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Wood-derived acid leaching of biomass for enhanced production of sugars and sugar derivatives during pyrolysis: Influence of acidity and treatment time

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ABSTRACT

Inorganic matter in biomass (especially alkali and alkaline earth metals) acts like intrinsic catalysts during pyrolysis and influences the composition of derived liquids. In this work, the influence of acidity and time on leaching of inorganics with wood pyrolysis-derived acids was investigated in order to understand their effect on the biomass characteristics and the composition of pyrolysis products, as well as to study the mechanism of leaching of different inorganic elements. Aqueous solutions of 5 and 10 wt% acetic acid (main acid in pyrolysis products and in similar concentrations) were used for demineralizing softwood at 85 °C for 30–90 min. Biomass characteristics, composition of intrinsic inorganics and primary pyrolytic vapors from different pretreatment cases are presented. Results show that removal of inorganics was in all cases enhanced by higher acidity; time of treatment was only seen to have a positive effect at lower acidity. The volatile matter of biomass was not affected by the pretreatment, confirming the conditions investigated being relatively mild. Results from Py-GC/MS of leached biomass show an increased selectivity towards sugars and sugar derivatives and simultaneous suppression of the relative composition of carbonyls and phenolic compounds in derived vapors. Sugars and sugar derivatives was enhanced by increasing the leaching time at higher acidity, without seeing a clear correlation to removal of alkali and alkaline earth metals. It is therefore suggested that other factors might influence the pathway of formation of primary pyrolysis products than what has previously been suggested by others. Because of the enhanced production of sugars and sugar derivatives from pyrolysis of leached biomass, this procedure might serve as a pathway to be enable the utilization of pyrolytic liquids as feedstock for existing fermentation-based biorefineries.

1. Introduction

The demand on energy, food and transportation is increasing worldwide with the globalization and the rapid population growth. Renewable alternatives to replace solutions that today are based on fossil resources is the only permanent solution to these growing demands and to global warming. At the same time, fuel production should not be contradictive to the food production due to ethical issues [1]. Liquids derived from fast pyrolysis of lignocellulosic biomass is a promising route for supplying renewable alternatives to today's dependence to liquid fossil resources [2]. The challenge of this process lies in increasing the yields of desirable products and the organic liquid itself in order to increase its long-term feasibility. One way to overcome this challenge is to catalytically upgrade pyrolytic vapors [3]. Another way, or combined with a catalyst, is internal recycling of non-condensable vapors as a reactive carrier gas during pyrolysis [4]. In this work, the utilization of aqueous pyrolytic liquids for removal of inorganic matter in biomass prior to pyrolysis is investigated, in order to affect the thermochemical degradation pathways of biomass and the composition of pyrolysis products. It is known that biomass contains inorganic matter that affects the composition of derived pyrolytic liquids. Alkali and alkaline earth metals (AAEMs) are well-known for their influence on vapor composition during pyrolysis of lignocellulosic biomass, found in previous studies [5–8]. Piskorz et al. [9] claimed that depolymerization reactions during fast pyrolysis of cellulose can take two different pathways: formation of anhydrosugars (e.g. levoglucosan) or lower molecular weight compounds (e.g. carboxylic acids, aldehydes) where the presence of AAEMs suppresses the formation of anhydrosugars. Also, AAEMs act like intrinsic catalysts, reducing the overall molecular weight and yield of vapors through secondary cracking reactions

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[10,11] or by increasing the char yield [5]. Besides from influencing the composition of pyrolytic vapors, ash forming inorganics contribute to process related issues such as catalyst poisoning (especially AAEMs) [12], as well as causing damage to equipment wear in industrial processes, e.g. corrosion and reduced heat transfer rates [13]. Therefore, reducing the inorganic content in biomass prior to pyrolysis may suppress these issues, even for biomass with relatively low ash content. Available works on pyrolysis of leached biomass have shown that removal of inorganic matter in biomass prior to pyrolysis leads to composition changes in derived pyrolytic liquids. Inorganic acids, such as HCl, HNO_3, H_2SO_4, have previously been used as leaching agents. It has been found that using strongly acidic solutions during biomass leaching can lead to high leaching performance but also reduce the volatile matter in biomass by dissolution of hemicellulose through acidolysis [7,14]. The volatile matter can also be dissoluted by using high temperature during aqueous treatment of biomass [15]. However, leaching with inorganic acids might lead to environmental and downstream process issues. One example is traces of Cl and S that can lead to e.g. catalyst poisoning. A more promising alternative could be the utilization of organic acids. Organic acids are present in pyrolytic liquids, where they promote acid-catalyzed aging reactions (e.g. re-polymerization) during storage [16]. Instead such wood-derived acids can be utilized as leaching agents in biomass pre-treatment. Recently, the idea of using the aqueous fraction of pyrolytic liquids including wood-derived acids for demineralization of biomass was investigated [8,17,18]. Results show that leached biomass gives enhanced yields of both pyrolytic liquids as well as levoglucosan (LGA) compared to raw biomass. To further investigate the utilization of the aqueous fraction of pyrolytic liquids as a leaching liquid, it would be of importance to understand the leaching effect of individual compounds and concentrations in this complex liquid composition, to see their effect on inorganic removal, biomass characteristics and the composition of pyrolysis products. Also, the influence of leaching parameters such as the acidity of the solution and the leaching time, which are vital parameters for the pretreatment of biomass, have been sparsely investigated in previous works and need further studies in order to understand and optimize leaching as a pretreatment step for biomass pyrolysis.

In order to understand the leaching mechanism of inorganics from biomass, one must be familiar with their different presences in biomass. Inorganic matter in biomass can be present in different ways: as minerals (e.g. SiO_2), ionically bonded in the biomass structure (metal ions, mainly AAEMs), and covalently bonded in the biomass structure (phosphorus and sulphur) [19]. Metal ions bonded in the organic structure are ion-exchangeable with protons [20]. The ion-exchange reaction is a reversible reaction where ions are exchanged between a solution and a solid phase at electroneutral conditions, e.g. ionically bonded metal ions and protons [21]. This knowledge is crucial in order to be able to study the mechanism of different inorganic elements, and how they are affected by e.g. the process conditions of leaching.

Studies on industrial utilization of leaching have recently been done by other researchers [22]. Preferably, the pretreatment should be a time efficient step that leach inorganics without dissolving significant fractions of the volatile matter in biomass. Previous studies using strongly acidic solutions and/or high temperature pretreatments has proven to have contradictive results since they reduce the volatile matter of biomass which leads to reduced liquid yield and is thereby a drawback of the entire process. This issue might not arise when using mild acidic leaching solutions at lower temperatures, and thereby have a positive effect on biomass pyrolysis for production of liquid chemicals and fuels. The objectives of this work are to understand the effect of acidity and time in the mechanisms of leaching different inorganics in biomass using wood-derived acids, and how different leaching conditions affect the composition of pyrolytic vapors and biomass characteristics. For the study, acetic acid was chosen as a model compound since it is the major acid derived from biomass pyrolysis [8,23]. The elemental composition of biomass and its intrinsic inorganics was analyzed after leaching, as well as its thermal decomposition properties and volatile matter. Pyrolysis was performed in an online Py-GC/MS using Pyrola2000 to allow analysis of composition of primary pyrolysis products.

Table 1
Proximate and ultimate analysis of the biomass used in this study (dry basis). Oxygen is calculated by difference.

Proximate analysis	
Ash (wt%)	3.5
Volatile matter (wt%)	81.4
LHV (MJ/kg)	19.3
Ultimate analysis	
C (wt%)	50.8
O* (wt%)	39.4
H (wt%)	6.1
N (wt%)	0.3
Si (mg/kg)	9310
Ca (mg/kg)	2170
Al (mg/kg)	2080
K (mg/kg)	1520
Fe (mg/kg)	986
Na (mg/kg)	690
Mg (mg/kg)	429

2. Materials and methods

2.1. Materials

The biomass used in this study was Swedish softwood sawdust (spruce/pine mixture), an industrially available feedstock supplied by SCA BioNorr. Proximate and ultimate analysis of the material is presented in Table 1. Particle size of ≤125 μm was chosen to meet the instrument criteria for Py-GC/MS analysis.

For leaching tests, aqueous solutions of de-ionized water and acetic acid were used. The setup for leaching experiments was a modified reflux apparatus illustrated in Fig. 1. The setup allows a closed lab-scale

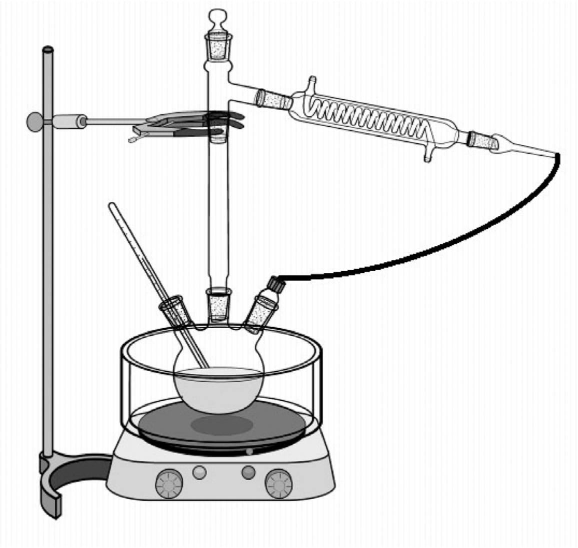

Fig. 1. Illustration of the experimental setup used for leaching of biomass – a closed batch glass reactor system consisting of a spherical three-neck glass, and a condensing loop. The condensing loop consisted of a glass tube, a water-cooled condenser, and a rubber tube. The reactor was heated in an oil bath while a magnetic stirrer was used to mix biomass with the aqueous solution during leaching. The temperature of the reactor was continuously measured during the leaching process to ensure isothermal conditions.