**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.

# 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](#_ENREF_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](#_ENREF_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.

## Inorganics

Biomass inorganics, which have been identified as the foremost pyrolysis catalyst [[3](#_ENREF_3), [4](#_ENREF_4)] act by increasing the reactivity of biomass and thus lowering the activation energy of undesirable reactions [[5](#_ENREF_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](#_ENREF_6)], although alkaline earth, transition metals, and non-metals can also be catalytic [[7](#_ENREF_7), [8](#_ENREF_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](#_ENREF_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](#_ENREF_10), [11](#_ENREF_11)].

## Moisture

Water appears to have an auto-catalytic role during pyrolysis [[12](#_ENREF_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](#_ENREF_13)]. 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](#_ENREF_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](#_ENREF_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.

## 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](#_ENREF_18)]. Partial oxygen removal to aldehydes and ketones may be beneficial because their required activation energy for deoxygenation is significantly lower [[18](#_ENREF_18)]; however, aldehydes and ketones are thought to cause stability issues when heating or storing bio-oil, and their production should be avoided [[19](#_ENREF_19), [20](#_ENREF_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](#_ENREF_21)]; or breakdown to form acetone, formic acid, and methanol [[22](#_ENREF_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](#_ENREF_16)], which increases water yields. Karimi *et al* [[23](#_ENREF_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](#_ENREF_24)]. Britt *et al* [[25](#_ENREF_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.

# Experimental

## 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.

## *Pretreatments*

Biomass pretreatment procedures with both leaching and torrefaction are based on the authors’ previous work [[26](#_ENREF_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 *Pinus radiata* after leaching, torrefaction, or both pretreatments were reported previously by Wigley *et al* [[26](#_ENREF_26)]. Leaching using deionised (DI) water and acetic, formic, hydrochloric, sulphuric, and nitric acid was investigated at 30 °C. Acid concentrations between 0.5-10 wt% were investigated for formic and acetic acid. Finally, leaching residence times between 1-8 h were investigated for acetic acid. The torrefaction residence time was optimised between 15-120 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 230-280 °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.

## *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 Figure 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.

## Bio-oil analysis

Proton nuclear magnetic resonance (1H-NMR) was used for a semi-quantification analysis of major bio-oil compounds. Thirty microliters of bio-oil was dissolved in 300 µL of dimethyl sulphoxide-d6 (DSMO-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](#_ENREF_27)], Diebold [[20](#_ENREF_20)], and Huber *et al* [[19](#_ENREF_19)] were identified in 1H-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](#_ENREF_28)] and shifts given by Hosoya *et al* [[29](#_ENREF_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-pentanol were either not detected or present in too small of a quantity to accurately determine the peak above the baseline noise. Peaks for aromatic compounds overlapped (phenol and furan derivatives such as syringol, guaiacol, phenol, methyl-2-furoate, furan, furfural, and hydroxymethylfurfural); therefore, these peaks were all grouped together and represented by the shift between 6.4 and 7.6 ppm because no olefins were identified after 6.4 ppm. Total aldehydes were represented by the shift between 9.5 and10.5 ppm and alkanes between 0.5 and 1.6 ppm [[30](#_ENREF_30), [31](#_ENREF_31)].

High-performance liquid chromatography (HPLC) was used to determine the bio-oil’s acetic acid content [[31](#_ENREF_31)]. Samples were prepared by adding 0.5 mL of DI water and mixing using an ultrasonic bath for 20 min and centrifuging for 20 min at 4000 rpm. A further 1 mL of DI water was added, and the sample was mixed and centrifuged againunder the same conditions. The aqueous fraction was decanted and filtered to 0.22 µm for HPLC analysis. The method used for HPLC analysis was described previously by Wigley *et al.* [[26](#_ENREF_26)]. The water content of samples was determined by Karl Fisher titration following ASTM E203 [[32](#_ENREF_32)]. Karl Fisher titrant 5 was used (5 mg H2O per mL), and titrations were carried out on a TitraLab TIM 550 Radiometer. One per cent water standards were used to calibrate the titrator and for quality control checks. A total of 0.1 mL of bio-oil was injected per test. Gel permeation chromatography (GPC) analysis was conducted by Scion in Rotorua, New Zealand. Samples were prepared by adding tetrahydrofuran to bio-oil to make a 5 mg.mL-1 solution. These samples were filtered to 0.45 µm before analysing at 30 °C in a Knauer/Polymer Standards Service GPC with a PSS SDV Lux 1000 Å column with a refractive index detector. 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 [[33](#_ENREF_33)] found that the average molecular weight of pyrolytic lignin is between 650 and 1300 g.mol-1; therefore, the molecular weight was estimated from the GPC fraction above 650 g.mol-1. An Anton Parr DMA60 was used for digital density measurements. The system was calibrated by measuring the density of water and air prior to injecting bio-oil samples. The carbon, hydrogen, oxygen, and nitrogen content of the solid samples were determined through complete oxidation [[34](#_ENREF_34)] with the elementary analyser at CRL Energy Ltd. in Wellington, New Zealand. The carbon, hydrogen, and nitrogen content were determined following standard ISO 29541:2010, and the oxygen content was calculated by difference. The heat of combustion was determined using Equation 1 reported by Channiwala and Parikh [[35](#_ENREF_35)].

(1)

where C, H, S, O, N, and A represent the dry mass % of carbon, hydrogen, sulphur, oxygen, nitrogen, and ash, respectively. The range for elements is as follows: C: 0-92.3%; H: 0.43-25.2%; N: 0-5.6%; S: 0-94.08%; O: 0-50%; and A: 0-71.4%. Measurement uncertainties are given in Table 1 for bio-oil from pyrolysis of raw biomass.

# Results and discussion

## Pyrolysis of leached biomass

Biomass leached at 30 °C for 4 h with DI water and acetic, formic, hydrochloric, sulphuric, and nitric acid was pyrolysed. The inorganic content of the samples after leaching is given in Table 2 and the pyrolysis yields are displayed in Figure 2. The bio-oil yield increased from 46.9 wt% for raw biomass to 51.2 wt% for DI water-washed biomass. This result is contradictory to results from other reports finding that the removal of water-soluble ions does not affect pyrolysis yields [[3](#_ENREF_3), [36](#_ENREF_36)]. Acid-soluble ions are thought to be more catalytic during pyrolysis, because they are bound tightly to the biomass and thus readily interact during vapour formation. However, water-soluble ions may catalyse secondary reactions during char and vapour entrainment from the reactor. During pyrolysis, the repeated desorption and adsorption of inorganics allows inorganics to reform into a thermally stable form in the char, either bonded to the char or as non-volatile compounds such as silicates [[37](#_ENREF_37)]. This process concentrates water-soluble and water-insoluble inorganics in the char fraction, which may enhance heterogeneous reactions as vapours exit through the outer char layer of a pyrolysing biomass particle or after entrainment. The extended length of the fluidised bed used in this research prolongs char and vapour interactions compared to other systems.

The bio-oil yield from pyrolysis of acetic and formic acid leached biomass increased to 54.6 and 54.8 wt%, respectively. These values were only slightly lower than the bio-oil yields from pyrolysis of nitric and hydrochloric leached biomass of 56.8 and 55.8 wt%, respectively. Leaching with sulphuric acid increased the bio-oil yield to only 52.4 wt% and gave the highest char yield. Sulphur became incorporated into the biomass after leaching, which may have catalysed char formation through the polymerisation of primary vapours. Char from acid leached biomass appeared to agglomerate more than char produced from raw or water-leached biomass, as indicated in Figure 3. This phenomenon has also been reported by Brown [[38](#_ENREF_38)].

Bio-oil properties are given in Table 3. The water and acetic acid content in the bio-oil decreased for all leached samples. Acetic acid is formed from alkali catalysed ring opening reactions [[6](#_ENREF_6)]. The pyrolytic water decreased, owing to the reduced dehydration of vapours. The reduction might also be due to the removal of inorganics that formed a crosslink between biomass polymers. Removing these inorganics would slightly reduce the crosslinking severity of the biomass. If these crosslinks are not removed, they will continuously be broken and reformed during pyrolysis, thus extending the reaction time for volatiles associated with the crosslinks and increasing cracking reactions, which can produce water as a by-product [[36](#_ENREF_36)]. The viscosity of the samples increased after the leaching, which is a common trend because of the lower water content [[39](#_ENREF_39)].

The yields of products and properties of bio-oil from pyrolysis of the biomass leached with 0.5, 1, and 5% acetic and formic acid solutions are presented in Table 4. The inorganic content did not vary when leaching with >1% solutions, and there was no additional mass loss during the leaching [[26](#_ENREF_26)]. However, the product yields from pyrolysis and properties of the bio-oil did vary. The higher bio-oil yield for strong leaching solutions is likely due to stronger leaching that altered the biomass’s structure. Radlein *et al* [[40](#_ENREF_40)] leached Avicel cellulose for 5.5 h at 90 °C in 5% H2SO4, and the inorganic content remained the same following the leaching. After the pretreatment, organic yields changed from 87.1 to 86.3 wt%, but the levoglucosan yield increased from 26.9 to 38.4 wt%, which indicates that inorganics affect pyrolysis product distribution; however the morphology and degree of hydrogen bonding in cellulose may also influence pyrolysis reactions [[41](#_ENREF_41)].

The pyrolysis of biomass leached with 1% acetic acid produced a higher concentration of acetic acid in the bio-oil compared to the other samples, most likely due to a small amount of acetic acid remaining in the biomass after the leaching, indicating that the presence of acetic acid during pyrolysis catalysed char and water formation. The biomass leached with 5% formic acid appeared to follow a similar trend while biomass leached with 5% acetic acid and 1% formic acid did not. DI water used for rinsing was stored at room temperature; this may have influenced the rinsing efficiency. Additionally, the filter cloth was prone to clogging which increased the soaking time of biomass in DI water for certain samples. Soaking the biomass in DI water may improve acid removal as even when the leachate reached a neutral pH, pH paper applied to the biomass indicated that it was still acidic.

Table 5 presents the results from pyrolysis of biomass leached with 1% acetic acid between 1-8 h. From Table 5, it was found that increasing the residence time beyond 4 h had a similar effect as increasing the concentration of the leaching solution: the bio-oil yield increased slightly, and the pyrolytic water decreased. This result may have occurred due to altering the biomass’s morphology during the prolonged leaching times. In general, increasing the leaching residence time had a minimal effect on the bio-oil composition, as determined by the 1H-NMR results shown in Figure 4. However, notable trends included increased alkanes, aromatics, and levoglucosan and decreased acetic acid, hydroxyacetone, and formic acid. From these results, a residence time of 4 h was considered the shortest residence time acceptable to reduce the inorganic content whilst minimising the pretreatment costs.

## Pyrolysis of torrefied biomass

Figure 5 shows the product yields from pyrolysis of biomass torrefied between 230 and 280 °C for 20 min. The yields presented take into account the mass loss during torrefaction. The bio-oil yield increased slightly with mild torrefaction at 230 °C, which was probably caused by reduced interactions between the biomass polymers [[42](#_ENREF_42)]. The total liquid yields in Figure 5 are the sum of the liquid generated from torrefaction and bio-oil from pyrolysis. The bio-oil production decreased with increasing torrefaction temperature but the overall liquid yield increased for most torrefaction temperatures, indicating that torrefaction alters the structure of the biomass to reduce interactions between the biomass polymers and also reduces acid- and water-catalysed reactions. Volatiles exiting the biomass particle interact less with other polymers and vapours when the biomass structure is slightly disturbed [[43](#_ENREF_43)]. Char yields increased as the torrefaction temperature increased due to carbon-carbon crosslinks formed by the dehydration of carbohydrate polymers during torrefaction.

The reduction in bio-oil for pyrolysis of torrefied biomass is partly due to the removal of light organics during torrefaction. The reduction is acceptable if the quality of the bio-oil improves. This factor was assessed in terms of the composition, molecular weight distribution, and oxygen content. Key bio-oil properties are given in Table 6. The acetic acid concentration in the bio-oil decreased significantly after the torrefaction temperature reached 260 °C. The acetic acid in bio-oil may be produced in reactions with moisture in biomass, cleavage of the acetyl content in the biomass, secondary interactions between sugar polymers, and possibly from hemicellulose decomposing to form acetic acid. Torrefaction temperatures up to 280 °C produced the same overall organic yields as from the pyrolysis of raw biomass, but the organic yield was higher between 230 and 270 °C.

An ultimate analysis of the bio-oil indicates increased carbon content but decreased amounts of hydrogen and oxygen in the bio-oil following torrefaction. The decreased hydrogen and oxygen content predominately originates from the reduced moisture content of the biomass, and the bio-oil oxygen content decreased from 41.9 to only 40.5% dry basis for torrefaction at 280 °C. This analysis shows that even severe torrefaction results in a minimal reduction of the bio-oil oxygen content of the organic fraction in bio-oil.

Carbon-carbon crosslinking during torrefaction may increase the bio-oil’s average molecular weight. This parameter was assessed using gel permeation chromatography (GPC), with curves given in Figure 6 and average values in Table 6. The results indicate that there was no substantial change to the average number, weight, or size of the bio-oil compounds following torrefaction but the curves in Figure 6 indicate slightly different molecular weight distributions for torrefied and raw samples. The fraction of the bio-oil with a molecular weight of 174 g.mol-1 was smaller for all torrefied samples compare to that of raw bio-oil, and the small peak at 222 g.mol-1 for raw bio-oil disappeared for torrefied samples. A peak at 255 g.mol-1 was present for torrefied samples. The compounds with molecular weight larger than 650 g.mol-1, which were considered the pyrolytic lignin fraction, decreased, as reported previously [[44](#_ENREF_44), [45](#_ENREF_45)]. Westerhof *et al* [[45](#_ENREF_45)] consider this decrease to be due to lignin partially crosslinking during torrefaction and forming char, as opposed to vapour during pyrolysis. When carbohydrate polymers form 3 adjacent carbon-carbon crosslinks during torrefaction, this structure is thought to be stable at pyrolysis conditions and will not break down further; therefore char forms and prevents the formation of high-molecular-weight compounds [[43](#_ENREF_43)]. The decrease might also be due to reduced secondary polymerisation reactions occurring during the pyrolysis of raw biomass, probably because of the decrease of acetic acid and water in the vapour stream.

The bio-oil’s composition was determined by 1H-NMR, and the results are given in Figure 7. The results indicate that concentrations of acetic acid, hydroxyacetone, and formic acid decreased with increasing torrefaction temperature. This is due to the increased levoglucosan and total aromatics compounds, and is consistent with the results reported by Westerhof *et al* [[45](#_ENREF_45)] for pyrolysis of torrefied pine wood and those by Ren *et al* [[46](#_ENREF_46)] for pyrolysis of torrefied Douglas fir. Aromatics increased because of the higher lignin fraction in the biomass following torrefaction, with dehydrated cellulose forming furans during pyrolysis. A slight depolymerisation of lignin may also enhance thermal decomposition to encourage aromatic release over char formation. There was no significant change to the aldehyde fraction, which was also observed by Zheng *et al* [[47](#_ENREF_47)]. Overall, the composition of the bio-oil can be considered to improve following torrefaction as a pretreatment.

## Pyrolysis of leached and torrefied biomass

### Effects of acid leaching conditions

Solely leaching biomass, as described in previously, resulted in small variances in the pyrolysis yields and bio-oil properties when using different leaching reagents. The subsequent effect of torrefaction was determined next. Samples were torrefied at 240 °C for 20 min following leaching with the different reagents. Yields from pyrolysis of the pretreated biomass are given in Table 7. The bio-oil yield from formic and acetic acid leached and torrefied biomass was higher than for biomass that was solely leached at 30 °C. However, all samples torrefied and leached with DI water or minerals acids (except for biomass leached with hydrochloric acid and torrefied) exhibited a decrease in the bio-oil yield compared to that of solely leached biomass. This finding indicates that acetic acid and formic acid leached biomass benefit from subsequent torrefaction to volatise acid residues and reveals the role of organic acids in catalysing secondary pyrolysis reactions.

Sulphuric acid leached biomass had a low bio-oil yield and a higher char yield compared to the other acid leached samples. This difference was due to the increased sulphur content in the biomass following leaching with sulphuric acid. The low water and acetic acid content in this bio-oil indicates that the mechanism for char formation did not enhance water or acetic acid formation. Leaching with hydrochloric acid produced high bio-oil yields, but the water and acetic acid content in the bio-oil were comparatively high, indicating that chloride (Cl) became incorporated into the biomass and enhanced secondary reactions or altered the primary reaction pathway to enhance the production of low-molecular-weight compounds. When hydrochloric acid leaching was not followed by torrefaction, the water and acetic acid yields were comparable to those of other leaching, likely because more Cl ions were incorporated into the second biomass sample or because torrefaction enhanced Cl ion interactions during vapour formation by transforming Cl into a stable form. This result demonstrates an advantage of using organic acids compared to mineral acids.

### Effects of torrefaction conditions

Biomass leached with 1% acetic acid for 4 h was torrefied between 240 and 280 °C for 20 min. Yields for pyrolysis of the pretreated biomass are displayed in Figure 8. The bio-oil yield obtained from severe torrefaction at 280 °C was still higher (52.4 wt% dry basis) than that from pyrolysis of raw biomass (46.9 wt% dry basis). The overall bio-oil yields were higher than for raw biomass between 240 and 270 °C when taking into the account the mass loss during the pretreatment; however, the overall yield decreased to 43.4 wt% at 280 °C. Torrefaction at 280 °C was associated with a sudden increase in the char yield. Thus, severe carbon-carbon crosslinking of the biomass carbohydrates occurred during torrefaction at 280 °C, and the degradation potential during pyrolysis was reduced as a larger proportion of the crosslinked carbohydrates formed char instead of decomposing to produce volatiles.

The bio-oil properties are given in Table 8. Increasing the torrefaction temperature decreased the acetic acid and water content in the bio-oil due to reduced acid-catalysed reactions. The organic yield was much higher than that of raw biomass, even when the mass loss due to the pretreatments was taken into account. GPC distribution curves are given in Figure 9 and average results are given in Table 8. The average GPC results indicate a small decrease in the average bio-oil molecular weight as the torrefaction temperature increased. This finding is associated with a general trend of decreasing pyrolytic lignin content. The decrease was probably due to reduced secondary polymerisation reactions, such as the oligomerisation of levoglucosan [[48](#_ENREF_48)]. The elementary analysis of pretreated samples indicates a minimal decrease in the bio-oil’s oxygen content on a dry basis. Although torrefaction decreased the biomass’s oxygen content, significant decreases cannot be accomplished without severe carbohydrate loss. Additionally, acid leaching increased the oxygen content in the bio-oil (to 51.8 wt% wet basis and 44.2 wt% dry basis for 1% acetic acid leached samples at 30 °C for 4 h), which offset the decrease caused by torrefaction. Therefore, when combining the pretreatments, only a marginal decrease in the bio-oil oxygen content was obtained on a dry basis.

Temperatures above 270 °C were required for a large decrease in the acetic and formic acid concentrations in the bio-oil. Organic acids cause bio-oil to be corrosive and promote aging reactions, such as aldol reactions to form carbon-carbon bonds between compounds, leading to the formation of high-molecular-weight compounds [[49](#_ENREF_49)]. Torrefaction at 270 °C was preferable to torrefaction at 280 °C because the bio-oil had similar water, acetic acid, pyrolytic lignin, and oxygen content. The molecular weight was also similar but the bio-oil yields were higher for torrefaction at 270 °C.

1H-NMR results for the bio-oils are given in Figure 10. There was a large increase in levoglucosan production for pretreated samples. Total aromatics also increased, whereas the alkane, acetic acid, acetaldehyde, and formic acid concentrations decreased. The levoglucosan concentration was higher than for samples that were solely leached or torrefied, indicating reduced secondary reactions of primary products when both pretreatments were implemented. The reduction in alkanes was most likely from hydroxyl removal during torrefaction, which produced a carbon-carbon double bond as opposed to a single carbon-carbon bond. The reduction may also be due to the reduced cleavage of primary products to produce low-molecular-weight alkanes.

## Comparison between pretreatments

Table 9 compares the biomass properties with and without pretreatment and the corresponding bio-oil yields of biomass that was solely leached with 1% acetic acid at 30 °C; biomass solely torrefied at 270 °C; and biomass leached with 1% acetic acid at 30 °C and then torrefied at 270 °C. The structural composition analysis shows that sugar decomposition was reduced for torrefaction of acid-leached biomass. This result indicates that inorganics may catalyse dehydration reactions during torrefaction via the removal of hydroxyl groups associated with cellulose and hemicellulose. Removal of these hydroxyl groups causes formation of the carbon-carbon double bond which appears as lignin in the fibre analysis [26]. It is desirable to limit hydroxyl removal during torrefaction because the carbon-carbon crosslinks are stable during pyrolysis and will not be cleaved to form volatiles [[43](#_ENREF_43)]. The acetyl removal, however, was not affected by the reduced inorganic concentration because the side branches of hemicellulose, which are highly oxygenated, were thermally reactive during torrefaction.

SEM images in Figure 11 show the morphology of the raw and pretreated biomasses. It was found that the characteristic shape of the tracheid cells remained (Figure 11d) in the pretreated biomass after leaching with 1% acetic acid at 30 °C and torrefaction at 270 °C for 20 min. These open tracheid cells maintained the high wood permeabilities in the pretreated biomass which allows the primary volatiles to exit the biomass particle rapidly during pyrolysis, resulting in a low char yield [51]. Additionally, the pretreated biomass is expected to have more unblocked passages in its structure, thus a higher permeability, compared with the raw biomass due to removal of extractives deposited inside the biomass vessels by acid leaching and torrefaction. Similar observations have been reported by Chen *et al.* [52] who found no change in Lauan wood after torrefied between 220-250 °C for 1 h, while temperatures above 280 °C indicated surface damage, with a tubular shaped surface formed instead of the tracheid cell shape.

Both the structural composition and morphological analysis of the raw and pretreated biomasses suggest that acid leaching preceding torrefaction is critical in achieving high bio-oil yield reported in Table 9.

Bio-oil properties were improved with the combined use of acid leaching and torrefaction in terms of the acetic acid and water content in the bio-oil. These results provide evidence that inorganics, acetic acid, and water all contribute to secondary reactions of pyrolysis vapours and that removal/reduction is required to significantly improve the bio-oil properties. Speculative reaction pathways indicated in Figure 13 were determined to explain how the product formation alters in response to different pretreatments. The water content in bio-oil decreased following the pretreatment, because of reduced water in the feed and reduced secondary reactions of volatiles that produce water as a by-product. The acetic acid production decreased for pretreated biomass, because of the lower acetyl content in the biomass and reduced production during pyrolysis resulting from fragmentation reactions catalysed by inorganics. Pyrolysis of pure cellulose produces no acetic acid [[48](#_ENREF_48)]; therefore, the acid originates from secondary reactions of primary products, inorganic catalysed reactions, or hemicellulose and lignin pyrolysis. Reducing the inorganic and acetyl content in biomass limited these reactions. The oxygen content of the bio-oil was not reduced following the combined pretreatments. Torrefaction decreased the oxygen content in raw biomass to produce a slightly oxygen-depleted bio-oil; however acid leaching increased the oxygen content of the bio-oil. The overall effect when integrating the pretreatments was a minimal change in the oxygen content of the bio-oil on a dry basis but a notable decrease on a wet basis.

Inorganics in biomass predominantly catalyse primary vapours as they escape the biomass particles [52] and products as they are formed. The fragmentation of polymers over depolymerisation is dominant in the presence of inorganic cations [[3](#_ENREF_3)], which enhances the formation of small oxygenated compounds over levoglucosan. Both these mechanisms were reduced for pyrolysis of pretreated biomass as leaching reduced the inorganic content and torrefaction loosened the biomass structure to reduce interactions between immobilised inorganics in the biomass or primary vapours. Rapid moisture removal from the amorphous regions of cellulose during torrefaction can rupture the biomass structure to reduce interactions [53] as well as breaking hydrogen bonds between biomass polymers.

Acid-catalysed reactions can enhance the formation of large aromatics and char [[9](#_ENREF_9)]. It is thought that pyrolysis temperatures above 375 °C are dominated by acid-catalysed reactions over free radical reactions [[25](#_ENREF_25)]. Average GPC results indicate a reduction in the weight and size average of the pretreated bio-oil. The pyrolytic lignin content (fraction >650 g.mol-1) halved, which confirms that secondary, acid-catalysed polymerisation reactions were reduced as a result of both a reduction in the acetic acid present in bio-oil and possibly to the existence of more pathways for the volatiles to escape from the biomass particle. GPC distributions curves are displayed in Figure 12. There was a large peak at 157 g.mol-1, which represented the leached torrefied biomass, and the fraction in the high-molecular-weight range is visually lower compared to the other samples.

# Conclusions

Pyrolysis of leached biomass increased the bio-oil yield for all acid reagents investigated. Char yields from pyrolysis were reduced with the biomass pretreatment, except for biomass leached with sulphuric acid because sulphur became incorporated into the biomass and catalysed charring reactions. The bio-oil’s water and acetic acid content decreased when samples were leached prior to pyrolysis. The optimal leaching conditions were 1% acetic acid leaching at 30 °C for 4 h. Leaching at these conditions reduced the inorganic content from 0.41 wt% for raw biomass to 0.16 wt% for leached biomass. The pyrolysis of biomass leached at the optimal conditions yielded 54.6 wt% bio-oil (dry basis) which contained 1.9 wt% acetic acid and 17.1 wt% water. The higher levoglucosan yield in the bio-oil confirm that secondary reactions were reduced in the inorganic limited environment.

Pyrolysis of biomass torrefied between 230 and 280 °C indicated only torrefaction at 230 °C produced more bio-oil compared to pyrolysis of raw biomass when the mass loss during torrefaction was taken into account. The char yield was higher following torrefaction, because of stable carbon-carbon crosslinks that formed via the dehydration of biomass carbohydrates during torrefaction. Pyrolysis of biomass torrefied at 270 °C for 20 min yielded 46.1 wt% bio-oil. This result equated to an overall yield of 38.9 wt% bio-oil when the mass loss during torrefaction was taken into account. The bio-oil contained 0.6 wt% acetic acid and 6.1 wt% water. The bio-oil was slightly enriched in levoglucosan and aromatics compared to raw bio-oil.

The optimal pretreatment sequence was 1% acetic acid leaching at 30 °C for 4 h followed by torrefaction at 270 °C for 20 min. This condition yielded 55.4 wt% bio-oil, which equated to an overall bio-oil yield of 48.0 wt%, taking into account the mass loss during the pretreatments. The bio-oil produced from pyrolysis of pretreated biomass at the optimal conditions contained 0.15 wt% acetic acid and 4.3 wt% water. Reducing the biomass’s acetyl content limited organic acid formation in the early stages of pyrolysis, leading to a reduction in acid-catalysed reactions; therefore, the pyrolytic lignin content was also reduced in the bio-oil. Inorganics in biomass promote fragmentation reactions over depolymerisation reactions, which enhance the production of organic acids. Thus, reducing the inorganic content during leaching further reduced acid catalysed reactions during pyrolysis. The water content in the bio-oil was extremely low because torrefaction dried the biomass. Water is thought to play an auto-catalytic role to promote the production of pyrolytic water; therefore, dry biomass decreased pyrolytic water formation. Additionally, less water was produced from secondary condensation or dehydration reactions due to the lower inorganic content. The high levoglucosan yield of 17.0% confirmed that secondary reactions were limited to a much higher degree when both pretreatments were implemented and all three biomass catalysts (organic acids, water, and inorganics) were reduced/removed.

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