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The use of demineralisation and torrefaction to improve the properties of biomass intended as a feedstock for fast pyrolysis

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ABSTRACT

Pre-treatments of biomass were investigated to reduce its undesirable properties which may affect the quality of fast pyrolysis bio-oil. A pre-treatment sequence was developed in this study to incorporate both biomass demineralisation and torrefaction. Demineralisation was performed by dilute acid leaching, primarily to reduce the inorganic concentration in raw biomass, whereas torrefaction targeted a reduction of the carboxyl, moisture and oxygen content. The liquid produced during torrefaction was recycled back as the leaching reagent for demineralisation. This solution contained dilute organic acids; therefore, the viability of leaching with organic acids (acetic and formic acid) compared to commonly used mineral acids (sulphuric, nitric and hydrochloric acid) was validated. Synthetic leaching solutions reduced the inorganic content in raw biomass from 0.41 wt% to 0.14 wt% when leached with 1% formic acid and to 0.16 wt% when leached with 1% acetic acid, which was comparable to leaching with the mineral acids. Recycled torrefaction liquid that contained other acidic compounds in small quantities reduced the inorganic content to 0.14 wt%, suggesting it is effective to use the recycled torrefaction liquid as the leaching solution. From the experimental results, the optimal conditions for biomass torrefaction were 260 °C for 20 min to minimise the char formation during pyrolysis, based on the increase in the acid-insoluble fraction of the biomass. However, the torrefaction temperature may be increased to 280 °C if further reductions in acetyl and oxygen content are required. Higher temperatures are associated with severe biomass loss and the initiation of hydrogen loss. It should be noted that even at 280 °C, the oxygen reduction is minimal. If oxygen reduction is the principal target when pre-treating biomass, it is suggested that torrefaction alone is not a suitable method to obtain bio-oil with a low oxygen content due to the low pyrolysis yields obtainable. This study demonstrated that the combined use of demineralisation and torrefaction as biomass pre-treatments has the ability to decrease the inorganic, acetyl and moisture content of biomass, which reduces undesirable catalytic reactions during fast pyrolysis to improve the quality of bio-oil produced.

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1. Introduction

Pinus radiata residues are a major by-product of the wood processing industry in New Zealand. In 2001, approximately 1.3 Mm³ of wood processing residues remained unused and additional forest residues were not extracted [1]. New Zealand already has many sources of renewable electricity (such as solar, hydro, wind, geothermal and wave power [2,3]). It would be beneficial if a transportation fuel could be produced from the wood residues. Since conversion of softwoods to ethanol is not currently effective [4],

focus should be placed on processes such as gasification and fast pyrolysis.

Fast pyrolysis is a thermal process in which biomass polymers are fragmented into light compounds that are able to volatilise, thereby producing a product referred to as bio-oil. High heating rates and short vapour residence times employed during fast pyrolysis are preferred to maximise the liquid yield, opposed to slow pyrolysis which enhances char production [5]. The focus for bio-oil production is typically as an alternative to petroleum transportation fuels; however, the high acidity, reactivity, solids content, water content, viscosity and distillation residue restrict the direct use of bio-oil in combustion engines. The high oxygen content of biomass is reflected in the bio-oils elementary composition, subsequently decreasing its heating value and stability during storage or upon heating. The water content can reach 30 wt%, further

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decreasing the heating value to approximately half that of petroleum fuels. Typical properties for bio-oils are summarised and compared to those of a heavy fuel oil in Table 1.

Upgrading crude bio-oil through either catalytic cracking or hydroprocessing has been extensively studied [14–27], however, the upgrading process is complicated due to the complexity of the bio-oil, resulting in low yields and high processing costs. Pre-treating biomass prior to pyrolysis has the potential to improve the quality of crude pyrolysis bio-oil and thus, increase the efficiency of upgrading via catalytic cracking and hydroprocessing processes through reduced reactor clogging and catalyst deactivation. The approach of combining demineralisation and torrefaction as pre-treatments has the capability to reduce the oxygen, carboxyl, water and ash content of biomass, subsequently decreasing the negative attributes of bio-oil that limit the efficiency of conventional refining techniques. If small, de-centralised pyrolysis plants could directly produce bio-oil of sufficient quality, the bio-oil could then be transported to existing petroleum refineries for co-processing with petroleum crude. Fig. 1 presents a simplified version of the proposed system. The primary objective of this paper was to investigate the effectiveness of pre-treatments for reducing the negative attributes of biomass for subsequent fast pyrolysis.

In the pre-treatment stages, biomass is initially demineralised during acid leaching, followed by the removal of excess moisture. Biomass is then torrefied, which also represents the drying stage. The liquid produced during torrefaction mainly contains water and organic acids; therefore, this liquid is recycled back into the demineralisation unit as the acid leaching reagent. The use of dilute organic acids (<1%) compared to commonly used mineral acids has not been reported so far; only 10% acetic acid solutions have been tested previously [28]; therefore, the secondary objective of this study was to compare the efficiency for demineralisation with organic acids to mineral acids.

1.1. Acid leaching

Demineralisation typically involves leaching biomass in water or a dilute acid to reduce the inorganic content (ash). It is well documented that inorganics catalyse dehydration and cracking reactions during pyrolysis, lowering the bio-oil quality [29–33]. Additionally, inorganics facilitate coke formation during the catalytic upgrading of bio-oil. Alkali and alkaline earth metals (AAEMs) are typically considered as detrimental compounds in ash. Encinar et al. [34] demonstrated that certain transition metals actually decreased the bio-oil yield more than common AAEMs. Non-metals and halogens (with the exception of silica, which is generally considered inert [35]) can also have a catalytic effect during pyrolysis; therefore, the inorganics targeted during demineralisation were considered as the total inorganic fraction, assuming that silica decreases proportionally to the other elements.

Previous studies indicate that water washing cannot fully remove inorganics from biomass, suggesting that they are present in at least two forms in biomass: either soluble salts or as cations

bound to reactive sites in biomass. The latter is most likely as functionalities of cellulose or of acid groups associated with lignin, hemicellulose and extractives. Soluble salts can be removed through simple water leaching, whereas cations require the presence of an acid for ion exchange to occur [29]. The removal of soluble salts via water leaching has been reported to have negligible effect on the bio-oil yield and composition. Cations are bound more tightly to biomass polymers and are thought to interact more readily during pyrolysis by facilitating dehydration and cracking reactions. The removal of acid-soluble cations typically decreases the amount of pyrolytic water, increases the bio-oil yield and significantly alters its composition, primarily by increasing the levoglucosan yield [29,36].

1.2. Torrefaction

Torrefaction is a mild version of slow pyrolysis, characterised by slow heating rates, long residence times and temperatures between 200 and 320 °C. The process is relatively new, with development aimed at increasing the energy density of biomass for pelletising [37–39]. The predominant product is a darkened biomass, with minor by-products of a liquid and non-condensable gas [40]. Torrefaction can be classified as mild, moderate or severe depending on the temperature and residence time. During mild torrefaction (<220 °C), non-reactive drying and particle shrinkage occur initially, followed by reactive drying, bond breaking, and volatilisation of lipophilic extractives and other light compounds [39]. Moderate torrefaction (220 to 250 °C) is distinguished by the release of water, CO, CO₂, CH₄, light volatiles and organic acid [41]. Under severe torrefaction conditions (>250 °C) the majority of hemicellulose is decomposed, with cellulose and lignin decomposition initiating when residence times are prolonged [37]. The fibrous biomass structure is destroyed during torrefaction. This reduces the energy for grinding by up to 90% [41]. The solid product from torrefaction exhibits increased particle sphericity when ground, which improves the flow characteristics and increases the bulk density [38,42–44].

Several authors have considered torrefaction as a pre-treatment for pyrolysis biomass [37,41,45–48]. It was reported that the quality of the bio-oil improved due to a reduced content of water, oxygen, organic acids and light components [45]. Meng et al. [41] observed that the bio-oil under consideration was rich in pyrolytic lignin and anhydrosugars and low in light oxygenates and aldehydes. Chang et al. [47] reported that the levoglucosan yield increased after torrefaction, and speculated that this was caused by the reduction of catalytic interactions between the major biomass components resulting from the slightly disturbed wood structure. Under severe torrefaction conditions, the total liquid yield (torrefaction plus pyrolysis) decreases due to the formation of stable carbon–carbon cross-links during torrefaction that can undergo further polycondensation reactions to form char during pyrolysis [48]. Cross-links are formed when hydroxyl groups are removed during dehydration reactions. Adjacent cross-links form stable compounds that appear

Table 1
Properties of bio-oil compared to a heavy fuel oil and the effects of these properties on the oil's quality.

Property	Pyrolysis oil [6]	Heavy fuel oil [6]	Effect on the quality in terms of fuel use
HHV (MJkg ⁻¹)	14–20	40	Larger volumes required [7–9]
Water content (wt%)	15–30	0.1	Lowers the heating value, viscosity, density, and ignition rate [10,11]
pH	2–3	–	Corrosive to pipes and vessels [10,11]
Solids (wt%)	0.2–1	1	Enhances bio-oil aging, corrosion and equipment blockages [10]
Ash (wt%)	0–0.2	0.1	High temperature corrosion, hard deposits, and bio-oil aging [11,12]
Viscosity (cP at 50 °C)	40–100	180	High pressure drop, increased equipment costs, and ruptures [10]
Density (kgL ⁻¹)	1.2	0.85	Higher density can cause pumping issues [7]
Oxygen content (wt%)	30–40	–	Bio-oils immiscible with petroleum based fuels [11]
Safety (flammable class)	3	3	Potentially harmful [13]

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