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Pretreating biomass via demineralisation and torrefaction to improve the quality of crude pyrolysis oil

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ABSTRACT

Pretreating biomass prior to pyrolysis was investigated. Three undesirable catalysts naturally present in biomass were identified: inorganics, acids, and water. A pretreatment sequence incorporating acid leaching and torrefaction was developed to reduce/remove these catalysts. Acid leaching targeted reducing the biomass's inorganic content. The acidic liquor produced during torrefaction was rich in acetic and formic acid; this solution was recycled as the acid leaching reagent. The optimal leaching conditions were at 30 °C with 1% acetic acid for 4 h, which decreased the inorganic content from 0.41 wt % to 0.16 wt% for leached biomass. Torrefaction targeted reducing the biomass's moisture and acetyl content and was optimal at 270 °C for 20 min. Bio-oil from pyrolysis of demineralisation and torrefied biomass was depleted in organic acids, pyrolytic lignin, and water but was rich in levoglucosan and aromatics. Decreasing the biomass's acetyl and inorganic content reduced organic acid formation. The water content in the bio-oil was lower because less water entered the system, and water plays an auto-catalytic role during pyrolysis, promoting the production of pyrolytic water. The high levoglucosan yield confirmed that secondary reactions were limited to a much higher degree when both pretreatments were implemented compared to demineralisation or torrefaction alone.

1. Introduction

Fast pyrolysis is the oxygen-deficient process of thermally decomposing carbonaceous solids (such as biomass) to produce a liquid, referred as bio-oil, char and non-condensable gas. The differentiation of slow, fast, and flash pyrolysis is controversial, but fast pyrolysis is generally defined as conditions that give the highest liquid yield [1]. Bio-oil has the potential to be used as an alternative transportation fuel if upgraded through catalytic cracking or hydro-deoxygenation. However, catalyst deterioration is excessive during upgrading as a result of catalyst sintering, degradation of the support, coking, and loss of sulphide from the catalyst [2]. Most of the deactivation can be attributed to the acidity, inorganic content, water content, and oligomeric lignin derivatives in bio-oil. Pretreating biomass prior to pyrolysis has the potential to improve the quality of crude bio-oil, thus increasing the efficiency of catalytic cracking or hydroprocessing. The combined use of demineralisation (acid leaching) and torrefaction targets the inorganic, organic acid, and moisture in biomass.

1.1. Inorganics

Biomass inorganics, which have been identified as the foremost pyrolysis catalyst [3,4], act by increasing the reactivity of biomass and thus lowering the activation energy of undesirable reactions [5]. Ring-opening reactions are catalysed through fragmentation, depolymerisation, and cracking of primary pyrolysis vapours, which causes liquid yields to decrease and gas yields to increase. Alkali metals are thought to be the most catalytic [6], although alkaline earth, transition metals, and non-metals can also be catalytic [7,8]. Therefore, the catalytic fraction was referred to as the total inorganic (ash) fraction. Inorganics become concentrated in the char fraction, thus, vapour residence times are restricted as inorganics in char heterogeneously catalyse the vapour phase until char separation [9]. This condition limits reactor configurations and means fluidised bed must be shallow, which increases the fluidising gas requirements. Inorganics in bio-oil cause high-temperature corrosion and hard deposits in engines, may contribute to bio-oil aging, and hinder secondary upgrading processes [10,11].

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1.2. Moisture

Water appears to have an auto-catalytic role during pyrolysis [12], but varied results have been obtained for the pyrolysis of dry biomass in terms of the bio-oil yield and composition changes [13–15]. These findings clearly indicate that moisture in biomass affects pyrolysis, possibly by causing the hydrolytic scission of glucosidic bonds and thereby lowering the degree of polymerisation in cellulose [16]. Removing excess moisture from biomass decreases its thermal conductivity; therefore if inorganics are present, dry biomass particles may take longer to reach the pyrolysis temperature and thus increase the activity of inorganic catalysts. This process was demonstrated by Gary et al. [17] who showed that wet (and inorganic free) biomass produces significantly less volatiles and more char at approximately 500 °C, suggesting that some chemical interaction with water occurs in wet biomass compared to dry and inorganic free biomass. Conversely, if inorganics were not removed, then wet biomass gave higher bio-oil yields compared to dry biomass due to faster biomass heating, indicating that inorganics are more catalytic than moisture.

1.3. Organic acids

Acetic acid in bio-oil cause corrosion issues during combustion applications and can deactivate refining catalysts. It also requires high activation energies for decarboxylation [18]. Partial oxygen removal to aldehydes and ketones may be beneficial because their required activation energy for deoxygenation is significantly lower [18]; however, aldehydes and ketones are thought to cause stability issues when heating or storing bio-oil, and their production should be avoided [19,20]. Primary acids are produced during the initial stages of pyrolysis through the low-temperature cleavage of carboxyl compounds and breakdown of extractives; therefore, acids are present to catalytically interact with vapours either during or after formation. Carboxyl groups associated with hemicellulose produce carboxylic acids; whereas extractives remain as resin acids; form esterified versions [21]; or breakdown to form acetone, formic acid, and methanol [22]. The main organic acid in bio-oil is acetic acid, produced from acetyl groups and during secondary reactions. Acid catalysts favour dehydration over depolymerisation [16], which increases water yields. Karimi et al. [23] reported that acid-catalysed condensation reactions lead to resin formation and phase separation of the bio-oil. Even in the presence of weak organic acids, the reaction rate for certain compounds increased, such as enhanced homolysis cracking reactions [24]. Britt et al. [25] added acidic silica-alumina to pyrolysis, which enhanced the rate of decomposition during the pyrolysis of lignin. Acid-catalysed cracking and polymerisation reactions altered the products produced, with fewer alkenes and increased large aromatics, char, and coke formed.

2. Experimental

2.1. Materials

Pinus radiata wood chips (<6 mm) were obtained from the SRS Sawmill in Rolleston, New Zealand. The biomass was dried in a condition controlled room with relative humidity and temperature of 50% and 40 °C, respectively, until the moisture content stabilised at 8.4 wt%. Dried biomass was knife milled to 2 mm and then sieved to remove the fines below 295 μm. The removal of fines reduced errors during pretreatments as these block filters.

2.2. Pretreatments

Biomass pretreatment procedures with both leaching and torrefaction are based on the authors' previous work [26]. Biomass was initially leached, and this was followed by torrefaction. The liquid produced during torrefaction was recycled as the acid leaching reagent, containing mainly acetic and formic acid. The compositional changes to *P. radiata* after leaching, torrefaction, or both pretreatments were reported previously by Wigley et al. [26]. Leaching using deionised (DI) water and acetic, formic, hydrochloric, sulphuric, and nitric acid was investigated at 30 °C. Acid concentrations between 0.5 and 10 wt% were investigated for formic and acetic acid. Finally, leaching residence times between 1 and 8 h were investigated for acetic acid. The torrefaction residence time was optimised between 15 and 120 min, and the temperature was optimised between 230 and 280 °C. Biomass samples leached with DI water and acetic, formic, hydrochloric, sulphuric, and nitric acid were then torrefied.

Acid leaching was carried out in caped 2 L conical flasks on magnetic hot plates. Seventy grams of biomass was added to 700 mL of leaching solution. After the leaching, samples were neutralised with DI water and then dried. Torrefaction was carried out in a modified bomb calorimeter which was heated on a hot plate to between 230 and 280 °C. The residence time for all experiments was 20 min, and 37.5 g of biomass was used with a moisture content of 25 wt% as torrefaction represented the drying stage.

2.3. Pyrolysis

A fast pyrolysis reactor with a feeding rate of 0.36 kg h^{-1} of biomass was used for the experiments. The pyrolysis reactor was a fluidised bed, which operated at a controlled temperature of 500 °C. Preheated nitrogen was used as the fluidising gas and silica sand with particle sizes between 600 and 710 μm was used as the inert bed material. The fluidised bed had an internal diameter of 35.1 mm and height of 500 mm, with the top 100 mm tapered to 9.7 mm. Char was separated in a high-efficiency Swift cyclone, which was traced-heated to maintain at a temperature of 450 °C. Bio-oil vapours were condensed in a series of 3 shell and tube condensers. Remaining aerosols were collected in an electrostatic precipitator and a final cotton wool filter. A schematic of the system is given in Fig. 1. Samples that were torrefied were oven-dried prior to pyrolysis, whereas all other samples had a moisture content of 10 wt%. All yields from pyrolysis are reported on dry basis.

2.4. Bio-oil analysis

Proton nuclear magnetic resonance (^{1}H NMR) was used for a semi-quantification analysis of major bio-oil compounds. Thirty microlitres of bio-oil was dissolved in 300 μL of DSMO-d6 (dimethyl sulphoxide-d6); the sample was then filtered to 0.22 μm before being placed in NMR tubes. Spectra were acquired at 26 °C on an Agilent 400 MR with a Varian 7600-AS auto-sampler operating at 400 MHz. Individual compounds that are commonly present in bio-oil from Zhang and Kong [27], Diebold [20], and Huber et al. [19] were identified in ^{1}H NMR by determining the individual shift for each compound. Individual shifts were confirmed using a shift predicator supplied by the Institute of Chemical Sciences and Engineering [28] and shifts given by Hosoya et al. [29]. The following peaks were identified: formic acid (8.10 ppm), acetaldehyde (9.58 and 2.08 ppm), levoglucosan (3.27, 3.84–3.85, 4.31–4.33, and 5.13 ppm), glycolaldehyde (9.55 ppm), hydroxyacetone (4.01 ppm), and acetic acid (1.88 ppm). Propanoic acid, octanoic acid, hexanoic acid, acetone, ethanol, glyoxal, methanol, 1-heptanol, and 1-