated species. Molecules with low H/C_{eff} ratios (i.e. carbohydrates: $H/C_{eff} = 0$) will not produce any hydrogen if they produce coke, therefore, other modes of hydrogen transfer must operate as catalytic cracking of sugars produces olefins and aromatics. Hydrogen can also be transferred from petroleum feedstocks which are rich in H_2 to biomass feedstocks which are poor in H_2.[48]

Hydrogenation reactions usually occur on metal surfaces, where H_2 is dissociated and then undergoes reaction. Metal or metal oxide impurities on a zeolite surface may dissociate H_2 and could then be used for hydrogenation reactions. Alkenes, aromatics, aldehydes, and ketones have also been hydrogenated with acid catalysts.[53–55] The key step in the mechanism is the reaction between a carbenium ion and molecular hydrogen. Gas-phase H_2 is observed under our reaction conditions. We have shown that the H_2-to-CO ratio is low for the catalytic cracking of glycerol, indicating that most of the H_2 produced is consumed in the reaction.[48]

The highest theoretical yield of propylene from FCC of glycerol according to Equation (7) is 77 % based on carbon. In this reaction, the oxygen is removed as CO_2 and H_2O. If oxygen is removed from the glycerol as CO and H_2O [Eq. (8)], the maximum theoretical carbon yield of propylene is 66 %. If oxygen is only removed as water by dehydration [Eq. (9)], then the maximum theoretical carbon yield of propylene is 33 %. Therefore, to increase the maximum theoretical yield of propylene the oxygen should be rejected as both CO_2 and H_2O, and the coke levels should be minimized. A similar analysis can be performed for aromatics, olefins, or other alkanes if they are the targeted product. The maximum theoretical yield is a function of the H/C_{eff} ratio of the feed, and decreasing the H/C_{eff} ratio of the feed decreases the maximum theoretical yield of the desired olefin or aromatics. For example, the maximum carbon theoretical yield of propylene with sorbitol feedstock is 72 % according to Equation (10), which is lower than that of glycerol-based feedstocks (77 %).

$$^{9}/_{7}\,C_3H_8O_3 \rightarrow C_3H_6 + {}^{6}/_{7}\,CO_2 + {}^{15}/_{7}\,H_2O \tag{7}$$

$$1.5\,C_3H_8O_3 \rightarrow C_3H_6 + 1.5\,CO + 3\,H_2O \tag{8}$$

$$3\,C_3H_8O_3 \rightarrow C_3H_6 + 6\,C + 9\,H_2O \tag{9}$$

$$^{9}/_{13}\,C_6H_{14}O_6 \rightarrow C_3H_6 + {}^{15}/_{13}\,CO_2 + {}^{24}/_{13}\,H_2O \tag{10}$$

We have studied the catalytic cracking of aqueous sorbitol and glycerol feedstocks in a microactivity test (MAT) reactor.[48] Products from this reaction include olefins (ethylene, propylene, butenes), aromatics, light paraffins (methane, ethane, propane), CO, CO_2, H_2, and coke. ZSM-5 as catalyst produces lower levels of coke (less than 20 % molar carbon yield) and higher levels of aromatics and olefins, whereas other catalysts, including a fresh commercial FCC catalyst containing Y-zeolite in a silica-alumina matrix, a commercial equilibrium FCC catalyst with V and Ni impurities (ECat),

Al_2O_3, and a Y-zeolite, gave rise to high yields of coke (30–50%) and lower levels of aromatics and olefins. The maximum molar carbon yield of olefins and aromatics versus yields of coke at 500°C for ZSM-5 and ECat is shown in Figure 3. The maximum theoretical molar carbon yield for propylene [77% at 100% conversion or 62% at 80% conversion as defined in Eq. (9)] is not approached by either of these catalysts. According to Figure 3, the ECat catalyst affords a 20% yield of olefins and aromatics and 26% yield of coke when the total conversion is 80%. This is similar to Equation (10) at an 80% conversion. ZSM-5 gives rise to a lower yield of coke and a higher yield of olefins and aromatics which approaches 45% at a conversion of 80%. This result is similar (but still lower) to the yield of olefins and aromatics for ZSM-5 according to Equation (10), which would give a maximum theoretical yield of 53% at 80% conversion.

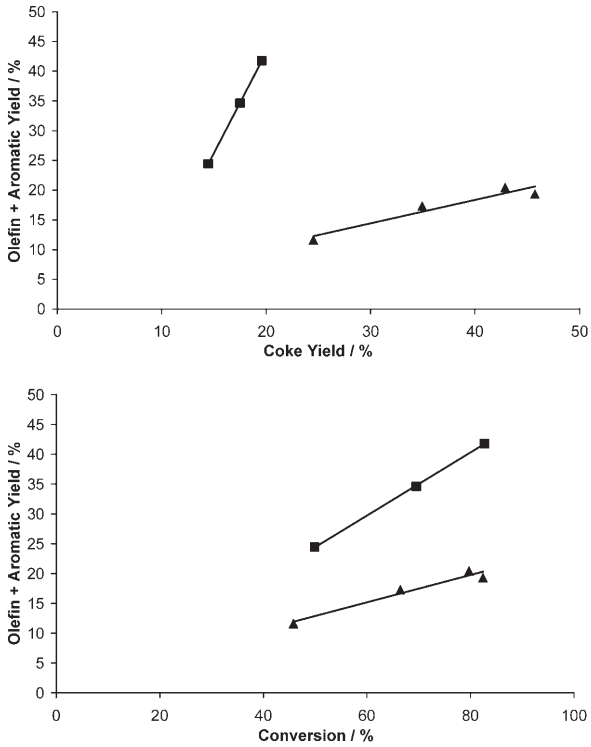
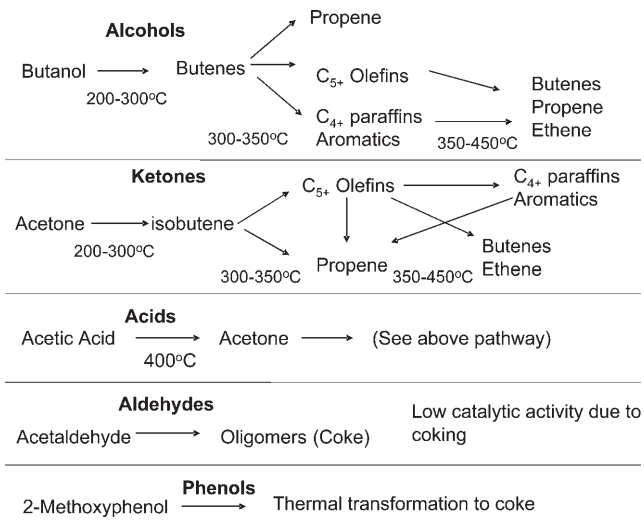


Figure 3. Yields of olefins and aromatics versus the yield of coke (top) and the total conversion (gas, gases, and aromatics; bottom) for the catalytic cracking of a glycerol/water mixture (50 wt% glycerol) in a MAT reactor for ZSM-5 (■) and an equilibrium FCC catalysts (ECat, ▲).

Neither of these catalysts comes close to achieving the maximum theoretical yield, which suggests that future improvements can be made to further improve the yields of olefins and aromatics. These experiments suggest that zeolitic conversion of glycerol is a shape-selective process and that reaction products change depending on the structure of the catalyst. Future catalysts and reactors should be designed to 1) minimize the formation of coke, 2) increase the rate of hydrogen transfer, 3) maximize the production of CO, and 4) maximize the production of CO_2 by increasing the water gas shift reaction.

3.2.2. *Catalytic Cracking of Bio-oils*

The reactivity and reaction pathways for some model bio-oil compounds using ZSM-5 catalysts has been studied by Gayubo and co-workers (Scheme 2).[50,56,57] These feeds have higher H/C_{eff} ratios than would be present in most bio-oils. Nevertheless, these experiments do teach us some of the chemistry involved, as these molecules would be important intermediates in the conversion of biomass-derived molecules into olefins and aromatics. Alcohols convert into olefins at temperatures around 200°C, then into higher olefins at 250°C, and into paraffins and a small proportion of aromatics at 350°C.[50,56,57] Phenol has a low reactivity on ZSM-5 and only produces small amounts of propylene and butanes. Both 2-methoxyphenol and acetaldehyde have a low reactivity on ZSM-5 catalysts and undergo thermal decomposition to generate coke.[56] Acetone, which is less reactive than alcohols, is first dehydrated and then undergoes disproportionation to isobutene at 250°C and then converts into C_{5+} olefins at temperatures above 350°C. These olefins are then converted into C_{5+} paraffins, aromatics, and light alkenes. Acetic acid produces acetone, by a complex chemical pathway, which is converted into acetone derivatives. Products from zeolitic upgrading of acetic acid and acetone produce considerably more coke than products from alcohol feedstocks do. Thus, different molecules in bio-oils display a significant difference in reactivity and rates of coke formation.



Scheme 2. The conversion of model bio-oil compounds with ZSM-5 (adapted from Gayubo et al.[50,56]).

Gayubo et al. have recommended that the oil fractions that lead to thermal coking (such as aldehydes, oxyphenols, and furfurals) be removed from the bio-oil prior to upgrading over zeolites. Bio-oils can be separated by fractionation using mainly water to produce an oil layer (with mostly lignin-derived components) and an aqueous carbon-containing layer (Figure 4).[26] The patent literature lists processes for the selective removal of phenolic compounds from bio-oils by

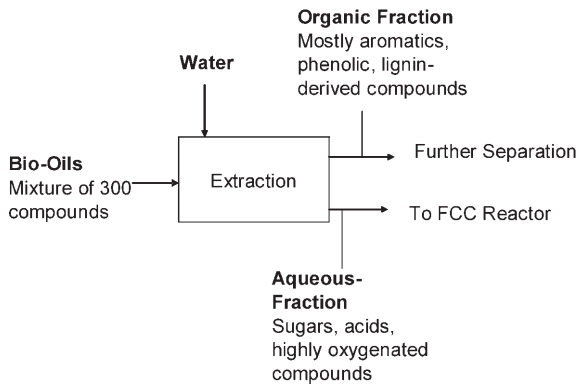


Figure 4. Separation and conversion of bio-oils.

liquid–liquid extraction, where the phenolic compounds are then used to make phenol-formaldehyde resins.[58,59] These different fractions could then be a feed to a catalytic cracker or hydrotreater, or converted into chemicals.

The conversion of wood-derived bio-oils produced by fast pyrolysis was tested in a flow reactor at temperatures of 290–410 °C and catalyst residence times of 30 min with acidic catalysts including ZSM-5, H-Y-zeolite, H-mordenite, silicalite, and silica-alumina (Table 2).[60–63] The zeolite catalysts gave rise to higher yields of hydrocarbon than the silica-alumina and silicalite catalysts. ZSM-5 produced the highest amount (34 wt % of feed) of liquid organic products.[61] The organic products formed comprised mostly aromatics for ZSM-5 and aliphatics for SiO_2-Al_2O_3. Between 30 and 40 wt % of the bio-oil was deposited on the catalyst as coke or in the reactor as char. Gaseous products include CO_2, CO, light alkanes, and light olefins. Large amounts of coke (6–29 wt % of feed), char (12–37 wt % of feed), and tar (12–37 wt % of feed) formed during upgrading over zeolites. Importantly, bio-oils are thermally unstable and thermal cracking reactions occur during upgrading on zeolites. Bakhshi and co-workers developed a two-reactor process, where only thermal reactions occur in the first empty reactor and catalytic reactions occur in the second reactor that contains the catalyst.[63] The advantage of the two-reactor system is that it improves the life of the catalyst by reducing the amount of coke deposited on the catalyst.

Table 2: Comparison of different zeolite catalysts for upgrading of wood-derived bio-oils obtained by fast pyrolysis at 370 °C.[60–62]

Catalyst	HZSM-5	SiO_2-Al_2O_3 (ratio 0.14)	SAPO-5
Properties			
pore size [nm]	0.54	3.15	0.80
BET surface area [$m^2 g^{-1}$]	329	321	330
acid area [$cm^2 g^{-1}$][a]	224.9	–	125.5
Product Yields [wt % of feed]			
organic liquid product	33.6	24.9	22.2
gas	–	6.1	10.3
coke + char[b]	20.5–30.2	40	30.0
tar[c]	0–4.1	–	9.5
aqueous fraction	–	25.0	24.2
Composition Organic Liquid Product [wt %]			
total hydrocarbons	86.7	45.6	51.0
aromatics	85.9[d]	2.1	27.5
aliphatics	18.6	43.5	23.5

[a] Acid area is measured by ammonia temperature-programmed desorption and represents Brønsted and Lewis acid sites. [b] Coke is defined as organics that could only be removed from the catalyst by calcinations. Char is defined as organics deposited in the reactor as a result of thermal decomposition which were not on the catalyst. [c] Tar refers to the heavy oils deposited on the catalysts that were only removed with a hexane/acetone wash. [d] Toluenes and xylenes are the most common aromatics for HZSM-5, whereas benzene is the most common aromatic for SAPO and MGAPO catalysts.

3.2.3. *Catalytic Cracking of Lignin*

Lignin, which consists of polyaromatic oxygenated compounds, is especially challenging to convert as a result of its stable (nonreactive) aromatic structure. As discussed above, phenols, which have chemical structures similar to lignin, produce large amounts of coke on ZSM-5 catalysts. Thring et al. studied zeolite upgrading of Alcell lignin with ZSM-5 catalyst at 500–650 °C in a fixed-bed reactor (Table 3).[64] The highest liquid yield was 43 wt %, and the yields of coke and char were 15–50 wt %. As the temperature increased, the yields of gas increased, those of char and coke decreased, and those of liquids decreased. The major liquid components were toluene, benzene, and xylene, which can disproportionate and isomerize on acid catalysts. Small FCC pilot-plant tests have been carried out with pyrolysis lignin oil fractions, pyrolysis oil, VGO, and blends with pyrolysis oil lignin fraction with VGO (Table 4).[9] The pyrolysis oil was separated into a lignin

Table 3: Zeolite upgrading of lignin with ZSM-5 catalyst (WHSV = 5 h^{-1}).[64]

Temperature [°C]	500	550	600	650
Yield of Products [%]				
gas	11	19	54	68
liquid	39	43	30	11
char + coke	50	38	16	21
Major Liquid Product [wt %]				
benzene	8.6	9.4	13.6	14.4
toluene	33.1	36.7	42.4	43.7
xylene	31.5	33.0	22.7	21.0
ethylbenzene	3.0	2.1	1.9	1.3
propylbenzene	4.2	2.5	1.3	1.0
C_{9+} aromatics	9.0	5.1	6.0	3.0
Gas Composition [wt %]				
methane	8.7	5.3	4.4	13.9
ethylene	6.6	19.5	16.2	24.3
ethane	4.5	2.6	2.8	2.9
propylene	8.2	21.1	11.4	13.4
propane	34.6	13.7	6.6	2.6
C_4	18.5	13.2	4.4	3.0
C_{5+}	4.8	2.4	1.0	3.9
CO	3.1	9.4	23.5	6.6
CO_2	10.9	12.4	29.7	19.6
H_2	0.2	0.3	0.1	0.1

Table 4: Yields [wt%] from fluid catalytic cracking of VGO, mixtures of VGO and either pyrolysis oil or pyrolysis oil lignin fraction, and pyrolysis oil lignin fraction.[9]

Product	VGO	VGO + 20 wt% pyrolysis oil	VGO + 20 wt% lignin fraction	Lignin fraction
Ethylene	2.0	3.3	3.6	3.8
Propane	1.2	2.1	2.4	0.7
Propylene	5.9	6.1	6.3	2.6
Butanes	11.1	13.5	14.3	2.7
Gasoline	42.7	40.6	41.3	28.8
LCO[a]	14.8	9.1	9.7	15.6
CSO[b]	18.5	4.8	4.7	6.2
Coke	3.8	7.1	9.2	16.1
Water + CO_2	0.0	13.5	8.5	23.5

[a] Light cycle oil. [b] Clarified slurry oil.

fraction by adding water to the bio-oil followed by phase separation. As shown in Table 4, the lignin in the pyrolysis oil can produce gasoline, olefins, and light cycle oil.

3.2.4. *Catalytic Cracking of Biomass-Derived Feedstocks Mixed with Petroleum-Derived Feedstocks*

We have processed mixtures of VGO with glycerol (50 wt% glycerol in water) and pure VGO as feedstocks in a MAT reactor with a fresh FCC catalyst at 500 °C (Figure 5) to simulate co-feeding of biomass-derived feedstocks with petroleum-derived feedstocks.[48] The mixed feeds consisted of 9:1 and 2:1 volumetric mixtures of VGO/glycerol solution which correspond to molar carbon ratios of VGO to glycerol of 31:1 and 7:1, respectively. These experiments showed that mixtures of VGO with biomass-derived feedstocks can help to transfer hydrogen from the VGO to the biomass molecules.

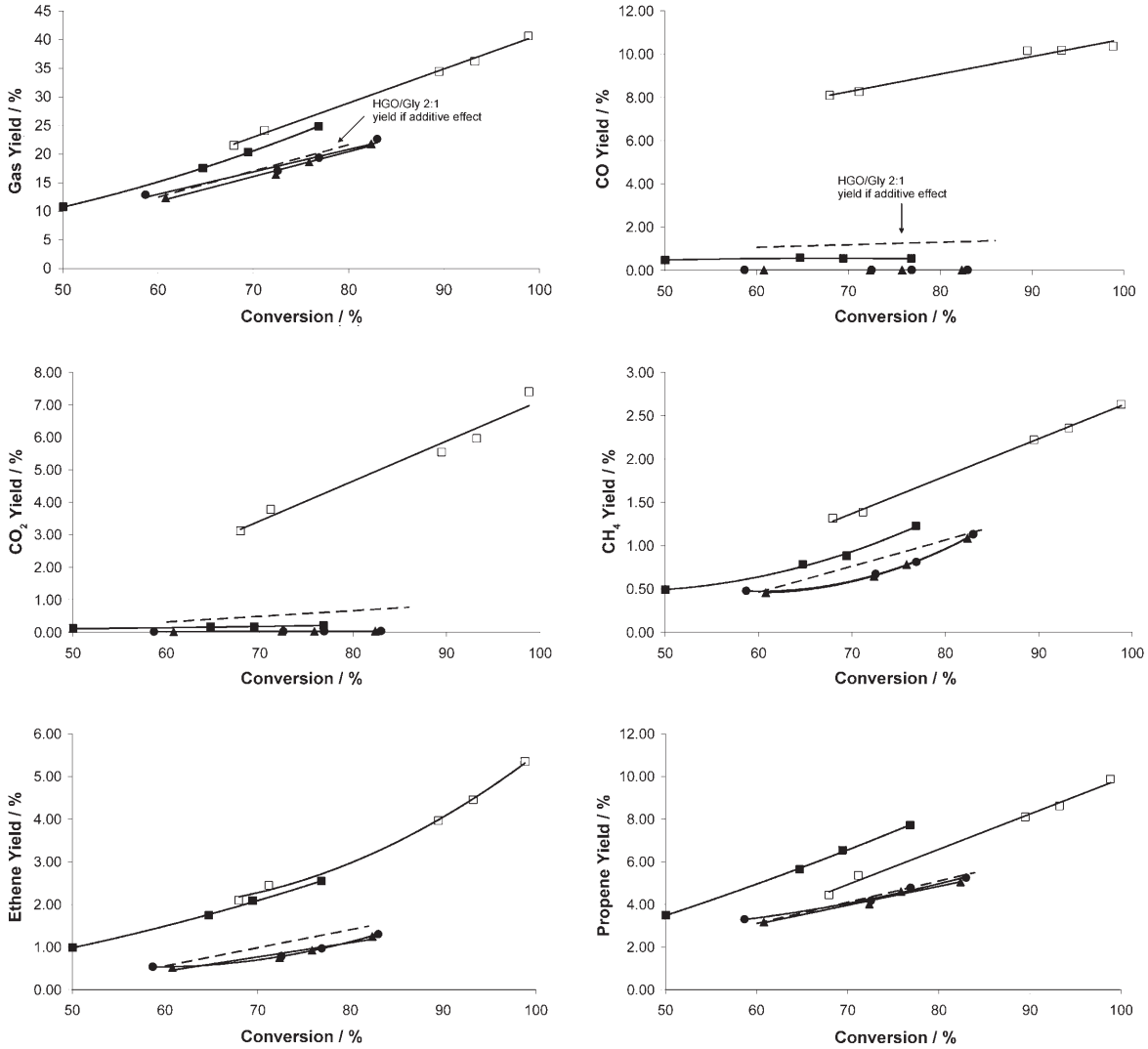
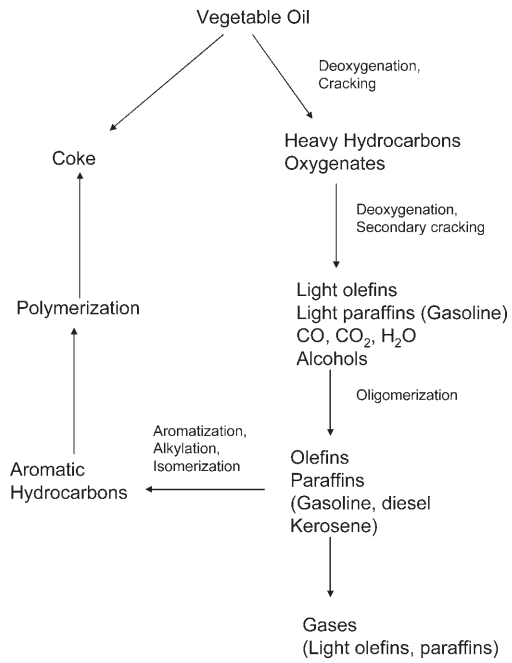


Figure 5. Gas-phase yields produced for catalytic cracking of mixtures vacuum gas oil (VGO) with 50 wt% glycerol using a FCC1 catalyst in a MAT reactor at 500 °C (□: glycerol; ■: glycerol/VGO (1:2); ●: glycerol/VGO (1:9); ▲: VGO). Glycerol was fed into the reactor as a 50 wt% glycerol/water mixture. The dotted lines represent the yields if an additive effect of glycerol and VGO was observed. Yields are based on carbon molar selectivity, and the molecular weight of VGO is estimated to be that of phenylheptane. The conversions for VGO and glycerol/VGO mixtures include the gases, coke, and gasoline fraction from a simulated distillation. The conversions for a pure glycerol feed include coke, gases, and aromatics.

These results are consistent with those of Marinangeli et al., who also showed that VGO can act as a hydrogen donor.[9] The dashed line in Figure 5 corresponds to the product molar carbon yields if glycerol and VGO-derived molecules did not react or if the mixture effect were purely additive (additive effect, calculated by adding the yields obtained with glycerol solution and VGO runs, with respect to the mass ratio of both feeds, and normalizing to 100%.) In comparison to VGO, glycerol cracking produces significant amounts of CO and CO_2, a similar yield of hydrogen, more methane and ethylene but less ethane, more propylene but less propane, and much less butenes and butane. The ratios of olefins to paraffins are much higher for glycerol cracking. Importantly, adding glycerol to VGO increases the yields of ethylene and propylene more than what would be expected for an additive effect of mixtures of VGO and glycerol. The yields of gases for glycerol/VGO mixtures are higher than what would be expected from an additive mixture, indicating that some synergetic effect is occurring. However, the yield of coke was similar to the yields obtained for an additive effect. These experiments were carried out with standard FCC catalysts, which do not produce large amounts of olefins. One option for further improving the yields of olefins and aromatics for co-feeding of glycerol and petroleum-derived feedstocks into an FCC reactor would be to add ZSM-5 to the FCC catalyst, as ZSM-5 produced more olefins and less coke than the FCC1 catalyst.

3.3. Catalytic Cracking of Triglyceride-Based Feedstocks

Catalytic cracking and pyrolysis of vegetable oils can be used to produce liquid fuels that contain linear and cyclic paraffins, olefins, aldehydes, ketones, and carboxylic acids. Vegetable oils are thermally unstable, and therefore homogeneous non-catalytic reactions occur when they are rapidly heated without air present. Catalytic cracking of vegetable oils involves the pyrolysis of vegetable oils in the presence of solid catalysts that can improve the product yield. For catalytic cracking of vegetable oils, both the homogeneous and heterogeneous components need to be understood. The cracking of vegetable oils has been studied since 1921,[65] and pyrolysis products of vegetable oils were used as a fuel during both world wars.[66] Mainly zeolite catalysts have been tested for this reaction, including HZSM-5, β-zeolite, and USY.[67,68] Leng et al. proposed a reaction pathway for catalytic cracking of vegetable oils as shown in Scheme 3:[69] The vegetable oil first undergoes deoxygenation and cracking reactions to produce heavy hydrocarbons and oxygenates. These are then cracked by secondary reactions and deoxygenation to produce light olefins, light paraffins, CO, CO_2, H_2O, and alcohols. The light olefins then undergo oligomerization reactions to produce olefins and paraffins, which could be used as gasoline, diesel, and kerosene. Aromatic hydrocarbons are also produced by aromatization, alkylation, and isomerization. The aromatics can undergo polymerization to produce undesired coke. The gasoline, diesel, and kerosene fractions can undergo cracking reactions to produce light olefins and paraffins.



Scheme 3. Proposed reaction pathway for the cracking of vegetable oils with HZSM-5 (adapted from Leng et al.[69]).

UOP has also investigated the catalytic cracking of vegetable oils.[9,70] Table 5 lists the yields for catalytic cracking of VGO and vegetable oil with a process optimized for the production of gasoline and olefins. As can be seen, vegetable oil can be used to produce both olefins and gasoline with yields that are similar to those obtained from VGO. Twaiq et al. used ZSM-5 as catalyst to produce gasoline, kerosene, and diesel fuel in yields of 28, 9, and 5%, respectively, from a palm oil feed.[68] Catalytic cracking of vegetable oils appears to be a process for the production of gasoline and olefins, however, the chemistry of this process is not well understood. It is likely that the process can be improved by understanding the chemistry better and by developing better catalytic materials and reactors.

Table 5: Yields [wt%] from catalytic cracking of VGO and mixtures of VGO and vegetable oil/fat.[70][a]

Product	Optimized for Gasoline		Optimized for Olefins	
	VGO	Vegetable oil/fat	VGO	Vegetable oil/fat
Mathane/Ethane	–	–	4.1	4.1
Ethylene	1.5	1.9	8.6	8.7
Propane	0.7	0.8	2.0	2.1
Propylene	4.0	4.6	22.0	22.4
C_4 fraction	7.9	6.6	15.0	13.5
Gasoline	45.5	45.4	27.3	23.0
LCO	17.5	11.4	9.5	5.0
CSO	19.5	13.1	5.0	3.0
Coke	3.4	4.5	6.5	6.5
Water	0	11.7	0	11.7
RON[b] of gasoline	92.1	94.8	94.8	96.8

[a] Based on MAT tests, modeling, and yield-estimating tools. [b] Research octane number.

3.4. Steam Reforming of Coke Deposits from Biomass during Catalytic Cracking

Large amounts of coke are produced during catalytic cracking of cellulosic molecules with standard FCC catalysts. The coke is typically burned to provide process heat for the FCC process; however, the coke could in principle be converted into syngas, thereby producing a valuable product that can be used elsewhere in the refinery. The patent literature has discussed the conversion of coke from the FCC process into syngas. In the 1980s, Hettinger et al. from Ashland Oil published two patents on an FCC process for CO_2 reforming of coked FCC catalysts[71–73] in which the CO_2 reacts with the coke to form CO and H_2O. This process could also be used to decrease CO_2 emissions during the FCC process.[71] They proposed a two-stage regenerator system: in the first stage CO_2 removes most of the hydrogen on the coke as well as some carbon, and in a second regenerator the remaining coke is burned to release enough heat for the cracking reaction. The FCC catalyst was modified by introduction of a metal to improve the activity of carbon reforming, and the activities of several FCC catalysts with 1 wt% metal impurities were tested in reforming coke with CO_2.

Steam reforming has also been reported as a method of regenerating coked FCC catalysts. The first mention of steam reforming of coked FCC catalysts appeared in 1950 in a patent assigned to Phillips Petroleum.[74] They reported two experiments in which a coked FCC catalyst was regenerated at 650 °C with air and with a steam/oxygen mixture. The outlet gas from the catalyst regenerated with air contained primarily N_2, CO_2, CO, and O_2. The outlet gas from the catalyst regenerated with the steam/oxygen mixture contained 38% CO_2, 30% CO, and 32% H_2 (by volume).

In principle, biomass could be added, with H_2O or CO_2, to a FCC regenerator section to produce syngas if the injection is carried out in a zone that contains low levels of oxygen. In this zone, several reactions may occur, including the decomposition of biomass to syngas, formation of coke, steam reforming of coke, CO_2 reforming of coke, and water gas shift. We will calculate the thermodynamics for the formation and reforming of coke in an FCC process by using ethylene glycol as a biomass-derived oxygenate and graphite as the carbon product. Ethylene glycol can decompose into syngas [Eq. (11)] or into carbon and water [Eq. (12)]. Carbon dioxide reforming (Boudouard reaction) involves the reaction of coke with CO_2 to form CO as shown in Equation (13). Steam reforming of the coke involves reaction of the coke with water to produce CO and H_2 as shown in Equation (14). Two other reactions that may also be involved in this process are the water gas shift reaction and methanation [Eq. (15) and (16), respectively]. We also use benzene as a model for an aromatic coke species and report steam and CO_2 reforming of benzene as Equations (17) and (18), respectively.

$$C_2H_6O_2 \rightarrow 2\,CO + 3\,H_2 \quad (11)$$

$$C_2H_6O_2 \rightarrow 2\,CO + 3\,H_2O \quad (12)$$

$$C + CO_2 \rightarrow 2\,CO \quad (13)$$

$$C + H_2O \rightarrow CO + H_2 \quad (14)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (15)$$

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O \quad (16)$$

$$C_6H_6 + 6\,H_2O \rightarrow 6\,CO + 9\,H_2 \quad (17)$$

$$C_6H_6 + 6\,CO_2 \rightarrow 12\,CO + 3\,H_2 \quad (18)$$

The thermodynamics of the reactions in Equations (11) and (12) are such that both are thermodynamically favorable at temperatures between 200 and 900 °C with a standard Gibbs free energy (G/RT) of less than $-10\,kJ\,mol^{-1}$(C). This indicates that syngas and coke can indeed be produced from ethylene glycol (and also glucose) at these conditions. Figure 6 shows the standard Gibbs free energy for CO_2 reforming of carbon [Eq. (13)], H_2O reforming of carbon

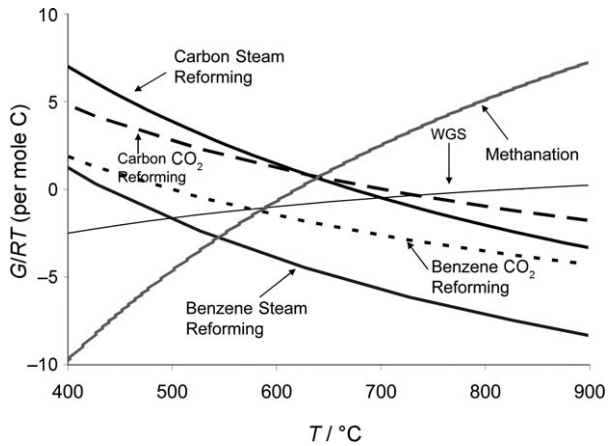


Figure 6. Thermodynamics for reactions involving steam and CO_2 reforming of biomass-derived compounds. WGS: water gas shift.

[Eq. (14)], water gas shift reaction [Eq. (15)], and methanation [Eq. (16)]. As the coke may be an aromatic species that contains hydrogen, we have included H_2O and CO_2 reforming of benzene [shown in Eq. (17) and (18), respectively] in this figure. All values in Figure 6 are normalized per mole of carbon. H_2O and CO_2 reforming of carbon are thermodynamically favorable at temperatures above 700 °C. Reforming of benzene is thermodynamically favorable at temperatures above 450 and 500 °C for H_2O and CO_2 reforming, respectively. All of the CO_2 and H_2O reforming reactions are endothermic, and increasing the reaction temperature increases the Gibbs free energy. The water gas shift and methanation reactions are exothermic, and increasing the reaction temperature decreases the Gibbs free energy. The water gas shift reaction is thermodynamically favorable at temperatures below 800 °C. If the aim is to produce hydrogen, an additional lower-temperature water gas shift reactor will be required to convert CO and H_2O into H_2 and CO_2. The methanation reaction is thermodynamically favored at temperatures below 600 °C; therefore, CH_4 levels will be low at temperatures above 700 °C.

Temperature-programmed desorption experiments were performed to verify if syngas could be produced from biomass on FCC catalysts.[75] Aqueous solutions of glucose (30 wt% glucose) were impregnated onto FCC catalysts prior to the experiments. The glucose/catalyst mixture was then heated in flowing He or He saturated with H_2O in a temperature-programmed desorption system. Mass spectrometry analyses revealed the major products to be H_2, CO, and CO_2. After reaction, the carbon content of the remaining catalyst was analyzed with an elemental analyzer. Two catalysts were tested, namely, a fresh FCC catalyst and a FCC catalyst impregnated with 2 wt% Ni.

When only He was used as the gas (no water present), only small amounts of H_2, CO, and CO_2 were produced, and 36% of the carbon was removed from the catalyst as gas-phase products.[75] When He is saturated with water (Figure 7), large amounts of H_2 and CO are observed along with the consumption of water. The H_2 and CO peaks are significantly higher for the Ni-containing catalyst, indicating that Ni—as, for instance, Ni-deposited on the catalyst during FCC operation—promotes this reaction. These experiments show that syngas can be produced from biomass-derived compounds (glucose) using a standard FCC catalyst and a modified FCC catalyst and that the coke formed during catalytic cracking of biomass can be converted into syngas.

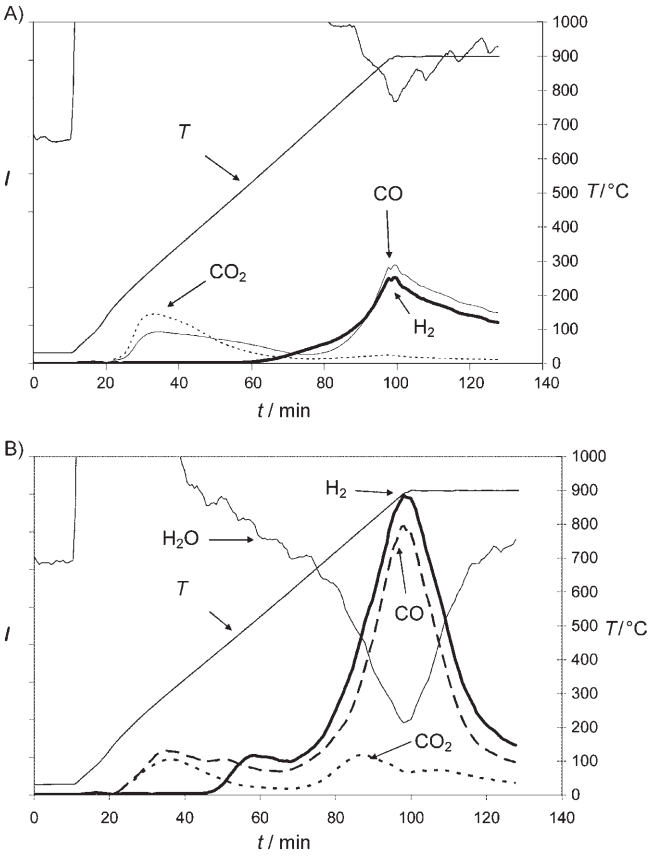


Figure 7. Temperature-programmed reaction of He saturated with water with FCC catalysts impregnated with aqueous glucose solution (30 wt% glucose): A) steamed commercial FCC catalyst (FCC); B) 2 wt% Ni/FCC catalyst. Temperature profile: ramp 10 K min^{-1} to 900°C and held for 30 min at 900°C. Catalysts impregnated with 0.75 g aqueous glucose solution (30 wt% glucose) to 1.00 g catalyst.

4. Hydrotreating of Biomass-Derived Feedstocks

4.1. Petroleum Technology

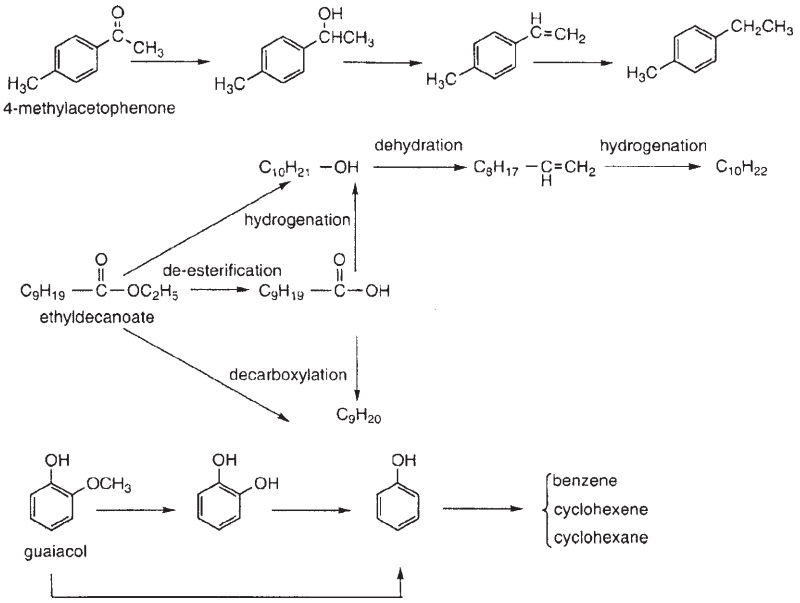
Hydrotreating is typically more expensive than catalytic cracking because it requires H_2. Today, in a typical petroleum refinery, vacuum gas oil is also hydrotreated. The objective of hydrotreating in a petroleum refinery is to remove sulfur (hydrodesulfurization, HDS), nitrogen (hydrodenitrogenation, HDN), metals (hydrodemetalation, HDM), and oxygen (hydrodeoxygenation, HDO) from polyaromatics from the heavy gas oil feedstock. Hydrogen is added with the heavy gas oil feed. Typical catalysts used for hydrotreating include sulfided Co-Mo and Ni-Mo, and typical reaction conditions employed are temperatures of 300–450°C, pressures of 35–170 bar H_2, and liquid hourly space velocities (LHSVs) of 0.2–10 h^{-1}.

4.2. Hydrotreating of Cellulosic Feedstocks

4.2.1. Hydrotreating of Bio-oil Model Compounds

Hydrotreating, or hydrodeoxygenation, can be used to convert bio-oils into a more stable fuel with a higher energy density that has the potential to be blended with petroleum-derived feedstocks. In a petroleum refinery, hydrotreating is carried out at temperatures of 300–600°C and H_2 pressures of 35–170 atm with sulfided Co-Mo- and Ni-Mo-based catalysts. Most hydrodeoxygenation of bio-oils has focused on sulfided Co-Mo- and Ni-Mo-based catalysts, which are used for hydrotreating industrial feedstocks. When sulfided Co-Mo and Ni-Mo catalysts are used, sulfur must be added to the bio-oil, otherwise catalyst deactivation will occur. Non-sulfided catalysts, including Pt/SiO_2-Al_2O_3,[76] vanadium nitride,[77] and Ru, have also been used for hydrodeoxygenation. During hydrodeoxygenation, the oxygen in the bio-oil reacts with H_2 to form water and saturated C—C bonds. Partial hydrotreating (greater than 5 wt% oxygen) results in an increase in oil viscosity, and deoxygenation to less than 5 wt% oxygen is required for a low viscosity such as that required for fuel applications.[78] It is also desirable to avoid hydrogenation of aromatics in the bio-oils, since this would decrease the octane number of the gasoline produced and increase H_2 consumption. Furminskyu[79] and Elliot et al.[23] have written reviews on hydrodeoxygenation.

Delmon and co-workers studied the hydrodeoxygenation of model bio-oil compounds with sulfided Co-Mo and Ni-Mo catalysts to elucidate the main reaction pathways, the influence of the important reaction parameters, and the possible catalytic poisons.[80–84] The model bio-oil feedstock was a mixture of guaiacol, 4-methylacetophenone, and ethyl-decanoate (Scheme 4), and thus contained ketone, ester, aromatic, and phenol groups. During the conversion process, carboxylic acids and alcohols are also formed. The ketone group in 4-methylacetophenone is easily and selectively hydrogenated into a methylene group above 200°C.[82] Carboxylic groups and guaiacyl groups are not as reactive as ketone groups, and temperatures greater than 300°C are required for their conversion. Carboxylic groups undergo



Scheme 4. Hydrodeoxygenation pathways of 4-methylacetophenone, ethyl decanoate, and guaiacol from Ferrari et al.[80] (Reprinted from reference [80], with permission.)

both hydrogenation and a parallel decarboxylation process.[82] Guaiacol was hydrogenated into catechol and then to phenol. Guaiacol caused deactivation of the catalyst owing to coking reactions. Increasing acidity of the catalyst support led to increased rates of decarboxylation and hydrogenation of ethyl decanoate as well as formation of coke from guaiacol. According to Delmon, carbon, which has low acidity, is a good catalytic support for hydrodeoxygenation because it reduces undesired coking reactions.

Elliott and co-workers developed a two-step hydrotreating process for the upgrading of bio-oils using sulfided Co-Mo/Al_2O_3 or sulfided Ni-Mo/Al_2O_3 catalysts.[32,78,85] The yield of the process is 0.4 L of refined oil per liter of bio-oil feed, with the refined oil containing less than 1 wt% oxygen. The first step involves a low-temperature (270°C, 136 atm H_2) catalytic treatment that hydrogenates the thermally unstable bio-oil compounds, which would otherwise undergo thermal decomposition to form coke and plug the reactor. The second step involves catalytic hydrogenation at higher temperature (400°C, 136 atm H_2). Upgraded bio-oils have a research octane number (RON) of 72 and an aromatic/aliphatic carbon ratio of 38:62 to 22:78. During this process, 20–30% of the carbon in the bio-oil is converted into gas-phase carbon, decreasing the overall yield. Catalyst stability and formation of gums in the lines were identified as points of major uncertainty of the process, and future work is needed to develop improved hydrotreating catalysts.

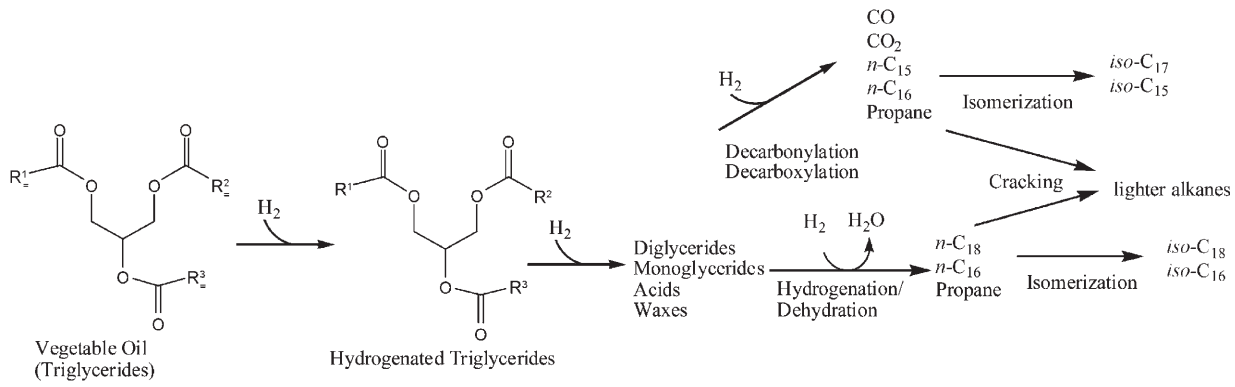
4.2.2. *Hydrotreating of Lignin*

Lignin, from paper mills, cellulosic ethanol plants, or the lignin component in bio-oils, can be converted into fuels or chemicals by hydrotreating. Previous dehydroxygenation experiments of lignin-derived feedstocks have used standard hydrotreating catalysts (sulfided Ni-Mo and Co-Mo) at temperatures of 250–450°C to produce phenols, cyclohexane, benzene, naphthalene, and phenanthrene with liquid oil yields of 61% based on the initial lignin.[86–89] A process to convert lignin into a high-octane oxygenated gasoline additive has been developed and designed by the National Renewable Energy Laboratory (US).[90,91] The first step in this process involves base-catalyzed depolymerization of lignin with NaOH and methanol or ethanol as solvent at 320°C and 120 atm.[90,92] The liquid products are separated from the solids and neutralized with sulfuric acid, and the lignin is extracted in a toluene stream. The lignin, which contains mono-, di-, and polyalkylated phenols and benzenes with minor amounts of alkyoxyphenols and alkyoxybenzene, is then separated from the toluene stream and fed to the hydroprocessing unit. The hydrotreating unit consists of two reactors for hydrodeoxygenation and hydrocracking/ring hydrogenation, both with standard sulfided hydrotreating catalysts. The products consist of C_7–C_{11} alkylbenzenes, C_5–C_{11} multibranched paraffins, and mono-, di-, tri-, and polyalkylated cyclohexanes and cyclopentanes. The products are comprised of 65% aromatics with an octane number of 100–110. The production cost (in US dollars, USD) of the high-octane reformulated fuel additive, assuming 100% solubilization of the lignin and an overall yield of 70%, is estimated to be 0.28 USD L^{-1}.

4.3. *Hydrotreating of Triglycerides*

Vegetable oils can be hydrotreated to produce liquid alkanes that have very high cetane numbers (80–100) and good fuel properties (Table 5).[70] Also listed in Table 5 are the fuel properties of biodiesel and fuel oil. It can be seen that hydrogenated vegetable oils have better fuel properties than biodiesel. A 10-month on-road test of six postal delivery vans running on blends of petrodiesel with hydrogenated tall oil showed that engine fuel economy was greatly improved.[93] Neste Oil has also developed a process to produce diesel fuel, marketed as NExBTL fuel, by a modified hydrotreating process.[10] The advantages of hydrotreating over transesterification are that the former is compatible with current infrastructure as well as existing engines and there is some flexibility with respect to the feedstock.[94]

The reaction pathway for hydrogenating vegetable oils is shown in Scheme 5.[95] The first step is the hydrogenation of the C=C bonds of the vegetable oils. The hydrogenated vegetable oils then form free fatty acids, diglycerides, and monoglycerides. Acids form under hydrotreating conditions, and the reactor must be designed so that acids do not cause corrosion problems. The acids, diglycerides, and monoglycerides can also form waxes in the reactor, and these waxes can cause plugging if they are not removed or converted into alkanes. At lower space velocities and temperatures, the free



Scheme 5. Reaction pathway for the conversion of vegetable oils into alkanes by hydrotreating.

fatty acids, diglycerides, monoglycerides, triglycerides, and waxes undergo two different pathways to produce normal alkanes. The first is decarbonylation, which produces normal liquid alkanes (C_{17} if from a C_{18} free fatty acid), CO or CO_2, and propane. This pathway requires the least amount of hydrogen. Alternatively, triglycerides undergo a dehydration/hydrogenation pathway to produce a liquid *n*-alkane (e.g. C_{18} if from a C_{18} acid) and propane. The straight-chain alkanes can undergo isomerization and cracking to produce lighter and isomerized alkanes. It is likely that organic acids produced in the hydrotreating process catalyze the isomerization and cracking reactions. If straight-chain alkanes are desired, which is typically the case for diesel fuel, then the isomerization and cracking reactions should be minimized. However, isomerization would be required for production of such fuels as jet fuel. Large amounts of straight-chain alkanes may also increase the cloud point of diesel fuel, and so the straight chains may have to be isomerized to reduce this problem.[9]

It has been shown that vegetable oils including canola, sunflower, soy bean, rapeseed, and palm oils as well as the fatty acid fraction of tall oil and mixtures of the above compounds can be hydrotreated to produce liquid paraffins (mainly n-C_{15}–n-C_{18} alkanes).[96] Hydrotreating conditions involved temperatures of 350–450 °C, H_2 partial pressures of 48–152 bar, LHSVs of 0.5–5.0 h^{-1}, and standard hydroprocessing catalysts including cobalt molybdenum (Co-Mo) and nickel molybdenum (Ni-Mo). Liquid alkanes can also be produced by hydrotreating of tall oil, a by-product from Kraft pulping of pine and spruce trees, which has little economic value and contains large amounts of unsaturated fatty acids (30–60 wt %).[97]

In a petroleum refinery, hydrotreating may be carried out not only with petroleum-derived feedstocks but also with mixtures of vegetable oils and VGO as we have reported (Figure 8).[95] However, blending the vegetable oil with VGO dilutes the VGO, and therefore the contact time has to be adjusted to maintain high rates of conversion of sulfur and nitrogen. This change may cause the catalysts to deactivate faster and thereby decrease the catalyst cycle length.[9] Water produced from hydrotreating of vegetable oils may also increase the rate of deactivation in the hydrotreating reaction. Vegetable oils with high acidity, such as yellow or brown grease, are difficult to process in standard hydrotreating reactors owing to constraints of the reactor metallurgy. Our results have also shown that hydrotreating catalysts can remove sulfur or nitrogen from the VGO when vegetable oils are present, at flow rates similar to those used for pure VGO.[95] The yield of straight-chain alkanes (n-C_{15}–n-C_{18}; Figure 8E) increases with increasing concentration of sunflower oil. For feeds containing large amounts of sunflower oil (30 and 50 wt %), the yield of n-C_{15}–n-C_{18} alkanes decreases when the reaction temperature is increased above 350 °C as the alkanes are cracked to lighter products at higher temperatures and probably also because of a higher concentration of acidic molecules in the reactor.

Figure 8F shows the percentage maximum n-C_{15}–n-C_{18} alkanes yields (PMCYs) for the different mixtures of VGO/sunflower oil. The PMCY value is defined as the yield of n-C_{15}–n-C_{18} alkane minus the yield of n-C_{15}–n-C_{18} alkane from the VGO, divided by the maximum n-C_{15}–n-C_{18} yield if all of the fatty acids present in the triglyceride were converted into n-C_{15}–n-C_{18} alkanes. The PMCY increases as the temperature increases for the 5 wt % sunflower oil feed, and the value for this feed is 65–70 % at temperatures from 350–450 °C. The PMCY for the 15 wt % sunflower oil feed increases from 9 % to 83 % as the temperature increases from 300 to 350 °C, while a further increase in the temperature to 450 °C decreases the PMCY to 40 %. The PMCY for the 30 wt % sunflower oil feed decreases from 85 % to 56 % to 26 % as the temperature increases from 350 °C to 400 °C to 450 °C, respectively. The PMCY for the 50 wt % sunflower oil feed decreases from 70 to 26 % as the temperature increases from 350 °C to 450 °C.

Figure 8G shows the increase in sulfur conversion in the VGO with temperature. Figure 8 illustrates that the optimal conditions for hydrotreating of VGO are different than the optimal conditions of hydrotreating of vegetable oils. Therefore, in an industrial setting the vegetable oils could be injected into a different reactor section than the VGO. The injection section would vary depending on the temperature and the type of feed injected. A detailed kinetic model of hydrotreating of vegetable oils needs to be developed to find this optimal condition. We believe that future work in understanding the chemistry involved in the hydrotreating

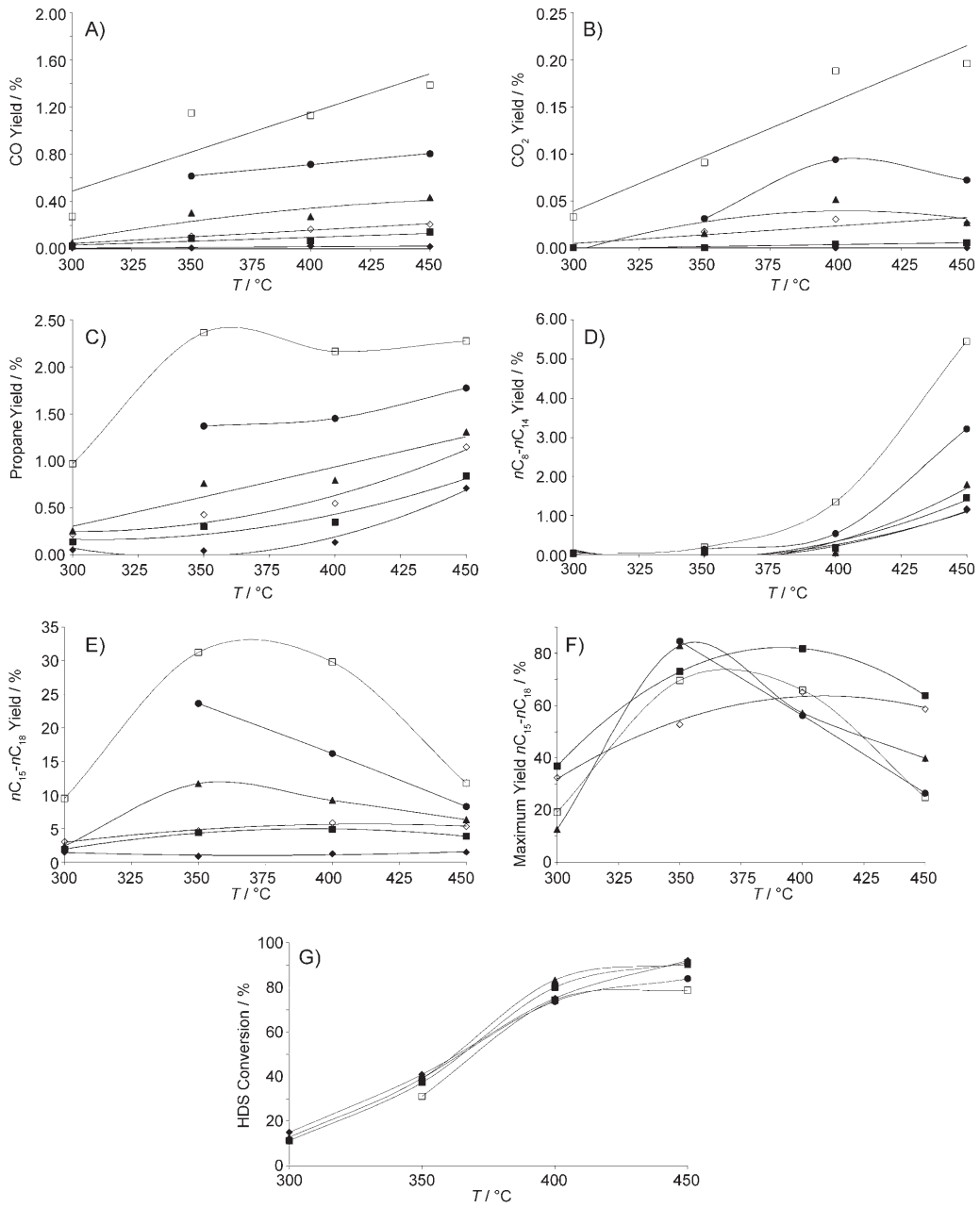


Figure 8. Product molar carbon yields (A–E), maximum yield for n-C_{15}–n-C_{18} alkanes (F), and sulfur conversion (G) for hydrotreating of mixtures of vacuum gas oil and sunflower oil with Ni-Mo/Al_2O_3 catalyst at 5.2 h^{-1} LHSV and 50 atm H_2. Each data point was collected after 6 h on-stream (◆: 100 wt% VGO; ■: 95 wt% VGO and 5 wt% sunflower oil; ◇: 90 wt% VGO and 10 wt% sunflower oil; ▲: 85 wt% VGO and 15 wt% sunflower oil; ●: 70 wt% VGO and 30 wt% sunflower oil; □: 50 wt% VGO and 50 wt% sunflower oil).

of vegetables oils and vacuum gas oil combined with the development of better catalysts will lead to efficient processes for the hydrotreating of such mixtures in a petroleum refinery.

5. Summary and Outlook

As petroleum prices continue to increase, it is likely that biofuels will play an ever-increasing role in our energy future. The processing of biomass-derived molecules by catalytic cracking and hydrotreating is a promising alternative for the future to produce biofuels. These methods allow the utilization of existing infrastructure which would have low capital costs. Future work should focus on understanding the reaction pathways for feeding of biomass-derived feedstocks, with the ultimate goal of designing new catalysts that display higher selectivities. Biomass feedstocks include cellulosic biomass, starch-based biomass, and vegetable oils. Vegetable oils are the easiest feedstock to convert into liquid fuels because of their high energy density, low oxygen content, and the fact that they are already liquid fuels. Gasoline and diesel fuel can be produced from catalytic cracking and hydrotreating,

respectively, of triglycerides. Diesel fuel produced from hydrotreating of vegetable oils has been reported to have better fuel properties than biodiesel (Table 6).[70]

Table 6: Comparision of properties of biodiesel and hydrogenated vegetable oil.[70]

Properties	Biodiesel	Hydrogenated vegetable oil
Cetane number	50	80–90
Density [g mL^{-1}]	0.883	0.78
Change in NO_x emissions [%]	+10	0 to −10
Distillation [°C]	340–355	265–320
Sulfur content [ppm]	<10	<10
Lower heating value [MJ kg^{-1}]	38	44
Oxygen content [wt%]	11	0
Cloud point [°C]	−5	−5 to −30

Cellulose-based biomass, which is the cheapest and most abundant form of biomass, is more difficult to convert into a biofuel because it is a solid with a low energy density. The first step for utilization of cellulosic biomass in a petroleum refinery is to overcome the recalcitrant nature of this material and convert it into a liquid product, which is done by fast pyrolysis or liquefaction to produce bio-oils or by hydrolysis routes to produce aqueous sugars and solid lignin. Catalytic cracking of bio-oils, sugars, and lignin produces olefins and aromatics from biomass-derived feedstocks. Unfortunately, large amounts of coke form under typical FCC conditions. This coke can be used to provide process heat or converted into syngas through steam or CO_2 reforming; otherwise, the reaction conditions must be improved to crack these products without forming large amounts of coke. Hydrotreating of bio-oils and lignin can produce diesel and gasoline range fuels, but the process requires high-pressure hydrogen. However, it is likely that in the future this hydrogen could be produced by using renewable energy sources such as the sun, wind, or biomass. Many options are available for the utilization of biomass-derived feedstocks in a petroleum refinery, and as we continue to develop processes for the production of biofuels our society will move towards a sustainable economy.

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[1] D. L. Klass, *Biomass for Renewable Energy, Fuels and Chemicals*, Academic Press, San Diego, **1998**.
[2] D. L. Klass, *Encyclopedia of Energy*, *Vol. 1* (Ed.: C. J. Cleveland), Elsevier, Dordrecht, **2004**.
[3] L. R. Lynd, J. H. Cushman, R. J. Nichols, C. E. Wyman, *Science* **1991**, *251*, 1318.
[4] European Biomass Industry Association, http://www.eubia.org (accessed December, 2005).
[5] L. R. Lynd, C. E. Wyman, T. U. Gerngross, *Biotechnol. Prog.* **1999**, *15*, 777.
[6] "Fuel Cycle Evaluations of Biomass-Ethanol and Reformulated Gasoline": K. S. Tyson, Report No. NREL/TP-263–2950, DE94000227, National Renewable Energy Laboratory, **1993**.
[7] C. E. Wyman, *Appl. Biochem. Biotechnol.* **1994**, *45*/46, 897.
[8] C. E. Wyman, N. D. Hinman, *Appl. Biochem. Biotechnol.* **1990**, *24*/25, 735.
[9] "Opportunities for Biorenewables in Oil Refineries": R. Marinangeli, T. Marker, J. Petri, T. Kalnes, M. McCall, D. Mackowiak, B. Jerosky, B. Reagan, L. Nemeth, M. Krawczyk, S. Czernik, D. Elliott, D. Shonnard, Report No. DE-FG36-05GO15085, UOP, **2006**.
[10] Neste Oil, http://www.nesteoil.com (accessed January, 2006).
[11] J. Biswas, I. E. Maxwell, *Appl. Catal.* **1990**, *63*, 197.
[12] R. J. Farrauto, C. Bartholomew, *Introduction to Industrial Catalytic Processes*, Chapman & Hall, London, **1997**.
[13] R. R. Davda, J. W. Shabaker, G. W. Huber, R. D. Cortright, J. A. Dumesic, *Appl. Catal. B* **2005**, *56*, 171.
[14] D. Dayton, *National Renewable Energy Laboratory*, Golden, CO, **2002**.
[15] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044.
[16] "Preliminary Screening—Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas": P. L. Spath, D. C. Dayton, National Renewable Energy Laboratory, Report No. NREL/TP-510-34929, **2003** (http://www.osti.gov/bridge).
[17] "Update of Hydrogen from Biomass—Determination of the Delivered Cost of Hydrogen": P. L. Spath, M. K. Mann, W. A. Amos, NREL, Report No. NREL/MP-510-33112, **2003** (http://www.osti.gov/bridge).
[18] C. E. Wyman, S. R. Decker, M. E. Himmel, J. W. Brady, C. E. Skopec, L. Viikari in *Polysaccharides*, 2nd ed. (Ed.: S. Dumitriu), Marcel Dekker, New York, NY, **2005**.
[19] C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch, Y. Y. Lee, *Bioresour. Technol.* **2005**, *96*, 1959.
[20] B. Kamm, P. R. Gruber, M. Kamm, *Biorefineries—Industrial Processes and Products*, Wiley-VCH, Weinheim, **2005**.
[21] A. V. Bridgwater, G. V. C. Peacocke, *Renewable Sustainable Energy Rev.* **2000**, *4*, 1.
[22] D. C. Elliott, E. G. Baker, D. Beckman, Y. Solantausta, V. Tolenhiemo, S. B. Gevert, C. Hörnell, A. Östman, B. Kjellström, *Biomass* **1990**, *22*, 251.
[23] D. C. Elliott, D. Beckman, A. V. Bridgwater, J. P. Diebold, S. B. Gevert, Y. Solantausta, *Energy Fuels* **1991**, *5*, 399.
[24] D. Mohan, C. U. Pittman, P. H. Steele, *Energy Fuels* **2006**, *20*, 848.
[25] T. A. Milne, F. Agblevor, M. Davis, S. Deutch, D. Johnson in *Developments in Thermal Biomass Conversion* (Eds.: A. V. Bridgwater, D. G. B. Boocock), Blackie Academic and Professional, London, **1997**, p. 409.
[26] S. Czernik, A. V. Bridgwater, *Energy Fuels* **2004**, *18*, 590.
[27] C. E. Wyman, *Annu. Rev. Energy Environ.* **1999**, *24*, 189.
[28] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapple, M. Ladisch, *Bioresour. Technol.* **2005**, *96*, 673.
[29] L. T. Fan, M. M. Gharpuray, Y. H. Lee, *Cellulose Hydrolysis*, Springer, Berlin, **1987**.
[30] N. S. Mosier, C. M. Ladisch, M. R. Ladisch, *Biotechnol. Bioeng.* **2002**, *79*, 610.
[31] US Department of Energy "Feedstock Composition Gallery" US Department of Energy, **2005** (http://www.eere.energy.gov/biomass/feedstock glossary.html).
[32] D. C. Elliott, A. Oasmaa, *Energy Fuels* **1991**, *5*, 102.
[33] C. L. Peterson in *The Biodiesel Handbook* (Eds.: G. Knothe, J. Krahl, J. V. Gerpen), AOCS Press, Champaign, IL, **2005**.
[34] D. R. Erickson, E. H. Pryde, O. L. Brekke, T. L. Mounts, R. A. Falb, *Handbook of Soy Oil Processing and Utilization*, American Soybean Association and the American Oil Chemist's Society, St. Louis, Missouri, and Champaign, IL, **1980**.

[35] "Urban Waste Grease Resource Assessment": G. Wiltsee, National Renewable Energy Laboratory, Report No. NREL/SR-570-26141, **1998** (http://www.osti.gov/bridge).
[36] G. Knothe, J. Krahl, J. V. Gerpen, *The Biodiesel Handbook*, AOCS Press, Champaign, IL, **2005**.
[37] F. Ma, M. A. Hanna, *Bioresour. Technol.* **1999**, *70*, 1.
[38] A. Corma, P. J. Miguel, A. V. Orchilles, *J. Catal.* **1994**, *145*, 171.
[39] A. Corma, *J. Catal.* **2003**, *216*, 298.
[40] A. Corma, *Chem. Rev.* **1995**, *95*, 559; A. Corma, V. Fornés, E. Ortega, *J. Catal.* **1985**, *92*, 284.
[41] A. Chica, A. Corma, *J. Catal.* **1999**, *187*, 167.
[42] A. Corma, M. J. Diaz-Cabanas, J. L. Jorda, C. Martinez, M. Molinell, *Nature* **2006**, *443*, 842.
[43] K. G. Strohmaier, D. E. Vaughan, *J. Am. Chem. Soc.* **2003**, *125*, 16035.
[44] M. A. Camblor, A. Corma, A. Mifsud, J. Pérez-Pariente, S. Valencia, *Stud. Surf. Sci. Catal.* **1997**, *105*, 341.
[45] W. Adam, A. Corma, T. I. Reddy, M. Renz, *J. Org. Chem.* **1997**, *62*, 3631.
[46] A. V. Bridgwater, *Appl. Catal. A* **1994**, *116*, 5.
[47] N. Y. Chen, J. T. F. Degnan, L. R. Koenig, *Chemtech* **1986**, *16*, 506.
[48] A. Corma, G. W. Huber, L. Sauvanaud, P. O'Connor, *J. Catal.* **2007**, *247*, 307.
[49] P. Cheung, A. Bhan, G. J. Sunley, E. Iglesia, *Angew. Chem.* **2006**, *118*, 1647; *Angew. Chem. Int. Ed.* **2006**, *45*, 1617.
[50] A. G. Gayubo, A. T. Aguayo, A. Atutxa, R. Aguado, M. Olazar, J. Bilbao, *Ind. Eng. Chem. Res.* **2004**, *43*, 2619.
[51] G. J. Hutchings, P. Johnston, D. F. Lee, A. Warwick, C. D. Williams, M. Wilkinson, *J. Catal.* **1994**, *147*, 177.
[52] A. Corma, B. W. Wojciechowski, *Catal. Rev. Sci. Eng.* **1985**, *27*, 29.
[53] S. Senger, L. Radom, *J. Am. Chem. Soc.* **2000**, *122*, 2613.
[54] C. Walling, L. Bollyky, *J. Am. Chem. Soc.* **1961**, *83*, 2968.
[55] J. Wristers, *J. Am. Chem. Soc.* **1975**, *97*, 4312.
[56] A. G. Gayubo, A. T. Aguayo, A. Atutxa, R. Aguado, J. Bilbao, *Ind. Eng. Chem. Res.* **2004**, *43*, 2610.
[57] A. G. Gayubo, A. T. Aguayo, A. Atutxa, B. Valle, J. Bilbao, *J. Chem. Technol. Biotechnol.* **2005**, *80*, 1244.
[58] R. M. Gallivan, P. K. Mattschei (American Can Company, USA), US Patent 4233465, **1980**.
[59] H. L. Chum, S. K. Black (Midwest Research Institute, USA), US Patent 4942269, **1990**.
[60] J. D. Adjaye, S. P. R. Katikaneni, N. N. Bakhshi, *Fuel Process. Technol.* **1996**, *48*, 115.
[61] S. P. R. Katikaneni, J. D. Adjaye, N. N. Bakhshi, *Energy Fuels* **1995**, *9*, 1065.
[62] R. K. Sharma, N. N. Bakhshi, *Energy Fuels* **1993**, *7*, 306.
[63] S. T. Srinivas, A. K. Dalai, N. N. Bakhshi, *Can. J. Chem. Eng.* **2000**, *78*, 343.
[64] R. W. Thring, S. P. R. Katikaneni, N. N. Bakhshi, *Fuel Process. Technol.* **2000**, *62*, 17.
[65] C.-C. Chang, S.-W. Wan, *Ind. Eng. Chem.* **1947**, *39*, 1543.
[66] D. G. Lima, V. C. D. Soares, E. B. Ribeiro, D. A. Carvalho, E. C. V. Cardoso, F. C. Rassi, K. C. Mundim, J. C. Rubim, P. A. Z. Suarez, *J. Anal. Appl. Pyrolysis* **2004**, *71*, 987.
[67] T. A. Milne, R. J. Evans, N. Nagle, *Biomass* **1990**, *21*, 219.
[68] F. A. Twaiq, N. A. M. Zabidi, S. Bhatia, *Ind. Eng. Chem. Res.* **1999**, *38*, 3230.
[69] T. Y. Leng, A. R. Mohamed, S. Bhatia, *Can. J. Chem. Eng.* **1999**, *77*, 156.
[70] M. J. McCall, T. L. Marker, J. Petri, D. Mackowiak, S. Czernik, D. Elliott, D. Shonnard, *Abstracts of the 230th American Chemical Society National Meeting* (Washington DC, USA), **2005**.
[71] W. P. Hettinger, *Catal. Today* **1999**, *53*, 367.
[72] W. P. Hettinger, S. M. Kovach, J. F. Hoffman (Ashland Oil, USA), US Patent 4450241, **1984**.
[73] W. P. Hettinger, S. M. Kovach, J. F. Hoffman (Ashland Oil, USA), US Patent 4425259, **1984**.
[74] J. A. Guyer (Phillips Petroleum Company, USA), US Patent 2518775, **1950**.
[75] A. Corma, G. Huber, L. Sauvanaud, P. O'Connor (BioeCon), European Patent Application 061189825-1211, **2006**.
[76] Y.-H. E. Sheu, R. G. Anthony, E. J. Soltes, *Fuel Process. Technol.* **1988**, *19*, 31.
[77] S. Ramanathan, S. T. Oyama, *J. Phys. Chem.* **1995**, *99*, 16365.
[78] D. C. Elliott, G. G. Neuenschwander in *Developments in Thermochemical Biomass Conversion*, *Vol. 1* (Eds.: A. V. Bridgwater, D. G. B. Boocock), Blackie Academic and Professional, London, **1996**, p. 611.
[79] E. Furimsky, *Appl. Catal. A* **2000**, *199*, 147.
[80] M. Ferrari, R. Maggi, B. Delmon, P. Grange, *J. Catal.* **2001**, *198*, 47.
[81] A. Centeno, E. Laurent, B. Delmon, *J. Catal.* **1995**, *154*, 288.
[82] E. Laurent, B. Delmon, *Appl. Catal. A* **1994**, *109*, 77.
[83] E. Laurent, B. Delmon, *Appl. Catal. A* **1994**, *109*, 97.
[84] E. Laurent, B. Delmon, *J. Catal.* **1994**, *146*, 281.
[85] D. C. Elliott, E. G. Baker, J. Piskorz, D. S. Scott, Y. Solantausta, *Energy Fuels* **1988**, *2*, 234.
[86] J. Piskorz, P. Majerski, D. Radlein, D. S. Scott, *Energy Fuels* **1989**, *3*, 723.
[87] P. M. Train, M. T. Klein, *Fuel Sci. Technol.* **1991**, *9*, 193.
[88] M. A. Ratcliff, D. K. Johnson, F. L. Posey, H. L. Chum, *Appl. Biochem. Biotechnol.* **1988**, *17*, 151.
[89] A. Oasmaa, R. Alen, D. Meier, *Bioresour. Technol.* **1993**, *45*, 189.
[90] J. S. Shabtai, W. W. Zmierczak, E. Chornet (The University of Utah Research Foundation, USA), US Patent 5959167, **1999**.
[91] "Lignin Process Design Confirmation and Capital Cost Evaluation": L. Montague, National Renewable Energy Laboratory, Report No. NREL/SR-510-31579, **2003** (http://www.osti.gov/bridge).
[92] J. E. Miller, L. Evans, A. Littlewolf, D. E. Trudell, *Fuel* **1999**, *78*, 1363.
[93] A. Wong, E. Hogan in *Biomass: A Growth Opportunity in Green Energy and Value-Added Products* (Eds.: R. P. Overend, E. Chornet), Elsevier Science, Oakland, CA, **1999**, p. 837.
[94] M. Stumborg, A. Wong, E. Hogan, *Bioresour. Technol.* **1996**, *56*, 13.
[95] Hydrotreating of Vegetable Oil/Vacuum Gas Oil Mixtures: G. W. Huber, R. S. Martinez, A. Corma, *Appl. Catal. A*, in press.
[96] W. K. Craig, D. W. Soveran, US Patent 4992605, **1991**.
[97] J. Monnier, G. Tourigny, D. W. Soveran, A. Wong, E. N. Hogan, M. Stumborg (Natural Resources Canada, USA), US Patent 5705722, **1998**.
[98] D. C. Elliott, G. F. Schiefelbein, *Am. Chem. Soc. Div. Fuel Chem. Prepr. Pap.* **1989**, *34*, 1160.