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Analysis and comparison of bio-oils obtained by hydrothermal liquefaction and fast pyrolysis of beech wood

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HIGHLIGHTS

- Bio-oils from beech wood by hydrothermal liquefaction and fast pyrolysis.
- Physical and chemical properties of bio-oils are presented.
- Bio-oils generally have a high acidity, iodine values and residual carbon.
- Hydrothermal bio-oil has a high viscosity and low volatility.

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ABSTRACT

There are many different ways to convert biomass into liquid fuels, mostly referred to as bio-oils. This paper presents the analysis of bio-oils produced by hydrothermal liquefaction and fast pyrolysis of beech wood. Both processes have a wide panel of parameters that can be optimised influencing the oil quality. Results of the analysis show that both oils have high acidities. Iodine values indicate a high degree of unsaturations. These two qualities seem to be inversely proportional in the case of pyrolysis oils. In the case of hydrothermal conversion, additives to adjust the pH such as sodium hydroxide increase oil yields, lower its viscosity but do little to further improve the quality of the oils. For pyrolysis oils, increasing the severity does reduce acidity but at the expense of more unsaturations and a loss in yield. The results show that without extensive upgrading or refining, commercial fuel standards cannot be met. Specific norms and standards are being elaborated for pyrolysis used in specific installations. This paper shows how detailed analysis can help to optimise process parameters with an objective that goes beyond the mass or energy yield.

1. Introduction

In the search for replacement of fossil liquid fuels, a wide panel of different conversion techniques have been proposed. These include hydrothermal liquefaction, fast (or flash) pyrolysis (aided by catalysts or not) and various gasification processes followed by catalytic fuel synthesis (Fischer–Tropsch amongst others). The yield and quality of the produced liquid fuel are extremely variable from process to process.

Hydrothermal liquefaction (HTL) converts biomass in subcritical water [1]. Typical operating conditions are 260–350 °C and 8–20 MPa. At lower temperatures, hydrothermal carbonisation is favoured, while higher temperatures, especially above the critical point, favour gasification. Hydrothermal liquefaction is particularly suited for wet resources as no preliminary drying is required. Wet resources that are often considered for this process include sewage sludge [2,3], food processing residues [4,5] and algae [6]. Dry resources have also been studied, including wood and forestry residues [7,8] and agricultural residues [9–11]. It has been extensively shown that additives can improve bio-oil yields [2,8].

Pyrolysis is an ancient technique to produce charcoal from wood. By heating the wood in absence of an oxidising agent to 400–600 °C, it decomposes in charcoal, tar and gas. Fast pyrolysis (often referred to as flash pyrolysis) applies the same principle except that the heating rate is much higher (500–1000 °C s^{-1}). Under these conditions the production of tar and condensable compounds are favoured at the detriment of char and gas [12].

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The quality of the bio-oils produced depends on the process but also on the resource. Typically hydrothermal oils are very viscous, strong smelling black oils with a relatively high heating value, up to 35–40 MJ/kg. Pyrolysis oils have a smoky odour, are less viscous and have a much lower heating value (similar to that of the parent biomass). Hydrothermal oils are typically proposed as a diesel substitute after catalytic upgrading [13]. Pyrolysis oils are often thought of as an alternative for fuel oil.

The objective of this paper is to present bio-oils produced by hydrothermal liquefaction and pyrolysis of beech wood, and to characterise them as much as possible. In this study, we tested various analysis techniques on six different bio-oils from HTL and entrained flow pyrolysis processes. The objective is to determine values for some of the important properties qualifying a liquid fuel. We are interested here in determining some physical and chemical properties, by testing standard methods developed to characterise biodiesel and conventional fuels.

2. Review of analysis techniques

There are many standards for commercial fuels, for heating and transportation applications. Each application requiring fuel is typically designed for a particular fuel for optimal performance. Inversely, most fuels target a particular application. A fuel is characterised with properties relevant to its application, including manipulation, storage and combustion. There is a very large panel of standardized tests that are applied to different fuels that are commercially available. Some of these tests are relevant to potential applications concerning bio-oils.

All commercial fuels have criteria related to storage. The iodine value (standard EN 14111) is determined to indicate if biodiesels contain compounds with unsaturated long chains like fatty acids or their derivatives resulting from the conversion of lipids. This technique has already been applied to pyrolysis oils [14]. The presence of unsaturated compounds can produce polymerisation reactions during storage. Iodine value measures the amount of unsaturation in the form of double bonds, which react with iodine compounds. The higher the iodine number, the more C=C bonds are present in the bio-oil. The total acid number (TAN) is used as an index of fuel acidity, one of the parameters to estimate corrosion. This is an important quality measurement to avoid corrosion risk to machinery and storage tanks (standards EN 14104 and ASTM D664). Biodiesel and pyrolysis oils are often characterised with this parameter [15,16].

One of the major fuel qualities is its heating value expressed by its Lower Heating Value (LHV) or Higher Heating Value (HHV) (standard NF EN 14918). Nazari et al. [17] report hydrothermal bio-oils with higher heating values in the range of 25–32 MJ kg^{-1}. Vaporisation is the first stage in the combustion process. Some applications require very small amounts of residual carbon after vaporisation. This is evaluated by measuring the Conradson Carbon Residue (CCR, standards EN ISO 10370 and ASTM D4530). It is obtained after heating a fuel, and is the main indicator to identify residual carbon. Transportation fuels such as petrol, jet fuel and diesel have more narrow specifications in terms of combustion properties, for example Research Octane Number (RON, standard ASTM D2699) and cetane number (standard EN ISO 5165 and ASTM D613). These latter two are of little interest for bio-oils.

Ultimate analysis is not usually a criterion for fuels but does give interesting insights to the quality of a fuel. Typical oxygen contents for hydrothermal oils vary in the literature. Hydrothermal oils from woody biomass in batch autoclave experiments contain 20–30% oxygen according to Nazari et al. [17], 34% according to Doassans-Carrère et al. [18] and Gan and Yuan report 28% oxygen content for hydrothermal oil obtained from corn cobs [10]. Continuous liquefaction reactors produce biocrudes with lower oxygen content for similar biomasses, Elliot at al. report 12% [19,20] while Hoffman et al. report 5% for oil produced in supercritical conditions. Pyrolysis oils contain more oxygen, around 50% on water free basis according to Doassans-Carrère et al. [18] while Zhang et al. report 35–40% [21].

Few authors presenting hydrothermal oils complete these results in terms of functional fuel properties such as viscosity, density, volatility and stability during storage. The properties of bio-oils can be easily compared with commercial standards. This directs the use of bio-oils towards certain applications for example transport or heating.

Viscosities of HTL bio-oils are rarely mentioned in the literature, high values were found up to 1000 Pa s [7]. Furthermore, according to Mohan et al. [22] the viscosity of bio-oils increases due to the aging effect. It is well agreed that rheological properties of bio-oils change over time at elevated temperature by many factors like polymerisation, oxidation and others. For pyrolysis oils much more data is available. Studies on rheological properties and on the aging effects of bio-oil can be performed to give an indication on how bio-oil viscosity changes upon time depending on temperature and other storage conditions [15,23]. The fuel pumpability, assessed via the measure of viscosity (standards EN ISO 3104 and ASTM D445), is another important parameter.

The characterisation of chemical species in bio-oils is often performed using separation techniques such as gas chromatography coupled with mass spectrometry (GC/MS). These techniques provide an indication of the chemical nature of the bio-oil but they do not allow the quantification of all of its compounds [24,25].

Another major parameter is related to the volatility of the fuel. For storage purposes the product should be stable, vapour pressure expressed as the Reid Vapour Pressure (standard ASTM D323) should be inferior to a certain value (seasonal parameter). The boiling point range and the end of the distillation (standard ASTM D86) are also important parameters to be regulated.

Characterisation by a full distillation curve (standard ASTM D86) is rarely presented for bio-oils because they are available in small amounts at the laboratory scale. To understand the evaporation behaviour of bio-oils, other analysis techniques are applied, such as thermogravimetric analysis (TGA). TGA is applied to any type of sample that will undergo a mass change over time under the effect of temperature in a given atmosphere. The evaporation and thermal decomposition are part of the changes that will be detected by thermogravimetry. TGA is often used to predict the thermal behaviour of the major macromolecular components of biomass during their thermal conversion to biofuel [26]. In other published works, TGA is used to simulate distillation or to show the volatility of products resulting from biomass conversion. The distillation of biodiesels produced from different vegetable oils as resources are compared in term of percentage of weight loss at different temperatures [27]. Zhu et al. compared HTL bio-oils obtained from different operating conditions [28]. TGA can also be used as an alternative method to the Conradson carbon residue (CCR) method [29].

3. Materials and methods

3.1. Biomass and chemicals characteristics

The same biomass was used to produce oils by HTL and pyrolysis. The biomass is beech wood supplied by SPPS company. The raw wood is finely ground with particles having sizes ranging from tens to a few hundreds of microns. Narrow particle distributions were obtained by sieving. The wood water content was determined after drying at 105 °C according to the standard NF-EN-14774. Ash content was determined by burning the sample in air at 550 °C