



Fast pyrolysis of organic acid leached wood, straw, hay and bagasse: Improved oil and sugar yields



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ABSTRACT

Organic acid leaching of pine wood, straw, bagasse and hay effectively reduced the amount of catalytically active alkali and alkaline earth metals (AAEMs). Using the (acetic) acid produced by pyrolysis as leaching agent, the AAEMs content could be reduced to 90–600 mg/kg. Tests with AAEMs impregnated Avicel cellulose (1–1000 mg/kg) showed that even at such low concentrations of AAEMs (100 mg/kg) the sugar yield was significantly suppressed. After leaching, single phase oils (condensed at 20 °C) were obtained even for straw and hay. A large increase in the yields of organic pyrolysis oil (e.g. straw: 37–58 wt%) and pyrolytic sugar (e.g. bagasse: 3–22 wt%) was observed for all acid leached biomasses. The increase in sugar yield can be ascribed to less intense dehydration and ring fragmentation reactions. A comparison of the sugar yields of the leached biomasses with those of AAEMs impregnated cellulose showed clearly that the concentration of AAEMs is not the only factor determining the sugar yield.

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1. Introduction

Fast pyrolysis of lignocellulosic biomass is a thermal depolymerization process aiming at the production of renewable bio-oil. This bio-oil is an intermediate for the production of transportation fuels and contains interesting chemicals like anhydrosugars (e.g. levoglucosan) and aromatics [1]. Anhydrosugars can be used as feedstock in fermentation processes to obtain e.g. bio-ethanol [2,3] and in (catalytic) conversions to for example methyl levulinate [4].

Next to cellulose, hemicellulose, lignin and extractives, lignocellulosic biomass contains inorganic compounds including alkali and alkaline earth metals (AAEMs) [5,6]. According to literature the presence of AAEMs during pyrolysis increases the char and water yield via dehydration reactions [7] and increases the yield of light oxygenates via ring-fragmentation reactions of carbohydrates [8]. These two AAEMs catalyzed reactions explain, at least partly, the low selectivity towards anhydrosugars and the presence of many small oxygenated molecules in the bio-oil. The increased water production is unwanted since too high water contents in bio-oil can easily lead to phase separation into an aqueous and an organic phase [9]. Phase separated bio-oil may cause serious problems during storage, transportation and in applications.

To minimize the catalytic effects of AAEMs during pyrolysis, three different approaches are reported in literature, namely: (i) mineral acid leaching, in which the AAEM salts react with the acid to water soluble compounds and the cations bound to the biomass structure are ion-exchanged by a proton [10]. Many papers on the fast pyrolysis of mineral acid leached biomass are available in literature [8,11–13]. (ii) Reducing the catalytic effects of AAEMs on the sugar production by infusing strong acids into the biomass [14,15], resulting in passivated (also called thermally stable) salts [14] and (iii) acid leaching with organic acids, the principle is identical to mineral acid leaching. In general all these papers report an increase in the anhydrosugar and oil yields. However there is less consensus in the reported yields of water and pyrolytic lignin. Piskorz et al. showed a large decrease in the produced water for poplar wood (12.2 versus 1 wt% after acid leaching) [8] whereas Brown et al. measured an increase of 9.7 versus 11.7 wt% for swithgrass and 2.6 versus 10.6 wt% for cornstover [12]. Mourant et al. report doubling of the pyrolytic lignin yield for mallee wood pyrolysis [13] while Brown et al. showed that the yield was approximately halved for both swithgrass and cornstover after acid leaching [12].

In our previous paper we utilized organic acids produced in the pyrolysis process itself to reduce the AAEMs content [16]. The organic acids were concentrated, by applying fractional condensation of the pyrolysis vapors, and collected as a separated aqueous phase. This aqueous phase was successfully used to leach the AAEMs from pine wood (to 88 mg/kg) which resulted in high bio-oil and levoglucosan yields after pyrolysis [16]. The same con-

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cept is applied in present paper for straw, hay and bagasse. These biomasses were analyzed for their extractives, sugar (xylose, mannose, arabinose and glucose), lignin (aromatics) and AAEMs (K, Na, Ca, Mg) content. Fast pyrolysis of these untreated and acid leached feedstocks was carried out in a 150 g per run fluidized bed reactor operated at 530 °C.

The first aim of this paper is to evaluate the effect of organic acid leaching on the chemical composition of biomass and the AAEMs removal efficiency for the broad selection of feedstocks. The second aim is to produce high yields of single phase bio-oils containing a high amount of hydrolysable sugars by reducing the AAEMs content by the aforementioned procedure. Yields of organic oil, char, gas, water, sugar and water insolubles of untreated and pretreated biomass are compared. These yields are also presented and analyzed as a function of AAEMs content. In our work, the importance of the AAEMs remaining in the biomass after leaching, is studied by comparing the yields of the selected biomasses with the pyrolysis results of Avicel cellulose (1 mg/kg, as received) and AAEMs (100–1000 mg/kg) impregnated Avicel cellulose.

2. Experimental

2.1. Materials

Pine wood (Lignocel 9, Rettenmaier & Söhne GmbH), wheat straw (Purchased from Praxis. Brand: Puik original, two different batches), hay (obtained from a local farm) bagasse (kindly supplied by Shell) and cellulose (Avicel ph 101 particle size ~50 µm) were used in this study. The synthetic leaching solution consisted out of 10 wt% of acetic acid (SAFC, purity 99.5 wt%), 3.75 wt% of acetone (Assink Chemie, purity >99.5 wt%), 3.75 wt% of ethanol (Assink Chemie, purity 99.8 wt%), 1.5 wt% of guaiacol (SAFC, purity >98 wt%), 1.5 wt% of propionic acid (SAFC, purity >99.9 wt%) and 79.5 wt% of demineralized water (Milli-Q). The salt used for impregnating cellulose was potassium carbonate (Sigma-Aldrich, purity 99.7%). In the fast pyrolysis experiments silica sand, sieve fraction 212–300 µm with a particle density of 2600 kg/m³, was used as fluidized bed material.

2.2. Experimental and methods

2.2.1. Acid leaching

The biomass samples were ground in a knife-mill and sieved to obtain a particle size fraction of 0.5–2 mm. Half of the amount of biomass samples was leached with a synthetic acidic aqueous solution, mimicking the second condenser liquid from the pyrolysis process. The use of this synthetic mixture instead of the real condenser stream has been validated in our previous work [16]. Below, the leaching method [16] is described briefly.

The biomass samples were leached in a 1 l glass reactor. The reactor was filled with the leaching solution and preheated to 90 °C. A water-cooled reflux condenser was used to condense the low boiling vapors. When the desired temperature was reached, biomass was added (0.10 g dry biomass per 1 g of leaching solution). The biomass slurry was mixed using a flat blade stirrer (660 rpm) combined with a baffle mounted on the reactor wall. After 2 h the leaching liquid was drained from the reactor through a perforated plate (pore size 0.5 mm), leaving the solid biomass inside the reactor. The biomass remaining in the reactor was rinsed with Milli-Q water, to remove the leaching liquid remaining in the pores, until the pH of the effluent solution was higher than 6.0. Hereafter the biomass was dried for 24 h in a hot air oven at 105 °C.

2.2.2. Cellulose impregnation

Cellulose was impregnated with 100 and 1000 mg/kg of potassium (in the form of K₂CO₃). The amount of K₂CO₃ used for

Table 1
Operational conditions of fast pyrolysis and acid leaching experiments.

Pyrolysis	
Run time	45–60 min
$M_{\text{sand,initial}}$	1.0 kg
$\Phi_{V,N_2}/\Phi_{m,\text{biomass}}$	1.5 Nl/g
T_{reactor}	530 °C
τ_{vapors}	1.8 s
U/U_{mf}	2.5
$T_{\text{outgoinggasfirstcondensor}}$	80 °C
$T_{\text{outgoinggassecondcondensor}}$	–5 °C
Acid Leaching	
Run Time	120 min
V_{vessel}	1 l
$V_{\text{leachingliquid}}/M_{\text{biomass}}$	10
Stirrer speed	660 RPM
$T_{\text{acidleaching}}$	90 °C

impregnation was chosen based on the concentrations of AAEMs remaining in the biomass after acid leaching. Therefore, the pyrolysis outcome of cellulose can be compared with that of biomass after acid leaching. The cellulose samples were impregnated by dissolving the desired amount of K₂CO₃ in Milli-Q water. The dissolved K₂CO₃ solution was mixed with the cellulose (fully wetted). Hereafter the water was evaporated in a rotary evaporator (40 °C, 60 m bar and continuous stirring).

2.2.3. Fast pyrolysis

The biomass samples were pyrolyzed in a fluidized bed reactor at a temperature of 530 °C. This setup is explained in more detail in our previous paper [16]. Short recap: preheated nitrogen was used as fluidization gas and silica sand was used as bed material. The process conditions are summarized in Table 1. Per experiment around 150 g of biomass was fed manually in batches of 2–5 g together with 4–8 g sand, via a gas lock system consisting out of two valves, into the fluidized bed reactor during a period of 30–40 min. After the experiment the bed was maintained at 530 °C for 15 min before cooling down to ensure full conversion of biomass. The char was removed from the gas/vapor stream using two wire-mesh filters (pore size 9 µm and 5 µm). The vapors were condensed in two fractions using an electrostatic precipitator (ESP), operated at 80 °C (outgoing gas temperature), and a double walled glass condenser, operated at –5 °C (outgoing gas). Half of the liquids collected in the 1st and 2nd condenser were mixed to simulate liquid collected in a single condenser (operated at 20 °C). A gas filter (10 µm) was used to collect the remaining liquid (±2 wt% of total oil) in order to complete the mass balance. The char yield was determined by collecting the char/sand mixtures from the reactor and char-filters and subtracting the initial weight of sand present at the start of the experiment and the amount of sand fed during the experiment. In contrast to our previous paper on biomass leaching [17] the char yield was also corrected for the amount of ash present in the pyrolyzed biomass.

$$Y_{\text{char,d.a.f.}} = \frac{\sum_{\text{reactor,filter}} (\text{kg char collected} - \text{kg of ash in biomass})}{\text{kg biomass fed} \times (1 - \text{water fraction biomass} - \text{ash fraction biomass})}$$

The liquid production was measured by weighing both condensers and the gas filter before and after the experiment. The amount of produced gasses was calculated by difference.

For comparison between, pyrolysis of untreated or acid leached biomass, the yield is expressed on initial dry ash free (d.a.f.) biomass (intake of process, $Y_f f = \text{feed}$). When the effect of biomass composition on the lumped product classes and individual compounds is studied the yield is expressed on biomass fed to the pyrolysis reactor ($Y_r r = \text{reactor}$). For the hydrolysable sugars the recovery is defined as the ratio between the amount of individual sugar (e.g. glucose, xylose) in the pyrolysis oil (after hydrolysis) and their cor-

responding concentration initially in the pyrolyzed biomass (after hydrolysis).

2.3. Analytical techniques

The analytical techniques used to analyze the feedstocks and quantify the produced products are shown in Table 2. The extractives, structural carbohydrates and lignin content of the different biomasses were analyzed using the NREL LAP methods “Determination of Ethanol Extractives in Biomass” [18] and “Determination of Structural Carbohydrates and Lignin in Biomass” [19]. The ash content of the biomass was determined by quantifying the residue remaining after 24 h of dry oxidation at 575 °C. The ash composition was determined with X-ray fluorescence (XRF) spectroscopy (Phillips PW 1480 spectrometer). The biomasses and produced oils were analyzed by elemental analysis (Thermo Scientific -FLASH 2000CHN analyzer) for their C, H and N content. The oxygen content was calculated by difference ($O = 100 - C - H - N - \text{Ash}$). Duplicate measurements were performed, if the difference was larger than 1 wt% the measurement was repeated until satisfying results were obtained. The gasses produced during pyrolysis were analyzed using a gas chromatograph (Varian CP 4900) equipped with two columns (i) 10 m molsieve 5A operated at 70 °C, and (ii) 10 m PPQ operated at 80 °C. Helium was used as carrier gas. The first column measured H₂, O₂, N₂, CH₄ and CO and the second column CO₂, C₂H₄, C₂H₆, C₃H₆. The compounds were detected by two thermal conductivity detectors. The water content of the pyrolysis oil was measured by Karl Fischer titration (Metrohm 787 KF Titrino, titrant Hydranal Composite 5 and solvent 3/1 methanol dichloromethane). Duplicate titrations were carried out, if the difference was larger than 0.5 wt% the titration was repeated until satisfying results were obtained. The identification and quantification of levoglucosan and acetic acid was done by GC–MS analysis (GC 7890A MS 5975C Agilent Technologies) equipped with a capillary column (Agilent HP-5MS, HP19091S-433) and helium as carrier gas (inlet pressure programmed for constant 1st column flow of 2 ml/min). Samples were dissolved in acetone (50 mg oil/gr acetone) and filtered before analysis (Whatman 0.2 µm filter). The injection volume was 1 µl, injector temperature 250 °C, split ratio 20:1 (FID:MS), at injection the column was 4 min at 45 °C where after it was heated to 280 °C (by 3 °C/min) at which it was maintained for 20 min. The hydrolysable sugar content of the oil was quantified using NREL LAP method “Determination of sugars, byproducts, and degradation products in liquid fraction process samples” [20]. The oil was first separated using the cold water extraction method [21] (1 g of 1st condenser oil per 100 ml cold water) followed by hydrolysis (3.5 vol% H₂SO₄ for 60 min at 120 °C) of the water soluble fraction. The samples were hereafter neutralized by adding BaCO₃ and filtered (Whatman 0.2 µm filter) before HPLC analysis (Agilent 1200 series, column Hi-Plex-pb operated at 70 °C, eluent milli-q water (0.6 ml/min)).

3. Results and discussion

The reproducibility of the successive experiments (acid leaching followed by pyrolysis) was tested for pine wood ($n = 5$) and straw batch 2 ($n = 3$). The differences in the char yield between the experiments with pine wood or the experiments with straw was smaller than 2 wt%, Similar differences were obtained for gas, water and organic oil, for both biomasses. Therefore it could be concluded that the reproducibility was good.

3.1. The effects of acid leaching on the biomass composition

Pine wood, hay, bagasse and two different wheat straw batches were selected as pyrolysis feedstocks relevant to practice. Table 3

shows the composition of these feedstocks before and after acid leaching and subsequent water rinsing. Acid leaching reduced the AAEMs content of the tested biomasses by 97%. Only for bagasse the removal efficiency was 91%. Notice, bagasse was already washed with water during the sugar extraction process. The ash remaining in the biomass after acid leaching consisted for more than 85 wt% of silica. During the acid leaching step the AAEM salts dissolve in the water or react with the acid to form readily soluble salts. The fraction of AAEMs which are ionically bound to the biomass structure (i.e. to proteins [22] and carboxylic groups [23,24]) are exchanged by protons [24]. Additional acid leaching and rinsing with excessive amounts of water did not further reduce the AAEM content. Comparable studies on acid leaching of biomass confirm this finding [25,26]. An explanation for the incomplete removal of the AAEMs content might be that the AAEMs are partially located in inaccessible region for the rinsing liquid, like inside proteins. The oxygen and nitrogen content of the biomasses before and after acid leaching did not change much.

Next, the polysaccharide (hemicellulose and cellulose) and lignin content of the initial biomasses after water and ethanol extraction (between brackets) were compared to the acid leached biomasses. These data show that under our leaching conditions (pH 2.1 and 90 °C) hardly any loss of hydrolysable sugars or lignin to the leaching liquid did occur due to the acidity of the acid leaching solution. Moreover, the mass loss of the biomass caused by the acid leaching was nearly identical to the sum of the AAEMs and water- and ethanol extractives in the biomass. The nitrogen content was hardly affected (in case of straw batch 1 and hay a slight increase due to removal of extractives) by acid leaching. Jiang et al. presented also a relative low (10–20 wt%) decrease in the nitrogen content after water- and acid leaching (5 wt% CH₃COOH, HCl, HNO₃ or H₂SO₄) from rice straw [25]. Moreover experiments by Kootstra et al. showed that only 5 wt% of the proteins were extracted from *Jatropha* press cake by water- or acid leaching at 100 °C, increasing the leaching temperature resulted in higher protein removal (25 wt% at 140 °C) [27].

From the results it is evident that the chemical composition of the biomass in terms of the hemicellulose, cellulose and lignin content is not affected by our organic acid leaching method. Contrary, mineral acid leaching, at pH below 1, changes the physical structure and chemical composition (removal of hemicellulose) of biomass significantly already at 25 °C [25].

Table 3 shows that both the water soluble and ethanol soluble extractives vanished after acid leaching. In light of producing sugars from biomass it was analyzed if sugars are lost as extractives. Therefore the water solution after extraction was hydrolyzed and analyzed by HPLC. The water soluble extractives from bagasse and straw (batch 2) showed the presence of roughly 15 wt% hydrolysable sugars (<2 wt% of original biomass), for pine, hay and straw (batch 1) this amount was less.

3.2. Pyrolysis experiments

3.2.1. Yields of char, gas and oil

Fig. 1 shows the pyrolysis yields of biomasses with and without acid leaching. The product yields are expressed on initial biomass input (Yf). The initial biomass input is defined as the dry ash free biomass before leaching and thus the product distribution includes the (losses of) extractives in the leaching step. Fig. 2 shows the pyrolysis yields expressed on basis of the dry ash free biomass fed into the pyrolysis reactor during an experiment. The organic oil yield increases after acid leaching for all feedstocks (Figs. 1 and 2) despite of organic losses in the leaching step (Fig. 2). A decrease in the water, char and gas yield can be observed. Nevertheless, the gas yield is still quite high because of the high pyrolysis temperature (530 °C) chosen for the experiments. Our tests confirm [28–30] that

Table 2
Overview of analytical techniques applied.

Compounds/quality properties	Technique	Reference
Biomass feed		
Extractives	Soxhlet extraction with H ₂ O and EtOH	[18]
Lignin and sugar content	Acid hydrolysis + HPLC	[19]
Ash content	Dry oxidation @ 575 °C	[40]
Ash composition	XRF	
C/H/N content	Element analyser	
Bio oil		
C/H/N content	Element analyser	
Water	Karl Fischer	
Levoglucosan and acetic acid.	GC/MS	
Hydrolysable sugars	Acid hydrolysis + HPLC	[20]
Water insolubles	Cold water precipitation	[21]
Gas		
Gas composition	Micro-GC	

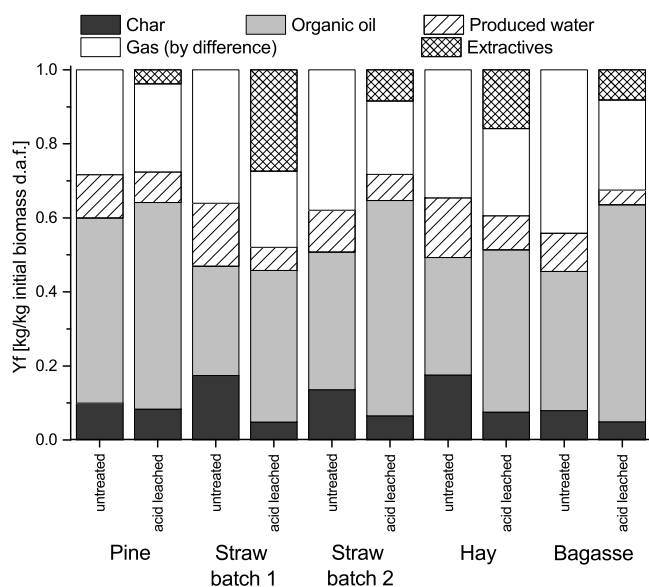


Fig. 1. Pyrolysis yields obtained from the different feedstocks with and without acid leaching. $T_{\text{reactor}} = 530\text{ °C}$. Data for pine from reference [16]. The yields are expressed on basis of initial biomass (before leaching).

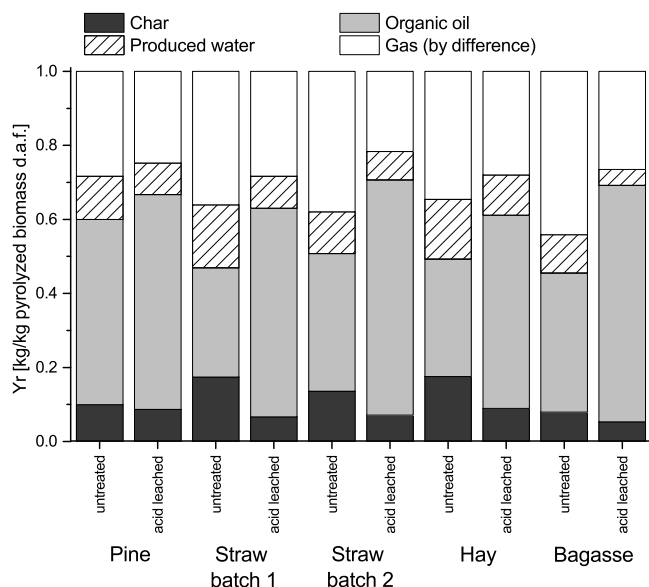


Fig. 2. Pyrolysis yields obtained from the different feedstocks with and without acid leaching. $T_{\text{reactor}} = 530\text{ °C}$. The yields are expressed on basis of biomass fed to the pyrolysis reactor.

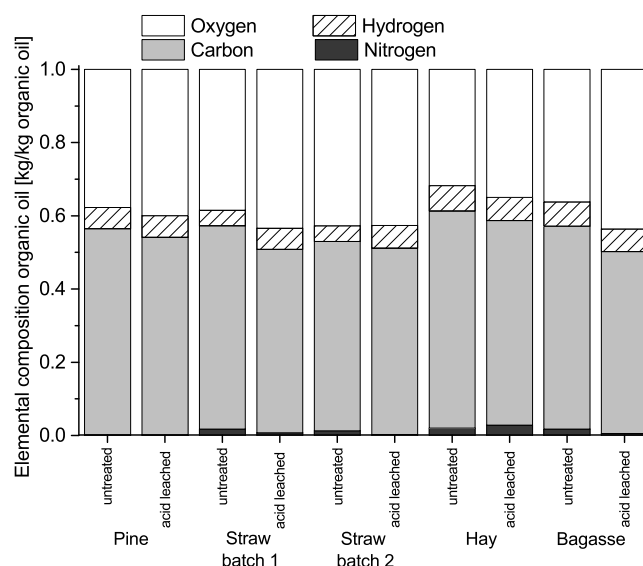


Fig. 3. Elemental composition of the organic oil obtained from the different feedstocks with and without acid leaching. $T_{\text{reactor}} = 530\text{ °C}$.

pyrolysis of untreated straw, hay and bagasse results in lesser oil with a higher water content as compared to woody biomass. However, this was not the case after acid leaching of these biomasses. The pyrolysis yields (on reactor intake basis, see Fig. 2) of the acid leached biomasses became more comparable. This is an advantage for pyrolysis plants processing various biomass feedstocks, also from an operational point of view (e.g. no large fluctuations in the amount of char to the combustor and load of the condenser system).

Fig. 3 shows the elemental composition of the organic oils from the different biomasses with and without acid leaching. After acid leaching a decrease in the carbon content and an increase in the oxygen content was obtained. This can be explained by the less intense dehydration reactions after acid leaching. Fig. 4 shows the carbon recovery, which is defined as the amount of carbon in the oil divided by the carbon initial in the feed (before leaching), for the different biomasses. This graph clearly shows that the carbon recovery increased after acid leaching, especially for biomasses with a high AAEM content and low amount of water and ethanol extractives.

Fig. 5 shows the organic oil yield (on reactor intake basis) as function of the AAEMs content of the different biomasses. The data points of the initial and accompanying acid leached biomass are connected by a dashed line. The observed increase in organic oil yield as a result of lower AAEMs content is in line with the finding of other researchers for untreated biomasses [28,31]. However, it appeared that a comparable AAEMs content doesn't result in the

Table 3
Biomass composition before and after acid leaching.

	Pine		Straw (batch 1)		Straw (batch 2)		Hay		Bagasse	
	Initial	Acid leached	Initial	Acid leached	Initial	Acid leached	Initial	Acid leached	Initial	Acid leached
Compositional analysis (kg/kg daf)										
H ₂ O Extractive	0.03	–	0.26	–	0.06	–	0.13	–	0.06	–
EtOH Extractive	0.01	–	0.02	–	0.02	–	0.02	–	0.02	–
Total extractives	0.04	0	0.27	0	0.08	0	0.16	0	0.08	0
Glucose	0.51 (0.53 ^a)	0.53	0.35 (0.49 ^a)	0.50	0.47 (0.51 ^a)	0.48	0.41 (0.48 ^a)	0.46	0.44 (0.48 ^a)	0.50
Xylose	0.05 (0.05 ^a)	0.04	0.16 (0.21 ^a)	0.23	0.24 (0.27 ^a)	0.25	0.18 (0.20 ^a)	0.19	0.20 (0.22 ^a)	0.24
Galactose	0.02 (0.02 ^a)	0.02	0.00 (0.01 ^a)	0.01	0.00 (0.01 ^a)	0.01	0.01 (0.01 ^a)	0.01	0.00 (0.00 ^a)	0.00
Arabinose	0.01 (0.01 ^a)	0.01	0.03 (0.04 ^a)	0.04	0.03 (0.04 ^a)	0.04	0.03 (0.04 ^a)	0.04	0.02 (0.03 ^a)	0.02
Mannose	0.12 (0.13 ^a)	0.13	0.00 (0.01 ^a)	0.00	0.01 (0.01 ^a)	0.01	0.00 (0.00 ^a)	0.00	0.00 (0.00 ^a)	0.01
Total (poly) saccharides	0.70 (0.73^a)	0.73	0.54 (0.74^a)	0.78	0.78 (0.83^a)	0.79	0.64 (0.71^a)	0.68	0.66 (0.73^a)	0.77
Acid soluble lignin	0.04 (0.04 ^a)	0.05	0.05 (0.07 ^a)	0.06	0.05 (0.05 ^a)	0.05	0.05 (0.06 ^a)	0.07	0.05 (0.05 ^a)	0.05
Acid insoluble lignin	0.24 (0.25 ^a)	0.24	0.10 (0.14 ^a)	0.18	0.12 (0.13 ^a)	0.15	0.11 (0.14 ^a)	0.13	0.18 (0.20 ^a)	0.18
Total lignin	0.28 (0.29^a)	0.29	0.15 (0.21^a)	0.25	0.17 (0.18^a)	0.20	0.17 (0.20^a)	0.20	0.23 (0.25^a)	0.23
Total Ash^c	0.01	0.00	0.06	0.02	0.08	0.05	0.06	0.01	0.01	0.01
Ultimate analysis (wt%, daf)										
C	50.1	49.7	48.0	48.5	48.5	47.9	47.6	48.2	49.3	48.9
H	6.1	6.2	6.2	6.2	6.2	6.0	6.2	6.2	6.1	6.1
N	0.1	0.0	0.5	0.8	0.4	0.2	1.1	1.4	0.2	0.1
O ^b	43.7	44.1	45.3	44.5	44.9	45.8	45.1	44.2	44.4	44.9
Ash composition (mg cation/kg dry biomass)										
Na ⁺	60	2	2365	62	117	22	737	26	24	18
K ⁺	398	9	11786	285	12595	55	28826	104	1792	123
Mg ²⁺	387	9	1093	30	427	15	1361	63	402	21
Ca ²⁺	1771	68	3037	218	2068	164	1795	207	700	56
Sum (AAEMs)	2626	88	18281	595	15208	256	32719	395	2558	218

^a On dry ash and extractive free basis.

^b By difference.

^c Including all non-organic material (metals, Si, etc).

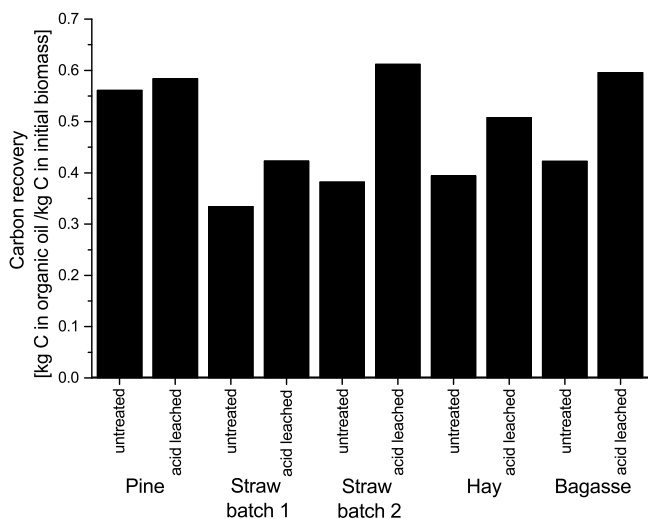


Fig. 4. Fraction of carbon recovered in the oils from the different feedstocks with and without acid leaching. $T_{\text{reactor}} = 530^\circ\text{C}$. The recovery is expressed on basis of initial biomass (before leaching).

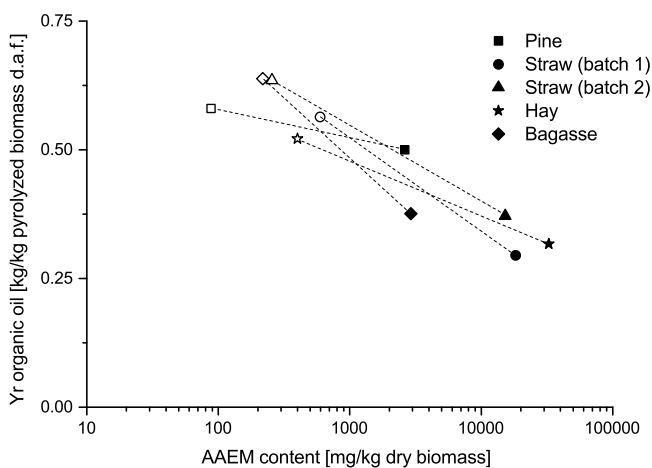


Fig. 5. Organic oil yield as function of the AAEM content of the feed. The organic oil yield is expressed on basis of biomass fed to the pyrolysis reactor. Open symbols: acid leached before pyrolysis. AAEM content is expressed as mg of cation.

same yield of organic oil. For instance, the increase in the organic oil yield for bagasse is much higher as compared to pine wood while starting from the same AAEMs content and with even more remaining AAEMs after acid leaching. Therefore, the organic oil yield is strongly but not solely determined by the overall AAEMs content of the feedstock. By plotting the organic oil yield versus the moles of monovalent AAEMs (K+Na) or the divalent AAEMs (Mg+Ca) in the biomass (shown in Table 3) still no clear trend was obtained for both the untreated and acid leached biomasses (figures not shown here). The type of AAEMs, the feedstock composition, other feedstock characteristics, and/or physical/chemical processes during pyrolysis can have an impact as well. Fig. 6 shows an overall trend of increasing char, produced water and gas yield with increasing AAEM content for the 5 different feedstocks. These figures also show that a comparable AAEM content doesn't necessarily result in the comparable yields. The observations support that also other parameters influence the pyrolysis outcome than solely the AAEMs content. Reported data sets relating the oil yield to the total ash content (thus not solely on AAEMs basis) show indeed quite some scatter [28]. It should be noticed that the ash content of our biomasses after acid leaching still largely varies (pine 0.02 wt% while straw batch 2 had 4.5 wt% of ash). The remaining ash, mainly

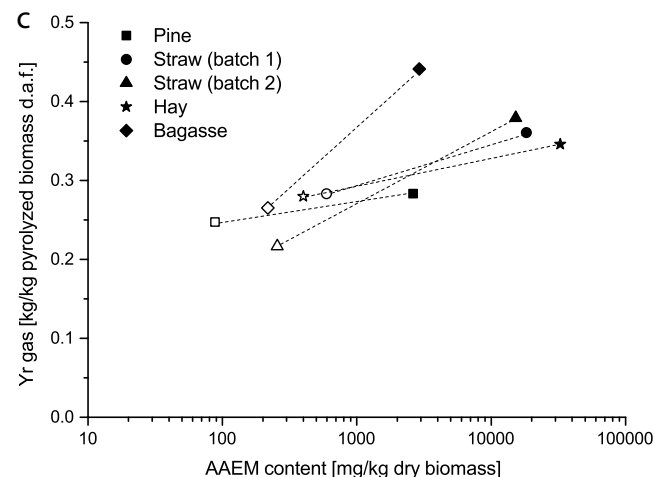
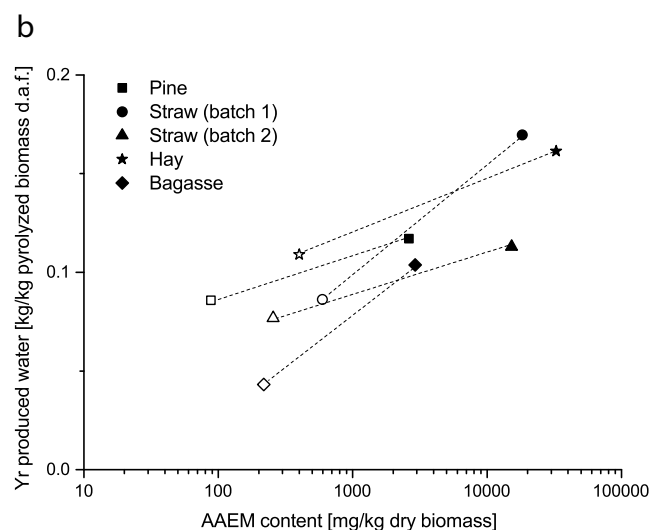
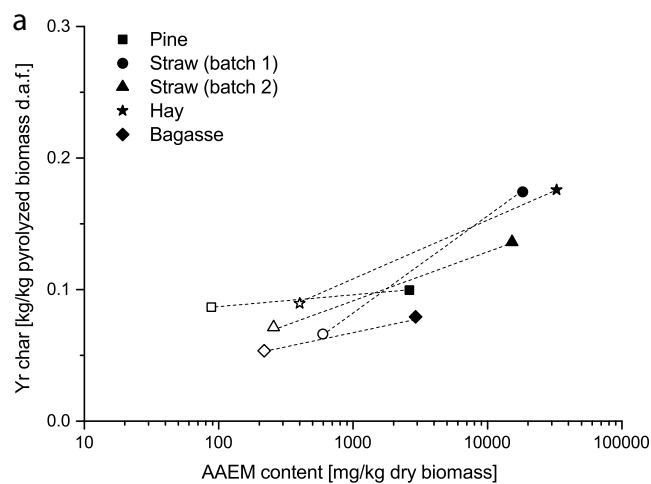


Fig. 6. Effect of AAEM content in pyrolysis feed on the (a) char yield (b) produced water yield (c) gas yield. The yields are expressed on basis of biomass fed to the pyrolysis reactor. Open symbols: acid leached before pyrolysis. AAEM content is expressed as mg of cation.

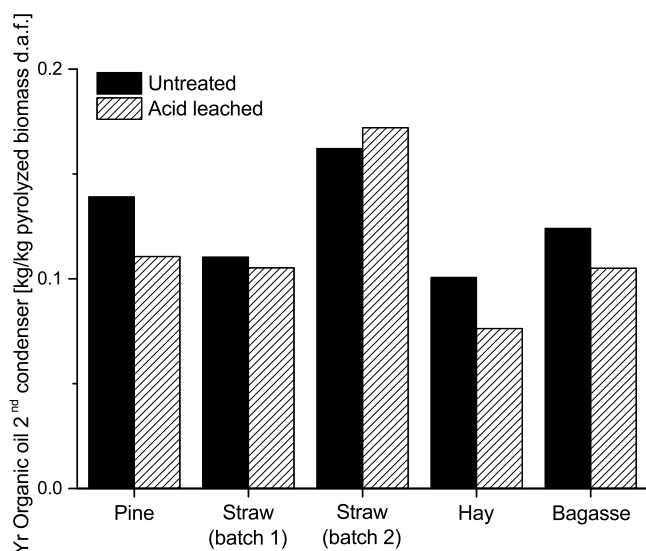


Fig. 7. Amount of organic oil recovered in the 2nd condenser for the different untreated and acid washed biomasses. The gas outlet temperature was 80 °C for the first condenser and –5 °C for the second condenser.

silica (not shown), doesn't seem to have a large influence on the pyrolysis results of acid leached biomass, since the organic and sugar production is quite constant (i.a. Figs. 2 and 10).

3.2.2. Light oxygenates

In our concept fractional condensation of the pyrolysis vapors is applied [32]. The first condenser was operated at thermodynamic vapor–liquid equilibrium [32] and had a vapor/gas outflow temperature of 80 °C. This condenser collects the heavy compounds like anhydrosugars and aromatics. It was previously shown that almost no light oxygenates (e.g. acetic acid, acetol, etc.) were collected in the first condenser [32]. The second condenser was operated at –5 °C and collected all the light oxygenates and water. Fig. 7 shows the amount of organic compounds (light oxygenates) collected in the 2nd condenser. As can be seen, pyrolysis of acid leached biomass produces slightly less light oxygenates compared to untreated biomass except for straw (batch 2). The overall trend is in line with mechanistic studies claiming that the presence of AAEMs enhance the formation of light compounds via ring scissoring [8,33]. However, the decrease in light oxygenates was relatively small considering the large differences in AAEM content between untreated and acid leached biomass (see Table 3).

Fig. 8 shows the acetic acid yield and concentration in the 2nd condenser liquid. A decrease in the acetic acid yield was obtained after acid leaching for all biomasses. However the acetic acid concentration in the second condenser liquid increased for all biomasses to 8–10 wt%, due to the large reduction in produced water after acid leaching. It should be noted that the acid concentration during acid leaching in practice will be lower than the 10 wt% applied in this work due to the amount of second condenser liquid produced per kilogram feed (0.15–0.20 kg/kg pyrolyzed biomass d.a.f.) and the amount of liquid required to fully wet a biomass particle (2–3 times the dry biomass mass). However leaching tests with lower acid concentrations still showed successful AAEM removal (data will be presented in a upcoming paper). Calculations show that the pyrolysis of AAEMs lean biomasses still produce enough acetic acids to remove the AAEMs from the tested biomasses (in case of straw batch 1 and hay a first water wash step is required to dissolve a fraction of the potassium). In these calculations it was assumed that dissolving one mole of K or Na consumes 1 mole of acetic acid and that 1 mole of Ca or Mg consumes 2 moles of acetic acid. It should be noticed that only acetic acid was used in these cal-

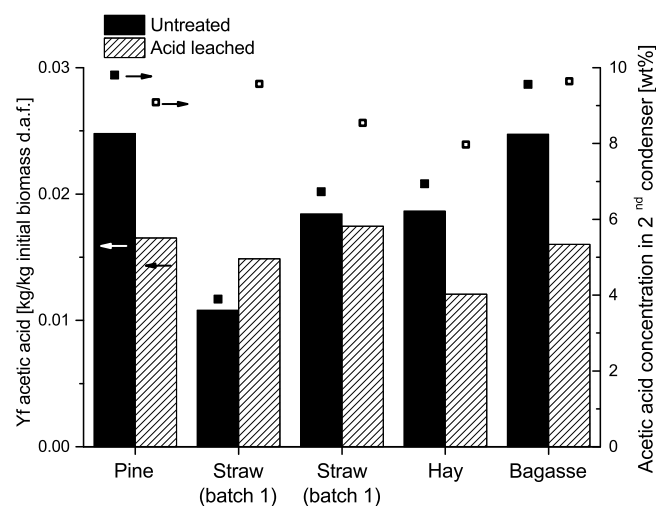


Fig. 8. Acetic acid yield and concentration in the 2nd condenser for the different untreated and acid washed biomasses. The gas outlet temperature was 80 °C for the first condenser and –5 °C for the second condenser.

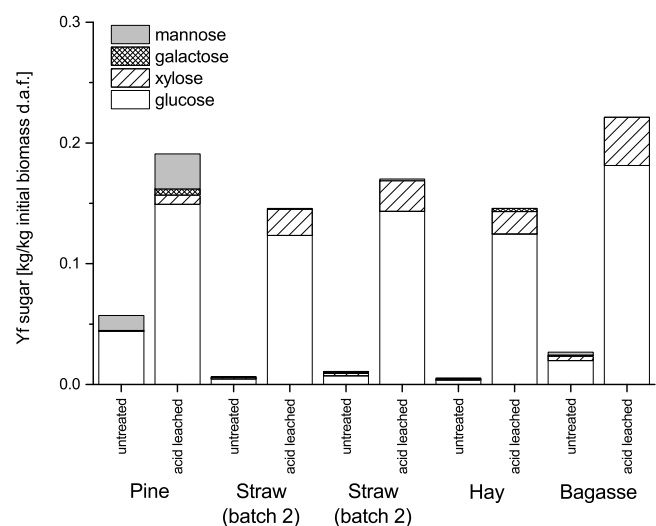


Fig. 9. Effect of acid leaching on the sugar yield (after hydrolysis of the oil). The sugar yield is expressed on basis of initial biomass (before leaching).

culations while also other acids are present in the second condenser liquid like formic and propionic acid.

3.2.3. Sugars

Fig. 9 shows the sugar yield, determined after hydrolysis of the oils, obtained from the untreated and acid leached biomasses. This figure shows that the sugar yields increased for all 5 feedstocks after acid leaching. Besides for glucose, also an increase in the galactose, mannose and xylose yield after acid leaching was found. The latter three sugars originate from hemicellulose. Notice, the mannose content in pine wood is quite high and the xylose content low whereas for agricultural waste streams the opposite can be observed. The sugars were mainly recovered in the 1st condenser (>95 wt% of the sugars). Besides sugars, the 1st condenser contains mainly aromatic oligomers, mono-aromatics and furans. The first condenser oil has a low water content (2–5 wt%) which could be beneficial for further processing, e.g. the recovery of the sugars from this mixture.

Fig. 10 shows the recovery of glucose in pyrolysis oil versus the AAEMs content of the biomass and cellulose. Glucose was measured after hydrolysis of the pyrolysis oils. Fig. 11 shows the hemicellu-

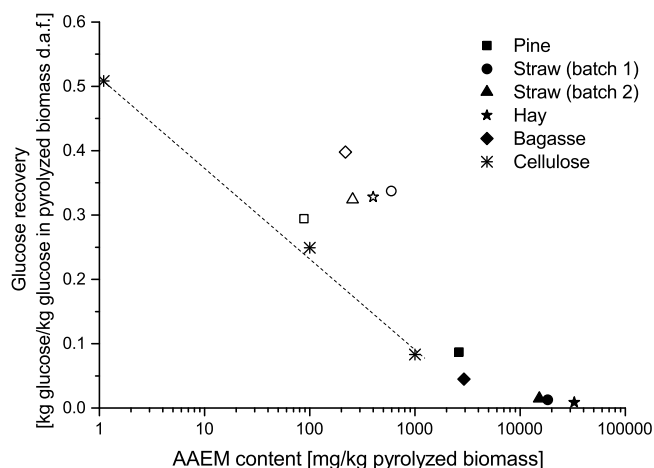


Fig. 10. Recovery of glucose in the oil versus the AAEM content of the feed. The sugar recovery is defined as the amount of glucose in the oil divided by glucose in the feed. AAEM content is expressed as mg of cation.

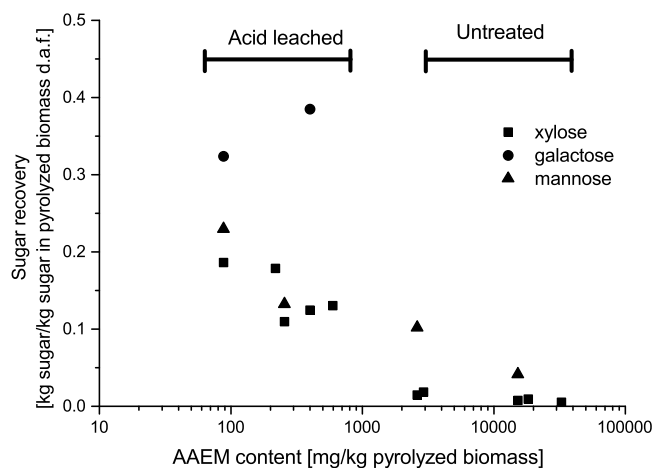


Fig. 11. Recovery of xylose, galactose and mannose in the oil versus the AAEM content of the feed. The recovery is defined as the amount of the sugar in the oil divided by the corresponding sugar in the feed. AAEM content is expressed as mg of cation.

lose derived sugars obtained after hydrolysis of the pyrolysis oils. Because further reduction of the AAEMs content of the biomasses was not possible, the glucose recovery of the tested biomasses was compared with the pyrolysis (identical setup and conditions) of Avicel cellulose with 1 mg/kg AAEMs (as received) and Avicel cellulose impregnated with 100–1000 mg cation/kg of AAEMs salts (K_2CO_3). As discussed earlier the recovery of sugars increased after acid leaching (see Fig. 10). When cellulose was used the glucose recovery steadily increased with decreasing AAEMs content (see Fig. 10). For the leached biomasses there did not seem to be a clear relation between the AAEMs content (90–600 mg/kg) and the sugar yield. It is noteworthy that the glucose recovery of the leached biomasses was higher than that of cellulose at equal AAEMs content. Based on these results we conclude that the sugar recovery, like the organic oil yield, is strongly but not solely determined by the overall AAEMs content of the feedstock. Also here, chemical reactions such as lignin/cellulose/hemicellulose interactions [34,35] and the characteristics of the biomass (e.g. composition or structure) may play a role as well. When the glucose recovery was plotted versus the moles of monovalent AAEMs (K+Na) or the divalent AAEMs (Mg+Ca) in the biomass (shown in Table 3) still no clear trend was obtained for the acid leached biomasses (figures not shown here). This means that the glucose recovery is not determined by the remaining of a specific AAEM. Additionally,

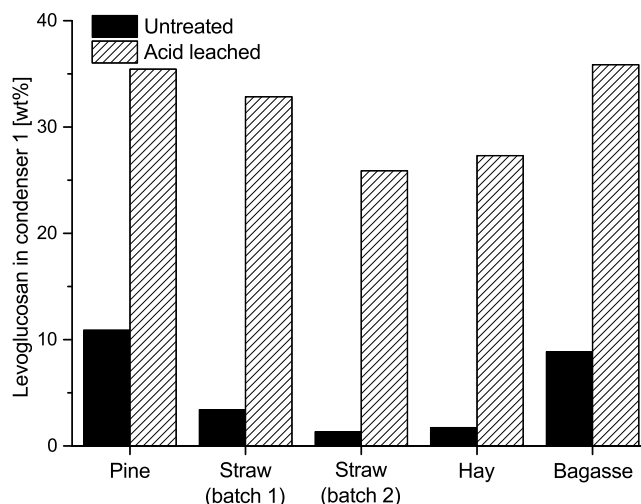


Fig. 12. Effect of acid leaching on the levoglucosan concentration recovered in the first condenser. The first condenser temperature was 80 °C.

the location of the AAEMs in the biomass could play an important role. In the cellulose experiments all the AAEMs were present in the cellulose whereas in the leached biomasses most of the AAEMs could be present in the hemicelluloses and proteins, like in natural materials [22–24]. The same observations and explanations hold for xylose, galactose and mannose, see Fig. 11.

Fig. 12 shows the levoglucosan concentration in the first condenser oil. The first condenser was operated at 80 °C. At this temperature light oxygenates and water remain in the vapor phase and are collected in a second condenser at 20 °C. This figure shows that levoglucosan concentrations between 26 and 38 wt% were obtained from acid leached biomasses while the concentration was between 3 and 10 wt% without acid leaching. The high concentration of levoglucosan offers opportunities for chemicals production via biotechnological routes [2,3] or acid catalyzed conversions [4,36]. Plotting the moles of monovalent AAEMs (K+Na) or the divalent AAEMs (Mg+Ca) in the biomass (shown in Table 3) gave no clear trend for both the untreated and acid leached biomasses (figures not shown here).

3.2.4. Water insolubles

Both the aromatics and sugars in the bio-oil are important products in the concept of chemicals production via pyrolysis. Analysis of the aromatic compounds in the pyrolysis oil was done by cold water precipitation (heavy fraction lumped as “water insolubles”).

Fig. 13 shows the water insoluble yield for the different untreated and acid leached biomasses. Analysis of water insolubles from different feedstocks showed that these compounds mainly consist of aromatic structures derived from lignin [37,38]. A decrease in the water insoluble yield was obtained after acid leaching whereas much more organic oil was produced (see Fig. 2). It seems that the extent of the decrease depends on the feedstock: for pine the decrease was marginal while for hay and bagasse the decrease was more than a factor of 2. It turned out not to be possible to relate the decrease in water insoluble to the feedstock composition, including the AAEMs content nor the type of AAEMs.

To study if the phase stability of pyrolysis oil was improved after acid leaching, the first and second condenser oils were mixed to simulate an oil condensed as a single batch at 20 °C. It was found that all oils produced from acid leached biomasses were single phase liquids. This was not the case for the straws and hay without acid leaching. Too high concentration of water insoluble compounds and water are the cause of physical instability (phase

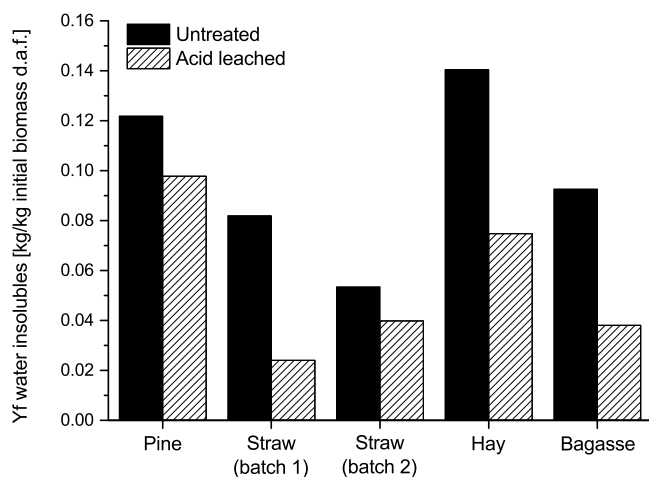


Fig. 13. Effect of acid leaching on the water insoluble yield. The water insoluble yield is expressed on basis of initial biomass (before leaching).

separation) of the bio-oils [39]. Thus the improved stability can be explained by lower water (Fig. 2) and water insoluble production for acid leached biomass and the resulting lower concentration of these compounds in the bio-oils.

4. Conclusions

The acidity of the organic leaching liquid (pH 2.1), resembling the liquid produced in the pyrolysis process, and the leaching temperature (90 °C) did not affect the carbohydrate and lignin content of the biomass feedstocks tested. However, acid leaching did lead to a loss in organic matter (e.g. 27 wt% for straw batch 1) that turned out to be water and ethanol extractives. Organic acid leaching removed most of the AAEMs naturally present in biomass, though the AAEMs content could not be reduced below 90 mg/kg. After acid leaching, the organic oil yield was largely increased for all biomasses. The carbon to oil conversion increased after acid leaching, especially for high AAEMs content biomasses. Moreover, the char, gas and oil yields, based on biomass fed to the reactor, became more comparable for the different biomasses after acid leaching. This may improve the operability of pyrolysis plants running on various types of biomasses. Only after acid leaching, pyrolysis of straw and hay resulted in production of single phase bio-oils (condensed at 20 °C) which makes them easier to handle. As a result of acid leaching the dehydration and ring fragmentation reactions of sugars are significantly suppressed. Consequently, 30–40 wt% of the initial glucose and galactose in the biomass was recovered as hydrolysable sugar in the oil and 10–22 wt% of the xylose and mannose. Unfortunately, even very small amounts of AAEMs (~100 mg/kg) suppressed the production of sugars significantly. It turned out that the catalytic activity of AAEMs is a dominant factor with respect to sugar production. However, results of the leached biomasses and AAEMs impregnated avicel cellulose showed, that next to AAEMs, there are other factors (e.g. reactions, biomass structure/composition) of influence with respect to the sugar yield. Bagasse gave the highest total sugar yield (22.1 wt% of the feed) after hydrolysis. The acetic acid yield reduced after acid leaching, however calculations showed that still sufficient acid is produced to demineralize the tested biomasses. By applying staged condensation, levoglucosan, the most abundant sugar in our pyrolysis oils, could be concentrated up to 38wt%.

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