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Catalytic pyrolysis of demineralized lignocellulosic biomass

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ABSTRACT

The effect of ash removal pre-treatment of lignocellulosic biomass prior to catalytic pyrolysis for producing biofuels was investigated. Non-catalytic and catalytic pyrolysis of demineralized and raw biomass was performed in Py-GC/MS and bench-scale experiments to study the performance of in-bed and ex-bed upgrading. Pre-treated biomass shows a significant increase in the organic liquid yield in experiments performed at 600 °C from 31 to 42 wt% compared to raw biomass, as well as a significant reduction of char yield. The performance of in-bed catalytic pyrolysis of pre-treated biomass over HZSM-5 is limited compared to the corresponding raw material. However, ex-bed catalytic pyrolysis of pre-treated biomass at 600 °C results in an overall increased yield of BTX compounds. Pyrolysis vapors from pre-treated biomass present a suitable composition for catalytic upgrading after secondary vapor-phase reactions. Additionally, demineralization reduces the total acid number of derived liquids in catalytic and non-catalytic pyrolysis.

1. Background

The search for renewable substitutes to the global reliance on fossil-based resources is rapidly gaining attention. Much focus is spent on resources/residues from the forestry and agricultural industries, but also on organic waste such as food and animal offal. A major challenge in the commercialization of renewable applications is the development of technically and economically reliable conversion routes to turn such resources into for example liquid feedstocks. One promising approach for converting forestry and agricultural feedstocks is pyrolysis since it allows a relatively low cost for converting solids into renewable liquids [1]. Such feedstocks mainly consists of lignocellulosic biomass, which is a complex fibrous polymeric material of varying composition and with global availability. Lignocellulosic biomass consists mainly of three polymeric structures: hemicellulose, cellulose, and lignin with varying thermal stabilities [2,3]. In pyrolysis, the material is depolymerized when heated to around 400–600 °C in inert atmosphere, which produces: (1) a hot gas of condensable organic compounds and permanent gases which mainly consists of derivatives from hemicellulose and cellulose [4], and (2) a solid carbonaceous material mainly derived from polycondensation reactions of lignin [5,6].

The composition of pyrolysis liquid derived from lignocellulosic biomass is dependent on its polymeric structure as well as its concentration and composition of inorganic elements. Elements such as alkali and alkaline earth metals (AAEMs) are known as intrinsic catalysts for the thermal decomposition of biomass as well as for reactions such as cracking and re-polymerization during the devolatilization of biomass and when vapors diffuse from the carbonaceous residue [7]. Previous works have identified two major pathways for thermal decomposition of carbohydrates that are dependent on the concentration of AAEMs: (1) formation of anhydrosugars in low concentration of AAEMs, and (2) formation of low molecular weight compounds such as aldehydes and carboxylic acids in high concentration of AAEMs [8]. This can be explained by AAEMs catalyzing the formation of smaller compounds during depolymerization and/or cracking of larger compounds, e.g. sugars and anhydrosugars, when leaving the carbonaceous solid residue [9]. By demineralizing biomass prior to pyrolysis, commonly performed through acid leaching, AAEMs and other inorganic elements can be removed. Recently, several studies have investigated the demineralization of biomass followed by characterizing its effect on the pyrolysis products. The results confirm the decomposition pathways presented above, where demineralized biomass shows an enhanced production of levoglucosan and other anhydrosugars and less smaller compounds [10–12], reflecting the pyrolysis of glucose [13].

Pyrolysis liquid is known for its complex organic composition and high oxygen content, which gives it a low heating value and makes it a complicated feedstock for handling in refining processes. In order to homogenize the liquid’s organic composition and to enhance its similarities to fossil crude oils, pyrolysis vapors can be catalytically upgraded prior to condensation. Catalytic pyrolysis of biomass has been widely studied in the recent years, mainly by evaluating the performance of different zeolitic catalysts known from the petrochemical
industry for promoting cracking, deoxygenation and aromatization reactions. One of the most promising catalysts for aromatization of pyrolytic vapors from biomass is HZSM-5 mainly because of its shape selectivity and narrow pore-size distribution, making it suitable for converting model compounds such as glucose and other sugars into aromatic hydrocarbons [14,15], but also for lignocellulosic biomass feedstocks [5,16]. Different pathways to further increase the conversion of biomass into aromatic hydrocarbons have been studied, for example by investigating the temperature of catalytic pyrolysis, modifying the catalyst’s acidity, metal-doping of the catalyst etc. [16–18]. However, little focus has been spent on the influence of the vapor stream composition that is subject to catalytic upgrading. By demineralizing biomass prior to catalytic pyrolysis, one can produce a vapor stream with enhanced concentration of anhydrosugars to be upgraded over the catalytic surface. Thereby, the vapor composition becomes more similar to the one from glucose, which has been used as a model compound for biomass when investigating the performance of different zeolites. Also, demineralization of biomass reduces the complexity of the bio-oil composition which should be preferable in downstream upgrading [11]. Therefore, combining pre-treatment for biomass demineralization with catalytic pyrolysis over HZSM-5 should be of interest. Ash removal prior to catalytic pyrolysis will also reduce irreversible catalyst poisoning caused by for example alkali metals during vapor upgrading [7]. Additionally, biomass demineralization can be performed utilizing wood-derived acids present in the aqueous phase of pyrolysis liquid by internal liquid recirculation [10,11]. Thereby, the use of additional feedstocks for demineralization can be reduced as well as the risk of contaminating biomass when using inorganic acids as leaching agents. Previous studies have identified the combination of acid-leaching and pyrolysis with internal recycling of chemicals to be a cost effective process to produce sugars and combustible liquids from biomass [19].

Based on this, a process scheme is suggested for combined biomass pre-treatment and catalytic pyrolysis utilizing internal acid recycling, presented in Fig. 1.

In this work, catalytic and non-catalytic pyrolysis of demineralized biomass was investigated and compared to raw biomass based on pyrolysis properties and the performance in catalytic upgrading. Lignocellulosic biomass was experimentally demineralized. Pyrolysis and catalytic upgrading was performed in Py-GC/MS as well as in a bench-scale reactor to study in-bed and ex-bed catalytic pyrolysis. Experiments were performed at different temperatures to study the thermal degradation behaviors and the influence of temperature on catalytic upgrading.

### Table 1

<table>
<thead>
<tr>
<th>Biomass characteristics</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile matter</td>
<td>SS-EN ISO 18123:2015</td>
</tr>
<tr>
<td>Elemental composition</td>
<td>SS-EN ISO 16948:2015</td>
</tr>
<tr>
<td>Ash content</td>
<td>SS-EN ISO 18122:2015</td>
</tr>
<tr>
<td>Ash composition</td>
<td>ICP/MS</td>
</tr>
</tbody>
</table>

#### 2. Materials and methods

Demineralized and raw biomass were compared based on their thermal degradation properties and characteristics in catalytic and non-catalytic pyrolysis. The lignocellulosic material used in this study was softwood sawdust with particle size range 0.35–0.5 mm, which was characterized based on properties presented in Table 1. Analysis results are presented in Table 3.

#### 2.1. Biomass pre-treatment

Biomass was demineralized by acid leaching pre-treatment based on previous works [11], where biomass was successfully demineralized without reducing its volatile matter. A 2 dm³ solution consisting of acetic acid (10 wt%) and de-ionized water was pre-heated to 85°C in a closed vessel. Thereafter, the solution was mixed with 100 g of pre-dried and pre-heated biomass and kept at constant temperature for 30 min under stirring. After the pre-treatment, biomass and the acidic solution was separated by filtration. The biomass was thereafter washed with de-ionized water in order to remove any residues from the acidic solution, such as acids and dissolved inorganics [10,20]. Several washing cycles were performed by mixing biomass with de-ionized water followed by filtration. When the water did not show any difference in pH after washing biomass, the biomass was placed in a drying oven operating at 105°C. Characterization results of pre-treated biomass is presented in Table 3.

#### 2.2. Catalyst preparation and characterisation

The catalyst used for catalytic pyrolysis was HZSM-5 supplied by Alfa Aesar (SiO₂:Al₂O₃ 30:1). The material was calcined in air at 610°C for 15h followed by preparation for catalytic pyrolysis. The catalyst was pelletized, crushed and sieved to different particle size for each pyrolysis unit: 0.125–0.180 mm for bench-scale experiments and 0.63–0.90 µm for Py-GC/MS.

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**Fig. 1.** Suggested process scheme for biomass demineralization and catalytic pyrolysis.
2.3. Pyrolysis experiments

Pyrolysis and catalytic pyrolysis experiments were performed both in a Py-GC/MS instrument as well as in a bench-scale setup. This allowed investigating in-bed and ex-bed catalytic pyrolysis respectively as well as the influence of different heating rate and treatment times. Experiments were performed at 400, 500 and 600 °C in order to study the thermal decomposition of the biomass samples, the performance of catalytic pyrolysis, as well as product yields.

2.3.1. Py-GC/MS

A Py-GC/MS setup was used to study in-bed catalytic pyrolysis of the two lignocellulosic samples, the thermal stability of raw and pretreated biomass as well as the composition of bio-oil formed in non-catalytic pyrolysis during rapid heating, short thermal treatment time and instantaneous vapor cooling. Catalytic and non-catalytic pyrolysis were conducted in a filament pyrolyzer Pyrol2000 coupled with an Agilent 7890A/5975C instrument. In order to separate the vapors from catalytic and non-catalytic pyrolysis respectively, different columns were used based on the vapors’ overall polar characteristics. The biomass was grinded and sieved to a particle size of 63–90 µm.

For non-catalytic pyrolysis, approximately 1 mg of biomass was placed on the filament and positioned in the Pyrol2000 device. The sample was soaked in acetone in order to increase the contact surface area between biomass and the filament. The temperature of the pyrolysis chamber was 175 °C. After the sample had been dried it was heated to the pyrolysis temperature within 8 ms by pyrolysis for 2 s at the set temperature. Formed vapors were carried by He into a mid-polar 60 m VF-1701 ms column (film thickness 0.25 µm) operating at 40 °C, with a split ratio of 30:1. The choice of column was based on the polar character of raw pyrolytic vapors from biomass. After keeping constant temperature for 2 min, the GC oven was heated by 4 °C/min until reaching 250 °C, where the temperature was kept constant for 30 min. The unit mass range was set to 45–550. Compounds were identified with Chemstation software and NIST11 library.

For catalytic upgrading in the Py-GC/MS setup, the experimental procedure was inspired by a previous work of catalytic pyrolysis in a Pyrola2000 unit [21]. Biomass was carefully mixed with HZSM-5 of similar particle size (mass ratio 1:1). Thereafter, the mixture was placed on the filament. The mixture was then soaked in acetone in order to increase the contact surface area between the biomass, the catalyst and the filament. After drying in the pyrolysis chamber operating at 175 °C, catalytic pyrolysis was performed at the desired temperature for 2 s reaction time after heating during 8 ms. The upgraded pyrolysis vapors were injected to a non-polar 60 m long HP5-ms column in order to study the non-polar products from catalytic upgrading. Split ratio was 30:1. After the column had been kept at 40 °C for 2 min, the GC oven was heated with 4 °C/min to 250 °C followed by 30 min holding time. The unit mass range was similar to the analysis of vapors from non-catalytic pyrolysis, as well as the software and library used for peak identification.

The results from non-catalytic and catalytic pyrolysis were analyzed by semi-quantification, where the average peak area over the weight of sample placed on the filament (biomass or biomass and catalyst respectively) was calculated and compared. The experimental cases were repeated and results are presented as an average including standard deviations. Chromatograms for Py-GC/MS analysis can be found as supplementary material.

Characteristic organic compounds found in the bio-oil were chosen for presenting the results from the pyrolysis experiments. For non-catalytic pyrolysis acetic acid, levoglucosan, furfural, guaiacol and furan were chosen. Acetic acid, furfural and levoglucosan are the main acid, aldehyde and anhydroxy sugar respectively found in pyrolysis liquid from lignocellulosic biomass and are derived from the holocellulosic structure [22]. Guaiacol (also known as 2-methoxyphenol) is a major phenol compound derived from the lignin structure [23]. Additionally, furan is presented as it is a known derivative from dehydration of levoglucosan and commonly used as model compound in catalytic pyrolysis studies [24, 25].

For catalytic pyrolysis, characteristic one- and two-ringed aromatic hydrocarbons were chosen for comparison since they serve as the main products from the catalytic upgrading over HZSM-5 [15, 26].

2.3.2. Bench-scale pyrolysis

A bench-scale fixed bed setup was used to study the composition of bio-oil formed during slow heating, a longer thermal treatment time and well as a longer residence time of vapors at the pyrolysis temperature prior to quenching. Also, the experimental setup was used for ex-bed catalytic pyrolysis of bio-oil formed from raw and demineralized biomass. The pyrolyzer consisted of a tubular steel pipe with an inner diameter of 5 cm mantled by a 60 cm three-heating zone furnace. The biomass sample was placed in a basket and kept in a water-cooled section above the furnace until it had reached a stable temperature of pyrolysis. The temperature of the biomass was measured by a thermocouple positioned in the centre of the fixed sample bed. In the bottom part of the heated zone, a fixed bed of catalyst or silica sand with a particle diameter range of 125–180 µm was positioned on a fine mesh platform prior to furnace heating. N2 was used as carrier gas in all cases with a flow rate dependent on the pyrolysis temperature to allow constant residence time of vapors in the pyrolyzer and in the fixed bed for each experimental case. The experimental setup is illustrated and further described in previous works [27–29]. When the pyrolyzer had reached a stable final temperature, the biomass sample was introduced to the heated zone and positioned above the fixed bed of catalyst/sand. The sample was heated to the furnace temperature set to 400, 500, and 600 °C respectively. Downstream the fixed bed of catalyst/sand, pyrolysis vapors were quenched at −17 °C in cold traps connected in-series in a cooling bath followed by passing through an aerosol trap. Results of bench-scale pyrolysis was evaluated by mass balance as well as analyzing the composition of pyrolysis liquids and permanent gases. Catalyst coke yield was analyzed by thermogravimetric analysis.

2.3.3. Analysis of permanent gases

The composition of permanent gases was analyzed in a micro-GC (Agilent 490) equipped with four columns with TCD-detectors and calibrated for analysis of CH4, C2H2–4, C3H6–8, CO, CO2, H2, N2 and O2.

2.3.4. Analysis of pyrolysis liquids

Liquids were analyzed based on characteristics presented in Table 2. The amount of liquid collected in the condensation system and in the aerosol trap was quantified by scaling.

For analysis of the organic composition in GC/MS, an Agilent 7890A/5975C setup was used. As for Py-GC/MS studies of catalytic and non-catalytic pyrolysis, the same columns were used for catalytic and non-catalytic tests (HP5-ms and VF-1701 ms) in order to identify their non-polar and polar compounds respectively. In both cases, similar GC programs to separate the organic compounds were used as for the Py-GC/MS analyses, with a split ratio of 30:1 and 10:1 for catalytic and non-catalytic tests respectively. Prior to sample injection to the GC column, the pyrolysis liquid was diluted with methanol. A solvent delay of 4 min was set for the MS. Dichloromethane was used as internal standard (2000 ppm). This allowed semi-quantification of the GC/MS results where the average peak areas and standard deviations from the

Table 2

<table>
<thead>
<tr>
<th>Method</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karl-Fischer titration</td>
<td>Water content</td>
</tr>
<tr>
<td>TAN titration</td>
<td>Total acid number</td>
</tr>
<tr>
<td>GC/MS</td>
<td>Organic composition</td>
</tr>
</tbody>
</table>
derived chromatograms are presented. For each case, multiple samples were taken for GC/MS analysis and is presented as an average.

3. Results and discussion

3.1. Pre-treatment and biomass characteristics

Results of ultimate and proximate analysis of pre-treated and raw biomass are presented in Table 3. The pre-treatment shows a 76 % removal of inorganics in the biomass structure without sacrificing the volatile matter. For the removal of individual elements, the results show that acid-leaching mainly removes AAEMs compared to transition metals, where for example 38 % of Fe and at least 91 % of Ca was removed. This could be explained by the chemical state of individual elements in the biomass structure. AAEMs are mainly present as water-soluble salts or ion-exchangeable from the organic structure using protons, whereas Fe is mainly present as minerals and ion-exchangeable elements [30,31]. Overall, the characterization results of the samples reflect similar observations from previous studies [11].

<table>
<thead>
<tr>
<th></th>
<th>Raw</th>
<th>Pre-treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash content (wt%)</td>
<td>0.21</td>
<td>0.05</td>
</tr>
<tr>
<td>Volatile matter (wt%)</td>
<td>84.4</td>
<td>86.3</td>
</tr>
<tr>
<td>C (wt%)</td>
<td>50.7</td>
<td>50.9</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>6.0</td>
<td>6.5</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>&lt; 0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>O* (wt%)</td>
<td>43.0</td>
<td>42.5</td>
</tr>
<tr>
<td>Ca (mg/kg)</td>
<td>349</td>
<td>&lt;30</td>
</tr>
<tr>
<td>K (mg/kg)</td>
<td>242</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Mg (mg/kg)</td>
<td>51.6</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Mn (mg/kg)</td>
<td>42.4</td>
<td>0.88</td>
</tr>
<tr>
<td>Fe (mg/kg)</td>
<td>7.97</td>
<td>4.95</td>
</tr>
<tr>
<td>Al (mg/kg)</td>
<td>5.24</td>
<td>4.34</td>
</tr>
</tbody>
</table>

* Calculated by difference.

3.2. Mass balance of bench-scale pyrolysis experiments

Fig. 2 presents the mass balance of products from non-catalytic and catalytic pyrolysis performed in the bench-scale fixed bed setup. Overall, a significant impact of the pre-treatment can be observed for the mass distribution of pyrolysis products. For non-catalytic pyrolysis, an increased organic liquid yield for pre-treated biomass was observed at higher temperatures. Pyrolysis of pre-treated biomass at 600 °C increases the organic liquid yield by 33 % compared to raw biomass, where also the yield of gas and water was reduced. These observations are associated with the lower concentration of AAEMs in pre-treated biomass which for example suppresses the magnitude of vapor cracking which leads to gas and water production [12]. Additionally, an increased organic liquid yield derived from pre-treated biomass for pyrolysis at higher temperatures could be associated with the higher temperature gradients during pyrolysis. Additionally, a clear reduction of the char yield at higher temperatures was observed for the pre-treated biomass compared to its corresponding raw material. At 600 °C demineralized biomass reduced the char yield with 20 %. This correlates with the above statement about the influence of AAEMs which are also known to promote char-ring reaction and the formation of secondary char [6]. The higher char yield for pre-treated biomass at 400 °C is speculated to be associated with the material’s increased thermal stability in the absence of inorganic elements. However, bench-scale experiments performed in this study and thermogravimetric analysis (TGA) from previous studies present different results in terms of the biomass samples’ relative char yield [11]. Compared to bench-scale experiments, TGA results present a reduced thermal degradation at lower temperatures as well as no significant difference in the yield of solid carbonaceous residues at higher temperatures. This can be explained by the different sample volumes used in TGA and the bench-scale experiments, i.e. different magnitudes of available surface area for charring reactions when vapors leave the solid residue of pyrolysis and thereby the exposure to AAEMs.

Moving on to the catalytic pyrolysis, the differences in yields of gas, organic liquid and pyrolytic water compared to non-catalytic tests reflect the catalyst activity [27,29]. Also, a reduced coke yield with the temperature of catalytic pyrolysis is in accordance with previous works [17]. The difference in coke yield between pre-treated and raw biomass will be further discussed in Section 3.4.2.

3.3. Composition of bio-oil

The results of bio-oil composition from experiments performed in Py-GC/MS and in a bench-scale fixed bed pyrolyzer at 400, 500 and 600 °C are presented in Figs. 3 and 4 in terms of chosen characteristic compounds from the different biomass constituents. Chromatograms

![Fig. 2. Mass balances of performed experimental cases. P.t. refers to pre-treated. *Gas yield is calculated by difference.](image-url)
can be found as supplementary information.

### 3.3.1. Py-GC/MS

Py-GC/MS analysis results of the biomass samples are presented in Fig. 3 as detected peak area over the sample mass. Pre-treated biomass presents a significant reduction of acetic acid compared to raw biomass together with a significantly enhanced concentration of levoglucosan with increasing temperature. At 600 °C the relative acetic acid yield is reduced by 17 % compared to raw biomass, whereas levoglucosan is increased by 339 %. These results can be attributed to the thermal decomposition pathway of holocellulose [8]. For the results of furfural, the yields from the two biomass samples do not show any clear influence of demineralization. Simultaneously, pre-treatment was observed to reduce the guaiacol production up to 88 % which confirms that leaching affects the thermal decomposition of lignin [10,11]. However, a deeper understanding on the influence of AAEMs during lignin devolatilization is left for future studies.

Additionally, an overall increase in product yields with increased temperature should be attributed to the short time of heating and thermal treatment in the filament pyrolyzer. Therefore, these results also indicate the thermal stability of the polymers in the biomass samples under such conditions.

![Fig. 3. Results of non-catalytic pyrolysis in Py-GC/MS.](image)

### 3.3.2. Bench-scale pyrolysis experiments

The composition of bio-oil derived from thermal treatment of raw and pre-treated biomass in a bench-scale fixed-bed pyrolyzer are presented in Fig. 4. Results of dichloromethane confirms an even dilution of bio-oil samples. Compared to Py-GC/MS analysis, the bench-scale tests are performed at lower heating rate and longer time of thermal treatment which allows complete devolatilization. As seen for Py-GC/MS results, pre-treated biomass results in a lower concentration of acetic acid at all temperatures with a maximum relative decrease of 74 %. Also, pre-treatment suppresses the production of furan, which can be linked with the reduced dehydration of anhydrosugars in a lower concentration of AAEMs [32,33]. As for studies in Py-GC/MS, demineralized biomass shows a reduction of guaiacol, which has also been observed in fluidized bed experiments [10].

Moving on to levoglucosan, a significantly higher production was observed for demineralized biomass at all temperatures compared to raw biomass which slightly decreases at 600 °C. The trend for the levoglucosan yield for pyrolysis of pre-treated biomass in the range 400–600 °C could be explained by a combination of reduced reactivity of the carbonaceous residue as well as the influence of secondary vapor-phase reactions. The high levoglucosan yield reflects a suppressed influence of pre-treated biomass and its carbonaceous residue when primary vapor compounds are transported through the vapor phase, correlating with observations in Section 3.2. As the reactor temperature
increases, the rate of secondary reactions in the vapor phase is enhanced where levoglucosan is decomposed and/or reacts with other compounds by for example thermal cracking and repolymerization reactions [34]. This observation is uniform for presented compounds where yields are reduced with increasing temperature.

By comparing the results to the observations from Py-GC/MS, where no vapor-phase reactions occur due to the low temperature of the pyrolysis chamber, the significance of such reactions in the bench-scale pyrolyzer is clear. Simultaneously, the results indicate that the composition of the derived bio-oil is also dependent on the concentration of inorganic elements in the biomass structure.

3.4. Catalytic upgrading of bio-oil

Catalytic upgrading of the bio-oil in vapor phase derived from the Py-GC/MS and the bench-scale fixed-bed setups were performed by heterogeneous reactions over HZSM-5. Results are presented in Figs. 5 and 6. Py-GC/MS analysis allowed in-bed catalytic pyrolysis whereas bench-scale experiments allowed ex-bed catalytic pyrolysis.

3.4.1. In-bed catalytic upgrading in Py-GC/MS

Results of in-bed catalytic upgrading in Py-GC/MS analysis are presented in Fig. 5 as detected peak area over the mass of biomass-
catalyst mixture placed in the Pyrola2000. In all cases, catalytic upgrading from raw biomass results in higher yields of aromatic hydrocarbons than for pre-treated biomass, especially as the temperature increases. The influence of temperature for raw biomass correlates with previous studies using ash-containing feedstocks [17]. One example is benzene which presents an 87 % reduced yield relative to raw biomass. Reasons for the difference in aromatic yield between the two feedstocks can be explained by studying the results from non-catalytic pyrolysis in Py-GC/MS. Primary pyrolysis of demineralized biomass gives a significant increase in the selectivity towards sugars and anhydrosugars compared to raw biomass. The kinetic diameter of such compounds (e.g. levoglucosan, 6.7 Å) is too wide to fit in the narrow and selective pore structure of HZSM-5 (5.5–5.6 Å), which limits them to react over the catalyst’s external surface area. However, the presence of inorganic elements, AAEMs in particular, promotes the formation of smaller compounds, either during biomass depolymerization or by decomposition of sugars and anhydrosugars when leaving the biomass structure, for example by cracking and dehydration reactions [15]. Thereby, the bio-oil derived from raw biomass in Py-GC/MS consists of a higher yield of compounds that can enter the porous structure and undergo

Fig. 5. Results of catalytic pyrolysis in Py-GC/MS.
heterogeneous reactions such as dehydration, oligomerization, decarbonylation and decarboxylation, e.g. acetic acid [15,32,33]. Overall, the vapor composition from raw biomass presents a higher yield of aromatic hydrocarbons than demineralized biomass in Py-GC/MS, i.e. catalytic upgrading of primary pyrolysis vapors.

3.4.2. Ex-bed catalytic upgrading in bench-scale reactor

Results of ex-bed catalytic upgrading of bio-oil from raw and pretreated biomass performed in the bench-scale setup are presented in Fig. 6. The peak areas of dichloromethane confirm uniform sample preparations. As for the comparison between the bio-oil composition...
from non-catalytic pyrolysis of raw and pre-treated biomass, the results are significantly different compared to Py-GC/MS results. At lower temperatures, raw biomass gives a higher concentration of mainly BTX compounds than that of demineralized biomass. However, when the temperature increases the overall production of aromatic hydrocarbons from vapors of demineralized biomass significantly increases. For ex- pressed catalytic pyrolysis performed at 600 °C, demineralized biomass presents an enhanced selectivity towards one- and two-ringed aromatic hydrocarbons than raw biomass. Most significantly is toluene, presenting a 140 % relative increased concentration compared to raw biomass. By comparing the results to in-bed catalytic pyrolysis the significance of the pyrolysis vapors' exposure to a hot vapor stream and the occurrence of vapor-phase reactions (i.e. secondary reactions) prior to catalytic upgrading, discussed in Section 3.3.2, can be clearly seen. This can also be seen in the results from non-catalytic pyrolysis performed in Py-GC/MS and in the bench-scale setup, presenting the significance of such secondary reactions. This can be explained by the combined effect of biomass devolatilization, the rate of vapor phase reactions and catalytic upgrading at different temperatures. A higher temperature of the pyrolyzer increases the heating rate of biomass as well as the rate of vapor-phase reactions. At 600 °C, the composition of pyrolysis vapors from demineralized biomass after being exposed to the hot vapor-phase results in a higher conversion into aromatic hydrocarbons over HZSM-5 than vapors from raw biomass. In other words, the chemical composition and molecular size range of bio-oil derived from demineralized biomass after being converted by secondary vapor-phase reactions is suitable for catalytic upgrading over HZSM-5. Additionally, the increased catalytic conversion of bio-oil from deminer- alized biomass at 600 °C is indicated by the increased catalyst coking seen in Fig. 2.

Based on these results, the vapor composition of bio-oil can be seen to have a significant impact on its performance in catalytic upgrading over HZSM-5. Also, both the devolatilization pathways’ dependence on the inorganics in biomass as well as the occurrence of secondary vapors have major impact on the performance of catalytic pyrolysis. Especially derivatives originating from secondary reactions of anhydrosugars should play a significant role for the production of aromatic hydrocarbons over zeolitic catalysts.

### 3.5. Total acid number

Table 4 shows the total acid number (TAN) on dry basis of the pyrolysis liquids derived from experiments performed in the bench- scale pyrolyzer. Results from non-catalytic pyrolysis shows that the TAN reduces with increasing pyrolysis temperature. This is explained by the thermal decomposition properties of the lignocellulosic structure and the formation of acids mainly at lower temperatures [28]. Liquids derived from pre-treated biomass present a TAN reduction of 21–32 mg KOH/g sample at investigated temperatures compared to liquid derived from raw biomass. This correlates with the reduced AAEM concentra- tion in pre-treated biomass as well as with the reduced concentration of acetic acid seen in Figs. 3 and 4 [11].

Catalytic upgrading of bio-oil presents a significant effect on the TAN results on dry basis. However, no clear trends based on tempera- ture could be observed when comparing to raw bio-ols. The most sig- nificant reduction of TAN was observed for bio-oil from catalytic pyr- olysis of pre-treated biomass at 600 °C. Overall, the results of the bio-oil analysis present the significance of acid leaching pre-treatment as well as the pyrolysis temperature on the bio-oil characteristics.

### 3.6. Composition of permanent gases

The composition of permanent gases from each studied case is presented in Table 5 on mass yield basis. The total gas yield was cal- culated by difference. At higher temperatures raw biomass presents an increased gas production compared to pre-treated biomass. Demin- eralized biomass shows a suppression of mainly CO production with in- creasing temperature. At 600 °C pre-treated biomass shows a 31 % re- duced CO production corresponding to 4.5 % of the total mass balance. The reduction of CO for demineralized biomass should therefore be associated with catalytic decarbonylation reactions over AAEMs in the biomass [35,36].

In catalytic pyrolysis, an increased total gas yield for both biomass samples was seen when increasing the pyrolysis temperature. A clear effect of liquid deoxygenation as CO and CO2 promoted by an increased temperature was observed, which correlates with the occurrence of decarbonylation and decarboxylation reactions. The highest gas pro- duction occurred for catalytic pyrolysis of pre-treated biomass at 600 °C.

### Table 4

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Non-catalytic pyrolysis</th>
<th>Catalytic pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw</td>
<td>Pre-treated</td>
</tr>
<tr>
<td>400</td>
<td>139.6 ± 1.1</td>
<td>109.2 ± 1.9</td>
</tr>
<tr>
<td>500</td>
<td>182.4 ± 1.7</td>
<td>140.0 ± 2.7</td>
</tr>
<tr>
<td>600</td>
<td>208.4 ± 1.7</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

### Table 5

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Non-catalytic pyrolysis</th>
<th>Catalytic pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H2</td>
<td>CH4</td>
</tr>
<tr>
<td>400</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>500</td>
<td>n.d.</td>
<td>0.7 ± 0.0</td>
</tr>
<tr>
<td>600</td>
<td>0.1 ± 0.0</td>
<td>2.0 ± 0.0</td>
</tr>
<tr>
<td>Pre-treated</td>
<td>n.d.</td>
<td>0.2 ± 0.0</td>
</tr>
<tr>
<td>500</td>
<td>n.d.</td>
<td>0.7 ± 0.0</td>
</tr>
<tr>
<td>600</td>
<td>0.1 ± 0.0</td>
<td>2.2 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>CH4</td>
</tr>
<tr>
<td>400</td>
<td>n.d.</td>
<td>0.1 ± 0.0</td>
</tr>
<tr>
<td>500</td>
<td>2.0 ± 0.0</td>
<td>10.0 ± 0.3</td>
</tr>
<tr>
<td>600</td>
<td>0.1 ± 0.0</td>
<td>2.9 ± 0.0</td>
</tr>
<tr>
<td>Pre-treated</td>
<td>n.d.</td>
<td>0.1 ± 0.0</td>
</tr>
<tr>
<td>500</td>
<td>0.7 ± 0.0</td>
<td>8.5 ± 0.0</td>
</tr>
<tr>
<td>600</td>
<td>0.2 ± 0.0</td>
<td>5.8 ± 0.0</td>
</tr>
</tbody>
</table>
which correlates with the highest production of aromatic hydrocarbons presented in Section 3.4.2.

4. Conclusions

Demineralization of AAEMs from lignocellulosic biomass prior to pyrolysis increased the bio-oil yield, significantly influenced its organic composition and suppressed char production compared to raw biomass. In-bed catalytic upgrading of bio-oil from demineralized biomass over HZSM-5 performed in Py-GC/MS presented limited performance due to the catalyst’s narrow pore-size distribution and the high concentration of levoglucosan with a larger kinetic diameter. However, ex-bed catalytic pyrolysis of demineralized biomass performed in a bench-scale setup resulted in higher yields of aromatic hydrocarbons when performed at higher temperatures. The results show that secondary reactions of pyrolysis vapors from demineralized biomass gives a vapor composition favorable for production of aromatic hydrocarbons over HZSM-5.

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Appendix A. Supplementary data

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References