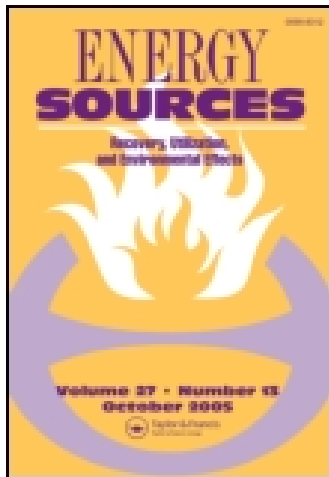


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An Overview of the Properties and Applications of Biomass Pyrolysis Oils

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Abstract *The aim of this article is to discuss the properties of pyrolysis liquid products and their primary applications. The pyrolysis of biomass is a promising route for the production of solid (charcoal), liquid (tar and other organics), and gaseous products. These products are of interest as they are possible alternate sources of fuels and chemicals. Pyrolysis liquid is referred to in the literature by terms, such as pyrolysis oil, bio-oil, bio-crude oil, bio-fuel oil, wood liquid, wood oil, liquid smoke, wood distillates, pyrolygneous tar, and pyrolygneous acid. Bio-oil from biomass pyrolysis mainly consisted of aromatic, aliphatic, and naphthenic hydrocarbons and oxygenated compounds, such as phenols, furans, alcohols, acids, ethers, aldehydes, and ketones. Bio-oil has a higher energy density than biomass, can be readily stored and transported, and can be used either as a renewable liquid fuel or chemical production.*

Keywords applications, biomass, bio-oil, properties, pyrolysis

Introduction

Since the energy crises of the 1970s, many countries have become interest in biomass as a fuel source to expand the development of domestic and renewable energy sources and reduce the environmental impacts of energy production. Biomass representing a source of gaseous, liquid, charcoal fuels, and chemical raw materials has led to the development of various research programs based on the following features: (1) all kinds of biomass incorporate almost the same components, (2) energy from conventional forestry and from plantations, (3) energy from wood powder and chips as an upgraded wood fuel, (4) macromolecular compounds existing in the biomass incorporate biosynthesis energy and their conversion to useful products, (5) oils by liquefaction of biomass “bio-oil” with different catalytic and noncatalytic processes, and (6) by conversion of biomass to solid, liquid, and gaseous fuels by carbonization, pyrolysis, supercritical fluid extraction, and gasification.

The pyrolysis of biomass is a promising route for the production of solid (charcoal) liquid (tar and other organics), and gaseous products. These products are of interest as they are possible alternate sources of fuels and chemicals (Demirbas, 2009). The pyrolysis liquids are complex mixtures of oxygenated aliphatic and aromatic compounds (Prakash and Karunanithi, 2009). Tars contain native resins, intermediate carbohydrates, phenols, aromatics, aldehydes, their condensation products, and other derivatives. Pyrolygneous acids consist of CH_3OH , $\text{C}_3\text{H}_6\text{O}$ (acetone, 50%), phenols, and water. CH_3OH can be

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produced by pyrolysis of biomass. CH_3OH arises from the methoxyl groups of uronic acid and from the breakdown of methyl esters and/or ethers from decomposition of pectin-like plant materials. Acetic acid comes from the acetyl groups of hemicelluloses. Pyrolysis gas mainly contains CO_2 , CO , CH_4 , H_2 , C_2H_6 , C_2H_4 , minor amounts of higher gaseous organics, and water vapor (Yaman, 2004).

The temperature range for the production of pyrolysis products is 625–775 K. Temperature is the most important factor for the product distribution of pyrolysis. Production of liquid products is at maximum at temperatures between 625 and 725 K. At higher temperatures, the rather large molecules present in the liquid and residual solid are broken down to produce smaller molecules that enrich the gaseous fraction (Demirbas, 2007, 2008). For maximization of yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, and short gas residence time process would be required (Demirbas, 2009).

Pyrolysis process has been used for commercial production of a wide range of fuels and chemicals from biomass feedstocks. The various pyrolysis processes are classified on heating rates and residence times as in Table 1. If the aim is the production of mainly liquid and/or gaseous products, a fast pyrolysis is recommended. In recent years, fast pyrolysis process for biomass has attracted a great deal of attention for maximizing liquid yields (Pütün, 2002). Figure 1 shows a block diagram of fast pyrolysis. Fast pyrolysis processes produce 60–75 wt% of liquid bio-oil, 15–25 wt% of solid char, and 10–20 wt% of noncondensable gases, depending on the feedstock used (Mohan et al., 2006). The liquid bio-oil produced by fast pyrolysis has the considerable advantage of being storable and transportable, as well as the potential to supply a number of valuable chemicals that offer the attraction of much higher added value than fuels (Bridgwater, 2003, 2007; Czernik and Bridgwater, 2004). Advantages of using fast pyrolysis liquids as fuel are listed in Table 2.

During the last 25 years of fast pyrolysis development, a number of different reactor designs have been explored that meet the heat transfer requirements noted above, while also attempting to address the cost issues of size reduction and moisture content of the feed (Ringer et al., 2006). The current pyrolysis reactors are fixed beds, augers, ablative processes, rotating cones, fluidized beds, and circulating fluidized beds. Apart from fixed beds, the other three from the first have scale-up problems and no large-scale commercial

Table 1
Pyrolysis technology variant

Process	Residence time	Heating rate	Temperature, K	Products
Carbonation	Days	Very low	673	Charcoal
Conventional	5–30 min	Low	873	Oil, gas, char
Fast	0.5–5 sec	Very high	923	Bio-oil
Flash-liquid	<1 sec	High	<923	Bio-oil
Flash-gas	<1 sec	High	<923	Chemicals, gas
Ultra	<0.5	Very high	1,273	Chemicals, gas
Vacuum	2–30 sec	Medium	673	Bio-oil
Hydro-pyrolysis	<10 sec	High	<773	Bio-oil
Methano-pyrolysis	<10 sec	High	>973	Chemicals

Source: Prakash and Karunanithi, 2009.

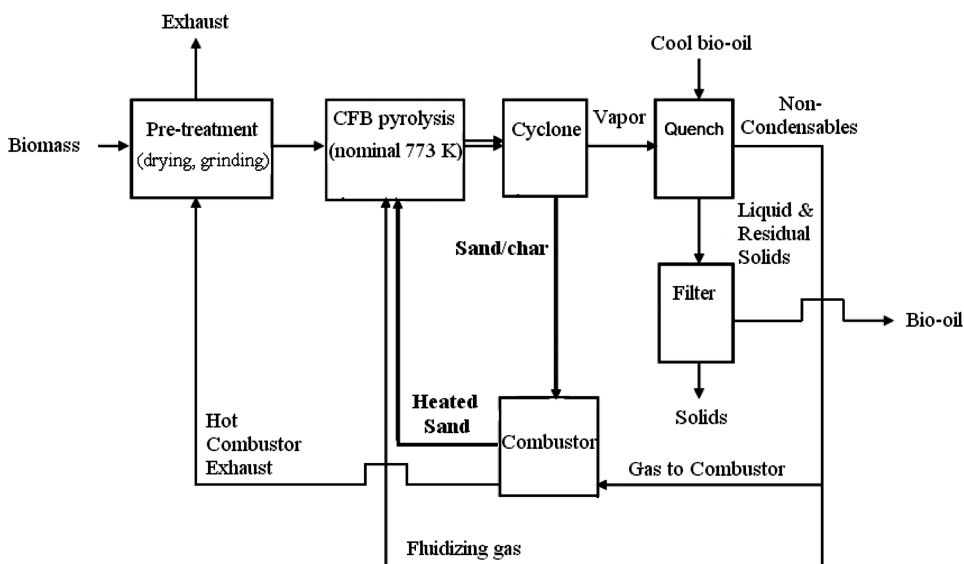


Figure 1. Block diagram of fast pyrolysis. (Source: Jones et al., 2009.)

implementations have been found. In the fluidized bed, the challenges lie in scaling up the endothermic pyrolysis reactor, particularly concerning heat transfer, and in improving the quality and consistency of the bio-oil. Circulating fluidized beds can be easily scaled up, but, it is rather complex and the products are much diluted, which greatly complicates the recovery of the liquid products (Prakash and Karunanithi, 2009).

Bio-oil

Pyrolysis liquid is referred to by many names, including pyrolysis oil, bio-oil, bio-crude oil, bio-fuel oil, pyroligneous tar or acid, wood liquid, wood oil, liquid smoke, wood distillates, and liquid wood (Bridgwater, 2003). Bio-oil is not a product of thermodynamic

Table 2

Advantages of using fast pyrolysis liquids as fuel

- Pyrolysis liquid is the lowest cost liquid biofuel, and its CO₂-balance is clearly positive
- Possibility of utilization in small-scale power generation systems as well as use in large power stations (co-firing)
- Possibility to decouple solid biofuel handling from utilization (reduced capital and operation costs in utilization)
- Storability and transportability of liquid fuels
- High-energy density compared to atmospheric biomass gasification fuel gases
- Intermittent operation feasible
- If light fuel oil is replaced, middle distillates are released to be used for transportation
- Potential of using pyrolysis liquid in existing power plants

Source: Chiamonti et al., 2007.

equilibrium during pyrolysis, but is produced with short reactor times and rapid cooling or quenching from the pyrolysis temperatures. This produces a condensate that is also not at thermodynamic equilibrium at storage temperatures. During storage, the complex chemical composition of the bio-oil changes toward thermodynamic equilibrium under storage conditions, resulting in changes in the viscosity, molecular weight, and co-solubility of its many compounds (Diebold, 2000).

Bio-oil can be made from a wide variety of forest and agricultural waste materials, including sugar cane bagasse, rice hulls and straw, peanuts hulls, oat hulls, switchgrass, wheat straw, and wood. In North America and Europe, bio-oil is produced from forest residues (sawdust, bark, and shavings). In Central and South America, the Caribbean and South Pacific, Australia, Asia, and Africa, it is produced from sugar cane bagasse and other agricultural wastes. Other abundant potential feedstocks include wheat and other straws, rice hulls, coconut fiber, etc. (Mohan et al., 2006). Bio-oil from wood generally has a high heating value (HHV) about 50% that of heavy fuel oil. Bio-oils produced at the Eastern Regional Research Center (ERRC) from agricultural feedstocks have had HHV values up to 75% of heavy fuel oil (Mullen and Boateng, 2008a).

Yields of bio-oil from wood, paper, and other biomass were in the range of ~60–95 wt%, depending on the feedstock composition. The bio-oil yields from wood are in the range of 72–80 wt%, depending on the relative amount of cellulose and lignin in the material. High lignin contents, such as that found in bark, have a tendency to give lower liquid yields (60–65%) (Mohan et al., 2006).

Properties of Bio-oil

Bio-oil from biomass pyrolysis mainly consisted of aromatic, aliphatic, and naphthenic hydrocarbons and oxygenated compounds, such as phenols, furans, alcohols, acids, ethers, aldehydes, and ketones. Bio-oil is made up of the following constituents (Shaw, 2006): 20–25% water, 25–30% water insoluble pyrolytic lignin, 5–12% organic acids, 5–10% non-polar hydrocarbons, 5–10% anhydrosugars, and 10–25% of other oxygenated compounds.

The chemical composition of bio-oil is important because it may give insights into its quality, stability, or suitability for downstream upgrading. The chemical compositions of the bio-oils are compared with what is known about the compositions of the feedstocks (Mullen and Boateng, 2008b). The compositions of bio-oil from four feedstocks are listed in Table 3. Excellent reviews on the chemical composition of bio-oil as a source of fuels and chemicals can be found elsewhere (Park et al., 2004; Chen et al., 2006; Ronghou et al., 2007; Mullen and Boateng, 2008b; Zheng et al., 2008).

Park et al. (2004) analyzed the compositions of bio-oils from rice straw pyrolysis by gas chromatography/mass spectroscopy (GC–MS). In the study, some typical components, such as acetic acid, phenol and alkylated phenols, furan derivatives, furfural, and anhydrosugars were identified. The bio-oil from sawdust (Chen et al., 2006) is mainly comprised of oxygen-containing aromatic compounds, such as phenol, alcohol, fluorene, aldehyde, and ketone according to the GC–MS analysis.

Bio-oils are multi-component mixtures of different size molecules derived from depolymerization and fragmentation of cellulose, hemicellulose, and lignin (Zhang et al., 2007). Bio-oil characteristics vary somewhat, depending on the production technology and the type of biomass feedstock from which the bio-oil is produced. This means that bio-oil fuel specifications are likely to be fairly important (Easterly, 2002). The lower heating value (LHV) of bio-oils is only 40–45 wt% of that exhibited by hydrocarbon fuels.

Table 3
Bio-oil components

Compound, wt%	Switch-grass	Alfalfa stems full flower	Guayule bagasse	Chicken litter
Water	11.04	18.45	1.44	24.46
Cellulose/hemicellulose-derived compounds				
Acetic acid	2.94	3.49	1.29	0.70
Furfural	0.62	—	—	—
Hydroxyacetaldehyde	2.40	—	—	0.04
Acetol	2.75	2.35	0.73	0.05
Levoglucosan	6.38	0.37	1.37	0.27
Lignin-derived compounds				
Guaiacol	0.18	0.46	0.39	0.41
Isoeugenol	0.45	0.73	0.65	0.24
2,6-Dimethoxyphenol	0.20	0.43	0.73	0.11
Phenol	0.66	0.95	0.65	0.51
Protein-derived compounds				
Pyrrole	—	—	—	0.07
Benzyl nitrile	Trace	0.06	Trace	0.06
Indole	—	0.01	—	0.13

Source: Mullen and Boateng, 2008a.

The LHV of bio-oils on a volume basis is ~60% of the heating value of hydrocarbon oils, because of the high oxygen content, the presence of water, and the higher bio-oil density. A typical heating value of bio-oil is ~17 MJ/kg (Mohan et al., 2006). Bio-oil is expensive as a transport fuel, but it presents the advantage of easy handling, transport, storage, combustion, retrofitting, and flexibility in production and marketing (Pütün et al., 2006). Typical properties of wood pyrolysis bio-oil and of heavy fuel oil are given in Table 4.

Bio-oil, is dark brown in color, approximates to biomass in elemental composition and is a complex mixture of oxygenated hydrocarbons and an appreciable amount of water (Maher and Bressler, 2007). Bio-oil has a content of water as high as 15–30 wt% derived from the original moisture in the feedstock and the product of dehydration during the pyrolysis reaction and storage. The presence of water lowers the heating value and flame temperature, but on the other hand, water reduces the viscosity and enhances the fluidity, which is good for the atomization and combustion of bio-oil in the engine (Zhang et al., 2007).

The oxygen content is dependent on the bio-oil's water content. Bio-oil without water contains 22–30 wt% oxygen. Proximate analysis of the bio-oil gives a chemical formula of $\text{CH}_{2.5}\text{O}_{0.4}$. The difference in oxygen content present in the feed versus that in the bio-oil is related to the oxygen content in the gases and the amount present as water in the oil (Mohan et al., 2006).

Viscosity is important in many fuel applications. The viscosity of the bio-oil as produced can vary from as low as 25 cSt to as high as 1,000 cSt (measured at 313 K) or more depending on the chemical nature of the feedstock, the water content of the oil, the amount of light ends that have been collected, and the extent to which the oil has aged (Diebold et al., 1997). The density of the oxygenated bio-oils is much higher, i.e., 1,150

Table 4
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 (MJ/kg)	16–19	40
Viscosity, at 773 K (cP)	40–100	180
Solids (wt%)	0.2–1.0	1
Distillation residue (wt%)	Up to 50	1

Source: Zhang et al., 2007.

to 1,300 kg/m³, than petroleum derived hydrocarbon oils. The bio-oils having relatively higher densities typically have lower water contents. Wood-derived pyrolysis liquid has a density of typically 1,200 kg/m³ for a water content of 25 wt% at 293 K (Islam et al., 2003). Bio-oil is moderately acidic, having a pH in the range of 2.5 to 3.0 (similar to the acidity of vinegar) (Easterly, 2002). For this reason, the oils are corrosive to common construction materials, such as carbon steel and aluminum, and can affect some sealing materials (Bridgwater, 2004).

Bio-oil Applications

Bio-oil has a higher energy density than biomass, can be readily stored and transported, and can be used either as a renewable liquid fuel or chemical production. Bio-oil applications are compared with fossil energy applications for the same heat and power duty. Bio-oil is treated effectively as a commodity, and the production of the bio-oil is considered separately from its utilization. An application is defined here as an installation for the conversion of bio-oil to energy, with a specific technology, purpose (power, heat, or CHP), and location, at a range of scales (rated output in MW) (Brammer et al., 2006). Possibilities for bio-oil applications are given in Figure 2.

The properties of bio-oil result in several significant problems during its use as a fuel in standard equipment, such as boilers, engines, and gas turbines constructed for combustion petroleum-derived fuels. Poor volatility, high viscosity, coking, and corrosiveness are probably the most challenging and have so far limited the range of bio-oil applications (Bridgwater, 2004). Some problems related to using pyrolysis liquids as a fuel in boilers, engines, and turbines are given in Table 5. It is necessary to conduct large-scale and long-duration tests on boilers, engines, and gas turbines before accepting pyrolysis liquids as commercial fuels. These tests will require a substantial supply of liquids with specified properties established by the producers and users (Oasmaa and Peacocke, 2001).

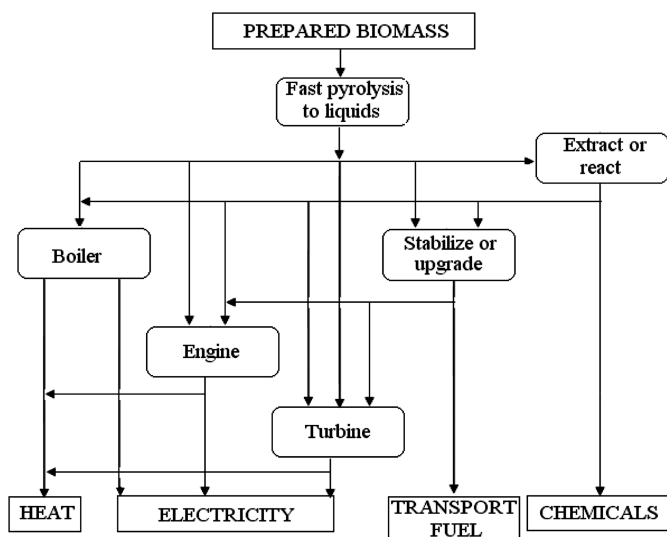


Figure 2. Applications for bio-oil. (Source: Bridgwater, 1999.)

The heating value of bio-oil is lower than that for fossil fuel, because of the large number of oxygenated compounds and a significant portion of water. Nevertheless, flame combustion tests showed that fast pyrolysis oils could replace heavy and light fuel oils in industrial boiler applications (Bridgwater, 2003; Mohan et al., 2006). In its combustion characteristics, the oil is more similar to light fuel oil, although significant differences in ignition, viscosity, energy content, stability, pH, and emission levels are observed. For pyrolysis liquids to be used or to be acceptable for boiler applications, the following minimum requirements must be achieved: (1) preheating to 345–355 K immediately prior to combustion, to reduce the viscosity to 2–4 cSt, and no recirculation of heated product back to the storage tank (because this can cause polymerization), (2) startup and shutdown on conventional fuel, to avoid deposition and coking of nozzles, and (3) ensuring a sufficiently low concentration of solids (<0.1 wt%) (Oasmaa et al., 2005). Co-firing of bio-oil has been demonstrated in a 350 MW gas-fired power station in Holland, when 1% of the boiler output was successfully replaced. It is in such applications that bio-oil can offer major advantages over solid biomass and gasification due to the ease of handling, storage, and combustion in an existing power station when special start-up procedures are not necessary (Bridgwater, 2002).

Medium and slow speed diesel engines are known for their ability to run on low quality fuels, even such fuels as coal slurries. In the early 1990s, researchers began investigating the use of bio-oils in these engines (Ringer et al., 2006). Bio-oil has a heating value of about 40% (on a weight basis) that of diesel (Wagenaar et al., 2000), but can be used directly in diesel engines or gas turbines. Bio-oil has been successfully fired in a diesel test engine, where it behaves very similar to diesel in terms of engine parameters and emissions (Bridgwater, 1999). At least 400 h of operation has been achieved on a 250 kWe specially modified dual-fuel engine and limited experience has been gained on a modified 2.5 MWe industrial gas turbine (Bridgwater, 2003). Long-term demonstration of bio-oil in diesel engines and gas turbines has not been possible due to a lack of large quantities of bio-oil (Bridgwater, 2002). For engine applications, the minimum property

Table 5
Issues related to using pyrolysis liquids as a fuel in boilers, engines, and turbines

Property	Specification to be met	Current value by present technology	Problem(s)	Possible solution(s)
Variation Water	Max. 10% <27 wt%	>50% 18–40	Changes in feed and process parameters Inhomogeneity, phase separation (>30 wt% water)	Quality control system Feedstock drying increase (<323 K) of condensation temperature
Total solids ^a	<0.01 wt%	≤0.5 wt%	Wear of injectors, increased liquids instability, high CO emissions	Homogeneous particle size distribution of the feed, hot vapor filter, three cyclones on reactor exit, liquids filtration/centrifugation
Inorganics ^b	<0.01 wt%	<0.1 wt%		Feedstock choice, hot vapor filter, three cyclones on reactor exit, liquids filtration/centrifugation
Homogeneity	Single-phase	Variation	Uneven liquid quality	Feedstock moisture <12 wt%, liquid water content <27 wt%
Stability	Max. 100% increase in viscosity in aging test (24 h 353 K, viscosity measurement at 313 K)	50–150%	Changes in liquid properties during storage and use	Alcohol addition [methanol preferred, but ethanol/2-propanol safer to use]
Flash point	Dependent on country	>313 K	Safety regulations for transportation	Adjusting the liquid condensation temperature
pH	FDS ^c	2–3	Corrosion of fuel lines	All pipework, vessels, and gaskets must be acid resistant
LHV	FDS ^c	16–19 MJ/kg	50% lower than fuel oil, does not auto-ignite at start-up	Increase pump pressure to injectors, increase diameter of fuel lines, dual fueling (%), combustion chamber modification
Viscosity	FDS ^c	>50 cSt at 293 K	Too high for most fuel injectors	Preheat liquids to reduce viscosity, add cosolvent (alcohol), use of emulsions
Lubricity	FDS ^c	Not determined	Buildup of lacquer on the injection needle and fuel pump plunger	Improvement in lubricity/flow properties, additives

^aIncludes char, ash, and sand.

^bIncludes ash and sand.

^cFDS cannot be influenced or specified.

Source: Oasmaa et al., 2005.

specifications required are as follows: (1) solids content of <0.1 wt%, (2) viscosity in the range of 10–20 cSt, and (3) maximum physical and chemical property variation. For turbine applications, the minimum requirement is that the particle size must be $<10\ \mu\text{m}$. For turbine applications, the minimum property specification required is a solids content of <0.1 wt% (Oasmaa et al., 2005).

Bio-oil can also be used for the production of chemicals. For many centuries, wood pyrolysis liquids were a major source of chemicals, such as methanol, acetic acid, turpentine, tars, etc. At present, most of these compounds can be produced at a lower cost from other feedstocks derived from natural gas, crude oil, or coal (Bridgwater, 2004). Hundreds of the components of bio-oil are determined, and reclaiming one or more kinds of small and valuable chemicals arouses great interest among scholars and businessmen. There are many substances that can be extracted from bio-oil, such as phenols used in the resins industry; volatile organic acids in the formation of de-icers; levoglucosan; hydroxyacetaldehyde; and some additives applied in the pharmaceutical, fiber synthesizing, or fertilizing industry; and flavoring agents in food products (Zhang et al., 2007). The only current commercially important application of bio-oil chemicals is that of wood flavor or liquid smoke. Several companies produce these liquids by adding water to the bio oil (Mohan et al., 2006).

Upgrading of Bio-oil

Currently, bio-oil cannot be used as a transportation fuel due to several of its drawbacks including: high viscosity, acidic nature, low heating value, high water and oxygen content, and incompatibility with conventional fuels. Hence, an upgrading process to convert bio-oil to tangible fuels is necessary (Vispute and Huber, 2009). Hydrodeoxygenation and catalytic cracking are two widely studied bio-oil upgrading approaches.

Hydrodeoxygenation

The necessary upgrading of bio-oil, in which the oxygen content is reduced, can be achieved by hydrodeoxygenation, which entails the elimination of oxygen and the formation of hydrocarbons in the presence of hydrogen on sulphided hydroprocessing catalysts (Şenol et al., 2007a). Figure 3 shows the simplified flow diagram for the stand-alone upgrading portion of the plant. The catalysts are much more active in their sulphided

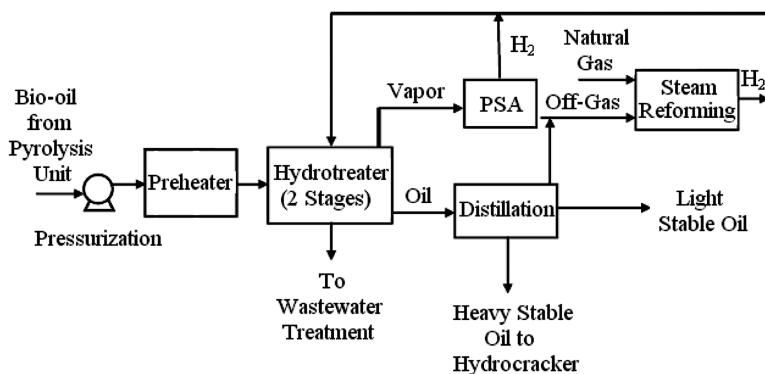


Figure 3. Block diagram of bio-oil upgrading. (Source: Jones et al., 2009.)

form, and the oxygen content of the feed has a deleterious effect on the sulphide structure of the catalysts, causing losses in activity and changes in product distribution (Şenol et al., 2007b). Since the sulphur content of bio-oils is typically very low, addition of a sulphiding agent to the feed seems to be a reasonable means of maintaining the catalyst in its sulphided state (Şenol et al., 2007b). Catalytic hydrogenation refers to the process in which crude bio-oil is hydrotreated under hydrogen pressure (10–20 MPa) in the hydrogen-donor solution (Guo et al., 2004). Most hydrodeoxygenation of bio-oils has focused on sulfided $\text{CoMo}/\text{Al}_2\text{O}_3$ and $\text{NiMo}/\text{Al}_2\text{O}_3$ catalysts, which are used for hydrotreating industrial feedstocks. These catalysts have been shown to be active in the upgrading of bio-oils.

ZrO_2 -supported noble metal (Rh, Pt, and Pd) catalysts offer a new possibility to carry out hydrodeoxygenation in the absence of sulfur: they have been found to be active and selective in the hydrodeoxygenation of 2-methoxyphenol (guaiacol), used as a model component for wood-based pyrolysis oil. Higher selectivity to benzene and lower carbon deposition were obtained with the noble metal than with the sulfided catalyst at 573 K. Due to these promising results, it is of interest to test the noble metal catalysts in the hydrodeoxygenation of methyl heptanoate, which can be used as a model component for vegetable oils (Gutierrez et al., 2009).

Catalytic Cracking

One approach to improve the quality of the bio-oil is stabilization by mild catalytic cracking. Catalytical thermal cracking is a process in which crude bio-oil is thermally treated in a gas-solid phase at atmospheric pressure without hydrogen (Guo et al., 2004). The simplified flow diagram for the hydrocracking and product separations areas is shown in Figure 4. Various catalysts have been introduced in pyrolysis in order to improve the quality of the bio-oil produced. The catalytically produced oils present a series of improved properties, such as stability and deoxygenation, but the amounts produced are lower than in the non-catalytic runs (Antonakou et al., 2006).

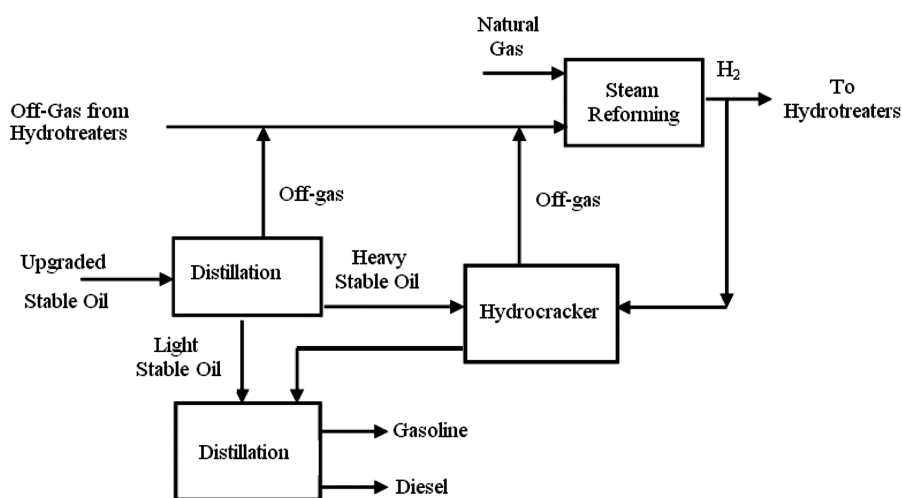


Figure 4. Block diagram of hydrocracking and product separation. (Source: Jones et al., 2009.)

Table 6
Comparison of different catalysts for zeolite upgrading of
wood-derived fast pyrolysis bio-oils

	Silica-alumina				
	HZSM-5	(SiO ₂ -Al ₂ O ₃ ratio 0.14)	SAPO-5	SAPO-11	MgAPO-36
Catalyst properties					
Pore size (nm)	0.54	3.15	0.80	0.56	0.75
BET surface area (m ² /g)	329	321	330	205	196
Acid area (cm ² /g) ^a	224.9		125.5	76.0	15.5
Product yields (wt% of feed)					
Organic liquid product	33.6	24.9	22.2	19.9	16.3
Gas		6.1	10.3	12.2	10.1
Coke + char ^b	20.5–30.2	40	30.0	25.5	38.7
Tar ^c	0–4.1		9.5	11.9	10.1
Aqueous fraction		25.0	24.2	26.3	23.1
Composition organic liquid product (wt%)					
Total hydrocarbons	86.7	45.6	51.0	56.8	51.6
Aromatics	85.9 ^d	2.1	27.5	29.1	26.7
Aliphatics	18.6	43.5	23.5	24.4	23.4

Reaction temperature 643 K.

^aAcid area is measured by ammonia TPD and represents Bronsted plus Lewis acid sites.

^bCoke is defined as organics that could only be removed from the catalyst by calcinations. Char is defined as organics deposited in the reactor due to thermal decomposition, and these compounds were not on the catalyst.

^cTar is the heavy oils deposited on the catalysts that were only removed with a hexane/acetone wash.

^dToluenes and xylenes are the most common aromatics for HZSM-5, whereas benzene is the most common aromatic for SAPO and MgAPO catalysts.

Source: Huber et al., 2006.

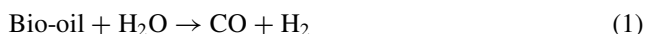
The use of zeolitic catalysts can maximize the yield of aromatic hydrocarbons in the cracking process (NSF, 2008). Temperatures of 625–775 K and atmospheric pressure are used for zeolite upgrading. The advantages of using a zeolite catalyst are that no hydrogen is required, atmospheric processing reduces operating costs, and the temperatures are similar to those for bio-oil production (Huber et al., 2006; Farrell and Gopal, 2008). The catalyst, HZSM-5, has been demonstrated to be particularly useful in this regard, producing aromatic yields with up to 5 times the aliphatic content. Other zeolites produce an aromatics to aliphatics ratio of about 1 to 1 (NSF, 2008). Table 6 shows the results for zeolite upgrading of wood-derived fast-pyrolysis bio-oils with different catalysts. It is expected that zeolite-related materials with bigger pores would allow larger pyrolysis products, particularly lignin-derived compounds, to enter, reformulate, and exit the catalyst matrix with less chances of coke deposition and blocking of pores (Pattiya et al., 2008).

Although catalytic cracking is regarded as a cheaper route by converting oxygenated feedstocks to lighter fractions, the results seem not promising due to high coking (8–25 wt%) and poor quality of the fuels obtained (Zhang et al., 2007).

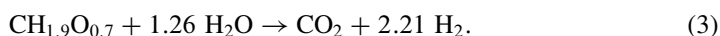
Steam Reforming

Hydrogen production from bio-oil provides a new route for utilization of bio-oil. Hydrogen production from renewable bio-oil is an attractive idea for fuel, energy, and

agricultural applications. In recent years, hydrogen production via steam reforming of bio-oil has attracted more and more attention. But because of the complicated composition of bio-oil and carbon deposition on the catalyst surface in the reaction process, currently the studies mainly focus on the steam reforming of model compounds in bio-oil and reforming catalysts (Wu et al., 2007). The bio-oil can be stored and shipped to a centralized facility where it is converted to hydrogen via catalytic steam reforming and shift conversion (Evans et al., 2003). Catalytic steam reforming of bio-oil at 1,025–1,125 K over a Ni-based catalyst is a two-step process that includes the shift reaction (Nath and Das, 2003; Evans et al., 2003):



The overall stoichiometry gives a maximum yield of 0.172 g H₂/g bio-oil (11.2% based on wood) (Nath and Das, 2003; Evans et al., 2003):



The first step in pyrolysis is to use heat to dissociate complex molecules into simple units. Next, reactive vapors, which are generated during the first step, convert to hydrogen (Nath and Das, 2003).

Studies on Pyrolysis Oil Upgrading

The development of bio-energy has drawn great attention from researchers since the early 1980's and upgrading of crude bio-oil from pyrolysis of biomass to prepare fuel oil of high quality has now become an area attracting more R&D efforts (Guo et al., 2004). The current research on bio-oil upgrading focuses on two technological routes: catalytic hydrogenation (Şenol et al., 2005; Gutierrez et al., 2007; Zhang et al., 2009; Fisk et al., 2009) and catalytic cracking (Sharma and Bakhshi, 1993; Vitolo et al., 2001; Peng et al., 2009).

Gutierrez et al. (2007) studied hydrodeoxygenation of guaiacol in a batch-reactor system using commercial alumina supported CoMo and NiMo catalysts under a total pressure of 8.0 MPa in the temperature range from 475–625 K. The results of the study showed that the conversion of guaiacol and the amount of hydrodeoxygenation products were higher on the NiMo than on the CoMo catalyst at the lowest temperatures tested (475–575 K). Thus, the NiMo catalyst was more active than the CoMo in this temperature range.

The liquid phase upgrading of a model bio-oil over Pt supported catalysts was studied by Fisk et al. (2009). In this study, Pt/Al₂O₃ showed the highest activity for deoxygenation, the oxygen content of the model oil decreasing from an initial value of 41.4 wt% to 2.8 wt% after upgrading.

Sharma and Bakhshi (1993) studied the upgrading of a fast pyrolysis bio-oil and its two fractions in a fixed bed microreactor using HZSM-5 as a catalyst at atmospheric pressure in the temperature range of 613–683 K. The objective of this study was to maximize the desired organic distillate product with a high concentration of aromatic hydrocarbons. The maximum organic distillate from the upgrading of whole bio-oil was 19 wt% of bio-oil and the highest concentration of aromatic hydrocarbons in the distillate was 83 wt%.

In one study (Peng et al., 2009), the pyrolysis oil from rice husk was upgraded in sub- and super-critical ethanol using HZSM-5 as the catalyst. The results of this study showed that the super-critical upgrading process performed more effectively than the sub-critical upgrading process.

Recently, Mahfud et al. (2007) reported a new method for the upgrading of flash pyrolysis oil using an improved alcohol treatment method. The method consists of treating pyrolysis oil with a high boiling alcohol like *n*-butanol in the presence of a (solid) acid catalyst at 323–353 K under reduced pressure (<10 kPa). Using this approach, the water content of the pyrolysis oil is reduced significantly and values less than 5 wt% were obtained using sulfuric acid (Mahfud et al., 2007).

Zheng et al. (2008) studied fast pyrolysis of cotton stalk at temperatures between 753 and 803 K in a fluidized bed and obtained the maximum yield of bio-oil (55%) at a temperature of 783 K. The results of the study showed that the bio-oil obtained under these conditions can be directly used as a fuel oil for combustion in a boiler or a furnace without any upgrading.

Conclusions

Pyrolysis is the fundamental chemical reaction process that is the precursor of both the gasification and combustion of solid fuels, and is simply defined as the chemical changes occurring when heat is applied to a material in the absence of oxygen. Pyrolysis of biomass is a promising route for the production of solid (char), liquid (bio-oil/tar), and gaseous products. These products are of interest as they are possible alternate sources of energy. The most important advantage of biomass pyrolysis for liquid production is the decoupling nature of the plant.

Bio-oil can be used as a fuel in boilers, diesel engines or gas turbines for heat and electricity generation. The properties of bio-oil result in several significant problems during its use as a fuel in standard equipment, such as boilers, engines, and gas turbines constructed for combustion petroleum-derived fuels. Poor volatility, high viscosity, coking, and corrosiveness are probably the most challenging problems and so far have limited the range of bio-oil applications.

The development of bio-energy has drawn great attention from researchers since the early 1980s and upgrading of crude bio-oil from pyrolysis of biomass to prepare fuel oil of high quality has now become an area attracting more R&D efforts. The current research on bio-oil upgrading focuses on two technological routes: catalytic hydrogenation and catalytic cracking.

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