



Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: <http://www.elsevier.com/locate/biombioe>

## Research paper

## Effect of temperature on the fast pyrolysis of organic-acid leached pinewood; the potential of low temperature pyrolysis

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## ARTICLE INFO

## Article history:

Received 15 August 2015

Received in revised form

10 December 2015

Accepted 17 December 2015

Available online xxx

## Keywords:

Fast pyrolysis

Acid leaching

Agglomerates

Sugars

Lignin

Alkali and alkaline earth metals

## ABSTRACT

In this paper, we have evaluated the potential of organic acid (mixture of acetic, formic and propionic acid) leaching of biomass and subsequent fast pyrolysis to increase the organic oil, sugars and phenols yield by varying the fluidized bed temperature between 360 °C and 580 °C (360 °C, 430 °C, 480 °C, 530 °C, and 580 °C). The pyrolysis of acid leached pinewood resulted in more organic oil and less water and residue compared to untreated pinewood over the whole temperature range. Below 500 °C the difference was most profound; for acid leached pinewood at 360 °C the organic oil was already 650 g kg<sup>-1</sup> pine with a sugar yield of 230 g kg<sup>-1</sup> pine. At this low pyrolysis temperature no bed agglomeration was observed for acid leached pine whereas at the higher temperatures tested agglomerates were found, which were identified to be clusters of fluidization sand glued together by sticky pyrolysis products (melt). Low reactor temperatures also favored the production of monomeric phenols, though their absolute yields remained low for both untreated and leached pine (maximum: 23 g kg<sup>-1</sup> pine, 80 g kg<sup>-1</sup> lignin). GPC, GC/MS and UV-fluorescence spectroscopy showed that acid leaching did not influence significantly the yield and molecular size of the aromatic fraction in the produced pyrolysis oils. Back impregnation of the removed AAEMs into leached biomass revealed that the effects of the applied acid leaching, both with respect to the product yields and bed agglomeration, can be mainly assigned to the removal of AAEMs.

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## 1. Introduction

Fast pyrolysis is a promising rapid process (seconds) to decompose solid biomass into an oil that can be used directly for power production or further refined to liquid fuels [1,2] and/or chemicals [3]. The oil composition depends largely on the biomass feedstock, process conditions and the oil recovery method. Since different oil applications require different specifications, control over the oil composition would be desirable.

Lignocellulosic biomass contains next to cellulose, hemicellulose, lignin and extractives, also inorganic compounds, including alkali and alkaline earth metals (AAEMs) [4,5]. These AAEMs catalyze (ring) cracking [6] and dehydration reactions [7] of the initial formed anhydrosugars (e.g. levoglucosan) from hemicellulose and cellulose. Minimizing these catalytic effects of the AAEMs during pyrolysis can be achieved by removing them via organic acid (e.g.

acetic acid) [8,9] or mineral acid leaching [6,10–12] or passivating via mineral acid infusion [13–16]. The anhydrosugars are then produced at higher yields making them an interesting feedstock for biological [17–19] and/or chemical conversion (see the review of Radlein [20]).

Recently, we have proposed a process concept in which the AAEM removal from the biomass is done via leaching with pyrolytic acids, produced and concentrated within the same process [8]. The products of interest are (fermentable) sugars, phenols and light oxygenates. In the first paper the proof of principle of the proposed concept was presented. In a follow-up paper we applied the concept (fixed reactor temperature of 530 °C) to 5 different biomasses, including high AAEM content agricultural waste streams [21]. A large increase in the organic oil yield as well as sugar recovery (30%–40% weight fraction of the initial glucose) was obtained for all biomasses. However it has been found that it is impossible to remove all AAEMs from biomass via organic acid leaching, and that these remaining AAEMs (88 mg kg<sup>-1</sup> for pinewood) still suppress the hydrolysable sugar recovery considerably.

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The pyrolysis temperature is undoubtedly an important parameter to steer the pyrolysis yield and product composition from untreated feedstocks [22–24]. So far all studies on pyrolysis of acid leached biomass have been carried out at temperatures between 450 °C and 530 °C (single temperature in each paper). Pernikis et al. did study a temperature range (340 °C–460 °C), however a hydrolyzed feedstock was used [25]. It is generally found that hemicellulose and cellulose are already fully converted at 300 °C [26] and 360 °C [27] respectively. Therefore such high pyrolysis temperatures (>450 °C) might not be necessary to obtain high organic oil and sugar yields from acid leached feeds.

Lignin pyrolysis yields a large variety of light organics and monomeric and oligomeric phenols [28]. Especially the oligomeric phenols are difficult to identify and quantify. This fraction is therefore often reported as the lumped group “water insolubles”, which is determined by the cold water precipitation method [29]. However, Garcia Perez et al. [23] showed that a significant fraction of the phenolic oligomers are overlooked when only the water insolubles are determined. The question whether AAEMs affect the lignin derived products has been studied in much lesser detail than the cellulose fraction and led to, sometimes, conflicting reports in the literature. Patwardhan et al. [30] claimed a negligible effect of impregnating AAEMs into lignin (no data were presented). Kleen and Gellersted [31] showed that sodium catalyzed the demethylation and dehydration of the monomeric phenols while the total peak area of detected monomeric phenols per gram of feed remained constant. Dalluge et al. obtained after acid infusion a reduction of 55% and 49% in the monomeric phenols yield (0.028 kg kg<sup>-1</sup> to 0.013 kg kg<sup>-1</sup> and 0.024 kg kg<sup>-1</sup> to 0.012 kg kg<sup>-1</sup>) and 49% and 14% in the water insoluble yield (0.10 kg kg<sup>-1</sup> to 0.05 kg kg<sup>-1</sup> and 0.09 kg kg<sup>-1</sup> to 0.08 kg kg<sup>-1</sup>) for red oak and switch grass respectively [14]. Mourant et al. report a doubling of the pyrolytic lignin yield for mallee wood pyrolysis [11] while Brown et al. showed that the yield was approximately halved for both switchgrass and corn stover after acid leaching [12].

Many pyrolysis reactor concepts have been proposed (see Bridgwater [32]), though most operational and planned large scale processes are based on the fluid bed concept [32]. Radlein [20] and Dalluge et al. [14] reported that pyrolysis of mineral acid leached and acid infused biomass in fluidized bed setups both resulted in the formation of bed agglomerates, leading to operational problems (blocking and defluidization). Radlein ascribed these agglomerates from acid leached biomass to the formation of a “sticky” melt, a mixture of high molecular weight polymer that decomposes very slowly, which coats the bed particles leading to agglomeration [20].

The main goal of this paper is to investigate the effect of the fluidized bed temperature on the pyrolysis yields and oil composition using organic acid leached pinewood as feedstock. First, to get a better understanding of the acid leaching on the pyrolysis results it is investigated if the observed effects are mainly caused by the AAEM removal or that modification of the biomass induced by the acid leaching also play a role. Hereafter yields of organic oil, residue, gas, water, sugars, monomeric phenols and water insolubles from untreated and acid leached pinewood pyrolyzed at various fluidized bed temperatures are compared. GPC and UV-fluorescence are used to shed light on the effects of AAEMs and reactor temperature on the lignin derived products. Finally, observations concerning the formation of bed agglomerates when pyrolyzing acid leached pinewood and ways to prevent this will be discussed.

## 2. Material and methods

### 2.1. Materials

Pinewood (Lignocel 9, Rettenmaier & Söhne GmbH, particle size fraction 0.5 mm–2 mm) and wheat straw (Purchased from Praxis. Brand: Puik original, batch 2 in our previous paper) were used as feedstock in this study. A fraction of the wood and straw was leached with a synthetic acidic aqueous mixture, 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 and was found to lead to identical results [8]. The synthetic leaching solution was made from (on mass fraction): 10% of acetic acid (SAFC, 99.5%), 3.75% of acetone (Assink Chemie, purity >99.5%), 3.75% of ethanol (Assink Chemie, purity 99.8%), 1.5% of guaiacol (SAFC, purity >98%), 1.5% of propionic acid (SAFC, purity >99.9%) and 79.5% of demineralized water (milli-Q). The composition of the pinewood and straw before and after acid leaching is shown in Table 1. Silica sand, sieve fraction (212 µm–300 µm) with a particle density of 2600 kg m<sup>-3</sup>, was used as fluidized bed material during the pyrolysis experiments. The chemicals used for the hydrolysis and analysis of the oils were: sulfuric acid (Sigma Aldrich, purity 95.0–98.0%), barium carbonate (Sigma Aldrich ACS reagent purity >99%) methanol (Uvasol, purity >99.9%), acetone (Chromasolv, purity >99.8%) and tetrahydrofuran (Sigma–Aldrich, purity 99.9%). The AAEM salts used for impregnating acid leached pinewood and straw were sodium carbonate (Riedel de Haen, purity 99.8%), potassium carbonate (Sigma Aldrich, purity 99.7%), magnesium carbonate (Taendos purity >99%) and calcium carbonate (sigma Aldrich, purity >93%).

### 2.2. Experimental and methods

#### 2.2.1. Acid leaching

The leaching method was identical to the one described in our previous paper [8]. Briefly, the wood or straw particles were leached for 2 h at 90 °C in a 50 dm<sup>3</sup> vessel (0.1 kg dry biomass per kg of leaching solution) under continuous stirring. After 2 h the leaching liquid was drained from the vessel through a perforated plate (pore size 0.5 mm), leaving the wood or straw particles inside

**Table 1**  
Pinewood and straw<sup>a</sup> composition before and after acid leaching, data from Ref. [21].

	Pine		Straw <sup>a</sup>	
	Untreated	Acid leached	Untreated	Acid leached
<b>Compositional analysis, fraction in biomass da.f. (kg kg<sup>-1</sup>)</b>				
H <sub>2</sub> O extractive	0.03	0	0.06	0
EtOH extractive	0.01	0	0.02	0
<b>Total extractives</b>	<b>0.04</b>	<b>0</b>	<b>0.08</b>	<b>0</b>
Glucose	0.51	0.53	0.47	0.48
Xylose	0.05	0.04	0.24	0.25
Galactose	0.02	0.02	0	0.01
Arabinose	0.01	0.01	0.03	0.04
Mannose	0.12	0.13	0.01	0.01
<b>Total sugars</b>	<b>0.70</b>	<b>0.73</b>	<b>0.78</b>	<b>0.79</b>
Acid soluble lignin	0.04	0.05	0.05	0.05
Acid insoluble lignin	0.24	0.24	0.12	0.15
<b>Total lignin</b>	<b>0.28</b>	<b>0.29</b>	<b>0.17</b>	<b>0.20</b>
<b>Ash composition, concentration in dry biomass (mg kg<sup>-1</sup>)</b>				
Na <sup>+</sup>	60	2	117	22
K <sup>+</sup>	398	9	12,595	55
Mg <sup>2+</sup>	387	9	427	15
Ca <sup>2+</sup>	1771	68	2068	164
<b>Total AAEMs</b>	<b>2616</b>	<b>88</b>	<b>15,208</b>	<b>256</b>
<b>Total ash</b>	<b>5260</b>	<b>184</b>	<b>78,151</b>	<b>45,435</b>

<sup>a</sup> Batch 2 straw in Ref. [21].

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