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A detailed product analysis of bio-oil from fast pyrolysis of demineralised and torrefied biomass

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ABSTRACT

Acid leaching and torrefaction were investigated as biomass pretreatments for fast pyrolysis of *Pinus radiata*. Both pretreatments were required to limit competitive primary and secondary reactions of pyrolysis vapours catalysed by water, organic acids, and inorganics present in the biomass. Torrefaction reduces the cost of acid leaching by providing the leaching reagent and eliminating the need for biomass rinsing prior to the leaching. It also reduces the biomass grinding costs, which helps offset the additional process costs of pretreating biomass. Acid leaching was required because pyrolysis of solely torrefied biomass was constrained by the high torrefaction temperatures required for significant bio-oil improvements, leading to low bio-oil yields due to the mass loss during torrefaction and increased char formation during pyrolysis. Finally, the reduced thermal conductivity of dry torrefied biomass increased the time avaliable for inorganics to catalyse primary reaction pathways during the biomass heating. The optimal pretreatment conditions were 1% acetic acid leaching at 30 °C for 4 h followed by torrefaction at 270 °C for 20 min. Pyrolysis of raw biomass yielded (dry basis) 55.3 wt% bio-oil, 25.0 wt%, char, and 12.5 wt% non-condensable gas, whereas pyrolysis of pretreated biomass yielded 57.8 wt% bio-oil, 23.7 wt%, char, and 11.5 wt% non-condensable gas. Integrating leaching and torrefaction as biomass pretreatments significantly reduced the heterogeneous and homogeneous secondary reactions of pyrolysis vapours. This integrated pretreatment improved the bio-oil's quality in terms of the organic acid (2.46–0.16%), water (16.8–3.6 wt%), aldehyde (1.58–0.50%), high molecular weight compound (10.2–4.2%), and inorganic (0.162–0.091 wt%) content, as well as the stability.

1. Introduction

There are abundant biomass resources in New Zealand due to the fertile soils, suitable growing climate, and well-managed forest plantations. In 2009, plantation forests constituted 6% or 1.7 million hectares of land in New Zealand [1]. *Pinus radiata* is the predominant lignocellulose source, with more than 25 Mm^3 of round wood harvested per year, and of this, 25% becomes wood residue, equating to approximately 6.3 Mm^3 of residue per year. Wood residues are mainly used in the wood processing industry, but additional forest residues are not extracted from the landing site [2]. Forest residues are approximately 4–6% of the total harvested volume plus additional cutover trees (trees that break during harvesting and are left at the skid site). New Zealand already has many sources of renewable electricity (solar, hydro, wind, and geothermal [3,4]); therefore this research focused on producing a marine transportation fuel from the pine residues.

Lignocellulose biomass can be thermo-chemically converted into energy via gasification [3,5,6], pyrolysis, liquefaction [7,8], or combustion [3,9]. No process currently stands out as the superior option [10], however pyrolysis and liquefaction are the only processes that directly produce a liquid fuel [11,12]. The high-pressure technology associated with liquefaction is thought to be too sophisticated for the thermal conversion of biomass to biofuels [7], therefore, pyrolysis is the most suitable candidate for the direct production of a second-generation liquid fuel. The low quality of crude bio-oil produced from fast pyrolysis limits its use to direct stationary combustion applications or as a densification technique to reduce the transportation costs of shipping wood to a bio-refinery [13,14]. This research investigates the use of biomass pretreatments to alter the bio-oil properties.

Demineralisation (acid leaching) and torrefaction were used to pretreat the biomass. Fig. 1 indicates how these were integrated; a detailed version was presented previously by Wigley et al. [15]. The biomass was leached, followed by excess moisture removal

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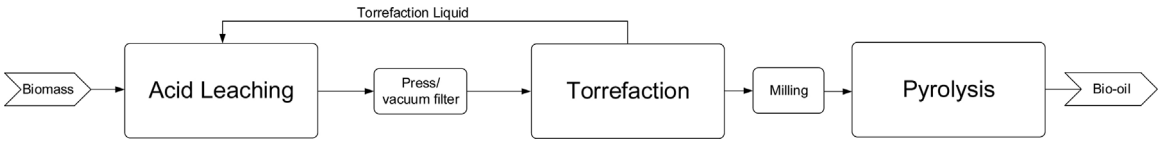

Fig. 1. Simplified pretreatment sequence for the direct production of a high quality crude bio-oil.

before torrefaction. The liquid produced during torrefaction contains mainly water and organic acids; this liquid was recycled as the leaching reagent. Our previous studies reported the biomass composition following the pretreatments as well as the bio-oil yield and properties from the pyrolysis of the pretreated biomass. These studies indicated that the pretreatments decrease the acetyl, inorganic, and moisture content in biomass, which limits secondary reactions during pyrolysis [15,16]. Controlling secondary reactions reduces reactions which produce small oxygenated compounds, high molecular weight compounds, pyrolytic water, and coke. These products further enhance secondary heterogeneous and homogeneous reactions which converts primary products such as levoglucosan and aromatics to produce additional small oxygenated compounds, high molecular weight compounds, pyrolytic water, and coke [16]. This paper provides a detailed product analyses of bio-oil produced from raw and pretreated biomass.

2. Experimental

2.1. Pretreatments

P. radiata between 0.295 and 2 mm was used for pyrolysis experiments. The biomass was either pyrolysed raw or pretreated. The pretreated biomass was produced by acid leaching followed by torrefaction. The acid leaching process was previously optimised as follows: a 1% acetic solution used for leaching at 30 °C for 4 h in a stirred vessel [15]. Leaching was carried out in a 25 L vessel stirred at 350 rpm. The vessel's temperature was controlled at 30 °C using two 60 W fish tank heaters. 1.5 kg of biomass was added to 15 kg of leaching solution per leaching. After the leaching was completed, the biomass was washed *in situ* by adding a cotton wool filter to the outlet and circulating DI water through the vessel until a neutral pH was obtained.

Torrefaction was optimised at 270 °C for 20 min previously by Wigley et al. [16]. The torrefaction vessel was constructed from 316 stainless steel pipe with a Kleanflow tri ferrule welded to the top of the vessel to allow a Kleanflow tri clamp to be used for sealing the vessel. The vessel was heated in an oven to the required torrefaction temperature. The N_2 feed tube was coiled within the oven to preheat the N_2 before it entered the vessel. A stainless steel single-pass condenser was used to condense the vapours exiting the reactor; the condensate was then filtered into a flask with a cotton wool filter at the top to capture any remaining vapours before the non-condensable gases (NCGs) were vented. Between 200 and 250 g of biomass with a moisture content of 25% was torrefied per run.

2.2. Pyrolysis

Fast pyrolysis in a fluidised bed reactor with a feed rate of 0.36 kg h^{-1} of biomass was used for the experiments, as described previously by Wigley et al. [16]. Preheated nitrogen was used as the fluidising gas and silica sand between 600 and 710 μm was used as the fluidising medium. Fast pyrolysis was carried out at 450 °C. Char was removed in a trace-heated Swift cyclone designed for high separation efficiency. Bio-oil vapours were condensed in a series of 3 shell and tube condensers. The remaining vapours and aerosols were collected in an electrostatic precipitator and a final cotton wool filter before the NCGs were analysed. Pretreated biomass was pyrolysed dry, whereas raw biomass had a moisture content of 10 wt%. For simplicity, the bio-oil produced from raw biomass is referred to as 'raw bio-oil', and bio-oil produced from the pyrolysis of pretreated biomass is referred to as 'pretreated bio-oil'. All yields are reported on a dry basis.

2.3. Analysis

Proton nuclear magnetic resonance (^{1}H NMR) was used for a semi-quantification analysis of the major bio-oil compounds. The procedure was described previously by Wigley et al. [16]. The shifts for major bio-oil compounds identified were as follows: 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). Aromatics were represented by the shift between 6.4 and 7.6 ppm, aldehydes between 9.5 and 10.5 ppm, and alkanes between 0.5 and 1.6 ppm.

High-performance liquid chromatography (HPLC) was used to determine the acetic acid content in the bio-oil and the acetic acid, formic acid and methanol content in the torrefaction liquor. The method used for HPLC analysis was described previously by Wigley et al. [16].

The water content of the samples was determined by Karl Fischer titration, following ASTM E203 [17]. Karl Fischer titrant 5 was used, and titrations were carried out on a TitraLab TIM 550 Radiometer.

Gel permeation chromatography (GPC) was conducted by Scion in Rotorua, New Zealand. The system was calibrated using polystyrene standards. The average number, molecular weight, and size were determined using Polymer Standards Service Win GPC Unichrom software. Scholze and Meier [18] found that the average molecular weight of pyrolytic lignin is between 650 and 1300 gmol^{-1}, thus, the pyrolytic lignin was estimated from the GPC fraction above 650 gmol^{-1}.

The carbon, hydrogen, oxygen, and nitrogen contents of the solid samples were determined through complete oxidation [19] using an elementary analyser at CRL Energy, Ltd. in Wellington, New Zealand. The carbon, hydrogen, and nitrogen contents were determined using standard ISO 29541:2010, and the oxygen content was calculated by the difference from unity. The higher heating value (HHV) was calculated using the equation reported by Channiwala and Parikh [20].

To test the stability of bio-oil, 5 mL was heated in an air-tight container to 80 °C for 25 h [21,22], which is reported to be similar to ageing at 25 °C for 6 months. The ageing was quantified by the change in the molecular weight, pyrolytic lignin, ^{1}H NMR spectra, and water content.

A scanning electron microscopy (SEM) was used to investigate char and biomass samples. Samples were gold plated prior to the analysis to improve conductivity. This process was conducted in a Polaron E5000 in argon to produce a positive charge for gold deposition on the sample. Samples were then analysed using a JEOL JSM 7000F field emission high-resolution scanning electron microscope at 3.0 kV.

The solids content was determine by the residue after filtering the bio-oil through a 0.45 μm polyethersulfone syringe filter followed by flushing with 50 mL of ethanol to wash through any