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Overview of Applications of Biomass Fast Pyrolysis Oil

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Fast pyrolysis of biomass is one of the most recent renewable energy processes to have been introduced. It offers the advantages of a liquid product, bio-oil that can be readily stored and transported. Bio-oil is a renewable liquid fuel and can also be used for production of chemicals. Fast pyrolysis has now achieved a commercial success for production of chemicals and is being actively developed for producing liquid fuels. Bio-oils have been successfully tested in engines, turbines, and boilers, and have been upgraded to high-quality hydrocarbon fuels, although at a presently unacceptable energetic and financial cost. The paper critically reviews scientific and technical developments in applications of bio-oil to date and concludes with some suggestions for research and strategic developments.

Introduction

Since the oil crisis in the mid 1970s, considerable effort has been directed toward development of processes for producing liquid fuels from ligno-cellulosic biomass. This led to the development of several fast pyrolysis technologies. Fast pyrolysis is a thermal decomposition process that occurs at moderate temperatures with a high heat transfer rate to the biomass particles and a short hot vapor residence time in the reaction zone. Several reactor configurations have been shown to ensure this condition and to achieve yields of liquid product as high as 70–80% based on the starting dry biomass weight.¹ They include bubbling fluid beds,^{2,3} circulating and transported beds,^{4,5} cyclonic reactors,^{6,7} and ablative reactors.⁸ In the 1990s, several fast pyrolysis technologies have reached near-commercial sta-

tus. Six circulating fluidized bed plants have been constructed by Ensyn Technologies with the largest having a nominal capacity of 50 t/day operated for Red Arrow Products Co., Inc., in Wisconsin. DynaMotive (Vancouver, Canada) demonstrated the bubbling fluidized bed process at 10 t/day of biomass and is scaling up the plant to 100 t/day. BTG (The Netherlands) operates a rotary cone reactor system at 5 t/day and is proposing to scale the plant up to 50 t/d. Fortum has a 12 t/day pilot plant in Finland.⁹ The yields and properties of the generated liquid product, bio-oil, depend on the feedstock, the process type and conditions, and the product collection efficiency. Though primarily biomass pyrolysis oils have been expected to become alternative liquid fuels, other potential applications have also emerged and will be reviewed in this paper.

Properties of Biomass Pyrolysis Oils

Bio-oils, also known under the names of pyrolysis oils, pyrolysis liquids, and others, are usually dark brown, free-flowing liquids having a distinctive smoky odor. The physical properties of bio-oils are described in several publications.^{10–12} These properties result from the chemical composition of the oils, which is significantly different from that of petroleum-derived oils. Bio-oils are multicomponent mixtures comprised of different size molecules derived primarily from depolymerization and fragmentation reactions of three key biomass building blocks: cellulose, hemicellulose, and lignin. Therefore,

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Table 1. 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 50 °C), cP	40–100	180
solids, wt %	0.2–1	1
distillation residue, wt %	up to 50	1

the elemental composition of bio-oil resembles that of biomass rather than that of petroleum oils. Basic data for bio-oils and conventional petroleum fuels are compared in Table 1, and those most important for combustion are discussed below. More detail on fuel-related characteristics is provided in ref 13.

Oxygen Content. The oxygen content of bio-oils is usually 35–40 wt %. This oxygen is present in most of the more than 300 compounds that have been identified in the oils. The distribution of these compounds mostly depends on the type of biomass used and on the process severity (temperature, residence time, and heating rate profiles). An increase in pyrolysis severity reduces the organic liquid yield due to cracking of the vapors and formation of gases but leaves the organic liquid with less oxygen. The single most abundant bio-oil component is water. The other major groups of compounds identified are hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics. Most of the phenolic compounds are present as oligomers having a molecular weight ranging from 900 to 2500.¹⁴

The presence of oxygen in many oil components is the primary reason for differences in the properties and behavior seen between hydrocarbon fuels and biomass pyrolysis oils. The high oxygen content results in a low energy density (heating value) that is less than 50% of that for conventional fuel oils and immiscibility with hydrocarbon fuels. An even more important consequence of the organic oxygen is the instability of bio-oil, which will be discussed later.

Water Content. Water in bio-oils¹⁵ results from the original moisture in the feedstock and as a product of the dehydration reactions occurring during pyrolysis. Therefore, the water content varies over a wide range (15–30%) depending on the feedstock and process conditions. At this concentration, water is usually miscible with the oligomeric lignin-derived components because of the solubilizing effect of other polar hydrophilic compounds (low-molecular-weight acids, alcohols, hydroxyaldehydes, and ketones) mostly originating from the decomposition of carbohydrates. The presence of

water has both negative and positive effects on the oil properties. It lowers its heating value, especially the LHV and flame temperature. It also contributes to the increase in ignition delay and in some cases to the decrease of combustion rate compared to diesel fuels.¹⁵ On the other hand, it improves bio-oil flow characteristics (reduces the oil viscosity), which is beneficial for combustion (pumping and atomization). It also leads to a more uniform temperature profile in the cylinder of a diesel engine and to lower NO_x emissions.

Volatility Distribution. Due to their chemical composition, bio-oils show a very wide range of boiling temperature. In addition to water and volatile organic components, biomass pyrolysis oils contain substantial amounts of nonvolatile materials such as sugars and oligomeric phenolics. In addition, the slow heating of the oils during distillation results in polymerization of some reactive components. Consequently, the oils start boiling below 100 °C but the distillation stops at 250–280 °C, leaving 35–50% of the starting material as residue. Thus, bio-oils cannot be used for applications requiring complete evaporation before combustion.

Viscosity and Aging. The viscosity of bio-oils can vary over a wide range (35–1000 cP at 40 °C) depending on the feedstock and process conditions, and especially on the efficiency of collection of low boiling components. It decreases at higher temperatures much faster than for petroleum-derived oils, so that even very viscous bio-oils can be easily pumped after a moderate preheating. A significant reduction in viscosity can also be achieved by addition of polar solvents such as methanol or acetone. An undesired effect, especially observed when the oils are stored or handled at higher temperature, is the viscosity increase with time.¹⁶ This is believed to result from chemical reactions between various compounds present in the oil, leading to the formation of larger molecules. There is also evidence of reaction with oxygen from air.

Corrosiveness. Bio-oils contain substantial amounts of organic acids, mostly acetic and formic acids, which results in a pH of 2–3. For this reason, the oils are corrosive to common construction materials such as carbon steel and aluminum¹⁷ and can affect some sealing materials. The corrosiveness is especially severe at elevated temperature and with the increase in water content. The oils are essentially noncorrosive to stainless steels. Polyolefins are usually an acceptable material of construction where other circumstances permit.

Combustion Behavior. These properties have an important impact on the behavior of bio-oils during combustion and consequently on the applications for energy production in standard equipment. Bio-oils are combustible but not flammable; because of the high content of nonvolatile components, bio-oil requires significant energy for ignition, but once ignited, it burns with a stable self-sustaining flame. An extensive study on the fundamentals of bio-oil combustion was done at Sandia National Laboratory using bio-oils produced at the NREL vortex reactor plant.^{18,19} Combustion tests performed on single droplets demonstrated a very

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unique, multistep process comprised of the following phases: ignition, quiescent burning (blue), droplet micro-explosion, disruptive sooty burning of droplet fragments (bright yellow), and formation and burnout of cenosphere particles. In contrast, petroleum distillate fuel oil demonstrated in the same conditions only quiescent, sooty burning from ignition through burnout. Despite large differences in fuel properties and combustion mechanisms, the burning times of bio-oils were comparable to those of No. 2 fuel oil under the same conditions. While the droplets of less severely cracked pyrolysis oils were found to exhibit an earlier but less effective micro-explosion and significantly longer burnout times than No. 2 fuel oil (180 ms vs 110 ms), the bio-oils that underwent more severe cracking during the pyrolysis process exhibited more violent micro-explosions, which resulted in more rapid burnout than light fuel oil. Also the adiabatic flame temperature for bio-oil is relatively high, 1700–2000 K compared to 2200–2300 K for standard fuels. This difference is much less than could be expected on the basis of heating values because of significantly lower stoichiometric air-to-fuel ratios for biomass pyrolysis oils (about 7 compared to 14 for standard fuels).

Macro-scale combustion tests performed in flame tunnels at MIT²⁰ and CANMET²¹ on fast pyrolysis bio-oil as well as those done at the International Flame Research Foundation,²² ENEL,²³ and COGIS²⁴ using slow pyrolysis liquid did not indicate fundamental differences in combustion behavior of wood pyrolysis oil and No. 2 fuel oil and confirmed that bio-oil could be burned with steady, self-sustaining flames similar to those from petroleum-based fuel oils. Emissions from bio-oil combustion, in general, showed higher particulate and CO levels than for petroleum fuels with NO_x concentration less than for No. 6 but higher than for No. 2 fuel oil.

Fuel Applications of Bio-oils

Over the last two decades there has been a growing interest in using biomass-derived fuels. Initially this interest was driven by concerns for potential shortages of crude oil, but in recent years the ecological advantages of biomass fuels have become an even more

important factor. Biomass fuels can be considered essentially CO₂ neutral and have a very low sulfur content compared to many fossil fuels. In addition, being a liquid, bio-oil can be easily transported and stored. However, the properties of bio-oil also result in several significant problems during its use as 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. In addition, bio-oil is not yet a commercial product and it lacks the quality standards necessary for commercial application.

The variability of its composition due to different feedstocks, reactor configurations, and recovery systems that results in differences in physical and chemical properties as well as combustion behavior makes large-scale applications even more difficult. However, compared to traditional biomass fuels such as black liquor or hog fuel, bio-oil presents a much better opportunity for high-efficiency energy production, and significant effort has been spent on research and development directed to the application of bio-oil for the generation of heat and power and for use as a transport fuel. In this paper, we review the state of the art in the area of combustion of bio-oil in boilers, diesel engines, gas turbines, Stirling engines, and upgrading to potential transport fuel.

Combustion in Burner/Furnace and Burner/Boiler Systems

Furnaces and boilers are common devices used for heat and power generation. They are usually less efficient than engines and turbines but they can operate with a great variety of fuels ranging from natural gas and petroleum distillates to sawdust and coal/water slurries. Bio-oil seems thus to be a suitable boiler fuel as long as it has consistent characteristics, provides an acceptable emissions level, and is economically feasible. Therefore, several companies have been interested in using bio-oil, especially for district heating to replace heavy fuel oil.

The only commercial system that regularly uses bio-oil to generate heat is at the Red Arrow Products pyrolysis plant in Wisconsin²⁵ and has been operated for over 10 years. The 5 MWth swirl burner uses different mixtures of byproducts, water-insoluble fraction of bio-oil (pyrolytic lignin), and char and gas from the plant dedicated to produce food-flavoring components. The bio-oil fraction is delivered to the combustor through a stainless steel nozzle and atomized with air, while char and gas are fed using separate lines. A 600 m² exhaust gas/air heat exchanger located at the combustor exit provides all space heating needs for the plant. Emission tests performed in 1994 showed CO at 17%, NO_x at 1.2%, and formaldehyde at 0.2% of the permitted levels.

Most research on bio-oil combustion in boilers has been carried out in Finland. Extensive tests have been

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performed at Neste Oy²⁶ in a 2.5 MW Danstoker boiler supplied with a dual fuel burner. The boiler operated satisfactorily in a dual fuel mode at different fuel oil to bio-oil ratios. The operation on pyrolysis oil without the auxiliary fuel required only relatively minor modifications to improve combustion stability. With such modifications, emissions of CO and NO_x were at acceptable levels (30 and 140 ppm, respectively) but particulates were still high (2.5–5 in the Bacharach scale). VTT Energy in collaboration with Oilon Oy²⁷ performed a series of tests on a wide range of bio-oils in an 8 MWth nominal capacity furnace operated at 4 MWth output. The main findings of these tests, which were consistent with those of Neste Oy, can be summarized as follows:

- Some modifications of the burner and boiler sections were required to improve combustion.
- The flame from bio-oil combustion was longer than that from burning standard fuel oil.
- A support fuel was necessary during start up and, in cases of lower quality bio-oils, even during operation.
- There were clear differences in combustion behavior and emissions for different bio-oils tested; those with high viscosity and water and solids content showed significantly worse performances.
- Emissions, in general, were lower than from burning heavy fuel oil except for particulates. They strongly depended on the proper handling of bio-oil (optimum was preheating to 50 °C and compressed air atomization) and its quality; for example, higher water content led to lower NO_x but higher particulates in flue gases.

An attractive option can be co-firing of bio-oil with fossil fuels. Large-scale tests have been carried out at the Manitowac power station,²⁸ where pyrolysis liquids from the Red Arrow operation were co-fired with coal for the commercial production of electricity. During a one-month period, bio-oil was co-fired for about 370 h, providing 5% of the thermal input to the 20 MWe boiler. The combustion of bio-oil was clean and efficient with no adverse changes on the boiler operation or on the emission levels.

In conclusion, a constant and better quality bio-oil available at an attractive price is necessary for commercial, large-scale applications. Problems of handling (storage, pumping, filtration, atomization) and optimization of the burner/boiler design to improve performances and reduce emissions seem to be possible to solve by relatively minor modifications to the existing equipment.

Combustion in Diesel Engines. While boilers are mostly used to produce heat, Diesel engines offer a high efficiency (up to 45%) in power generation and can also be adapted to the combined heat and power process (CHP). Medium- and slow-speed engines are known for fuel flexibility and can operate on low-grade fuels. The main concerns for operating diesel engines on bio-oils

are some specific properties of these liquids such as difficult ignition (resulting from low heating value and high water content), corrosiveness (acids), and coking (thermally unstable compounds). However, potential advantages of using bio-oils for power generation have led to important research activities in several countries.

In 1993 at VTT Energy, Solantausta et al.²⁹ using a 500 cm³ (maximum power 4.8 kW) high-speed, single-cylinder, direct injection Petter diesel engine with a compression ratio of 15.3:1, could not achieve auto-ignition of bio-oil without additives. A minimum of 5 vol % of a nitrated alcohol was required for stable engine operation (typically, 0.1–1 vol % of this component is added to standard fuels). Even with 9% of this additive, the ignition delay for bio-oil was 9 crank angle degrees (CAD), compared to 6 CAD for No. 2 fuel oil. In addition, coke formed during bio-oil combustion, resulting in rapid clogging of injection nozzles. CO, NO_x, and hydrocarbon emissions (after catalytic converter) from pyrolysis oil were comparable to those from diesel fuels. Further tests at VTT Energy³⁰ (84 kW engine) and Wärtsilä³¹ (1.5 MWe engine) showed that bio-oil could be efficiently used in pilot-ignited medium-speed diesel engines. The most important identified problems were difficulty in adjusting the injection system (excessive variability in composition of bio-oil), wear and corrosion of certain injection and pump elements (acids, particulates), and high CO emissions. However, it seems possible to overcome these problems with improvements to the pyrolysis process and use of better materials for injection nozzles and a catalytic converter for exhaust gases.

Suppes³² at University of Kansas found that ignition delay of a hot-filtered bio-oil (no particulates) measured in a combustion bomb was similar to that of 27 Cetane reference fuel. His tests on a blend of 72% pyrolysis oil, 24% methanol, and 4% cetane enhancer (tetraethyl-ene glycol dinitrate) performed in a single-cylinder, air-cooled Lister Petter diesel engine showed the same performance as for diesel oil.³³ The study concluded that the application of pure pyrolysis oils should be limited to low-speed diesel engines with relatively high compression ratios, but blends of biomass oil and methanol could be used in high-speed engines, especially with cetane-improving additives.

Shihadeh³⁴ at MIT tested the combustion behavior of biomass pyrolysis oils using a 0.45 L Ricardo single-cylinder direct injection diesel engine operating at a compression ratio of 19.8 and 2400 rpm. The tests showed that combustion of bio-oils was predominantly kinetically controlled, as opposed to the mixing-con-

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trolled combustion of diesel fuel. However, despite those differences, the thermal efficiency of bio-oils was approximately equal to that for diesel fuel, which has been confirmed by Ormrod.³⁵ Bio-oils required air preheating (55 °C) to ignite, but the engine operated smoothly even though the ignition delay (6–14 CAD) was longer than for diesel fuel. Hot-filtered bio-oils showed improved combustion characteristics (shorter ignition delay, shorter burn duration, less coking) mostly due to lower molecular weights resulting from vapor cracking during filtration and lower water content.

Ormrod Diesels³⁶ in the UK have accumulated more than 400 h of operation on a modified dual-fuel slow-speed diesel engine. Three cylinders of the six-cylinder 250 kW engine have been modified to run on bio-oil using up to 5% diesel as a pilot fuel to initiate combustion. Emissions other than CO were below those obtained while running on diesel fuel. The engine has been successfully operated entirely on bio-oil by shutting off the diesel supply to the un-modified cylinders.³⁵ The minimum diesel contribution as a pilot fuel to provide satisfactory operation was 5% in energy terms. Although black deposits formed on the pumps and injectors, these did not appear to affect performance in any way.

Baglioni et al.³⁷ at Pasquali Macchine Agricole (Italy) conducted a series of tests on emulsions of bio-oil in diesel fuel using a 6.25 kW single-cylinder engine (Lombardini 6LD400). They were able to operate the engine using emulsions with up to 50% of bio-oil. The main problems were deposits and erosion of the injectors. Recently Chiaramonti et al.³⁸ used bio-oil–diesel emulsions in four different engines and observed significant damage of the injectors and the fuel pumps, greater than that reported for pure bio-oil.

Combustion in Turbines. Gas turbines are used in a wide range of applications, most important of which are driving electric power generators and providing power to aircraft. Accordingly, the two main categories of turbines in use are industrial and aircraft types. However, both types of turbines are used in power plants. Though at present most gas turbines operate on petroleum distillates or gas fuels, if properly designed, they can essentially burn any fuel. Certainly, gas turbines can be modified or redesigned to accommodate some of the unusual properties of biomass pyrolysis oils. Moses³⁹ pointed out that modifications have to be done considering the effects of physical and chemical properties of bio-oils on atomization, combustion efficiency,

soot formation, and gaseous and particulate emissions. Also very important issues to address are compatibility of bio-oils with the materials used in fuel systems (acid corrosion) and in blades (erosion, alkali hot corrosion).

The first gas turbine tests on biomass slow pyrolysis liquids were carried out at Teledyne CAE (USA) by Kasper et al.⁴⁰ in the early 1980s using a J69-T-29 gas turbine combustor rig. The system consisted of an annular combustor and a centrifugal fuel injector rotating at shaft speed. The centrifugal injector was designed to provide good atomization of viscous fuels. The pyrolysis liquids used in the tests were produced from forest and agricultural residues and resembled typical fast pyrolysis bio-oils though they had higher carbon content and higher viscosity. The measured combustion efficiency in the rig using pyrolytic oil as fuel was 95% but it was expected it could exceed 99% in the engine at optimum conditions. Emissions of CO were higher, but CH and NO_x were within the limits observed for petroleum fuels. Also a slag buildup in the exhaust section resulting from ash in bio-oil was identified as a potential problem.

Since 1995 Orenda Aerospace Corporation (Canada) has been actively working on the application of bio-oil in gas turbines combustion. They selected a 2.5 MWe class GT2500 engine that was designed and built by Mashproekt in Ukraine as the most suitable for low-grade fuels including bio-oil. The main advantage of this engine is its “silo” type combustion chamber located above the turbine that can be easily modified and optimized for any fuel. Also, advanced coating of the whole hot section provides protection against contaminants (alkali). Andrews et al.⁴¹ tested the engine throughout the whole operational range, from idle to full power, and found that NO_x and SO₂ emissions from combustion bio-oil were less, while particulates were higher than those from diesel fuel.

Strenziok et al.⁴² at the University of Rostock (Germany) conducted bio-oil combustion tests in a small commercial gas turbine T216 with a rated electric power output of 75 kW. The combustion chamber of the turbine was modified and supplied with two separate fuel systems that included an ignition nozzle for diesel fuel and a main nozzle for bio-oil. The engine operated in a dual fuel mode at 73% of the full power that would be generated in a standard fuel mode, with about 40% of total power produced from bio-oil and 60% from diesel. Compared to the operation on diesel fuel, CO and HC emissions were significantly higher and NO_x less for dual fuel operation. The use of bio-oil in the turbine resulted in deposits in the combustion chamber and on the blades, and finding a solution to prevent fouling of the turbine is a priority requirement.

Combustion in Stirling Engines. Recently, in addition to boilers, diesel engines, and turbines, Stirling

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engines, which are suitable for small-scale combined heat and power (CHP) production, have been considered for the application of bio-oil as an alternative fuel. Bandi and Baumgart⁴³ at ZSW (Germany) used bio-oil in a 25 kW Stirling CHP unit supplied with a modified FLOX (flameless oxidation) burner that included an air pressure atomizer. The tests proved that bio-oil could be efficiently burned in such a burner without noticeable residues and with emissions below German standards. Electrical and thermal efficiencies of the CHP unit were not very satisfactory (50–60% overall), possibly because of the burning chamber geometry and not preheating air for atomization.

Upgrading of Bio-oil to Transport Fuels. The properties that negatively affect bio-oil fuel quality are foremost low heating value, incompatibility with conventional fuels, solids content, high viscosity, incomplete volatility, and chemical instability. Some of those deficiencies can be improved using relatively simple physical methods while others require more complex chemical processing. Maggi and Elliott⁴⁴ extensively reviewed the upgrading methods of bio-oils. In this paper, we will discuss only those that can lead to the use of bio-oil as transport fuel.

The simplest use of bio-oil as a transport fuel seems to be in combination with diesel fuel. Although biomass pyrolysis oils are not miscible with hydrocarbons, with the aid of surfactants they can be emulsified with diesel fuel. Processes for producing stable microemulsions with 5–30% of bio-oil in diesel have been developed at CANMET⁴⁵ (Canada) and at the University of Florence^{37,38} where emulsions from 10 to 90% bio-oil in diesel were produced. The resultant emulsions showed promising ignition characteristics. A drawback of this approach is the cost of surfactants and the high energy required for emulsification. In addition significantly higher levels of corrosion/erosion were observed in engine applications than with bio-oil or diesel alone.

Upgrading bio-oil to a conventional transport fuel requires full deoxygenation, which can be accomplished by two main routes: hydrotreating and catalytic vapor cracking. Hydrotreating of bio-oil carried out at high temperature, high hydrogen pressure, and in the presence of catalysts results in elimination of oxygen as water and in hydrogenation–hydrocracking of large molecules. The catalysts (typically sulfided CoMo or NiMo supported on alumina) and the process conditions are similar to those used in the refining of petroleum cuts.⁴⁶ Chemical methods for upgrading bio-oil by hydrotreating and zeolite cracking have been reviewed by Bridgwater.^{47,48} A projected typical yield of naphtha equivalent from biomass is about 25 wt % or 55% in energy terms excluding provision of hydrogen.⁴⁸

Catalytic vapor cracking makes deoxygenation possible through simultaneous dehydration–decarboxylation over acidic zeolite catalysts. At 450 °C and atmospheric pressure, oxygen is rejected as H₂O, CO₂, and CO producing mostly aromatics.⁴⁹ The low H/C ratio in the bio-oils imposes a relatively low limit on the hydrocarbon yield and, in addition, the technical feasibility is not yet completely proven. Catalyst deactivation still raises many concerns for both routes, although the coking problem with zeolites can in principle be overcome by a conventional FCC arrangement with continuous catalyst regeneration by oxidation of the coke. Some concern has been expressed over the poor control of molecular size and shape with orthodox zeolites and the propensity for formation of more noxious hydrocarbons.⁵⁰ The processing costs are high and the products are not competitive with fossil fuels.⁵¹ A projected typical yield of aromatics suitable for gasoline blending from biomass is about 20 wt % or 45% in energy terms.⁴⁸

Although upgrading to a liquid transport fuel does not currently look promising, bio-oil can become a source of the emerging transport fuel for the future – hydrogen. Production of hydrogen from biomass by pyrolysis and reforming has been extensively studied at the National Renewable Energy Laboratory (USA).^{52,53} The water-soluble (carbohydrate-derived) fraction of bio-oil was efficiently converted to hydrogen and CO₂ (>80% of theoretical conversion) in a fluidized bed process using commercial, nickel-based catalysts in the conditions similar to those for reforming natural gas. In such a concept, only 6 kg of hydrogen were produced from 100 kg biomass compared with 11–12 kg that could be obtained by direct gasification of biomass. However, the process makes economical sense providing that the lignin-derived fraction of bio-oil could be sold at half the price of phenol for the use as a phenol replacement in phenol-formaldehyde resins.⁵⁴

An alternative approach has recently been proposed whereby bio-oil or a bio-oil/char slurry is used as an energy carrier to more economically transport biomass to a central processing site where the liquid or slurry is gasified in an oxygen-blown pressurized gasifier to syngas for production of liquid fuels.⁵⁵ This offers the possibility of achieving high throughputs to take advantage of the economy of scale that is often absent in stand-alone bio-energy plants.

Summarizing, the application of bio-oils for heat and power generation is possible and usually only requires

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minor modifications of the existing equipment as demonstrated by the tests in boilers, diesel engines, and turbines. More research is needed in the area of handling bio-oils, especially on stabilization. Upgrading bio-oil to a quality transport liquid fuel still poses several technical challenges and is not currently economically attractive. An attractive future transportation fuel can be hydrogen produced by steam reforming of the whole oil or its carbohydrate-derived fraction.

Applications of Bio-oil for Producing 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. Though over 300 compounds have been identified in wood fast pyrolysis oil, their amounts are small and isolation of specific single compounds is seldom practical or economic as it usually requires complex separation techniques. Therefore, the development of technologies for producing products from the whole bio-oil or from its major, relatively easy separable fractions is the most advanced. In this paper we will discuss only the existing and potential short-term applications of bio-oil for producing chemicals. A more detailed review on this subject, including consideration of higher-value products, was published by Radlein.⁵⁶

Chemicals Produced from the Whole Bio-oil. The whole bio-oil can be converted into useful chemicals by taking advantage of its most abundant functional groups: carbonyl, carboxyl, and phenolic and react them in such a way that the nonreacting part of bio-oil would not have to be separated from the final product. For example, carboxylic acids and phenols can easily react with lime to form calcium salts and phenates. Based on this property, Dynamotive Corporation developed a product, BioLime,⁵⁷ which proved successful in capturing SO_x emissions from coal combustors. BioLime that typically contains 50% water and 7–14% calcium by weight is injected as a liquid suspension into a high-temperature flue gas stream. Compared to lime, those organic calcium compounds are about four times more efficient in capturing acid gases. With an appropriate calcium-to-sulfur ratio, BioLime can remove 90–98% SO_x from flue gases. Another advantage of BioLime is that oxidation of its organic, bio-oil derived part provides additional energy in the combustor. Furthermore, some components of BioLime proved to be efficient in destroying nitrogen oxides.⁵⁸ Although the technology for producing BioLime is well developed, the availability of low-cost lime makes marketing difficult.

Another promising application of the whole bio-oil exploits its high content of carbonyl groups. By reacting bio-oil with ammonia, urea, or other –NH₂ containing materials, various imide and amide bonds are formed between carbonyl carbons and nitrogen. In this fashion

about 10% nitrogen can be incorporated in an organic matrix that proved to have properties of an efficient biodegradable slow-release nitrogen fertilizer.^{59,60} Compared to mineral fertilizers, such a product has lower leachability, which results in less pollution of groundwaters. In addition, it is a good soil conditioning material containing humic type matter (lignin). Application of such a fertilizer returns carbon to the soil and can be also considered a method of carbon sequestration. Typical controlled-release nitrogen fertilizers sell for \$250–\$1250/ton, so bio-oil based fertilizer should be cost competitive on the market and is targeted for commercialization by Dynamotive.⁶¹

In addition to the above applications, the whole bio-oil has been recently proposed for use as an alternative wood preservative that could replace creosote.⁶² Some terpenoid and phenolic compounds present in bio-oil are known to act as insecticides and fungicides. It was proven that impregnating with bio-oil protects wood from fungi;⁶³ however the efficiency of bio-oil action was not long-lasting. When the retention of bio-oil in wood is improved, either the whole liquid or a fraction could be used as an environmentally friendly wood preservative.

Chemicals from Fractionation of Bio-oil. Bio-oil can be easily separated into two fractions based on water solubility. By simple water addition to bio-oil, a viscous mostly oligomeric lignin-derived fraction settles at the bottom while water soluble, mostly carbohydrate-derived compounds form a top layer. Although other solvent fractionation methods have also been developed, especially to improve the purity of the lignin-derived material,⁶⁴ water addition seems to be the favored option.

The water-soluble part of fast pyrolysis bio-oil has found an application that has been commercial for over 10 years. The aqueous extract of bio-oil includes both low-molecular-weight aldehydes that are effective meat browning agents (especially glycolaldehyde) as well as phenolic compounds that provide smoky flavors. Based on this, a range of food flavoring compositions have been patented and commercialized by Red Arrow Products Company,^{65,66} that successfully competes with similar products known as “liquid smoke” produced by a variety of slow pyrolysis processes in several countries.

A potential application of the water-soluble fraction

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of bio-oil is the production of calcium salts of carboxylic acids that can be used as environmentally friendly road de-icers.⁶⁷ Volatile organic acids, mostly formic, acetic, and propionic that are abundant in the aqueous extract of bio-oil can be distilled off as a sub-fraction. Although such a distillate also includes other volatile components (such as aldehydes and esters), they either can react with lime or are evaporated during the recovery of solid calcium salts. The scale-up of the production of biomass-derived de-icers is technically feasible but not currently economic. Calcium chloride is much less expensive and thus used as the most common de-icer, though it is known to have deleterious effects on plants.

The water-insoluble fraction that usually constitutes 25–30% of the whole bio-oil is often called pyrolytic lignin because it is essentially composed of oligomeric fragments originating from degradation of native lignin.^{68,69} So far, high-value applications of this fraction have not been commercialized; however, using pyrolytic lignin as phenol replacement in phenol-formaldehyde resins seems to approach that stage. The most important contributions in research and development on pyrolytic lignin-based resin formulation have been made at NREL^{70,71} and Biocarbons⁷² in the United States, Ensyn⁷³ and Pyrovac⁷⁴ in Canada, and ARI⁷⁵ in Greece. Although lignin is less reactive than phenol, 30–50% of phenol can be replaced by pyrolytic lignin in novolak and resole formulations producing high-quality resins. Those resins were successfully used as adhesives in plywood and particleboard manufacturing, showing high mechanical strength. Lower toxicity and lower cost compared to phenol make pyrolytic lignin an attractive component of adhesives. Consequently, resin and board manufacturers such as Louisiana Pacific, Weyerhaeuser, A. C. M. Wood Chemicals, and others have been heavily involved in commercialization of bio-oil derived adhesives.

Specific Chemicals from Bio-oil. As mentioned above, the production of specific chemicals from bio-oil is possible but because of the complexity of separation techniques has not been developed in larger scale, except from slow pyrolysis liquids where production of a few specific chemicals is viable by companies such as Chemviron in Germany, and until 2002, Usine Lambiotte in France. The most promising seems to be

glycolaldehyde (also known as hydroxyacetaldehyde) that is, besides water, the most abundant single component of fast pyrolysis bio-oil. Glycolaldehyde is also the most active meat-browning agent in “liquid smoke” and, therefore, it raised interest in the food flavoring industry. Red Arrow Products⁷⁶ and RTI⁷⁷ patented methods for isolation of glycolaldehyde based on crystallization. The production of glycolaldehyde is more attractive if cellulose is used instead of wood as feedstock for fast pyrolysis. In such a case, the lignin-free pyrolysis liquid contains a higher concentration of the desired product and isolation is easier, more efficient, and has been shown to be more economic, even allowing for the higher cost of cellulose compared to biomass.⁷⁸

Levoglucosan (1,6-anhydro- β -D-glucopyranose) and levoglucosenone (6,8-dioxabicyclo[3.2.1]oct-2-en-4-one) are not typical components of bio-oil produced for fuel application but can be generated with high yields by a similar pyrolysis processes from demineralized cellulose or biomass. For example, Dobeles⁷⁹ reported that 46% yield of levoglucosan and 24% of levoglucosenone were obtained by fast pyrolysis (pyroprobe) of acid-pretreated cellulose. A substantial review on the production and potential applications of levoglucosan was published by Radlein.⁸⁰ Several processes have been patented for pyrolytic generation, recovery, and purification of levoglucosan from cellulose and lignocellulosic materials, for example, the University of Waterloo fluidized bed process.⁸¹ The optimum process temperature for the production of levoglucosan is in the range of 400–500 °C, and different types of reactors can be used to provide about 50% yield based on cellulose in the feedstock. In the former Soviet Union, a 20 kg/h fluidized bed and a 30 kg/h cyclonic reactor were used to produce levoglucosan from acid-hydrolyzed biomass (lignocellulose).⁸² The approximate yield of levoglucosan from fast pyrolysis of lignocellulose was 20% in the condensate and 10% as a purified (96%) product. It seems that the main difficulty in the production of levoglucosan is not pyrolysis but rather its efficient isolation from the pyrolytic liquids. Though levoglucosan has potential for the manufacturing of pharmaceuticals, surfactants, biodegradable polymers, and others, the high production price, mostly due to the lack of low-cost recovery and purification procedures, makes unlikely its extensive use soon. Levoglucosenone was produced by fluidized bed pyrolysis of phosphoric acid-impregnated cellulose with the yield of 24%.⁵⁶ It can be relatively easily

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recovered from pyrolytic liquid by distillation. As with levoglucosan, it has potential in the synthesis of antibiotics and flavor compounds, but has not found yet a large-scale application.

In summary, some chemicals produced from the whole bio-oil or by its fractionation are already commercial products, for example liquid smoke, or have a chance for short-term commercialization, especially if a bio-refinery concept based on a fast pyrolysis process is implemented.⁸³ Commercialization of specialty chemicals from bio-oil requires more work on developing reliable low-cost separation procedures as well as working more closely with potential market outlets.

Conclusions

The liquid bio-oil product from fast pyrolysis has the considerable advantage of being a storable and transportable fuel as well as a potential source of a number of valuable chemicals that offer the attraction of much higher added value than fuels. Bio-oil has been successfully used as boiler fuel and also showed promise in diesel engine and gas turbine applications. Upgrading bio-oil to a quality of transport liquid fuel still poses several technical challenges and is not currently economically attractive. Some chemicals, especially those produced from the whole bio-oil (such as fertilizers) or its major fractions (such as liquid smoke or for wood resins), offer more interesting commercial opportunities.

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There are still many challenges to overcome before bio-oil finds large-scale application as fuel, including:

- Cost of bio-oil, which is 10% to 100% more than that of fossil fuel.

- Availability of material remains a problem, and there are limited supplies for testing.

- Lack of standards for use and distribution of bio-oil, and inconsistent quality inhibits wider usage. Considerable work is required to characterize and standardize these liquids and develop a wider range of energy applications.

- Incompatibility of bio-oil with conventional fuels and, therefore, the need for dedicated fuel handling systems.

- Users are unfamiliar with bio-oil.

- Environmental health and safety issues need to be completely resolved.

- Pyrolysis as a technology does not enjoy a good image.

More research is needed in the field of fast pyrolysis and bio-oil testing to develop large-scale applications. The most important issues that need to be addressed seem to be:

- Scale-up

- Cost reduction

- Better oil quality

- Norms and standards for producers and users

- Environmental health and safety issues in handling, transport, and usage

- Encouragement for developers to implement processes and for users to implement applications.

- Information dissemination.

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