▀▀▀▀ **CHAPTER 8**

Pyrolysis Oils From Biomass and Their Upgrading

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8.1 INTRODUCTION

The ongoing energy crisis and the accompanying environmental concerns, have caused the development of intense interest toward alternative fuels based on sources other than petroleum. Bio-oil is a renewable liquid fuel, having negligible contents of sulfur, nitrogen, and ash, and is widely recognized as one of the most promising renewable fuels that may one day replace fossil fuels. Fast pyrolysis of biomass technologies for the production of bio-oil have been developed extensively in recent years. The conversion of solid biomass into bio-oil using fast pyrolysis is carried out by the rapid (a few seconds) raising of temperature to around 450–550°C under atmospheric pressure and anaerobic conditions. The resulting products are short-chain molecules, which should be rapidly quenched to liquids. However, such biomass-based bio-oils are of high oxygen content, high viscosity, thermal instability, corrosiveness, and chemical complexity. These characteristics create many obstacles to the applications of bio-oils, precluding it from being used directly as a liquid fuel.[1] Consequently, bio-oils need to be upgraded to improve its fuel properties. Current upgrading techniques are hydrogenation, catalytic cracking, steam reforming, emulsification, converting into stable oxygenated compounds, extracting chemicals from the bio-oils. In this chapter, the preparation and properties of bio-oils will be reviewed with emphasis on advanced upgrading techniques.

8.2 BIO-OIL PREPARATION

Pyrolysis is the thermal decomposition of a material in the absence of oxygen. For biomass, the product of pyrolysis is a mixture of solids (char), liquids (bio-oil),

Table 8.1   Range of Typical Fast-Pyrolysis Conditions

Temperature (°C)	450–550
Gas residence time (s)	0.5–2
Particle size (mm)	0.2–2
Moisture (wt%)	2–12
Cellulose (wt%)	45–55
Ash (wt%)	0.5–3
Yields (wt%)	
Organic liquid	60–75
Water	10–15
Char	10–15
Gas	10–20

and gas (methane, carbon monoxide, and carbon dioxide). The pyrolysis processes are generally divided into "slow pyrolysis" and "fast pyrolysis." Just as its name implies, slow pyrolysis is operated by heating biomass to ∼500°C at a slow heating rate. The vapor residence time varies from 5 min to 30 min and the main product is charcoal.[2] On the contrary, fast pyrolysis is carried out by heating biomass feedstock at a rapid heating rate to around 450–550°C, followed by the rapid quenching of the product vapors to liquids. The aim of fast pyrolysis is to maximize the yields of bio-oil.
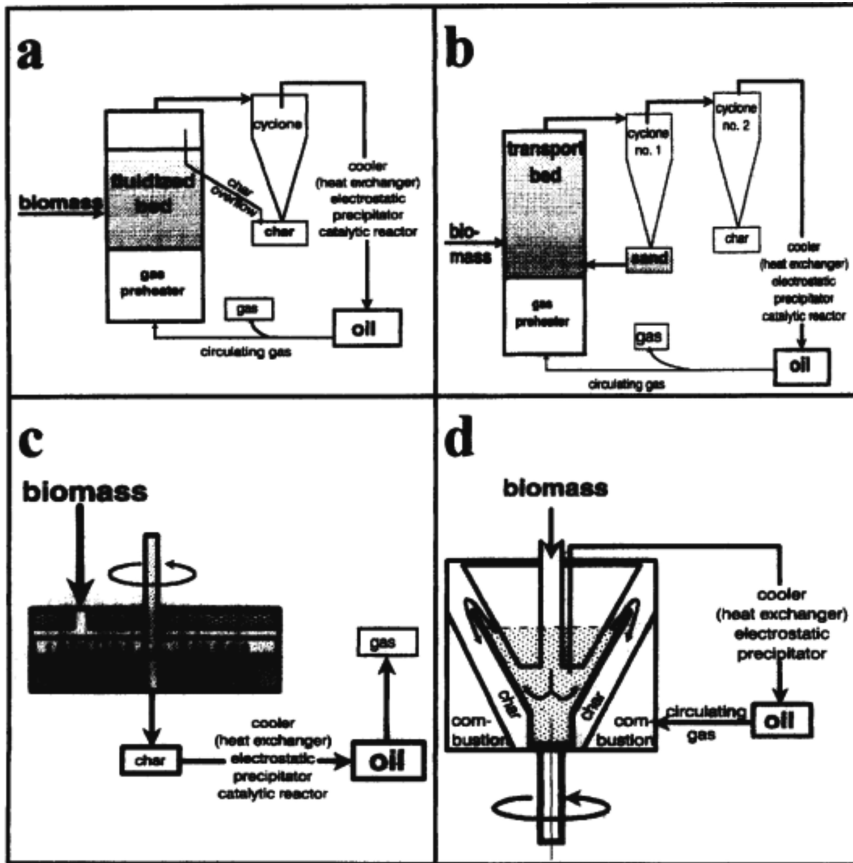
Currently, fast pyrolysis is the only feasible technology for the production of bio-oils at an industrial scale. To maximize the yields of bio-oil in a fast-pyrolysis process, various pyrolysis parameters such as temperature, heating rate, vapor residence time, feedstock properties, particle size, and moisture content, need to be optimized. Typical fast-pyrolysis conditions are shown in Table 8.1.[3]

Westerhof et al.[4] showed that the conventional view on pyrolysis taking place between 400 and 550°C with the aim to maximize oil yields must be reconsidered for temperatures below 400°C. Such temperatures have been shown to produce bio-oils of better quality for certain applications. Another factor determining the efficiency of such processes is the ash content of the feedstock biomass with dominant effects on the yield and composition of bio-oils.[3] In general, the yields of char and gas increase significantly for higher ash contents, while the yields of bio-oil decrease.

Present fast-pyrolysis reactors include bubbling fluidized-bed, circulating fluidized-bed, ablative, rotating cone, auger, and vacuum reactors. The major features of the first four reactors are listed in Table 8.2[2,5] and their schematic illustration is shown in Fig. 8.1.[6] The essential characteristics of a fast-pyrolysis reactor to maximize the yield of bio-oil are a very rapid heating rate, a reaction temperature of around 500°C, and a rapid quenching of the produced vapors.[3] With the development of fast-pyrolysis technologies, the primary method of heat transfer varies from solid–solid to gas–solid, and there is also a corresponding change of dominant mode of heat transfer from conduction to convection.[5]

Table 8.2 Summary of Characteristics of Some Common Pyrolysis Systems

Reactor Type	Ablative	Bubbling Fluidized Bed	Circulating Fluidized Bed	Rotating Cone
Carrier gas	No	Yes	Yes	No
Heating method	• Reactor wall/disc	• Heated recycle gas • Hot inert gas	• Particle gasification • Fire tubes	• Gasification of char to heat sand
Primary heat-transfer method	• Solid–solid	• Solid–solid • Gas–solid	• Solid–solid • Gas–solid	• Solid–solid • Gas–solid
Modes of heat-transfer (suggested)	–	• 95% conduction • 4% convection • 1% radiation	• 80% conduction • 19% convection • 1% radiation	• 95% conduction • 9% convection • 1% radiation
Main features	• Accepts large size feedstock • Very high mechanical char abrasion from biomass • Compact design • Heat supply problematical • Particulate transport gas not always required	• High heat-transfer rates • Heat supply to fluidizing gas or to bed directly • Limited char abrasion • Very good solids mixing • Particle size limit <2 mm in smallest dimension • Simple reactor configuration • Residence time of solids and vapors controlled by the fluidizing gas flow rate	• High heat-transfer rate • High char abrasion from biomass and char erosion leading to high char in product • Char/solid heat carrier separation required • Solid recycle required • Increased complexity of system • Maximum particle size up to 6 mm • Possible liquid cracking by hot solids • Possible catalytic activity from hot char • Greater reactor wear possible	• Centrifugal force moves heated sand and biomass • Small particle sizes needed

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Fig. 8.1 Schematic illustration of the reactor types for the fast pyrolysis of biomass: (a) bubbling fluidized bed; (b) circulating fluidized bed; (c) ablative pyrolysis; (d) rotating cone reactor.

8.3 BIO-OIL

8.3.1 Composition and Physicochemical Properties

There are big differences between bio-oil and petroleum-derived fuel, which can be shown in Table 8.3.[7]

8.3.1.1 Water The water content of bio-oils ranges between 15% and 30% depending on the feedstock and the operating conditions of the pyrolysis process. The presence of water has significant effects on the oil properties since it lowers its heating value and flame temperature. On a positive note, however, water reduces the viscosity of the oil, improving its fluidity leading to uniform combustion characteristics.

Table 8.3   A Comparison of Various Typical Properties of Wood Pyrolysis Bio-Oil and of Heavy Fuel Oil

Physical Property	Bio-Oil	Heavy Fuel Oil
Moisture content, wt%	15–30	0.1
pH	2.5	–
Specific gravity	1.2	0.94
Elemental composition, wt%		
C	54–58	85
H	5.5–7.0	11
O	35–40	1.0
N	0–0.2	0.3
Ash	0–0.2	0.1
HHV (higher heating value), MJ kg^{-1}	16–19	40
Viscosity (at 50°C), cP	40–100	180
Solids, wt%	0.2–1	1
Distillation residue, wt%	Up to 50	1

8.3.1.2 Oxygen   Bio-oil contains 35–40% oxygen as an integral part of the more than 300 chemical compounds present within. The distribution of these compounds can be altered by various biomass feedstocks and pyrolysis process conditions. The high oxygen content in bio-oil represents the biggest difference between bio-oils and hydrocarbon fuels. Due to the high oxygen content, bio-oils have about 50% lower energy density than conventional fuel oils[7] and are immiscible with hydrocarbon fuels. Moreover, bio-oils contain abundant reactive oxygen-containing functional groups such as carbonyl, carboxyl, methoxyl, and hydroxyl groups. Thus, bio-oils are acidic and unstable.

8.3.1.3 Viscosity   The viscosity of bio-oils can vary widely from 35 cP to 1000 cP at 40°C depending on the biomass source and operating conditions. The major factors affecting viscosity are temperature and water content. The temperature dependence of the viscosity becomes more pronounced when the viscosity of the oil increases. Minor factors that may affect oil viscosity were their acidity, particulates content, and micro-/nanostructure.[8] The viscosity of bio-oils can be reduced by the addition of a polar solvent such as methanol.

8.3.1.4 Acidity   The pH value of fast-pyrolysis bio-oils is low ranging between 2 and 3. Such acidity values are mainly due to the presence of large amounts of volatile acids (60–70%), with acetic and formic acids being the main constituents. Other groups of compounds present in fast-pyrolysis bio-oils, that also affect their acidity, include phenolics, fatty and resin acids, and hydroxy acids (e.g., colic acid).[9] The acids in biomass fast-pyrolysis oils are mainly derived from the degradation of hemicelluloses in wood. The high acidity of bio-oils can lead to severe corrosion of the storage containers and transportation lines such as carbon steel and aluminum.[10]

For these reasons bio-oils should be stored in acid-resistant vessels (e.g., stainless steel or polyolefin lined).

8.3.1.5 Heating Value Due to its high oxygen content and the presence of a significant amount of water, bio-oils are of lower heating value ($16–19\,MJ\,kg^{-1}$), compared to their fossil fuel counterparts ($42–44\,MJ\,kg^{-1}$).

8.3.2 Compositions of Bio-Oil

Bio-oil is a complicated mixture of highly oxygenated organic compounds including aldehydes, carboxylic acids, phenols, sugars, and aliphatic and aromatic hydrocarbons. A typical example of compositions of bio-oil is listed in Table 8.4.[11]

Understanding the composition of bio-oils is extremely valuable if one is to evaluate the bio-oils' stabilities, properties, and toxicity.[12] For example, raw bio-oils may contain some highly reactive oxygenated organic compounds which make pyrolysis oils unstable. During storage, chemical reactions can occur between these compounds to form larger molecules, resulting in increased viscosities over time.[7]

Mullen and Boateng[12] studied the chemical composition of bio-oils produced by fast pyrolysis of switchgrass and alfalfa stems. It was found that more nitrogen-containing compounds were found in the alfalfa stem derived bio-oils with

Table 8.4   Yields of Bio-Oil Compounds from the Pyrolysis of Southern Pine Wood

Compound	Yield (wt%)
Hydroxyacetaldehyde	3.07
Acetic acid	1.87
Hydroxyacetone	1.36
2-Furaldehyde	0.34
Furfuryl alcohol	0.37
Furan-(5H)-2-one	1.10
Phenol	0.04
Guaiacol	0.41
o-Cresol	0.05
p-Cresol	0.07
Levoglucosenone	0.19
4-Methyl guaiacol	0.65
2,4-Dimethyl phenol	0.13
4-Ethyl-guaiacol	0.12
Eugenol	0.22
5-(Hydroxy-methyl)-furaldehyde-(2)	0.99
Catechol	0.62
Isoeugenol	0.51
Vanillin	0.35
Acetoguaiacone	0.23
Guaiacyl acetone	0.45
Levoglucosan	4.86

correspondingly higher nitrogen content of the alfalfa stems biomass versus the switchgrass. Nitrogen-containing compounds found in the alfalfa stems bio-oils are 2,2,6,6-tetramethylpiperidone, benzylnitrile, pyridinol, indole, and methylindole. But for these nitrogen-containing compounds, only benzylnitrile was found in switchgrass.

A large amount of the water-soluble compounds is mainly derived from the decomposition of cellulose and hemicellulose.[13] Switchgrass biomass contains higher levels of cellulose and hemicelluloses rather than the alfalfa stems explaining why higher concentration of the water solubles can be determined for switchgrass-derived bio-oil.

8.4 UPGRADING OF BIO-OILS

While bio-oil production has achieved commercial success, overall poor character-istics limits the application as transportation fuels. The high oxygen and water contents of crude bio-oil are two key issues that make bio-oils unstable with high viscosity, thermal instability, corrosive characteristics, and chemical complexity. Therefore, it is imperative to develop efficient techniques to upgrade bio-oils. Nowadays, bio-oil upgrading techniques include hydrogenation, catalytic cracking, steam reforming, emulsification, converting them into stable oxygenated com-pounds, extracting chemicals from the bio-oils. In the following sections, such modern refining treatments are described in detail.

8.4.1 Hydrogenation

Hydrogenation is considered to be amongst the most effective method for bio-oil upgrading.[13] Typical catalysts used in the conventional hydrogenation process are metal sulfide catalysts such as cobalt or nickel doped molybdenum sulfides. However, these catalysts are sensitive to water and are readily poisoned by high concentrations of oxygen-containing compounds.[14] In addition, there are some drawbacks in the hydrogenation process, such as target products contaminated by sulfur, coke accumulation, and water-induced catalyst deactivation. Therefore, new catalysts are under development with the goal of increasing their catalytic selectivity and product yields.

In the conversion of aqueous phenolic bio-oil components to alkanes, Zhao et al.[15] developed a new and efficient (nearly 100% cycloalkane and methanol yields) catalytic route based on bifunctional catalysts combining Pd/C-catalyzed hydrogenation with H_3PO_4-catalyzed hydrolysis/dehydration. The final alkane products were easily separated from the aqueous phase. Moreover, Zhao et al.[14] developed a new green route based on low-cost RANEY® Ni catalysts and an environmentally friendly Brønsted solid acid, that is, Nafion/SiO₂. This process was claimed to convert the aqueous phenolic monomers (phenols, guaiacols and syrin-gols) within bio-oil to hydrocarbons and methanol. The new catalyst combination opens the possibility for the application in hydrodeoxygenation and hydrogenation of lignin-derived bio-products.

Due to the presence of many unstable compounds, bio-oils are of poor stability with aldehydes being the most reactive functional groups present in them. Consequently, it is essential to convert aldehydes to more stable compounds. A homogeneous catalyst based on ruthenium, $(RuCl_2(PPh_3)_3)$ was prepared for the hydrogenation of bio-oils, with a very significant catalytic performance on aldehydes and ketone hydrogenation in a single-phase system.[16] In this work, it was found that most of the aldehydes in a bio-oil fraction extracted with ethyl acetate could be converted to the corresponding alcohols under mild conditions ($70°C$, 3.3 MPa H_2). Thus the stability of bio-oils and as such the fuel quality could be improved.

Ionic liquids themselves are known to exhibit catalytic effect and be used as solvents and as catalysts for chemical transformations. Moreover, chemical reactions can be performed under mild conditions in ionic liquids. Yan et al.[17] reported the hydrodeoxygenation of lignin-derived phenols into alkanes by using metal nanoparticle catalysts combined with ionic liquids with Brønsted acidity, under mild conditions. This bifunctional system was used to transform a variety of phenolic compounds in both [bmim][BF$_4$] and [bmim][Tf$_2$N]. Only the Rh-nanoparticle containing system was able to convert the branched phenols into alkanes in high yields. Compared to previous systems with metal sulfite or with mineral acid-/supported metal catalysts in water, this system was found to be an efficient and less energy-demanding process to upgrade lignin derivatives.

Another novel strategy used to improve the properties of bio-oils involves hydrotreating the raw bio-oil under mild conditions reducing carboxylic acid compounds to alcohols which could subsequently be esterified with unconverted acids within the bio-oil.[18,19] The traditional severe conditions required for a hydrotreatment of bio-oil (high temperature $300–400°C$ and high hydrogen pressure 10–20 MPa) could thus be avoided. For example, bio-oil was upgraded as it emerged from the fast/vacuum pyrolysis of biomass over MoNi/γ-Al$_2$O$_3$ catalysts. The resulting GC-MS spectrometric analyses showed that both hydrotreatment and esterification had occurred over the 0.06MoNi/γ-Al$_2$O$_3$(873) catalyst during the upgrading process. Furthermore, the data showed that the reduced Mo-10Ni/γ-Al$_2$O$_3$ catalyst had the highest activity with 33.2% acetic acid conversion and the ester compounds in the upgraded bio-oil was found to be increased threefold.

Murata et al.[20] have reported that the pretreatment of cellulose in 1-hexanol at 623 K, followed by hydrocracking, catalyzed by Pt/H-ZSM-5(23) at 673 K, yielded up to 89% of C2–C9 alkanes with only 6% of CH$_4$/CO$_x$. The combination of alcohol pretreatment and Pt/H-ZSM-5-catalyzed hydrocracking was effective for the reaction. The findings suggested that the alcohol treatment could lead to lowering of the molecular weight of the cellulosic material, producing oxygenated intermediates such as monosaccharides and disaccharides, which could be further converted to C2–C9 alkane products by successive hydrocracking and condensation.

Pyrolytic lignins affect the bio-oil properties such as high viscosity, high reactivity, and low stability, which is difficult for bio-oil upgrading due to their nonvolatility and thermal instabilities. Tang et al.[21] converted pyrolytic lignins to stable liquid compounds through hydrocracking at $260°C$ in supercritical ethanol under a hydrogen atmosphere by the use of Ru/ZrO$_2$/SBA-15 or

$Ru/SO_4^{2-}/ZrO_2/SBA$-15 catalyst. The accumulated data demonstrated that under supercritical ethanol conditions, $Ru/ZrO_2/SBA$-15 and $Ru/SO_4^{2-}/ZrO_2/SBA$-15 were effective catalysts converting pyrolytic lignins to stable monomers such as phenols, guaiacols, anisoles, esters, light ketones (with the C_5–C_6 ring), alcohols, long-chain alkanes (C_{13}–C_{25}).

A potential way of valorizing bio-oils as a fuel is their cohydrotreatment with petroleum fractions. To meet environmental fuel standards, there is a need to study the simultaneous hydrodeoxygenation and hydrodesulfurization reactions before considering such a cotreatment. Pinheiro et al.[22] investigated the impact of oxygenated compounds from lignocellulosic biomass pyrolysis oils on gas oil hydrotreatment. They found that 2-propanol, cyclopentanone, anisole, and guaiacol were not inhibitors of catalytic performances under such operating conditions. On the contrary, propanoic acid and ethyl decanoate had an inhibiting effect on hydrodesulfurization, hydro-denitrogenation, and aromatic ring hydrogenation reactions.

8.4.2 Catalytic Cracking

Bio-oil vapors can be upgraded via catalytic deconstruction to hydrocarbons with their oxygen being removed as H_2O, CO_2, or CO in the absence of added hydrogen. Zeolites have been found to be promising catalysts for such upgrading. French and Czernik[23] have evaluated the catalytic performance of a set of commercial and laboratory-synthesized catalysts for upgrading of bio-oils via this route. In this effort, ZSM-5 type catalysts performed the best while larger-pore zeolites presented less deoxygenation activity. The highest yield of hydrocarbons (approximately 16 wt%, including 3.5 wt% of toluene) was obtained over nickel, cobalt, iron, and gallium-substituted ZSM-5 materials.

The presence of oxygenated compounds in the pyrolysis products results in a high level of acidity, which can lead to corrosion on internal combustion engines. Quirino et al.[24] studied the influence of alumina catalysts doped with tin and zinc oxides in the soybean oil pyrolysis reaction. It was observed that the presence of alumina catalysts doped with tin and zinc oxides during the pyrolysis can decrease undesirable carboxylic acid content up to 30%. Higher deoxygenating activities were achieved over solid $(SnO)_1(ZnO)_1(Al_2O_3)_8$ catalyst. Pyrolysis of vegetable oils is an acceptable process to convert vegetable oils into gasoline and diesel fuel. A. Demirbas[25] had documented that a gasoline like material can be obtained from sunflower oil via a pyrolysis process in the presence of Al_2O_3 catalyst treated with sodium hydroxide. The highest yield of gasoline was found to be 53.8% based on sunflower oil in the presence of 5% of catalyst.

8.4.3 Steam Reforming

Catalytic steam reforming of bio-oil offers a feasible option to produce hydrogen sustainably. Many literature accounts provide new developments in the area of hydrogen production via steam reforming of bio-oil in recent years. But due to the complexity of bio-oil and carbon deposition on the catalyst surface during the

reaction process, currently research studies mainly focus on the steam reforming of model compounds in bio-oil and reforming catalysts.[26]

Xu et al.[27] studied hydrogen production via catalytic steam reforming of bio-oil in a fluidized-bed reactor and selected nickel-based catalyst (Ni/MgO) as the reforming catalyst. It was found that the carbon deposition was not the main reason for catalyst deactivation. In fact, the fresh catalyst deactivation can be explained by the NiO grain sintered on the support surface.

Li et al.[28] applied the Ni/Mg/Al catalysts to the steam reforming of tar from pyrolysis of biomass. The optimized Ni/Mg/Al catalyst with a composition of Ni/Mg/Al=9/66/25 was found to exhibit high activity with high resistance to coke deposition, in particular, to coke formed by the disproportionation of CO which is an important product of the steam-reforming process.

Kan et al.[29] developed an efficient method for the production of hydrogen from the crude bio-oil via an integrated gasification-electrochemical catalytic reforming (G-ECR) process using a NiCuZnAl catalyst. The accumulated data showed that a maximum hydrogen yield of 81.4% and carbon conversion of 87.6% were obtained via the integrated G-ECR process. Compared to direct reforming of crude bio-oil, the deactivation of the catalyst was significantly suppressed by using the integrated gasification-reforming method. It was thus concluded that the integrated G-ECR process could be a potentially useful route to produce hydrogen from crude bio-oil.

8.4.4 Emulsification

One of the methods used to upgrade bio-oil to transportation fuels is to combine the bio-oil with other fuel sources by forming an emulsion. This results in a liquid fuel of a low viscosity, high calorific value, and high cetane number. It was observed that the emulsion of bio-oil with diesel fuel, at a suitable volume ratio, can lead to more stable emulsions compared to the original bio-oil.[30, 31] A stable bio-crude oil/diesel oil emulsion can be seen from Fig. 8.2.[30] The viscosity of emulsified bio-oil was substantially lower than the viscosity of bio-oil itself and the corrosivity of the emulsified fuels was also found to be reduced.[32]

Crossley et al.[33] reported a family of solid catalysts that can simultaneously stabilize water–oil emulsions and catalyze reactions at the liquid/liquid interface. By depositing palladium onto carbon nanotube–inorganic oxide hybrid nanoparticles, a biphasic hydrodeoxygenation and condensation catalytic reaction occurred. To illustrate the application of the catalytic nanohybrids in emulsions, a hydrodeoxygenation reaction was examined at the water/oil interface with vanillin as a test substrate and Pd-containing nanohybrid as the catalyst. During the reaction, different products were obtained depending on the reaction temperature and the degrees of hydrogenation, hydrogenolysis, and decarbonylation reactions. At 100°C, the primary product was found to be vanillin alcohol that remained within the aqueous phase. As reaction time progressed, the vanillin alcohol was consumed by hydrogenolysis to form p-creosol, which was found to migrate to the organic phase upon formation, preventing further conversion. At 250°C, the dominant reaction is the decarbonylation of the aldehyde group, leading primarily to guaiacol
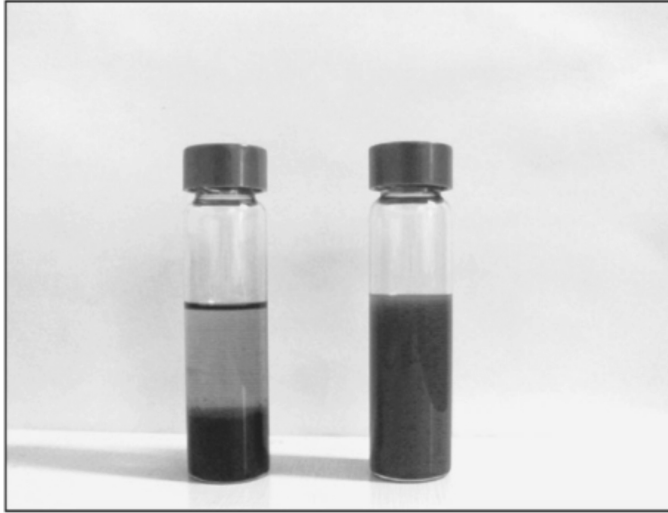
**Fig. 8.2** Bio-crude oil/diesel oil mixture (a) and emulsion (b)

which was also found to migrate to the organic phase. The carbon chains migrate to the organic phase after growing long enough to get the desirable products, whereas the shorter chains remained in the aqueous phase for further growth. This data illustrates that the concept of simultaneous reactions and separation of the intermediate products is possible since sequential reactions can be conducted within a single reactor.

Garcia-Perez et al.[34] reported on the fuel properties of fast-pyrolysis oil/bio-diesel blends. Commercial biodiesels are of lower oxidation stability and comparatively poor cold flow properties. When pyrolysis oil was blended with bio-diesel, the bio-diesel could extract selectively some of the fractions of the bio-oil, particularly those high in phenolic compounds. This could partially use bio-oils as additives for transportation fuels, while the oxidation stability of the bio-diesel could also be improved since phenolic compounds are known to be excellent antioxidants. However, other fuel properties such as solid residue and the acid number were found to deteriorate. This is because the solubilization of lignin-derived oligomers within the bio-diesel resulted in an increase of the solid residue. Consequently, solid residues need to be carefully monitored. Moreover, the solubility of bio-oil in bio-diesel was also found to be improved on addition of ethyl acetate.

8.4.5 Converting into Stable Oxygenated Compounds

Most bio-oil upgrading methods are based on deoxygenation of the crude bio-oils to reduce its oxygen content. Such processes are known to increase the upgrading costs while consuming large amounts of hydrogen. A useful approach is to convert
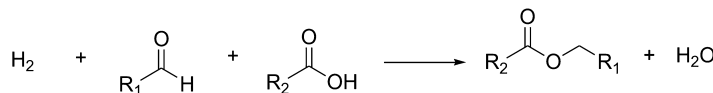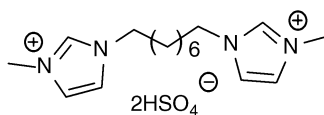
Scheme 8.1

chemically unstable and corrosive oxygenated components (acids, phenols, alde-hydes) into stable and flammable oxygenated compounds (esters, alcohols, and ketones). These stable oxygenated compounds can be developed into oxygenated fuels and can also be added into petroleum fuel to raise its combustion efficiency.

This upgrading approach can be classified based on two reaction categories: esterification and ketonization reactions. As far as esterification reactions are concerned, Tang et al.[35] designed hydrogenation–esterification of aldehydes and acids (Scheme 8.1) over a 5%Pt/HZSM-5 and a 5%Pt/Al$_2$(SiO$_3$)$_3$ at 150°C and 1.5 MPa of H$_2$ pressure. Acetaldehyde and butyl aldehyde were reduced *in situ* to ethanol and butanol, respectively, then found to react with acetic acid forming ethyl acetate and butyl acetate.

Peng et al.[36] upgraded the pyrolysis bio-oil from rice husks in sub- and super-critical ethanol using HZSM-5 as the catalyst. The data showed that a supercritical upgrading process was superior to a subcritical upgrading process. Acidic HZSM-5 was found to promote esterification reactions converting acids into a wide range of esters in supercritical ethanol. During supercritical upgrading, stronger acidic HZSM-5 (low Si/Al ratio) can more effectively facilitate the cracking of heavy components of crude bio-oil. Similar results were also obtained when the pyrolysis bio-oil was upgraded in supercritical ethanol using aluminum silicate as the catalyst.[37] Acidic aluminum silicate can facilitate the esterification to convert most carboxylic acids contained within the crude bio-oil into esters.

Upgrading bio-oil by catalytic esterification over solid acid (40SiO$_2$/TiO$_2$–SO$_4{}^{2-}$) and solid base (30K$_2$CO$_3$/Al$_2$O$_3$–NaOH) catalysts can lower the bio-oil's dynamic viscosity, enhance fluidity, and improve stability over time. The solid acid catalyst was found to achieve higher catalytic activity upon esterification than the solid base catalyst.[38]

Xiong et al.[39] synthesized a dicationic ionic liquid C$_6$(mim)$_2$-HSO$_4$ (Fig. 8.3) and used it as the catalyst to upgrade bio-oil through the esterification reaction of organic acids and ethanol at room temperature. It was found that no coke and deactivation of the catalyst were observed. The yield of upgraded oil reached 49%, and its properties were significantly improved with higher heating value of

Fig. 8.3   Structure of ionic liquid C$_6$(mim)$_2$-HSO$_4$.
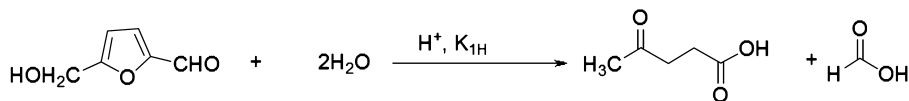
Scheme 8.2

$24.6\,MJ\,kg^{-1}$, an increase of pH value to 5.1, and a decrease of moisture content to 8.2 wt%. The data showed that organic acids could be successfully converted into esters and that the dicationic ionic liquid can facilitate the esterification to upgrade bio-oil.

Wang et al.[40] upgraded bio-oil by catalytic esterification over 732- and NKC-9-type ion-exchange resins. It was shown that the acid number of bio-oil was significantly reduced by 88.54 and 85.95% after bio-oil was upgraded over 732 and NKC-9 resins respectively, which represented that organic acids were converted to neutral esters. The heating values increased significantly, while the moisture contents and the densities decreased. Specifically, the viscosity was lowered from $81.27\,mm^2\,s^{-1}$ to $2.45\,mm^2\,s^{-1}$ (at 40°C) when bio-oil was upgraded over NKC-9-type ion-exchange resin. It was observed that the stability of upgraded bio-oil was improved.

With respect to the ketonization reaction, Deng et al.[41] proposed a novel method to upgrade the acid-rich phase of bio-oil via ketonic condensation over weak base CeO_2 catalysts. Most acetic acid was effectively transformed to acetone in model reactions:

$$2RCOOH \rightarrow RCOR + H_2O + CO_2.$$

During this reaction, furfural is known to exhibit significant deactivation. Consequently it is recommended to remove or decompose furans before upgrading the feed from bio-oil by hydrothermal treatment,[42] which is presented in Scheme 8.2.

Gärtner et al.[43] showed that ceria-zirconia was an effective catalyst for the upgrading of acids in bio-oils to produce larger ketones through ketonization reactions. At the same time, it was also found that esterification was an important side reaction that could compete with ketonization when alcohols were present in the hydrophobic mixture. Since esterification cannot be avoided over ceria-zirconia, it was suggested that esters could be converted to the desired ketones over the same catalyst through the direct ketonization, without the need to add water to the feed for the hydrolysis of the ester.

8.4.6   Chemicals Extracted From Bio-Oils

With the development of new pyrolysis technologies many studies have been carried out to increase the yields of the target products in bio-oils through specific pretreatments of biomass or catalytic pyrolysis of biomass. The pyrolytic treatment of biomass in the presence of various metal oxides is one such example. Six nano-structured metal oxides (MgO, CaO, TiO_2, Fe_2O_3, NiO, and ZnO) were used as

catalysts to upgrade biomass fast-pyrolysis vapors aimed at maximizing the forma-
tion of various valuable chemicals.[44] CaO was found to significantly decrease the
yields of phenols and anhydrosugars, and eliminate the acids, while also increasing
the formation of cyclopentanones, hydrocarbons, and several lighter products such as
acetaldehyde, acetone, 2-butanone, and methanol. ZnO was also a mild catalyst
which only slightly altered the pyrolytic product composition. The remaining four
catalysts (MgO, TiO_2, Fe_2O_3, NiO) all decreased the yield of linear aldehydes
dramatically while increasing the yields of ketones and cyclopentanones. With the
exception of NiO, they also decreased the anhydrosugars content. Furthermore,
Fe_2O_3 was found to promote the production of various hydrocarbons.

In general, the fast pyrolysis of cellulose generates low yields of furan com-
pounds. Lu et al.[45] studied the catalytic pyrolysis of cellulose with three sulfated
metal oxides (SO_4^{2-}/TiO_2, SO_4^{2-}/ZrO_2, and SO_4^{2-}/SnO_2) in order to obtain high
yields of light furan compounds. The oligomers were cracked into monomeric
compounds over these catalysts through catalytic cracking of the pyrolysis vapors.
The final primary pyrolytic products (such as levoglucosan and hydroxyacetalde-
hyde) were found to be decreased or completely eliminated while the yields of three
light furan compounds (5-methyl furfural, furfural, and furan) increased greatly. The
catalysts presented different selectivities on the targeted products with the formation
of 5-methyl furfural favored by SO_4^{2-}/SnO_2, furfural favored by SO_4^{2-}/TiO_2, and
furan favored by SO_4^{2-}/ZrO_2, respectively.

Lu et al.[46] found that Pd/SBA-15 catalysts could remarkably promote the
formation of monomeric phenolic compounds when biomass fast-pyrolysis vapors
were catalytically cracked over these catalysts. The Pd/SBA-15 catalysts presented
cracking capabilities to convert the lignin-derived oligomers to monomeric phenolic
compounds and further convert them to phenols. The removal of carbonyl group and
unsaturated C–C bond from the phenolic compounds indicated that Pd/SBA-15
catalysts presented decarbonylation activity and might have some hydrotreating
capability.

Lin et al.[47] examined the direct deoxygenation effect of CaO on bio-oil during
biomass pyrolysis in a fluidized-bed reactor. It was shown that at a CaO/white pine
mass ratio of 5, the oxygen content of the organic components in the bio-oil was
reduced by 21%. With increasing mass ratio, the oxygen-rich compounds in the
bio-oil, such as laevoglucose, formic acid, acetic acid, and D-allose, decreased
dramatically, which could reduce the total oxygen content of the bio-oil.

CCA (chromated copper arsenate) treated wood originally impregnated with
such metals for the preservation purposes was also examined as a source of
chemicals under low-temperature pyrolysis conditions, as an alternate method for
its disposal.[11] The work showed that the presence of chromated copper arsenate
within the structure of wood had a significant effect on the yields of the main
carbohydrate-degradation products under mild pyrolytic conditions. More specifi-
cally, the yield of levoglucosan from treated wood was found to increase while the
yields of hydroxyacetaldehyde and hydroxyacetone were seen to decrease.

In order to obtain high-yield commodity chemicals from pyrolysis oil, Vispute
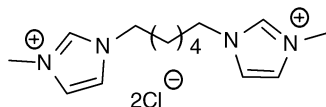et al.[48] used an integrated catalytic approach that combines low-temperature

Fig. 8.4   Structure of ionic liquid $[C_4(mim)_2]Cl_2$.

hydroprocessing of the bio-oils over a Ru-based catalyst and at higher temperature over a Pt-based catalyst, followed by a zeolite-conversion step. This combination of the hydrogenation steps with a zeolite-conversion step can reduce the overall hydrogen requirements as compared to hydrogen used for a complete deoxygenation of pyrolysis oil. The intrinsic hydrogen content of the pyrolysis oil increased through the hydroprocessing reaction. Polyols and alcohols could be produced through the hydroprocessing reaction. The zeolite catalyst then converted these hydrogenated products into light olefins and aromatic hydrocarbons with a yield much higher than that produced with the pure pyrolysis oil. Thus the combination of the hydrogenation steps with a zeolite-conversion step significantly raised the yields of olefins and aromatics. The direct zeolite upgrading of the water-soluble fraction of a pinewood bio-oil could offer 26.7% carbon yield of olefins and aromatics. Low-temperature hydrogenation before zeolite upgrading raised the yield to 51.8%, whereas the high-temperature hydrogenation resulted in higher yield of olefins and aromatics to 61.3%.

Ionic liquids have also been used in the field of biomass pyrolysis. More recently, Sheldrake and Schleck[49] have reported that dicationic molten salts ionic liquids were used as solvents for the controlled pyrolysis of cellulose to anhydrosugars. It was demonstrated that the use of dicationic $[C_4(mim)_2]Cl_2$ (Fig. 8.4) for the pyrolysis of cellulose gave levoglucosenone as the dominant anhydrosugar product at 180°C. A variety of other special catalytic systems have also been reported to effectively favor the production of various chemicals,[44] including the formation of levoglucosenone by using H_3PO_4,[50] 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one by nanoalumin⌷ titanate,[51] acetol by NaOH or Na_2CO_3,[52] furfural by $MgCl_2$[53] or $Fe_2(SO_4)_3$.[54]

8.4.7   Other Bio-Oil Upgrading Methods

High pressure thermal treatment (HPTT)[55] is a new process developed by BTG and University of Twente with the potential to economically reduce the oxygen and water content of oil obtained by fast pyrolysis. During the HPTT process, pyrolysis oil undergoes a phase separation at temperatures of 200–350°C with a residence time of several minutes (1.5–3.5 min) at 200 bar, yielding a gas phase, an aqueous phase, and an oil phase. The results showed that the oil obtained had lower oxygen (reduced from 40 to 23 wt%) and water content, and higher energy density (wet HHV ranging from 21.8 to 28.4 MJ·kg^{-1}). However, the adverse formation of high molecular weight components occurred during HPTT of pyrolysis oil, which was probably due to polymerization of the sugars present

within the pyrolysis oil. Miscibility tests showed that HPTT oil was immiscible with a conventional heavy refinery stream. It was recommended that further upgrading of the HPTT oil by hydrodeoxygenation was an option that could reduce the H_2 consumption during hydrodeoxygenation as compared to direct hydrodeoxygenation of pyrolysis oil.

Vispute and Huber[56] reported a new approach for the conversion of bio-oils via aqueous phase processing (APP). During the process, hydrogen, alkanes (ranging from C1 to C6) and polyols (ethylene glycol, 1,2-propanediol, and 1,4-butanediol) can be produced from the aqueous fraction of wood-derived pyrolysis oils. The pyrolysis oil was first phase separated into aqueous and nonaqueous fractions by mixing with distilled water. Then the aqueous fraction was subjected to a low-temperature hydrogenation with Ru/C catalyst at 125–175°C at 68.9 bar in order to thermally convert all unstable compounds to thermally stable compounds prior to APP. After the hydrogenation step, the polyols can be separated out if desired. In the ensuing steps, hydrogen was produced with high selectivity of 60% from the water-soluble part of bio-oil by aqueous-phase reforming. This is a feasible way to produce hydrogen from bio-oil. Alkanes can be produced from the water-soluble bio-oils by aqueous-phase dehydration/hydrogenation over a bifunctional catalyst (Pt/Al$_2$O$_3$–SiO$_2$). The results showed that an alkane selectivity of 77% was obtained with hydrogen being cofed to the reactor. Alternatively, an alkane selectivity of 45% was achieved when hydrogen was generated *in situ* from bio-oil. It can be seen that the advantage of this approach is that the aqueous phase of the bio-oil is processed differently from the organic phase, which can allow us to design catalysts that are well-suited for conversion of both the aqueous and organic phases, achieving higher overall yields for conversion of bio-oils into liquid fuels and chemicals.

8.5   CONCLUSIONS

Bio-oil has the potential to replace petroleum oil and also offers a source of valuable chemicals. The science and engineering pertaining to bio-oil upgrading has seen great progress in recent years with numerous challenges and limitations investigated, specially when considering large-scale application of bio-oil as a fuel. More specifically; the following issues need to be considered.

- Reducing the cost of bio-oil as compared to petroleum oil.
- Availability of raw material sources, handling and transportation issues.
- Addressing catalysts deactivation and coke-deposition issues.
- Effective procedures need to be developed when combining two or more bio-oil upgrading techniques.
- Reactors need to be designed so as to meet the product requirements.
- Environmental health and safety issues need to be given greater priority.
- Standards need to be set up for the quality monitoring and testing of bio-oils.

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