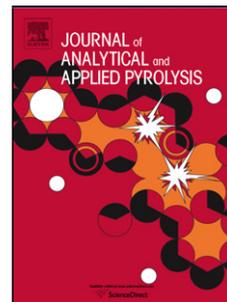


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# The Effect of Biomass Pretreatment on Catalytic Pyrolysis Products of Pine Wood by Py-GC/MS and Principal Component Analysis

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## Highlights

- Catalytic fast pyrolysis of pretreated pine wood was studied by Py-GC/MS and PCA
- PCA showed how feedstock and pyrolysis conditions affected pyrolysis products
- Temperature and catalyst loading were more important than biomass pretreatment
- Acid-leaching pretreatment slightly lowered the proportion of aromatic products
- The effects of acid-leaching and torrefaction were greatest in non-catalytic pyrolysis

## Abstract

Non-catalytic and catalytic pyrolysis of pretreated pine wood was conducted using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Biomass pretreatment included acid-leaching, torrefaction, and acid-leaching followed by torrefaction. Forty-five pyrolysis products were identified in the Py-GC/MS chromatograms and their peak area data evaluated by principal component analysis. In non-catalytic pyrolysis, acid-leaching pretreatment enhanced the levels of levoglucosan, while torrefaction pretreatment enhanced the proportion of catechols in the volatile products. Increasing both the temperature and catalyst loading in catalytic pyrolysis promoted the formation of aromatic hydrocarbons. At lower pyrolysis temperatures (450-500 °C), acid-leaching

pretreatment resulted in slightly low proportions of aromatics, while torrefaction pretreatment had the opposite effect. Overall, temperature and catalyst loading were considerably more important factors in catalytic fast pyrolysis of pine wood than biomass pretreatment as studied by Py-GC/MS.

## Keywords

Catalytic pyrolysis, Biomass pretreatment, Acid-leaching, Torrefaction, Pyrolysis-Gas Chromatography/Mass Spectrometry, Principal component analysis

## 1. Introduction

Biomass fast pyrolysis is a thermochemical process that aims to produce high yields of pyrolysis oil. Pyrolysis conditions typically include temperatures of 425-500 °C, a high heating rate, a short vapour residence time and rapid condensation of the hot vapour [1]. Pyrolysis oils, however, have undesirable properties that include high viscosity, poor volatility, corrosiveness and undesirable aging on storage [2]. Catalytic fast pyrolysis can be used to improve the quality of pyrolysis oils. This process combines fast pyrolysis with catalytic cracking [3], and can potentially be used to produce biofuels or value added chemicals [4].

Catalytic fast pyrolysis of lignocellulosic biomass with zeolite catalysts involves thermal pyrolysis of the biomass, followed by catalytic upgrading of the pyrolytic products [5]. The process can involve either pyrolysing the biomass with zeolite inside the reactor (in situ catalytic pyrolysis), or alternatively passing the hot vapours produced from standard fast pyrolysis through a bed of zeolite catalyst (ex situ).

Cellulose and hemicellulose are pyrolysed to various sugars and sugar derivatives, furans, light oxygenates and other compounds [6-9]. Lignin is pyrolysed to phenolic compounds including guaiacols, catechols and phenols [10,11]. These thermal pyrolysis products then undergo a series of reactions on the acid sites of the zeolite to form aromatic hydrocarbons [10]. For instance, the

sugars can be first transformed to furans, and further transformed to aromatic hydrocarbons [12,13]. Small lignin-derived products, such as guaiacol and 4-methylguaiacol, can enter the pores of the zeolite and undergo deoxygenation reactions to form aromatics [14]. Additionally, the light oxygenated pyrolysis products, such as acids and ketones, can undergo oligomerization, aromatization, hydrogen transfer and deoxygenation [5,10] to be converted to aromatics. Besides the above bio-oil products, significant by-products include non-condensable gases, water, char and coke [15]. The chemical reactions are extremely complex and further studies are required to improve the understanding of the reaction networks, kinetics and mechanisms involved in catalytic fast pyrolysis of lignocellulosic biomass [10].

Biomass pretreatment has been investigated as an approach to improving the properties of wood-derived fast pyrolysis oils [16-20]. Common pretreatments have included washing/leaching, steam explosion and torrefaction [21]. Biomass pretreatment via acid-leaching removes trace inorganics from the biomass and increases the yield of bio-oil in fast pyrolysis [22-24]. Torrefaction of biomass prior to fast pyrolysis leads to the production of more aromatics, and less water and acids, but also decreases bio-oil yield [21].

Biomass pretreatment, especially acid-leaching, for catalytic fast pyrolysis has not been studied in detail. Acid-leaching of biomass prior to in situ catalytic fast pyrolysis could conceivably prolong the lifetime of the catalyst. This is because inorganics in the biomass can cause irreversible deactivation of the zeolite catalyst during in situ catalytic fast pyrolysis [25-27]. This problem is less of an issue in ex situ catalytic fast pyrolysis as the inorganics are removed with the entrained char by the cyclone separators before the hot vapour reaches the catalytic bed. Torrefaction can be used to improve the selectivity of aromatic hydrocarbons in catalytic pyrolysis [28-30]. Optimal torrefaction conditions for catalytic pyrolysis are reported to be 210-240 °C for 40 minutes [28]. Torrefaction pretreatment can also enhance the production of aromatic hydrocarbons in catalytic pyrolysis of cellulose [31] and lignin [32]. Based on these studies, biomass pretreatment for catalytic fast pyrolysis was considered worthy of further investigation.

Performing catalytic fast pyrolysis experiments in large pyrolysis reactors and analysing the bio-oil products can be a time-consuming process, especially when investigating a number of experimental variables, such as the pretreatment technology, the catalyst loading and the pyrolysis temperature. One solution is to use pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) to rapidly screen a range of experimental conditions to better understand the parameters that have the greatest effect on the catalytic pyrolysis products. This technique can be applied semi-quantitatively to give information on the relative changes of particular products due to different pyrolysis conditions [33]. Only low molecular weight GC-volatile products are detected. The technique provides no information on the high molecular weight, non-volatile pyrolysis products. Py-GC/MS chromatograms of biomass feedstocks are typically very complex with hundreds of compounds detected. Only a proportion of these compounds can be confidently identified based on their mass spectra [34]. This is because of the low concentration of some compounds, co-elution of compounds on the GC column, and limitations of the mass spectral database. Absolute quantification is not usually performed in Py-GC/MS of lignocellulosics [34], as this requires calibration of the MS detector which responds differently to different compounds with responses not linear with respect to concentration. Hence the technique has its limitations and it is best to interpret the data in terms of general trends rather than specifics. One way to do this is to apply principal component analysis to the Py-GC/MS data [35-37].

Principal component analysis (PCA) is a statistical procedure that transforms a large number of possibly correlated variables into a smaller number of uncorrelated variables called principal components. It is useful in extracting information from complex data sets as it reduces a large set of variables into a smaller set without significant loss of the information. PCA has been successfully used by several researchers in analysing multivariate Py-GC/MS data [35-37].

In this study, Py-GC/MS analysis and principal component analysis was used to understand the effects of biomass pretreatment, pyrolysis temperature and catalyst loading on catalytic pyrolysis products. The effect of combined acid-leaching and torrefaction pretreatment on analytical pyrolysis of pine wood, under catalytic and non-catalytic conditions, is reported for the first time.

## 2. Experimental

### 2.1. Biomass pretreatment

Fresh wood chips (Radiata pine), obtained from a Rotorua sawmill in New Zealand, were dried to a moisture content of under 10 wt.% in a controlled drying room. The dried wood chips were ground and sieved to a particle size ranging from 0.25 mm to 2 mm.

Ground wood was acid-leached for 4 hours at 30 °C using a 1 wt.% acetic acid solution, and then washed with deionized water and oven dried [24]. Torrefaction of raw and acid-leached wood was carried out in a stainless steel vessel with N<sub>2</sub> purge and heated in an oven at 260 °C for 260 minutes before cooling to room temperature. The maximum temperature of the vessel was 258 ± 3 °C, the average heating rate was 0.9 °C/min and the average cooling rate was 2.0 °C/min.

The two pretreatments gave three feedstocks, acid-leached wood (ALwood), torrefied wood (Twood), and acid-leached and torrefied wood (ALTwood). Untreated raw wood (Rwood) was included in the study as the control. The woody feedstocks were ground and sieved to pass a 50 mesh screen and then oven-dried at 105 °C prior to chemical analysis (see Supplementary Information) and Py-GC/MS.

### 2.2. Catalyst and sample preparation for Py-GC/MS

The commercial zeolite catalyst, HZSM-5 (Si/Al=30:1) was purchased from Saint Chemical Material Company (Shanghai, China). The catalyst had a specific surface area  $\geq 350$  m<sup>2</sup>/g and binder content of 50 %. The non-catalytic aluminium oxide binder is added to improve attrition resistance. The catalyst was ground and sieved through a 50 mesh screen to obtain a fine powder which was then heated at 525 °C for 3 hours in a furnace to dry and activate the catalyst. A similarly-prepared silica sand powder was used for non-catalytic pyrolysis experiments.

For non-catalytic Py-GC/MS, the silica sand was mixed with the wood feedstocks in a ratio of 2.5:1 by weight. The samples were labelled as R00, AL00, T00 and ALT00 for Rwood, ALwood,

Twood and ALTwood, respectively. For catalytic Py-GC/MS, zeolite catalyst was mixed with the wood feedstocks at catalyst to biomass (C/B) ratios of 2.5:1, 4:1 and 6:1 by weight, and labelled accordingly (e.g. R25, AL25, T25, ALT25 for 2.5:1 samples etc.).

### 2.3. *Pyrolysis-gas chromatography/mass spectrometry*

The sixteen samples were pyrolysed at four different temperatures: 360 °C, 450 °C, 500 °C and 550 °C, giving a total of 64 different experiments labelled as sample\_temperature. For example, ALT25\_550 represented pyrolysis of ALTwood with a C/B ratio of 2.5:1 at 550 °C. Every experiment was carried out in triplicate to obtain average values and standard deviations.

The Py-GC/MS instrument was composed of a Frontier Lab pyrolysis furnace with an auto-shot sampler (Pyrolysis), an Agilent 7890A gas chromatograph (GC) and an Agilent 5973 mass selective detector. Gas chromatography was performed on a 30 m Zebron WaxPlus column (Phenomenex) with 0.25 mm inner diameter and 0.25 µm film thickness.

In each experiment, the sample contained  $0.6 \pm 0.05$  mg feedstock, and the residence time in the pyrolysis furnace was 6 seconds before the gas/vapour products were split at an injection split ratio of 30:1 into the GC/MS. The injection temperature was set at 280 °C, the interface temperature was 280 °C and the ion source temperature was 250 °C. The carrier gas was helium at a constant flow rate of 1 mL/min. The oven temperature program was set at 2 minutes isothermal heating at 60 °C, followed by a 4 °C/min ramp to 260 °C, then a hold at this temperature for 26 minutes. The mass spectra were recorded at 0.2 scan per second with an m/z 40-550 scanning range.

Agilent MassHunter software was used to collect and analyse the chromatographic peaks. Peaks with areas accounting for 5 % or more of the largest peak area in the chromatogram were included for identification. The compounds were identified using the MS library NIST 2011 with a high degree of certainty (over 80%) using distinctive ions based on selective ion mass spectrometry. The relative proportion of each identified compound was based on its selective ion peak area relative to the total selective ion peak area. The results are semi-quantitative as calibrating ion

abundances to concentration was not practical considering the large number of identified compounds, and the value and suitability of using an internal standard in this study. Hence, relative peak areas for grouped compounds (Table 1) was used to illustrate how different pretreatment or pyrolysis conditions affected the composition of the volatile pyrolysis products, with the results best interpreted in terms of the general trends.

The total number of integrated peaks per chromatogram ranged from 42 to 119 depending on the sample and pyrolysis conditions. The total ion peak area of the identified compounds as a percentage of the total ion peak area of all integrated peaks was calculated to show that the compounds that were identified and used in the PCA analysis were representative of the majority of the volatile pyrolysis products produced in each experiment.

#### 2.4. *Principal component analysis*

SIMCA 15 software (Sartorius Stedim Data Analytics AB, Sweden) was used for principal component analysis. In this analysis the catalytic pyrolysis experiments was set as the observations and the peak area percentages for the identified compounds in the Py-GC/MS chromatograms were set as the variables. The PCA method transformed this large set of variables into principal components. PCA models were then constructed using these principal components to show the variation between the different catalytic pyrolysis experiments. Differences in the selective peak area percentages of certain identified compounds contribute proportionally to the principal components based on the scale of the differences between the different pyrolysis experiments. The first two principal components of the variation, PC1 and PC2, were considered in this study and used to construct the PCA models. PC1 describes the largest possible variation, and PC2 the second highest variation. PC1 and PC2 are the horizontal and the vertical axes, respectively, in the score and loadings plots. A score plot is a PCA model of the observations (i.e. the pyrolysis experiments) and shows the distribution of the observations relative to each other. A loadings plot is the PCA model of the variables (i.e. the identified compounds) and shows the contribution of the variables to the principal components. The score and loadings plots need to be considered together in interpreting the results. Statistical data on the goodness of fit ( $R^2X$ ) and

goodness of prediction ( $Q^2X$ ) for the PCA models and for key individual variables in the models are provided in the Supplementary Information.

### 3. Results and discussion

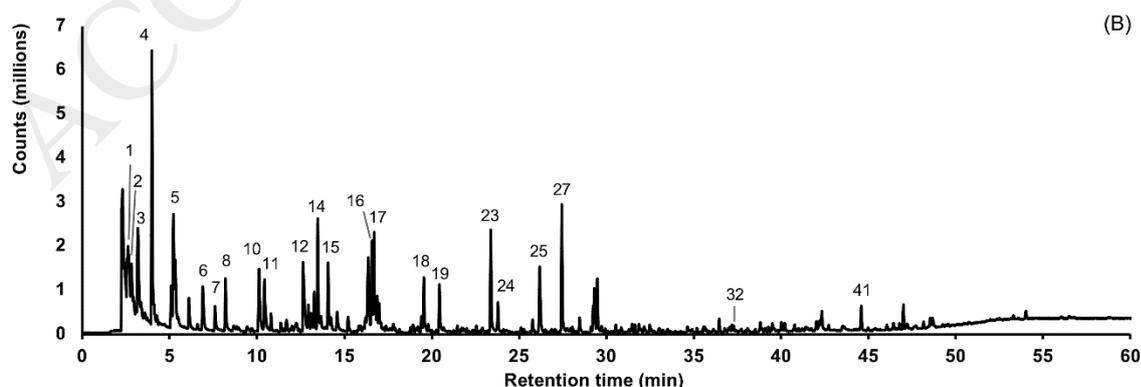
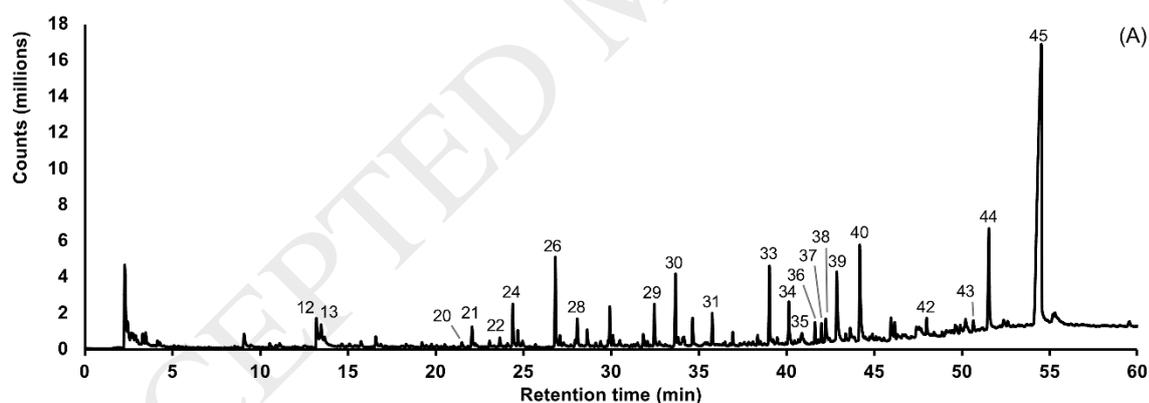
#### 3.1. Biomass pretreatment

The acid-leached wood was chemically very similar to the raw wood in terms of carbohydrate and lignin content, however its inorganic or ash content was substantially lower at 0.03 wt. % (Table S1, Supplementary Information). Inductively coupled plasma mass spectrometry (ICP-MS) analysis indicated that the alkali and alkali earth metals, K, Ca, Mg and Na were all substantially reduced compared to raw wood. Mild torrefaction pretreatments of raw wood and acid-leached wood resulted in 17 and 14 wt. % mass loss, respectively, mainly due to loss of hemicellulose components (Table S1). The apparent lignin content increased after torrefaction. The acid-leached and torrefied wood had a reduced inorganic content of 0.07 wt. %. These chemical changes (Table S1) were all consistent with previously reported results for acid-leached and torrefied softwood biomass [24]. The mass loss observed on the torrefaction pretreatment would affect the overall bio-oil yield in an industrial pyrolysis process [20]. Advantages and disadvantages of the various pretreatments will be discussed in a subsequent paper describing the results of catalytic pyrolysis of these feedstocks in a 0.35 kg/h (biomass feed) pyrolysis plant.

#### 3.2. Identified Py-GC/MS products

Forty-five compounds were identified in the chromatograms of the 64 different experiments (Table 1). Examples of chromatograms from non-catalytic pyrolysis and catalytic pyrolysis of ALTwood are given in Fig. 1, with identified products labelled with their retention time sequence. For non-catalytic pyrolysis experiments, 75-93 % of the total GC/MS peak area was accounted for by the identified compounds (Table 1). This number ranged from 71 to 79 % for the catalytic pyrolysis experiments. In general, the proportion of total identified peak area relative to total peak area was higher at the higher pyrolysis temperatures.

The data on the relative abundances of the identified compounds was analysed firstly by principal component analysis to: i) identify which experimental conditions resulted in the greatest variations in pyrolysis products and ii) identify those compounds or groups of compounds that made the greatest contributions to these variations. It was also beneficial to classify the identified compounds into nine groups based on their main chemical functionalities (Table 1), and to plot trends in the data. This approach of evaluating the relative abundances of groups of compounds has been successfully used by others [3,10]. Thermal pyrolysis products from cellulose and hemicellulose were grouped as furans, acetic acid, ketones, sugars and sugar derivatives (e.g. levoglucosan); while thermal pyrolysis products from lignin were grouped as guaiacols and phenols [10]. Catechols can be produced from polysaccharides and lignin. The catalytic pyrolysis products were classified into aromatics and oxygenated aromatics. Furans can also be products of catalytic pyrolysis, for example zeolites catalyse the dehydration of levoglucosan to 5-hydroxymethylfurfural [5].



**Fig. 1.** Py-GC/MS chromatograms obtained from thermal pyrolysis at 500 °C of acid-leached and torrefied wood (A) and catalytic pyrolysis at 500 °C of acid-leached and torrefied wood with C/B of 6:1 (B).

**Table 1:** Identified Py-GC/MS products and their assigned chemical groups.

ACCEPTED MANUSCRIPT

RT sequence	Compound	Group
1	Furan	Furans
2	2-Methylfuran	Furans
3	Benzene	Aromatics
4	Toluene	Aromatics
5	Xylene-p/o/m	Aromatics
6	1-Ethyl-(4/3/2)-methylbenzene	Aromatics
7	Styrene	Aromatics
8	1,2,4-Trimethylbenzene	Aromatics
9	1-Hydroxy-2-propanone	Ketones
10	Cyclopentenone	Ketones
11	Indane	Aromatics
12	Acetic acid	Acid
13	Furfural	Furans
14	Indene	Aromatics
15	Benzofuran	Oxygenated aromatics
16	2-Methylbenzofuran	Oxygenated aromatics
17	(1/3)-Methyl-1H-indene	Aromatics
18	1,3-Dimethyl-1H-indene	Aromatics
19	Naphthalene	Aromatics
20	2(5H)-Furanone	Furans
21	1,2-Cyclopentanedione	Ketones
22	2-Hydroxy-3-methyl-2-cyclopenten-1-one	Ketones
23	2-Methylnaphthalene	Aromatics
24	Guaiacol	Guaiacols
25	2,7-Dimethylnaphthalene	Aromatics
26	Creosol	Guaiacols
27	p/m/o-Methylphenol	Phenols
28	4-Ethylguaiacol	Guaiacols
29	Eugenol	Guaiacols
30	2-Methoxy-4-vinylphenol	Guaiacols
31	trans-Isoeugenol	Guaiacols
32	6-Methoxy-3-methylbenzofuran	Oxygenated aromatics
33	5-Hydroxymethylfurfural	Furans
34	Vanillin	Guaiacols
35	4-Propylguaiacol	Guaiacols
36	Apocynin	Guaiacols
37	Guaiacylacetone	Guaiacols
38	3-Methylcatechol	Catechols
39	Catechol	Catechols
40	4-Methylcatechol	Catechols
41	2-Methylantracene	Aromatics
42	4-(Ethoxymethyl)-2-methoxyphenol	Guaiacols
43	Coniferyl aldehyde	Guaiacols
44	Mannose	Sugars
45	Levogluconan	Sugars

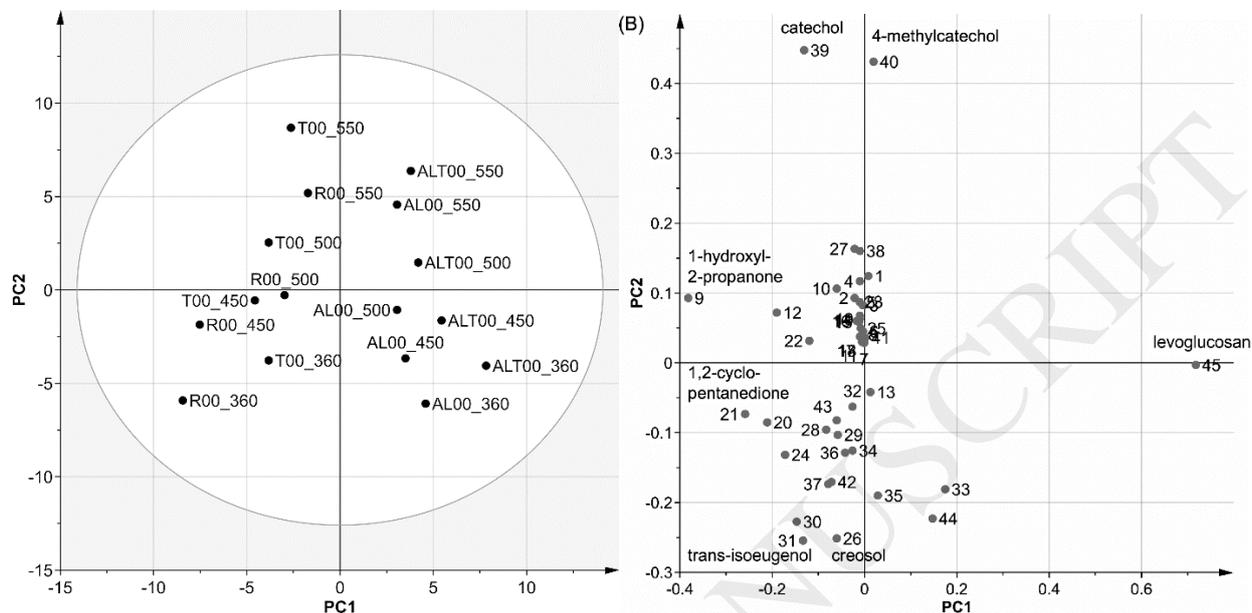
### 3.3. *Non-catalytic pyrolysis*

The score and loadings plots for non-catalytic Py-GC/MS are shown in Fig. 2. The score plot (Fig. 2A) shows how the 16 non-catalytic Py-GC/MS experiments are distributed relative to each other in terms of the two principal components of the variation between the experiments. In other words, clustering of experiments indicates the compositions of the pyrolysis products are similar. Separation of experiments indicates differences in the composition of the products. Principal component 1 (PC1) and 2 (PC2) account for 49 % and 39 % of the variation among the experiments, respectively. The loadings plot (Fig. 2B) shows the contributions of the 45 identified products (Table 1) to the variation in the experiments. Being located closer to the origin means that the compound contributes little to the principal component. Being located away from the origin indicates an important contribution to the principal component, with the spatial arrangement (positive or negative) defined by the score plot.

In the score plot (Fig. 2A) the experiments with acid-leaching pretreatment are located on the positive side of the origin on the PC1 axis, while experiments without acid-leaching pretreatment are located on the negative side. This implies that the acid-leaching pretreatment has the largest influence on the composition of the pyrolysis products. In the loadings plot (Fig. 2B), levoglucosan makes the major contribution to PC1 in the positive direction, while the ketones 1-hydroxy-2-propanone and 1,2-cyclopentanedione make important contributions in the negative direction. Hence the pyrolysis products of acid-leached woods (ALwood and ALTwood) mainly differ from those of Rwood and Twood in their levoglucosan and ketone contents.

PC2 in the score plot (Fig. 2A) distinguishes the experiments based on temperature, with higher temperatures driving the experiments in the positive direction on the PC2 axis. PC2 describes 39 % of the variation and so temperature is also an important factor influencing the composition of the pyrolysis products in non-catalytic pyrolysis. Torrefaction pretreatment affects PC2 with experiments with torrefied feedstocks (T00 and ALT00) located above the corresponding experiments with non-torrefied feedstocks (R00 and AL00) at all pyrolysis temperatures tested. In the loadings plot (Fig. 2B), PC2 is strongly positively correlated with catechol and

4-methylcatechol, and negatively correlated with creosol and the guaiacols, trans-isoeugenol and 4-vinylguaiacol. This indicates that increasing temperature, and to a lesser extent torrefaction pretreatment, contributes to a higher proportion of catechols in the GC volatile products.

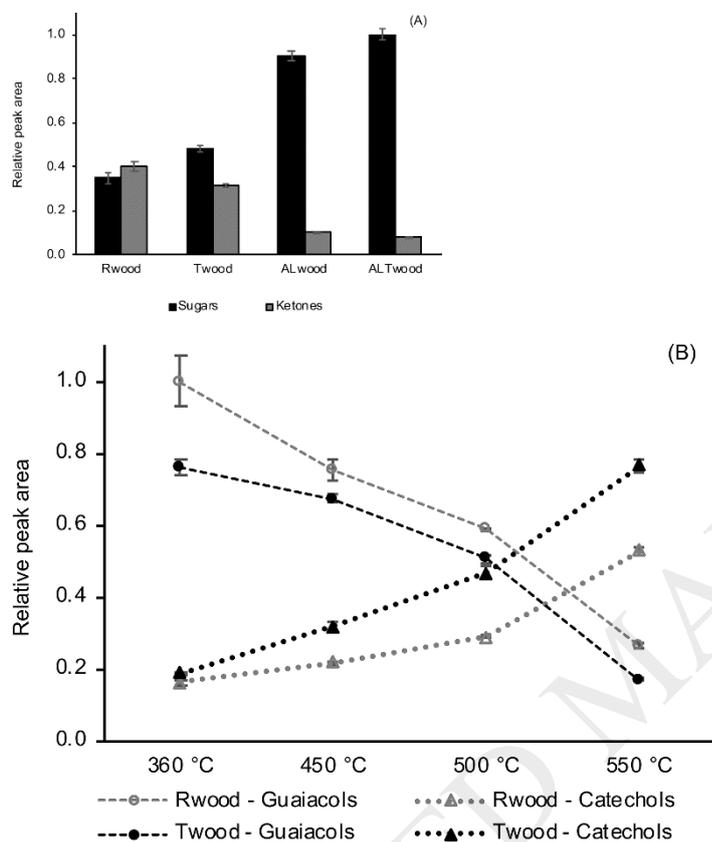


**Fig. 2.** Score (A) and loadings (B) plots of PC1 and PC2 for non-catalytic Py-GC/MS analysis with all feedstocks at all temperatures. The ellipse shown in the Score plot (A) is the Hotelling's  $T^2$  range for the 95% confidence region of the model.

Plotting the relative peak area results for the sugars and ketones groups for non-catalytic pyrolysis showed that acid-leaching enhanced the formation of sugars (mainly levoglucosan) with a resulting decrease in the relative proportion of ketones (Fig. 3A). Increased sugars yield on fast pyrolysis of acid-leached pinewood has been previously reported for a range of pyrolysis temperatures from 360 to 580 °C [38]. Inorganics in the biomass (e.g. alkali and alkaline earth metals) can promote the conversion of sugars to light oxygenates via reactions like fragmentation, ring-opening and cracking [39]. Hence the removal of these metal ions by acid-leaching suppresses these reactions.

Increasing the pyrolysis temperature increased the proportion of catechols and decreased the proportion of guaiacols in the volatile products for all four feedstocks (e.g. Fig. 3B for Rwood and Twood). Amutio *et al.* [40] found a similar result on fast pyrolysis of pine wood sawdust in a conical spouted bed reactor at 400 to 600 °C. The guaiacols possibly undergo thermal degradation

to contribute to the increased proportion of catechols. Torrefaction pretreatment has been reported to promote the formation of lignin-derived compounds in fast pyrolysis of pine wood [20,41]. Here we found torrefaction pretreatment favours higher proportions of catechols and lower proportions of guaiacols in the fast pyrolysis volatile products (Fig. 3B).



**Fig. 3.** Trends in relative peak areas of key pyrolysis products in non-catalytic Py-GC/MS for: all feedstocks at 450 °C (A); Rwood and Twood at 360 to 550 °C (B). Due to the nature of the Py-GC/MS data, peak area percentages have been normalised to the largest peak area % in each plot to illustrate the trends in the data. Hence, comparisons are only valid within each individual plot and not between plots.

### 3.4. Catalytic pyrolysis

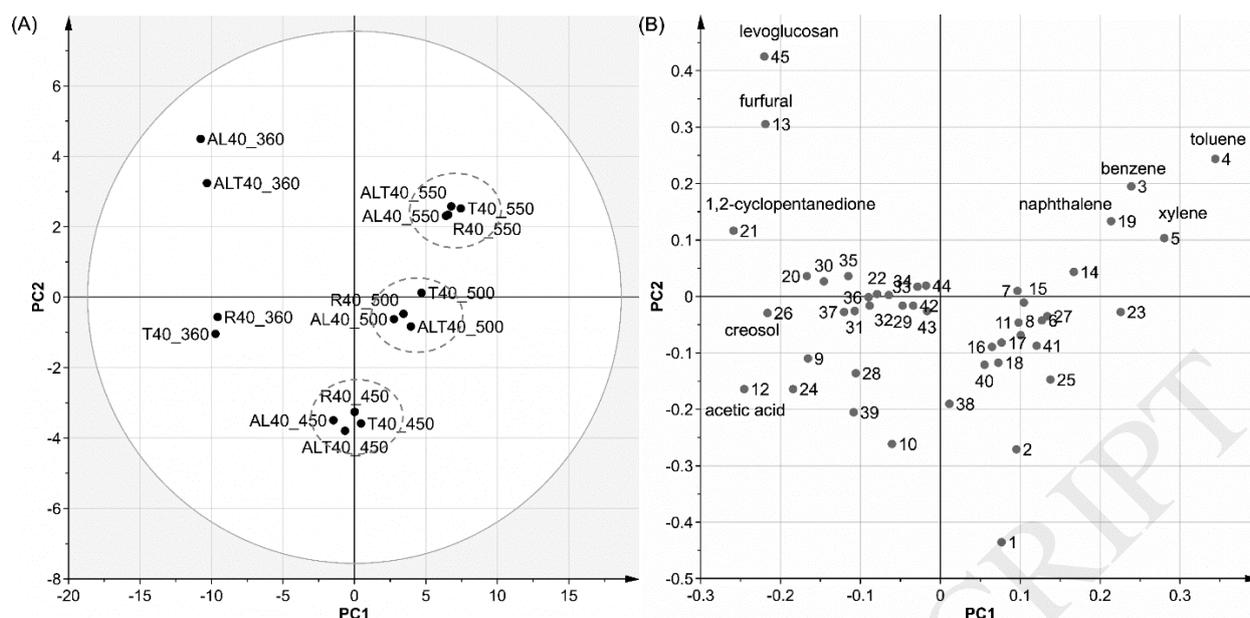
#### 3.4.1. Effect of pretreatment and pyrolysis temperature

The score and loadings plots for catalytic Py-GC/MS for all feedstocks at all temperatures, at a C/B ratio of 4:1, are shown in Fig. 4. The score plot (Fig. 4A) shows the distribution of these 16 experiments with PC1 and PC2 accounting of 73 % and 12 % of the variation among the experiments, respectively.

Experiments at the same pyrolysis temperatures are closely clustered together in the score plot (Fig. 4A) regardless of the pretreatment used, with the exception of experiments at 360 °C. This indicates that temperature was the most important factor determining the composition of the pyrolysis products at this catalyst loading. Experiments at 450, 500 and 550 °C are all tightly clustered together in three distinct groups (circled) according to temperature, with these groups shifted in the positive direction on the PC1 and PC2 axes with increasing temperature.

Experiments at 360 °C all appear at the same position on the PC1 axis, but are shifted in the negative direction relative to the higher temperature experiments. Additionally, experiments with acid-leached wood are shifted in the positive direction on the PC2 axis, relative to Rwood and Twood feedstocks which are located near the PC2 origin.

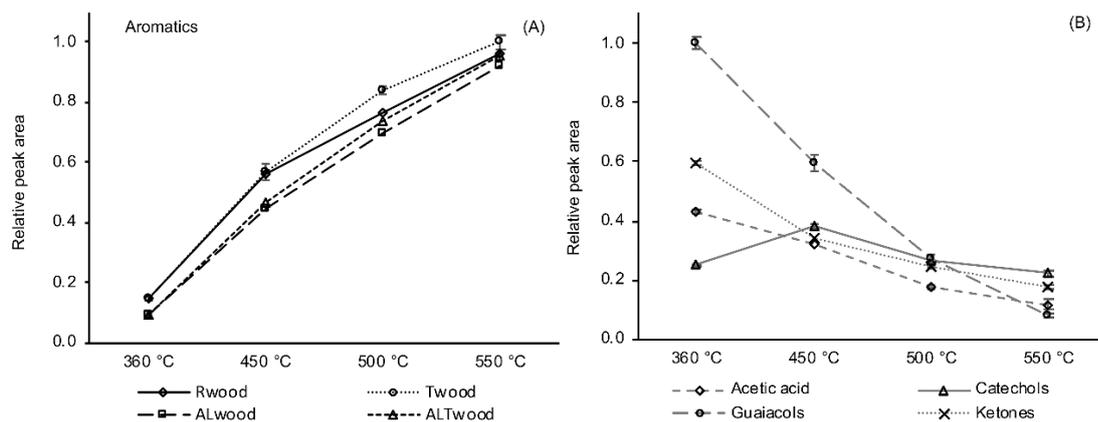
The loadings plot shows that PC1 is correlated in the positive direction with aromatic products, such as toluene, benzene, xylene and naphthalenes (Fig. 4B). PC1 is also correlated in the negative direction with thermal pyrolysis products, such as acetic acid, 1,2-cyclopentanedione, creosol and furfural. Hence, increasing pyrolysis temperature results in the formation of more aromatic hydrocarbons in catalytic pyrolysis, independent of whether biomass pretreatment is used or not (Fig. 5A). This is because the activity of HZSM-5 is increased with temperature. Acid-leaching pretreatment leads to slightly lower proportions of aromatics in the pyrolysis products compared to Rwood at lower pyrolysis temperatures (Fig. 5A). Conversely, torrefaction leads to slightly higher proportions of aromatics compared to Rwood at higher temperatures (Fig. 5A). This observation agrees with literature reports that state torrefaction pretreatment increased the selectivity of aromatic hydrocarbons in catalytic pyrolysis [28,41].



**Fig. 4.** Score (A) and loadings (B) plots of PC1 and PC2 for catalytic Py-GC/MS analysis with all feedstocks at all temperatures and a C/B ratio of 4:1. The ellipse shown in the Score plot (A) is the Hotelling's  $T^2$  range for the 95% confidence region of the model.

At low pyrolysis temperatures, e.g. 360 °C, the activity of the zeolite catalyst is low and so the products of thermal pyrolysis are important differentiators in the product composition.

Consequently, the influence of the acid-leaching pretreatment was more important at 360 °C (Fig. 4A) than at higher temperatures where the catalyst is more active. The proportions of thermal pyrolysis products, including acetic acid, guaiacols and ketones, were all substantially decreased with increasing pyrolysis temperature for all feedstocks (e.g. Fig. 5B), as these products were further converted by the catalyst. The relative proportion of catechols increased at 450 °C before decreasing again at 500 °C and above. It is speculated that as the temperature increases from 360 to 450 °C more sugars and guaiacols are converted to catechols. A further increase in temperature results in the catechols being more efficiently converted to aromatics.

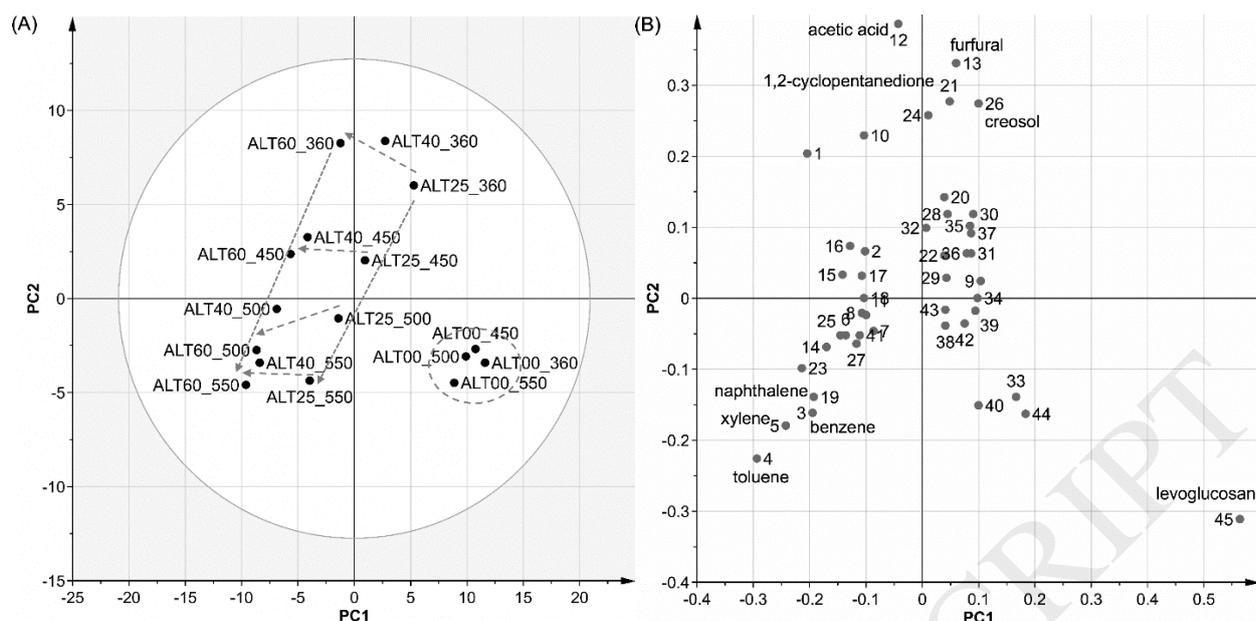


**Fig. 5.** Trends in relative peak areas of key pyrolysis products in catalytic Py-GC/MS for: aromatics for all feedstocks at all pyrolysis temperatures at C/B 4:1 (A); thermal pyrolysis products for ALTwood at all temperatures (B). Standard deviations are shown to give a representative indication of the level of experimental error, but only on selected data points for reasons of clarity of presentation.

### 3.4.2. Effect of catalyst to biomass ratio

The score and loadings plots for catalytic Py-GC/MS of ALTwood at all four temperatures and four C/B ratios are shown in Fig. 6. The score plot (Fig. 6A) shows the distribution of these 16 experiments with PC1 and PC2 accounting of 61 % and 23 % of the variation among the experiments, respectively. The score and loadings plots of the other three feedstocks Rwood, ALwood and Twood (Fig. S1-S3, Supplementary Information) show similar trends to those described for ALTwood.

In the score plot, catalytic Py-GC/MS experiments at the same temperature occurs at approximately the same position on the PC2 axis, but are shifted in the negative direction on PC1 axis with increasing C/B ratio (Fig. 6A). Additionally, catalytic Py-GC/MS experiments at the same C/B ratio are shifted in the negative direction on the PC1 and PC2 axes with increasing temperature. Therefore both the temperature and the C/B ratio affect the distribution of products in catalytic pyrolysis, with pyrolysis temperature appearing to have the larger influence in this study. In the case of the non-catalytic experiments, all four experiments are closely clustered together (Fig. 6A). Here the influence of temperature is relatively minor compared to the effect of catalysis.

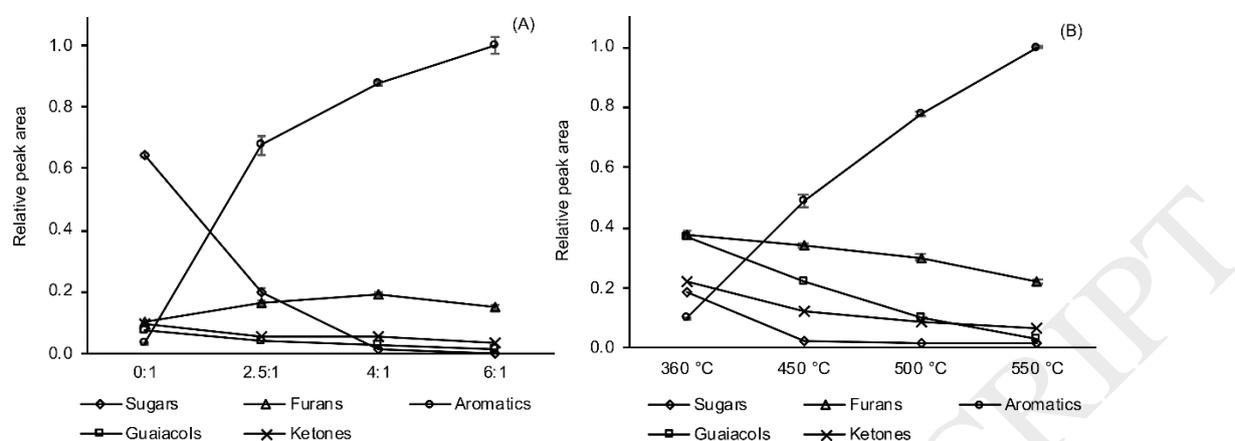


**Fig. 6.** Score (A) and loadings (B) plots of PC1 and PC2 for catalytic Py-GC/MS analysis of ALTwood at all temperatures and C/B ratios. The ellipse shown in the Score plot (A) is the Hotelling's  $T^2$  range for the 95% confidence region of the model.

The loadings plot (Fig. 6B) shows that PC1 is positively correlated to polysaccharide thermal pyrolysis products, such as levoglucosan, mannose, 5-hydroxymethylfurfural, and it is negatively correlated to aromatics, such as toluene, xylene, benzene and naphthalenes. Hence increasing temperature and increasing C/B ratio both drive the product composition towards the formation of aromatics. PC2 is positively correlated to light oxygenates and guaiacols, and negatively correlated to aromatic hydrocarbons. This indicates that increasing the temperature drives conversion of light oxygenates and guaiacols to aromatic hydrocarbons.

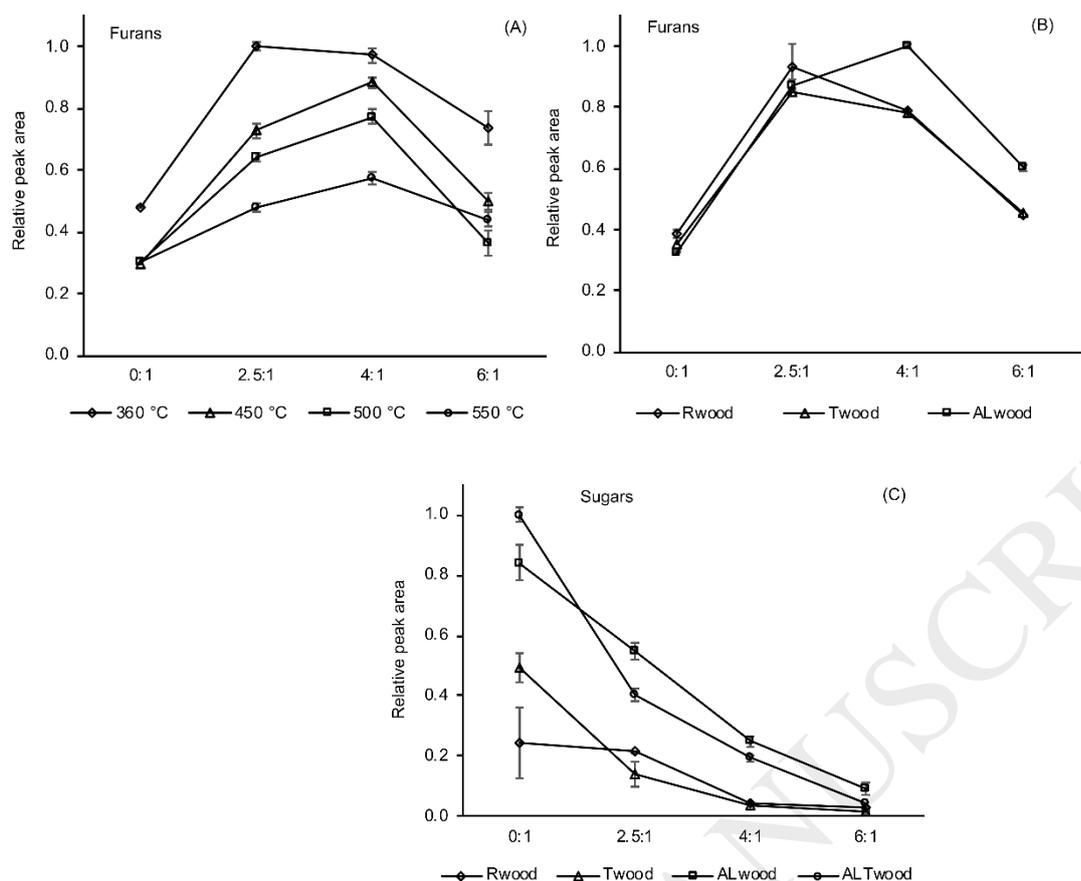
The proportion of aromatics in the pyrolysis products of ALTwood substantially increased when the C/B ratio and pyrolysis temperature were increased (Fig. 7A and 7B). This trend was observed for all four feedstocks. The proportions of sugars, guaiacols and ketones all decreased with increasing C/B ratio (at 550 °C) and increasing temperature (at C/B ratios of  $\geq 2.5:1$ ) (e.g. Fig. 7A and 7B for ALTwood). This indicates that HZSM-5 strongly promotes the conversion of thermal pyrolysis products to aromatics. This agrees with previous results that have shown the yield of aromatics is increased with an increase in C/B ratio in the range from 0:1 to 9:1 [42]. Because

zeolite activity is highly dependent on the availability of acid sites [43], increasing the C/B ratio provides more acid sites for converting thermal pyrolysis products.



**Fig. 7.** Trends in relative peak areas of key pyrolysis products in catalytic Py-GC/MS for: ALTwood at 550 °C and all C/B ratios (A); for ALTwood at C/B ratio of 4:1 at all temperatures (B). Standard deviations are shown on selected data points.

The proportion of furans increased with increasing C/B ratio up to a maxima at a C/B ratio of 4:1 (or in some cases 2.5:1) and then decreased again at a C/B ratio of 6:1. This general trend was evident at all pyrolysis temperatures (Fig. 8A) across all four feedstocks (Fig. 8B). Furans are intermediate products in catalytic pyrolysis [5,12,13,44] and are formed by catalytic dehydration of sugars before being further converted at high catalyst loadings. The proportion of sugars (mainly levoglucosan) in the Py-GC/MS chromatograms at 360 °C decreased significantly with increasing C/B ratio for all of the four feedstocks (Fig. 8D). High reactivity of levoglucosan on HZSM-5 at 550 °C is known [45], however this is the first time levoglucosan has been shown to be highly reactive on HZSM-5 at a pyrolysis temperature of 360 °C.



**Fig. 8.** Trends in relative peak area of pyrolysis products in catalytic Py-GC/MS for: furans in ALTwood at all temperatures and all C/B ratios (A); furans in Rwood, Twood and ALwood at 450 °C and all C/B ratios (B); sugars in all feedstocks at 360 °C and all C/B ratios (C). Standard deviations are shown on selected data points.

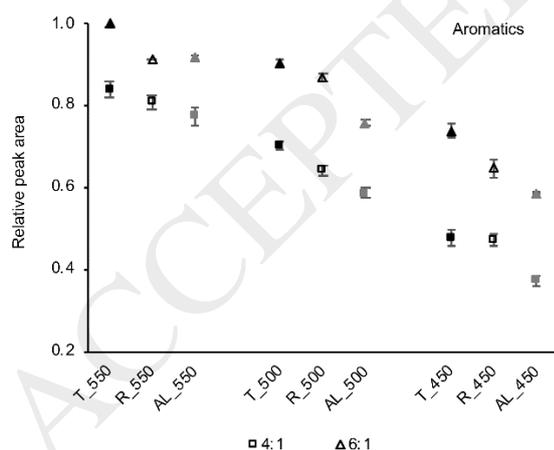
### 3.5. Effect of pretreatment on the chemistry of catalytic pyrolysis

In catalytic pyrolysis, the first step is thermal pyrolysis of the lignocellulosic biomass to release pyrolysis vapours, which then undergo a series of catalytic reactions on the zeolite to form aromatics and products with low oxygen contents (e.g. furans, benzofurans) [5,10]. This study has shown that acid-leaching and torrefaction pretreatments can affect the products of thermal pyrolysis. However, these pretreatments generally have only small influences on the products of catalytic pyrolysis compared to pyrolysis temperature and catalyst loading (C/B ratio).

Acid-leaching pretreatment significantly promoted the formation of levoglucosan in thermal pyrolysis, which is upgraded to aromatics [13] through furans intermediates [12]. At 550 °C the formation of aromatics is not restricted by the acid-leaching pretreatment (Fig. 9). However, at

lower temperatures (450 and 500 °C), there appears to be a slightly lower proportion of aromatics in the Py-GC/MS chromatograms of acid-leached wood compared to raw wood (Fig. 9). This is because HZSM-5 is unable to convert all of the excess levoglucosan produced with acid-leached wood to aromatics at these temperatures. Consequently, slightly higher proportions of furan intermediates are observed with acid-leached wood (at C/B ratios of 4:1 and 6:1) compared to raw wood (e.g. Fig. 8B).

Torrefaction pretreatment slightly increased the proportion of aromatics in catalytic Py-GC/MS compared to raw wood (Fig. 9). Torrefaction pretreatment favoured higher proportions of catechols and lower proportions of guaiacols in the thermal pyrolysis products relative to raw wood (Fig. 3B). The main catechols produced (e.g. catechol and 4-methylcatechol) were smaller molecules than many of the guaiacols produced (e.g. 4-ethylguaiacol, eugenol, 4-vinylguaiacol, isoeugenol and vanillin). Bulky guaiacols potentially have restricted access to the pores of the zeolite where the majority of the catalytic upgrading reactions occur [14]. Thus the higher proportion of catechols relative to bulky guaiacols is potentially responsible for the increased proportion of aromatics in the catalytic pyrolysis products of torrefied wood, as studied by Py-GCMS (Fig. 9).



**Fig. 9.** Trends in relative peak area of aromatic products from catalytic Py-GC/MS of Twood, Rwood and ALwood at 450-550 °C and C/B ratios of 4:1 and 6:1. Standard deviations are shown to give a representative indication of the level of experimental error.

## 4. Conclusions

Pretreatments of pine wood by acid-leaching or torrefaction influenced the products of thermal pyrolysis as analysed by Py-GC/MS. Acid-leaching promoted the formation of levoglucosan while leading to lower relative proportions of ketones in the GC volatile products. Torrefaction pretreatment affected the relative proportions of catechols and guaiacols in the pyrolysis products.

Temperature and catalyst loading were the major factors influencing the pyrolysis products in catalytic pyrolysis. Increasing both pyrolysis temperature and the catalyst to biomass ratio led to more aromatics being produced. Conversely, biomass pretreatments had only relatively minor effects in catalytic pyrolysis. Acid-leaching slightly lowered the relative proportion of aromatics in the pyrolysis products at 450-500 °C. This was due to the elevated levels of levoglucosan, which required high temperatures and catalyst loadings for complete conversion to aromatics via furan intermediates. Torrefaction slightly enhanced the relative proportions of aromatics in catalytic pyrolysis products possibly linked to increased proportions of catechols produced in the thermal pyrolysis step.

These analytical pyrolysis results provided insights into the catalytic pyrolysis behaviour of pretreated pine wood, which are useful in designing applied pyrolysis experiments to investigate impacts of biomass pretreatment on upgraded bio-oil yield and quality.

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