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Applications for Utilisation of Liquids Produced by Fast Pyrolysis of Biomass

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Introduction

Thermal biomass conversion has been investigated for many years as a source of renewable solid, gaseous, and liquid fuels. Compared to combustion, which is widely practised commercially, and gasification, which is being extensively demonstrated around the world, fast pyrolysis is at a relatively early stage of development. The process of fast pyrolysis is one of the most recent renewable energy processes to have been introduced and offers the advantages of a liquid product, bio-oil, that can be readily stored and transported and that can also be used for production of chemicals as well as being a fuel. The technology has now achieved some 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 an unacceptable energetic and financial cost.

Fast pyrolysis

Pyrolysis is by definition thermal decomposition occurring in the absence of oxygen. Three products are always formed, but the proportions can be varied over a wide range. The essential features of a fast pyrolysis process for producing liquids are:

- very high heating and heat transfer rates at the reaction interface, which usually requires a finely ground biomass feed,
- carefully controlled pyrolysis reaction temperature of around 500°C and vapour phase temperature of 400-450°C,
- short hot vapour residence times of typically less than two seconds,
- rapid cooling and coalescence of the pyrolysis vapours to give the bio-oil product.

Fast pyrolysis is an advanced process that requires carefully controlled parameters to give high yields of liquid. The main product, bio-oil, is obtained in yields of up to 75% wt on a dry feed basis, together with by-product char and gas which are typically used within the process so there are no waste streams other than flue gas and ash. However the char can be exported if there is a suitable market.

Fast Pyrolysis Liquid Bio-oil

Pyrolysis liquid is referred to by many names including pyrolysis oil, bio-oil, bio-crude-oil, bio-fuel-oil, wood liquids, wood oil, liquid smoke, wood distillates, pyroigneous tar, pyroigneous acid, and liquid wood. The crude pyrolysis liquid is dark brown and approximates to biomass in elemental composition. It is composed of a very complex mixture of oxygenated hydrocarbons with an appreciable proportion of water. Some important characteristics of this liquid are summarised in Table 1.

Table 1: Typical properties and characteristics of wood derived crude bio-oil

| Physical property | Typical value | Notes |
|---------------------------------------|---------------|--|
| Moisture content | 25 % | Water comes from moisture in the feed and reaction water and cannot be separated. |
| pH | 2.5 | The low pH comes from organic acids |
| Density | 1.20 | Very high at around 1.2 kg/litre compared to light fuel oil at around 0.85 kg/litre. Bio-oil has about 40% of the energy content of fuel oil on a weight basis, but 60% on a volumetric basis. |
| Elemental analysis | | Typically: C: 57%, H: 6.0%, O: 37%, N: trace |
| Ash | 0% | All ash is associated with the char. |
| HHV as produced (depends on moisture) | 18 MJ/kg | Bio-oil has a higher heating value of about 18 MJ/kg as produced with about 25% wt. water that cannot be separated. |
| Viscosity (at 40°C and 25% water) | 50 cp | Viscosity as produced can vary from 20 cSt to 1000 cSt (measured at 40°C) depending on feedstock, water content, light, and ageing. |
| Solids (char) | 0.2 % | 0.1 wt% is a good level |
| Vacuum distillation residue | 50% | Cannot be completely vaporised. Heating to 100°C causes production of a solid residue of around 50 wt% of the original liquid and distillate containing volatile organics and water. |
| Appearance | | Typically a dark brown free flowing liquid. |
| Odour | | A distinctive smoky smell. |
| Miscibility | | Water addition can be tolerated up to about 35% wt. Bio-oil is miscible with polar solvents such as methanol, but totally immiscible with petroleum-derived fuels. |

Applications for Bio-oil For Heat and Power

Bio-oil can substitute for fuel oil or diesel in many static applications including boilers, furnaces, engines, and turbines for electricity generation. The possibilities are summarised in Figure 1. There is also a range of products that can be extracted or derived including food flavourings, specialty chemicals, resins, agri-chemicals, fertilisers, and emissions control agents. Upgrading bio-oil to transportation fuels is feasible but currently not economic.

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 for power generation 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 is a suitable boiler fuel as long as it has consistent characteristics, provides acceptable emissions level, and is economically feasible.

Most research on bio-oil combustion in boilers has been carried out in Finland by Neste Oy and Oilon. The only commercial system that regularly uses bio-oil to generate heat is at the Red Arrow Products pyrolysis plant in Wisconsin USA and has been operated for over ten years. 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 in the USA, where pyrolysis liquids from the Red Arrow operation were co-fired with coal for the commercial production of electricity.

A consistent and better quality bio-oil at an attractive price is necessary for commercial, large-scale applications. Problems of handling (storage, pumping, filtration, and atomisation) and optimisation of the burner/boiler design to improve performances and reduce emissions can be solved by relatively minor modifications to the existing equipment.

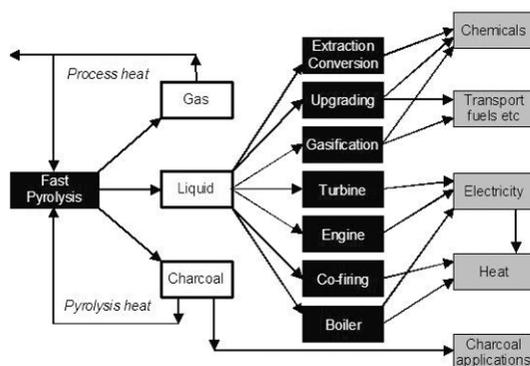


Figure 1: Applications for Bio-oil.

Combustion in diesel engines

While boilers are mostly used to produce heat, diesel engines offer high efficiency in power generation (up to 45%) and can also be adapted to combined heat and power (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.

Tests at VTT Energy and Wärtsilä (Finland) showed that the most important problems were difficulty in adjusting the injection system, wear and corrosion of certain injection and pump elements (acids, particulates), and high CO emissions. Testing has also been carried out at the University of Kansas (USA), MIT (USA), and Ormrod (UK) which showed that the thermal efficiency of bio-oils was approximately equal to that for diesel fuel. Emulsions of bio-oil and diesel have been tested in Italy, Germany, and the UK, but these caused substantial and rapid erosion of injectors and pumps.

Combustion in turbines

The first gas turbine tests on biomass slow pyrolysis liquids were carried out at Teledyne CAE (USA) in the early 1980s using a J69-T-29 gas turbine combustor rig. Emissions of CO were higher but CH and NO_x were within the limits observed for petroleum fuels.

Since 1995 Orenda Aerospace Corporation (Canada) has been actively working on the application of bio-oil in gas turbines combustion on a 2.5 MWe Mashproekt machine from the Ukraine. The main advantage of this engine is its 'silo' type combustion chamber located above the turbine that can be easily modified and optimised for any fuel. The engine has been tested throughout the whole operational range, from idle to full power, and found that NO_x and SO₂ emissions from combustion of bio-oil were less, while particulates were higher than those from diesel fuel.

The University of Rostock (Germany) has conducted bio-oil combustion tests in a small commercial 75 kW_e gas turbine. 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. CO and HC emissions were significantly higher and NO_x less for dual fuel operation.

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.

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 as described above.

Upgrading bio-oil to a conventional transport fuel requires full deoxygenation, which can be accomplished by two main routes: hydrotreating and catalytic vapour 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 and the process conditions are similar to those used in the refining of petroleum cuts. A projected typical yield of naphtha equivalent from biomass is about 25% by weight or 55% in energy terms excluding provision of hydrogen.

Catalytic vapour 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. 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. The processing costs are high and the products are

not competitive with fossil fuels. A projected typical yield of aromatics suitable for gasoline blending from biomass is about 20% by weight or 45% in energy terms.

Although upgrading to a liquid transport fuel does not currently look promising, bio-oil can become a source of hydrogen by reforming the water soluble fraction, as at the National Renewable Energy Laboratory (USA).

An alternative approach has recently been proposed whereby bio-oil or 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 pressurised gasifier to syngas for production of liquid fuels. This offers the possibility of achieving high throughputs to take advantage of the economy of scale that is often absent in stand-alone bioenergy plants.

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. Although 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.

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 non-reacting 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 to give product known as BioLime, which proved successful in capturing SO_x emissions from coal combustors.

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 imides 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 fertiliser. Compared to mineral fertilisers, such a product has lower leachability, which results in less pollution of ground waters.

Bio-oil has been recently proposed for use as an alternative wood preservative to replace creosote.

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, water addition seems to be the favoured option.

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 flavours. Based on this, a range of food flavouring compositions have been developed by Red Arrow Products (USA).

A potential application of the water-soluble fraction of bio-oil is the production of calcium salts of carboxylic acids that can be used as environmentally friendly road de-icers. 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. Pyrolytic lignin can be used as a phenol replacement in phenol-formaldehyde resins. The most important contributions in research and development on pyrolytic lignin based resin formulation have been made at NREL and Biocarbons in the USA, Ensyn and Pyrovac in Canada, and ARI 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.

Specific chemicals from bio-oil

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 viable production of a few specific chemicals by companies such as Chemviron in Germany, and until 2002, Usine Lambiotte in France. The most promising seems to be glycolaldehyde which is, apart from water, the most abundant single component of fast pyrolysis bio-oil.

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 commercialisation, especially if a bio-refinery concept based on fast pyrolysis process is implemented. Commercialisation 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 fertilisers) or its major fractions (such as for wood resins) offer more interesting commercial opportunities. 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 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.
- Incompatibility of bio-oil with conventional fuels and, therefore, 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 are:

- Scale-up,
- Cost reduction,

- Better oil quality,
- Norms and standards for producers and users,
- Environment health and safety issues in handling, transport and usage,
- Encouragement for developers to implement processes; and users to implement applications.
- Information dissemination.

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