Past, Present, and Future Production of Bio-oil

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Abstract

Bio-oil is a liquid product produced by fast pyrolysis of biomass. The fast pyrolysis is performed by heating the biomass rapidly (2 sec) at temperatures ranging from 350 to 650 °C. The vapors produced by this rapid heating are then condensed to produce a dark brown water-based emulsion composed of fragments of the original hemicellulose, cellulose and lignin molecules contained in the biomass. Yields range from 60 to 75% based on the feedstock type and the pyrolysis reactor employed. The bio-oil produced by this process has a number of negative properties that are produced mainly by the high oxygen content (40 to 50%) contributed by that contained in water (25 to 30% of total mass) and oxygenated compounds. Each bio-oil contains hundreds of chemical compounds. The chemical composition of bio-oil renders it a very recalcitrant chemical compound. To date, the difficulties in utilizing bio-oil have limited its commercial development to the production of liquid smoke as food flavoring. Practitioners have attempted to utilize raw bio-oil as a fuel; they have also applied many techniques to upgrade bio-oil to a fuel. Attempts to utilize raw bio-oil as a combustion engine fuel have resulted in engine or turbine damage; however, Stirling engines have been shown to successfully combust raw bio-oil without damage. Utilization of raw bio-oil as a boiler fuel has met with more success and an ASTM standard has recently been released describing bio-oil characteristics in relation to assigned fuel grades. However, commercialization has been slow to follow and no reports of distribution of these bio-oil boiler fuels have been reported. Co-feeding raw bio-oil with coal has been successfully performed but no current power generation facilities are following this practice. Upgrading of bio-oils to hydrocarbons via hydroprocessing is being performed by several organizations. Currently, limited catalyst life is the obstacle to commercialization of this technology. Researchers have developed means to increase the anhydrosugars content of bio-oil above the usual 3% produced during normal pyrolysis by mild acid pretreatment of the biomass feedstock. Mississippi State University has developed a proprietary method to produce an aqueous fraction containing more than 50% of anhydrosugars content. These anhydrosugars can be catalyzed to hydrogen or hydrocarbons; alternately, the aqueous fraction can be hydrolyzed to produce a high-glucose content. The hydrolyzed product can then be filtered to remove microbial inhibitor compounds followed by production of alcohols by fermentation. Production of bio-oil is now considered a major candidate as a technology promising production of drop-in transportation and boiler fuels.

What is Bio-oil?

For nearly three decades researchers have been developing the science of fast pyrolysis to produce liquid fuels. Fast pyrolysis entails the thermal decomposition of biomass at temperatures of 350 to 650°C in an oxygen-starved environment. This severe and rapid thermal treatment depolymerizes the cellular structure of the biomass to vapor that is rapidly condensed to a dark brown liquid termed pyrolysis oil or bio-oil.

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Table 1. Bio-oil yields.

40-65% organic condensate
10-20% char
10-30% gases (CO, CO_2, CH_4)
10-25% water

The term oil as a descriptive of the bio-oil product is an unfortunate one as the chemical compound produced from fast pyrolyzing biomass is not oil but, rather, a water emulsive suspension of thermally fractured cellular structure that was originally composed of hemicellulose, cellulose, and lignin structures. The typical water content of the water-based bio-oil ranges from 15 to 30% and, far from being oil, this emulsion is immiscible in petroleum-based hydrocarbons. Czernik and Bridgwater (2004) developed the information provided in Table 1 describing typical properties of raw bio-oil produced from fast pyrolysis of wood.

The violent decomposition of the lignocellulosic structure of the pyrolyzed feedstock results in numerous chemical fragments that result in the chemical complexity of bio-oil in which 100, or more, chemical compounds may be present in each bio-oil type. While these chemical compounds are too numerous to list, the general classes of compounds into which these numerous chemicals can be classified are provided in Table 2. By far the most abundant compound is water at 20-30% volume. Lignin is the next most abundant class of chemical compounds at 15-30%. This is followed by aldehydes (10-20%), carboxylic acids (10-15%), carbohydrates (5-10%), phenols (2-5%), furfurals (1-4%), alcohols (2-5%) and ketones (1-5%). Bio-oil yields typically range up to 65 to 70%, but yields are dependent on both biomass type and reactor efficiency.

A percentage of water will be produced in bio-oil during pyrolysis regardless of the water content of the biomass pyrolyzed. Even at 0% biomass water content the resultant bio-oil will still contain 12-15% water. The water produced from dry biomass is believed to result from carbohydrate dehydration and potentially from free radical reactions occurring between the hydrogen and oxygen produced during pyrolysis. It is usually considered prohibitively expensive to dry biomass for pyrolysis much below 10% with the result being water content usually between 25 and 30% in the final bio-oil.

Most of the chemical compounds comprising bio-oil are highly oxygenated, which results in a typical percentage of oxygen content of 45% by weight. In addition to the organic condensate comprising raw bio-oil, Table 1 indicates that 10 to 20% char, 10 to 30% non-condensable gases (CO, CO_2, and CH_4), and 10 to 25% water are produced.

Bio-oil contains combustible components but, because of high water content and the complexity of the remaining chemicals of which it is comprised, its use as a fuel is problematic. Mainly due to the high amount of oxygen that bio-oil has, a number of negative properties render it very difficult to utilize as a fuel when it is not upgraded in some manner. These properties are high acidity (pH of 2.0 to 3.0), viscosity increase over time, heating value of less than half that of No. 2 fuel oil (HHV of approximately 16 to 19 MJ/kg), pungent odor and high flashpoint that renders ignition difficult, and immiscibility with hydrocarbons that precludes direct mixing (Table 3). The high water content cannot be reduced by evaporation due to the reactivity of the remaining compounds contained in bio-oil that cause rapid polymerization with the application of heat.

Bio-oil, while difficult to ignite, burns as steadily as No. 2 fuel oil after ignition. Researchers have found that support fuels are helpful to assist in ignition and for smoother burning. Bio-oil emits higher particulate matter and CO_2 during combustion. However, compared to petroleum fuels, SO_x emissions are much lower and most research indicates that, for most applications, NO_x emissions are also lower (Czernik and Bridgwater 2004).

Table 2. Bio-oil chemical composition by group.

	Wt, %		Wt, %
Water	20-30	Phenols	2-5
Lignin	15-30	Furfurals	1-4
Aldehydes	10-20	Alcohols	2-5
Carboxylic acids	10-15	Ketones	1-5
Carbohydrates	5-10		

How is Bio-oil Made?

Various types of pyrolysis reactors have been developed since the concept of fast pyrolysis was developed. The most frequently applied design is the fluidized bed with two main variations of the fluidization concept applied. The bubbling fluidized bed has been used since the middle of the 20th century in the petroleum industry. This long history of use has resulted in their relatively

Table 3. Typical properties and characteristics of wood-derived crude bio-oil.

Physical property		Typical value
Moisture content		15-30%
pH		2.5
Specific gravity		1.2
Elemental analysis	C	56.4%
	H	6.2%
	O	37.3%
	N	0.1%
	Ash	0.1%
HHV as produced (depends on moisture)		16-19 MJ/kg
Viscosity (at 40°C and 25% water)		40-100 cp
Solids (char)		1%
Vacuum distillation residue		up to 50%

smooth adaptation to production of bio-oil from biomass. Numerous industrial prototypes based on the bubbling fluidized bed design are operational in research and demonstration facilities worldwide. The bubbling fluidized bed design passes hot gas through an inorganic particulate bed to provide a high heat-transfer temperature. In theory the bed is self cleaning but careful manipulation of the biomass particle size is required to realize this self-cleaning characteristic in actuality. Dynamotive Industries has adopted this design for their fast pyrolysis reactors. Despite long industrial experience and wide use, successful heat transfer to the bubbling bed has not been satisfactorily tested at large scale (Ringer et al. 2005).

The circulating fluidized bed design is a second design adopted from the petroleum refining industry. This design requires the circulation of the sand heating medium at 10 to 20 times the feedstock input rate requiring considerable capital cost provision for this feature. However, this feature allows for removal of char in a char combustion device (Ringer et al. 2005).

Ablative pyrolysis is a potential approach that was pioneered at National Renewable Energy Laboratory (NREL) in the early 1980s. The ablative approach depends on rapid conduction of heat from a hot surface to the biomass particle and this conduction can be achieved in many potential ways. NREL employed a vortex reactor that employed a carrier gas to impinge the biomass particles at high speed against the tubular vortex reactor wall resulting in very rapid vaporization. Drawbacks to the vortex design that prevented commercialization were failure to pyrolyze all particles on the first ablative application that required a feedback loop to return unpyrolyzed particles to the vortex throat; rapid wear occurred at the vortex throat due to the high-speed impact of feedstock particles; finally, scale-up issues have made application of the design to a larger reactor size for commercialization uncertain (Ringer et al. 2005).

The University of Twente in the Netherlands has performed research on a rotating cone pyrolysis reactor design since the early 1990s. Hot sand is introduced into a rotating cone turning at high rpm. The hot sand performs the fast pyrolysis and the cone rotation passes sand and biomass to the top lip of the cone to pass them on for char removal and sand reheating. Char is combusted in a separate fluidized bed to provide sand heating energy. This design, while successful, is somewhat more complex than the fluidized bed reactors and scale-up issues have not been resolved (Ringer et al. 2005).

Several organizations have designed auger reactors with Renewable Oil International, patenting a design that employs steel shot as the heat transfer medium (Badger and Fransham 2008). Mississippi State University (MSU) has developed its own auger reactor design that differs from the ROI design that employs hot steel shot as the heating medium. The major drawback of auger reactors is the difficulty of obtaining high heat transfer rates in the auger tube. The steel shot concept developed by ROI overcomes this problem by bringing the heated steel shot heat carrier into intimate contact with the biomass in a similar way as applied by fluidized bed and rotating cone concepts. We have not disclosed the MSU auger reactor design but we attain a bio-oil yield of 65% indicating the adequacy of the design for effective heat transfer.

How Has Bio-oil Been Used as a Fuel?

Despite the negative properties of bio-oil, early researchers attempted to utilize raw bio-oil as a liquid combustible fuel in a number of applications such as in engines, turbines, and boilers. The information regarding applications of bio-oil as liquid fuels has been largely paraphrased from a longer description published by Czernik and Bridgwater (2004); the authors gratefully acknowledge their heavy reliance on this invaluable source of hard-to-find information.

Boiler Fuel

Red Arrow Products, a Wisconsin company that manufactures liquid smoke flavorings from bio-oil, combusts the pyroligneous byproduct of their process combined with char and non-condensable exit gases to provide their process heat. The bio-oil is combusted at an air-atomizing nozzle with the char and gas input separately. This combustion boiler has successfully operated in this mode for many years (Czernik and Bridgwater 2004).

Finnish researchers have performed considerable research on boiler combustion of bio-oil. A dual fuel boiler was tested with various fuel oil to bio-oil proportion including without the co-fuel. A second set of tests was performed with raw bio-oil using an 8 MWth furnace operated at 4 MWth. The results of these tests showed that some minor modifications of burner and boiler are required to replace petroleum fuels with bio-oil; a petroleum fuel was required for ignition; emissions are lower for all emissions except particulates (Czernik and Bridgwater 2004).

A Co-feed with Coal

Using Red Arrow bio-oil, five percent of the BTUs for Wisconsin's Manitowoc Power Station were provided for electricity generation for a 370-hour test using a 20 MWe boiler. No modifications of the boiler were required and test results indicated good combustion with no operational or emissions issues (Czernik and Bridgwater 2004).

Diesel Engine Fuel

Medium- to low-speed diesel engines have the capacity to burn relatively low-grade fuels. For this reason researchers have investigated the potential for fueling them with raw bio-oil. VTT Energy attempted to fuel a high-speed, 500cc, single-cylinder Petter diesel engine with raw bio-oil in a 1993 test. However, ignition could not be achieved without more than 5% alcohol addiction. The main operational problem was rapid clogging of the injection nozzles by coke formed during the combustion process. Other tests by VTT Energy with medium-speed diesel engines allowed raw bio-oil to be combusted with pilot ignition. However, injection adjustment during combustion was difficult and injection and pump elements suffered rapid wear and corrosion (Czernik and Bridgwater 2004).

In a University of Kansas test, an air-cooled Lister Petter diesel engine was fueled with hot-filtered bio-oil and provided performance equivalent to that for petroleum diesel. Researchers also were able to fuel bio-oil methanol blends in a high-speed diesel engine but found that raw bio-oils would perform best in low-speed diesel engines with high compression ratio. Tests at MIT with a single-cylinder direct injection engine found that the raw bio-oil must be preheated to 55°C for proper ignition but combusted well following this step (Czernik and Bridgwater 2004).

Ormrod Diesels has performed tests of a dual-fueled slow-speed diesel engine for up to 400 hours. The engine was modified to combust bio-oil in three cylinders while the remaining three cylinders combusted diesel fuel. It was necessary to use diesel for ignition to start the engine. Deposits were noted on the pumps and injectors but no negative impact on engine performance resulted (Czernik and Bridgwater 2004).

Tests performed by Italian researchers combusted fuels comprised of emulsions of diesel and bio-oil. These emulsions have the potential to circumvent the lack of miscibility of bio-oil with petroleum hydrocarbons. These tests successfully combusted emulsions containing up to 50% raw bio-oil. However, damage to injectors worse than previous researchers noted for diesel combustion of raw bio-oil was observed (Czernik and Bridgwater 2004).

Turbines

Electricity production with bio-oil fueled turbines is an alternative investigated by researchers and demonstration projects. Tests in the early 1980s successfully fueled a turbine noting slag buildup in the exhaust area as a potential problem for long-term operation. Orenda Aerospace Corporation has performed long-term research on use of turbines fueled by bio-oil. They successfully fueled a 2.5 MWe turbine engine designed by the Ukrainian company Mashproekt that incorporates a relatively open combustion chamber that allows ease of modification to accommodate various fuel types. Tests were performed with no adverse drawbacks noted (Czernik and Bridgwater 2004).

A test by a German University of a small gas turbine of 75 kWe was performed in dual fuel mode to allow combustion of both diesel and bio-oil fuels. The turbine was able to combust the dual fuel mix but deposits on the turbine blades were observed, limiting the direct application of this approach (Czernik and Bridgwater 2004).

Sterling Engines

German researchers fueled a 25kW Sterling engine with a modified oxidative burner with air atomization. This experiment was successful without noticeable fouling and with acceptable emissions levels (Czernik and Bridgwater 2004).

Bio-oil Upgrading to Liquid Fuels

Due to the negative characteristics of raw bio-oils and past failures in successfully combusting these fuels as boiler and engine fuels, it is universally agreed that some type of upgrading of bio-oil is required to allow future production of fungible liquid fuels. The following upgrading technologies are under investigation by researchers:

Hydrodeoxygenation

Application of catalysts under heat and pressure in the presence of hydrogen to hydrodeoxygenate (HDO) bio-oil has been widely investigated since the early 1980s. Elliott (2007) traces the history of HDO from its inception until 2007. Elliott has been one of the most successful HDO practitioners of bio-oil HDO technology with multiple patents in the field. His application of two-stage catalysis to prevent early polymerization of the bio-oil has been copied by many investigators.

Elliott (2007) reports on Pacific Northwest National Laboratory bio-oil HDO tests performed in about 1995 on a continuous hydrotreater in downflow configuration with two commercial catalysts. The most successful of these catalysts was NiMo on alumina. Various first-stage lower temperatures, ranging from 148 to 150°C, and second-stage temperatures ranging from 349 to 380°C were applied over six experiments. Results were similar with biocrude yields (g/g) ranging from 38 to 53%. Deoxygenation reduced oxygen content by 94.4 to 98.6%. Elliott recently applied for a patent (Elliot et al. 2008) on palladium catalyst for HDO of bio-oil. Elliott and Universal Oil Products appear to be the only researchers who have progressed to packed bed continuous reactor for the practice of HDO bio-oil technology (Holmgren et al. 2005).

Recent research on single stage HDO of bio-oil with several catalysts was reported by Wildshcut and Heeres (2008). Best result was for Ru/C that provided a 60% yield of HDO bio-oil with oxygen content lowered to 6% (based on the weight of products to initial raw bio-oil weight). Water produced was approximately 35% and residual solids comprised 5% of the total mass. Total yield of all components was 93%. The water produced by the process formed a clear layer among the products such that separation was an easy step. A drawback is that the four-hour reaction time is much longer than reported for other successful hydrotreating catalysts.

MSU has developed a proprietary two-stage catalyst with the characteristics of the resulting hydrocarbon mix reported in this conference by Gajjela (Gajjela et al. 2011).

Regardless of the HDO catalyst applied, the results appear to be similar with the production of a hydrocarbon mix capturing approximately 50% of the carbon energy present in the original biomass. This mix has an HHV very close to that of petroleum products at over 44 MJ/kg (Gajjela et al. 2011).

Production of boiler fuel via HDO appears possible simply by applying only the single stage of the typical two-stage process. This stage largely eliminates the water content and produces a boiler fuel that has the potential for meeting the proposed ASTM standard boiler fuels manufactured from bio-oil.

Production of Lignocellulosic Biodiesel

MSU has developed a lignocellulosic biodiesel (L-B) product that meets the proposed ASTM standards for bio-oil boiler fuels (ASTM 2009). The process for producing this product is not disclosed but the properties as compared to raw bio-oil are given in Table 4. This table shows that the water content remains nearly the same with acid value cut by nearly 50%; viscosity is also decreased by approximately 50%; HHV is increased from 17.5 MJ/kg to 23.8 or by 36%; flash and pour point are largely unchanged. The L-B has been combusted successfully by MSU in a waste oil boiler and tests of L-B for fueling other boiler types are underway.

Production of Ethanol and Hydrocarbons from Pyrolytic Anhydrosugars

Levoglucosan (1,6-anhydro-β-D-glucopyranose) and other anhydrosugars are a product of cellulose combustion. When cellulose is heated to over 300°C, it undergoes various pyrolytic processes to produce anhydrosugars as a component in the resultant bio-oil. Several researchers have investigated means of increasing production of anhydrosugars from pyrolysis of lignocellulosic biomass (Shafizadeh 1980; Piskorz

Table 4. Chemical and physical properties and characteristics of L-B.

Property	Raw bio-oil	L-B
Water content (%)	24.2	25.8
Acid value (mg KOH/g)	89	46
Viscosity (cSt @ 40oC)	14.53	7.37
HHV (MJ/kg)	17.5	23.8
Flash point (oC)	52.2	47.9
Pour point (oC)	< -24	< -24

1989; Brown et al. 2001). Generally, anhydrosugars yields are approximately 3% by weight for untreated woody biomass and 30% to 40% for mild acid pretreated lignocellulosic biomass.

MSU has recently developed a method for increasing anhydrosugars in pyrolytic bio-oil to 50.8% based on oven-dry feedstock weight. Utilization of the pyrolytic anhydrosugars requires that the raw bio-oil is fractionated into the aqueous fraction and pyroligneous fractions. The aqueous fraction (71% of total raw bio-oil) contains the anhydrosugars produced during pyrolysis while the pyroligneous fraction (29% of total raw bio-oil) contains the acid-insoluble organic chemicals, such as phenols, aldehydes, and ketones, etc.

Researchers have recently developed technologies to convert the aqueous fraction anhydrosugars into either ethanol or hydrocarbons. The production of ethanol requires the hydrolysis of the anhydrosugars into glucose by standard hydrolysis procedures. Production of hydrocarbons entails aqueous phase reforming as described by Huber et al. (2005). MSU is pursuing development of technology to produce ethanol from the hydrolyzed anhydrosugars in the bio-oil aqueous phase.

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