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Upgrading and isolation of low molecular weight compounds from bark and softwood bio-oils through vacuum distillation

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ABSTRACT

In this paper an analysis of short-path vacuum distillation for the isolation of low molecular weight compounds (C1–C3) from softwood and bark bio-oils is reported. The short-path vacuum distillation was performed at 60–100 °C under vacuum (10 kPa) for 0.5–1 h. Although methanol and acrolein distilled completely, acetic acid and acetol failed to do so after 1 h. The acetic acid content and the total acid number of the residual oils decreased and their heating values doubled (to 19.6 kJ/g). Short-path vacuum distillation is an efficient method to both isolate low molecular weight feedstocks/fuels, and improve the quality of the residual bio-oil for blending with petroleum or biofuels.

1. Introduction

Forestry residues (e.g. saw chips, bark etc.) from the harvesting of timber and production of wood products are a potential source of bioproducts, ranging from fuels to biochemicals. Bark residue, for example, comprises 12–20 wt% of an average dried log, and represents potential bioproduct feedstock. However, the residues are traditionally treated as "waste" material due to challenges and costs associated with conversion and transport [1].

Fast pyrolysis bio-oil is a liquid produced by the pyrolysis (450–500 °C) of biomass. Fast pyrolysis has many advantages, including high oil yields (up to 70 wt%) and a higher energy density than the parent biomass [2,3]. However, the direct use of crude bio-oil as a replacement fuel is challenging due to the high water content and acidity, high viscosity, limited thermal stability, and low heating value [4–12]. Further, the acidity of the bio-oil (pH in the range of 2–4) is problematic leading to corrosion and safety issues. The primary drivers of the high acid content are low molecular weight organic acids, such as acetic and formic acid. Removal of these acids and other light organic fractions could improve the bio-oil quality while simultaneously generating a valuable feedstock for high-end chemicals used in industry.

Low molecular weight (LMW) compounds such as methanol, acrolein, glycolaldehyde, acetic acid, and acetol are platform chemicals used in the chemical industry. Bio-methanol fuel cells are promising energy conversion devices with high power density electrical energy potential [13,14]. The global acetic acid market is forecasted to be worth USD 13.65 billion by 2021 [15]. Acetol, which contains both hydroxyl and carbonyl functional groups, is used as a reagent in organic chemical reactions and is an important intermediate used to produce propylene glycol via hydrogenation [16].

Atmospheric, vacuum, fractional, and molecular distillation technologies have been used for the separation of bio-oil compounds [17–21]. However, in most cases where many compounds have been reported, there has been no focus upon the low MW compounds or their quantification. The value associated with this light fraction is important from a sustainability perspective. If the by-product of improving the bio-oil quality is in itself a valuable commodity, then the overall sustainability and cost effectiveness of the removal process is enhanced.

A phenolic concentrate with a guaiacolic fraction of 48.3 wt% was produced via a multistep extraction technique by Wang et al. [17]. Zhang et al. [18] were able to generate ~52 wt% separable carboxylic acids, furans, phenols, anhydrosugars, and carbonyl compounds by atmospheric distillation from co-pyrolysis. Microalgae pyrolytic bio-oil was separated by Nam et al. [19] into three fractions, using either fractional or vacuum distillation, consisting of paraffins and olefins, with the middle bio-oil fraction having a higher heating value (HHV) of 41.2 MJ/kg and < 1.25 wt% moisture. Capunitan et al. [20] fractionated corn stover bio-oil with 73–84% yield under atmospheric and vacuum distillation. The low density fractions obtained by Capunitan et al. contained aromatics and oxygenated compounds, whereas the heaviest fraction contained phenolics. Their focus was fractionation of the oil into multiple fractions and therefore temperatures up to 280 °C

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were used. Boucher et al. [21] on the other hand, attempted to distill bio-oil (for characterization purposes) under atmospheric pressure and 140 °C, but were rapidly hampered by coking and polymerization.

In atmospheric and vacuum distillation processes the extended time the oil is exposed to the hot surface can result in thermal degradation of the oil. Short-path vacuum path distillation has been used to circumvent this problem. In short-path vacuum distillation, like vacuum distillation used in refining of petroleum, the operating temperature is reduced (compared to atmospheric distillation) as is the exposure time to the hot surface (the exposure time is on the order of seconds) thereby limiting thermal decomposition of the oil. In short-path vacuum distillation the vapour molecules travel from the liquid phase to the condenser. The pressure used in the distillation apparatus should be sufficiently low and the condenser should be separated from the evaporator by a distance shorter than the mean free path of the vapour. In theory, the vapour molecules will not re-enter the liquid phase and the evaporation rate is specified by the rate of molecules that escape from the liquid surface. One of the key differences from conventional distillation is that the separation is not governed by phase equilibrium [22]. Zheng et al. [23] performed reduced pressure distillation of rice husk bio-oil at temperature 80 °C. They reported that the distilled yields of 61 wt% had a lower oxygen content of 9.2 wt%, higher heating value, lower corrosivity, and better overall stability compared to the original bio-oil. Wang et al. [24–27] used molecular distillation (a KDL5 molecular distillation apparatus) to separate bio-oil components and developed a separation factor system to identify conditions for isolating chemicals during distillation. They investigated the effects of the evaporation temperature on the separation of compounds of lauan sawdust bio-oil by molecular distillation at 70, 100, and 130 °C at 60 Pa [25]. They reported a maximum distillate yield of 85% at 130 °C without coking or polymerization.

The long term objectives of this work are to produce a bio-oil with enhanced fuel properties (e.g. low water and acid content) without thermally degrading the bio-oil and produce platform chemical(s) from the distilled fraction. With the lower operating temperatures and short contact times, short-path vacuum distillation has the potential to accomplish both of these objectives. In this study we investigated lab-scale short-path vacuum distillation of fast pyrolysis bio-oil derived from conifer bark and wood at relatively low temperatures (60–100 °C) with a very short distillation path (time) for isolation of low MW compounds (C1–C3), i.e., methanol, acrolein, acetic acid, and acetol, for potential use as chemical feedstocks or fuel cells while simultaneously improving the residual bio-oil quality.

2. Experimental section

2.1. Oil samples

The bio-oils used were generated from two different feedstocks, softwood shavings (SW shavings) and bark residues from a local sawmill. The samples were dried in an oven at 75 °C for 12 h and then ground to give particle sizes of 1–2 mm. Bio-oils were produced at Memorial University, from a pilot-scale (2–4 kg/h) auger medium pyrolysis reactor (ABRI-Tech Inc. Namur, Quebec, Canada) with steel shot as a heat carrier, and no sweeping gas, at 450 °C. The softwood bio-oil yield was 62.0 wt% with water content of 33.7 wt%. The bark bio-oil yield was 42.0 wt%. and was a two -phase mixture, the heavy (bottom) phase was 52.0 wt% and the light (top) phase was 48.0 wt%. The water content of the top and bottom layers were 46.2 and 20.0 wt%, respectively. The light (top) phase of the bark bio-oil was used in the bark experiments. Before the distillations, each bio-oil was filtered (Whatman Grade 1) to remove fine particles.

2.2. Short-path vacuum distillation of bio-oils

Bio-oil samples were distilled on a small scale by short-path vacuum distillation at low temperature. A sample of bio-oil weighing 25.0 g was placed in a modified 100 mL distillation apparatus (Fig. 1). The oil bath was set to 60, 80, or 100 °C and distilled under vacuum (10 kPa) for 0.5 or 1 h. The distillation of bio-oil was investigated to explore the effect of the distillation temperature and time on the isolation of the low MW components. All experiments were conducted in triplicate with the experimental error shown as the standard deviation for n = 3. The distillate and residual bio-oil were tightly sealed and stored in a refrigerator until analyzed.

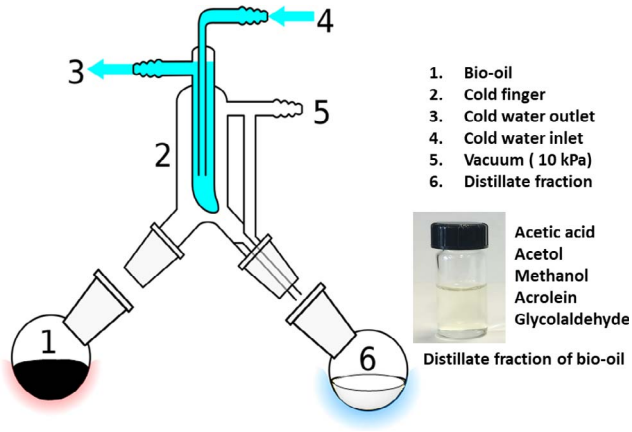

Fig. 1. Schematic diagram of short-path vacuum distillation of bio-oil.

2.3. Analysis of bio-oils and distillate fractions

The water content was measured using standard Karl Fischer titration (ASTM D-1744) using a Mettler Toledo titrator with Hydranal®-Coulomat AG-H (Sigma-Aldrich) as the titration reagent. The total acid number (TAN) was determined using the ASTM standard D664 potentiometric titration [28,29]. An oxygen bomb calorimeter (Model 1314 Plain Jacket Bomb Calorimeter, Parr Instrument Company, Moline, Illinois, USA) was used to determine the higher heating value (HHV) of the bio-oils.

2.4. GC-MS analysis

The bio-oil and oil residues were characterized by gas chromatography with mass spectrometry (GC–MS) equipped with a vertical microfurnace pyrolyzer [5]. Approximately 1.0 mg of sample was weighed inside a pyrolysis cup then introduced into a quartz tube vertical microfurnace pyrolyzer PY-2020D (Frontier laboratories Ltd., Yoriyama, Japan), coupled to a HP 5890 II gas chromatograph/HP 5971A mass selective detector (MSD) (Hewlett Packard, Palo Alto, CA, USA) with a ChemStation Data system. The MSD was operated under the following conditions: interface temperature, 280 °C; electron ionization energy, 70 eV; and scan range, 30–550 m/z. The GC injector and pyrolysis microfurnace temperatures were set at 270 °C. The carrier gas was helium with a constant flow of 2 mL/min. A Zebron ZB-1701 capillary column (30 m × 0.32 mm, 1.00 μm film thickness) was used. The GC oven was programmed to hold at 35 °C for 3 min to trap and focus the volatile compounds, ramp at 6 °C/min to 100 °C and then ramp at 15 °C/min to 260 °C and hold for 4 min. The identification of compounds was based on the National Institute of Standards and Technology (NIST) mass spectrum library and mass spectra found in the literature [30].

2.5. GC–FID analysis

The quantitative analyses of selected C1–C3 compounds in samples were determined by using a GC–FID (Thermo Scientific⁎ FOCUS GC Gas Chromatograph). A Zebron ZB-1701 capillary column (30 m × 0.32 mm, 1.00 μm film thickness) was used. The injector and