



# 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/m<sup>3</sup>, 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 K<sub>2</sub>CO<sub>3</sub>). The amount of K<sub>2</sub>CO<sub>3</sub> 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
$T_{\text{reactor}}$	530 °C
$\tau_{\text{vapors}}$	1.8 s
$U/U_{\text{mf}}$	2.5
$T_{\text{outgoinggasfirstcondensor}}$	80 °C
$T_{\text{outgoinggassecondcondensor}}$	–5 °C
Acid Leaching	
Run Time	120 min
$V_{\text{vessel}}$	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 K<sub>2</sub>CO<sub>3</sub> in Milli-Q water. The dissolved K<sub>2</sub>CO<sub>3</sub> 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-

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