REVIEW OF PYROLYSIS BIO-OIL APPLICATIONS

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Abstract

Pyrolysis bio-oil is a second-generation biofuel that could be used in mobile and stationary applications or as source of valuable oxygen-containing chemicals. Currently, bio-oils have been produced commercially in several countries. In the industrial-scale tests, bio-oils have been demonstrated to be a good option to replace heavy petroleum oils in district heating applications. This work reviews the possibilities and limitations of this and other possible applications of bio-oils and presents their current state-of-the-art.

Introduction

In the last decades, the importance of biomass as an energy source has significantly increased. This can be attributed to the increased awareness of the negative environmental effects associated with the use of fossil fuels and their gradual depletion. Biomass is a renewable and environmentally-friendly feedstock that can be used as an energy source directly by combustion or indirectly by conversion into valuable products via different thermochemical or biochemical processes. Among the processes suggested for biomass conversion, fast pyrolysis seems to be one of the most important ones[1,2].

In a fast pyrolysis process, biomass is rapidly heated to high temperatures without an access of air (oxygen) to produce high yields of liquid pyrolysis bio-oil (~75 wt%) and lower yields of gasses and solid char. Pyrolysis bio-oil is a renewable energy source with a low content of nitrogen, sulphur and metals that has, in comparison with raw biomass, about 2–10 times higher energy content per volumetric unit, which makes it easier to be handled, stored and transported than raw biomass[2]. Due to these properties, bio-oil is a promising product for further use in stationary applications, as transportation fuel or source of valuable chemicals. However, bio-oils are composed mostly of oxygen-containing compounds and high amount of water, see **Table I**, and have some significantly undesirable properties, especially high viscosity, acidic character (corrosive properties), 2–3 times lower LHV (lower heating value) than petroleum fuels, low chemical and thermo-oxidative stability, immiscibility with conventional petroleum fuels, etc. Majority of possible bio-oil applications requires improvement of these properties[3,4].

Table I
Comparison of typical properties of pyrolysis bio-oil and diesel[5-7]

Parameter	Bio-oil	Diesel
Water content [wt%]	15–30	<0.2
pH	2–3	–
Density (15 °C) [$kg\cdot m^{-3}$]	1100–1300	820–845
Viscosity (40 °C) [$mm^2\cdot s^{-1}$]	15–35	2.0–4.5
C [wt%]	54–58	87
H [wt%]	5.5–7.0	12.6
N [wt%]	<0.4	<0.02
S [wt%]	<0.05	<0.001
O [wt%]	35–50	0.4
Ash content [wt%]	0.01–0.1	<0.01
Lower heating value [$MJ\cdot kg^{-1}$]	13–18	42
Flash point [°C]	40–110	>55
Pour point [°C]	-9–36	-5 min
Cetane number	5–25	48–52

The aim of this work is to provide a brief overview of pyrolysis bio-oil applications, their possibilities and limitations and their current state-of-art.

Applications of Pyrolysis Bio-oils

An overview of possible bio-oil applications is presented in **Figure 1**. These applications are discussed in more detail in the next subsections.

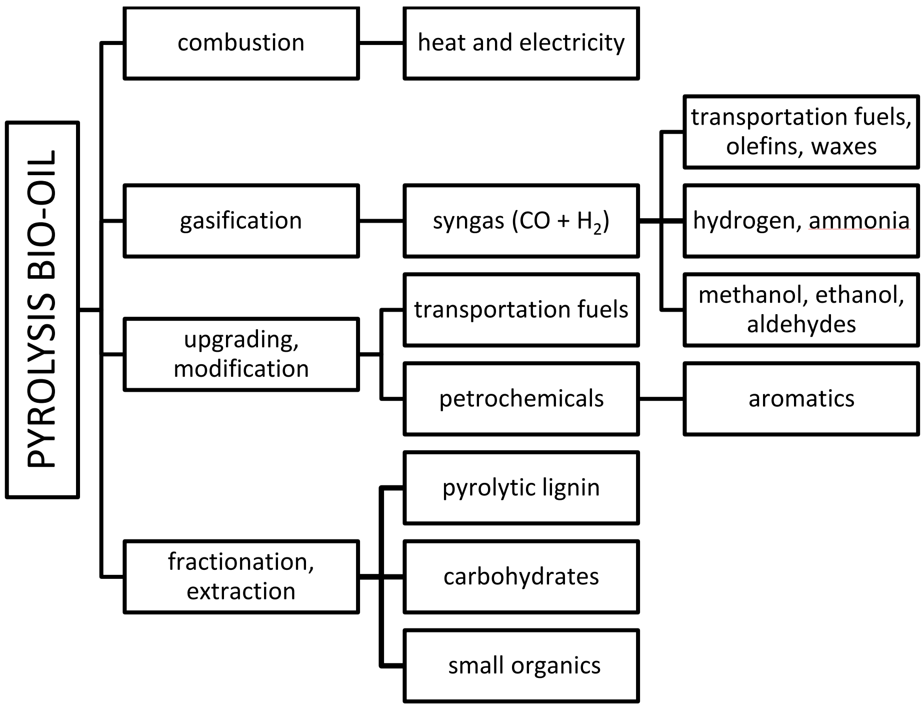

Figure 1. Scheme of possible bio-oil applications[4]

Combustion of pyrolysis bio-oils – production of heat and power

Pyrolysis bio-oils can be (co-)combusted in boilers, furnaces, diesel engines or turbines for producing heat or combined heat and power (CHP), i.e. in so-called stationary applications. Main advantages of these applications are savings of greenhouse gasses (even around 90 %) and reducing the dependency on prices of fossil fuels[8]. The (co-)combustion of bio-oils in decentralized applications, i.e. for district heating or in larger industrial companies producing their own heat and power, seems to be the most promising[8-10].

Boilers and furnaces. Bio-oils can be used as fuel in boilers and furnaces to produce heat, which is an easiest, straightforward application of bio-oils. Combustion of 100 % bio-oil and its co-combustion with fossil fuels was demonstrated. In these applications, boilers or furnaces primarily designed for combustion of fossil fuels do not have to be necessarily replaced as a whole, but it is necessary to use multi-fuel burners and moreover, pipes and storage tanks have to be produced from corrosion resistant material (i.e. stainless steel) due to corrosive properties of bio-oils. Currently, bio-oil is being produced in commercial-size installations (Finland, Netherlands and Brazil) to be used as fuel for district heating applications[10].

Diesel engines and gas turbines. Bio-oils can also be combusted in diesel engines or gas turbines for CHP purposes. Diesel engines have been tested by Wärtsilä[11] and VTT[12] (Finland), Pytec[13] (Germany) and BTG[14] (Netherlands). Gas turbines running on pyrolysis bio-oils have been developed by Magellan-Orenda (Canada) and Opra turbines (Netherlands) companies. However, to our best knowledge, none of these applications have been commercialized yet.

Gasification of pyrolysis bio-oils

Gasification, in general, is a process for producing syngas ($CO + H_2$) that can be used to produce synthetic fuels and various platform chemicals. Fossil fuels or biomass can be used as raw materials for gasification. In general,

there are two options for biomass gasification: (i) gasification of solid (raw) biomass in a centralized gasification unit or (ii) conversion of biomass into intermediates with higher energy density (e.g. bio-oils) in smaller decentralized units and transportation of these intermediates for processing into a centralized unit[15,16]. As gasification is a large-scale process, the second option may be economically feasible especially in areas with poor infrastructure or biomass availability.
Two-step gasification of biomass including conversion of biomass to bio-oil by fast pyrolysis and its subsequent gasification has been developed by several companies, i.e. BTG (Netherlands)[17], Karlsruhe Institute of Technology (Germany)[18], etc. However, the process has not been commercialized yet.

Upgrading and modification of pyrolysis bio-oils

As stated already in the introduction, bio-oils have some undesirable properties that need to be changed to achieve their more widespread use. These include especially high viscosity, acidic character (corrosive properties), 2–3 times lower LHV than petroleum fuels, low chemical and thermo-oxidative stability, immiscibility with conventional petroleum fuels, etc.

Emulsification. A direct use of bio-oils in blends with conventional petroleum fuels would be a great option of exploiting bio-oils in stationary or mobile applications. However, bio-oils have polar character and thereby they are immiscible with petroleum fuels. This can be overcome by preparing emulsions of bio-oils and conventional fuels using suitable emulsifiers. Emulsions of bio-oils with diesel or biodiesel have been studied[16,19,20]. However, commercialization has not been achieved yet.

Esterification. Another problematic property of pyrolysis bio-oils is their corrosive character that is associated with their high content of carboxylic acids, especially acidic and propionic acids. Via esterification, acids present in bio-oils can be converted to esters, which results in an decrease in the acidic character of bio-oils and their corrosive properties[16].

Hydrodeoxygenation (HDO). Difference between physico-chemical properties of bio-oils and petroleum fuels is associated with the high content of water and oxygen-containing compounds in bio-oils. Some of the undesirable bio-oil properties can be improved by decreasing the oxygen content in bio-oils by HDO. In HDO, bio-oil is treated with hydrogen at elevated temperature and pressure in the presence of a catalyst. Oxygen is removed in the form of water[21]. When deep deoxygenation is achieved, the obtained product could be used directly as a blending component of transportation fuels; in case of partial deoxygenation (stabilization), the product could be co-processed with petroleum fractions by existing refinery technologies.

Cracking using zeolite catalysts. This process in an alternative to HDO. Oxygen is removed in the form of water, CO and CO_2. The obtained product has strongly aromatic character that limits its potential use in transportation fuels, but makes it a suitable raw material for producing various aromatic compounds[21].

Fractionation and extraction of pyrolysis bio-oils

Use of whole bio-oils

There were reported some applications, in which whole bio-oils were converted into different useful products[22]. In these applications, abundant functional groups of bio-oils (e.g. carbonyl, carboxyl and phenolic) react with different reagents in such way that the non-reacting part of bio-oils does not have to be removed from the final product[22].

Biolime is a product developed by Dynamotive Corporation (Canada). The manufacturing of this product is based on reaction of carboxylic acids and phenols present in bio-oils with lime to produce calcium salts and phenates. This product was proven to be successful in capturing SO_x and NO_x emissions from coal combustors. Alternatively, lime can be used for this purpose, but Biolime was proven to have a higher efficiency (90–98 % vs. 75 % for capturing SO_x emissions). Although the technology for manufacturing Biolime is well developed, to our best knowledge, Biolime is currently not being manufactured likely due to its price and the availability of cheaper alternatives[22-24].

Carbonyl groups present in bio-oils can react with ammonia or urea to produce various imides and amides and incorporate nitrogen into the matrix of bio-oil (~10 wt%) and the obtained product could be used as efficient fertilizer. However, this application has not been commercialized likely due to the availability of cheaper alternatives[22].

Whole bio-oil was also proposed for use as a wood preservative[22].

<u>**Use of bio-oil fractions**</u>

Carboxylic acids are products mostly of hemicellulose and comprise typically about 4–15 wt% of bio-oils. Main representatives are acetic and also formic and propionic acids. In form of calcium or magnesium salts, they can be used as road de-icers[4,22].

Carbohydrates are typically decomposition products of cellulose and comprise about 20–35 wt% of bio-oils. Main representatives are levoglucosan, levoglucosenone and 1,4:3,6-dianhydro-α-D-glucopyranose. After hydrolysis, they can be fermented to bioethanol[4,22].

Pyrolytic lignin is a water-insoluble fraction of bio-oils that is composed mostly of oligomeric phenols and comprises about 25–30 wt% of bio-oils. It can be used as a replacement of phenol in phenol-formaldehyde resins or as a green alternative to bitumen for manufacturing roofing materials[4,22].

Phenols (monomeric) are products of lignin decomposition and comprise typically about 2–5 wt% of bio-oils[4,22].

Water soluble part of bio-oils can be used in food industry for production of meat browning agents (presence of glycolaldehyde) or food flavours (presence of phenolic compounds). This applications was commercialized by Red Arrows Products (USA)[4,22].

<u>**Specific chemicals from bio-oils**</u>

Hydroxyacetaldehyde (glycolaldehyde) is typically the most abundant organic compound in bio-oils (5–13 wt%) and the second most abundant bio-oil compound (after water). It can be used as a meat browning agent in “liquid smoke” in food industry[22].

Levoglucosan (1,6-anhydro-β-D-glucopyranose) is the main product of cellulose pyrolysis. It can be obtained in high yields (up to 40–45 wt%) when pure, demineralized cellulose is pyrolysed. Levoglucosan can be used to manufacture drugs, surfactants, biodegradable polymers etc. or after hydrolysis to glucose to produce bioethanol[22].

Levoglucosenone can be, similarly to levoglucosan, obtained in high yields (~24 wt%) when pure, demineralized cellulose is pyrolyzed. It has a potential to be used in the synthesis of antibiotics and flavour compounds[22].

Furfural is a typical product of holocellulose pyrolysis and can be obtained in yields of about 1.5–3 wt%. It is a frequently used organic solvent and can be used to produce of furfuryl alcohol, methylfuran, tetrahydrofurfuryl alcohol, 2-furoic acid, resins, drugs, food additives etc.

Acetic acid is a typical product of hemicellulose (or cellulose) pyrolysis with yields of about 2–10 wt%[4].

Conclusions

Pyrolysis bio-oil is a renewable liquid energy source with a promising potential, but it also has some undesirable properties that must be overcome to achieve its more widespread use. Moreover, chemical composition is not completely understood and thus, development in bio-oil analytics is necessary to design better processes for bio-oil upgrading. Currently, bio-oils are being produced at a commercial scale in several countries and used for district heating. Bio-oils have also achieved commercial use in food industry. For other applications, commercialization has not been achieved yet.

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