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Pyrolysis of pine and gasification of pine chars – Influence of organically bound metals

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HIGHLIGHTS

- ▶ Selective leaching of ash-forming elements from biomass.
- ▶ Adsorption of alkali and alkaline earth metals to the leached biomass sample.
- ▶ Pyrolysis of the leached and metal modified sample.
- ▶ Gasification of the pyrolysis chars.
- ▶ Strong influence on the pyrolysis and gasification by the metals.

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ABSTRACT

Pyrolysis of pine and gasification of pine chars was studied in this work, focusing on the influence of organically bound metals. Selective leaching of the major ash-forming elements in pine wood was performed with different acids, namely, nitric, sulfuric, hydrochloric and oxalic acids. No other major changes in the chemical composition of the biomass were observed except the removal of the metals. The effect of organically bound sodium, potassium, magnesium and calcium was studied in both pyrolysis and gasification. Removal of the metals had a positive effect on the pyrolysis, resulting in higher bio-oil, lower char and gas yields.

1. Introduction

Woody biomass can be transformed into liquid, solid and gaseous bio-products through pyrolysis and/or gasification. In pyrolysis the woody biomass is degraded into the above mentioned products in an atmosphere free of oxygen at 400–500 °C (Bridgwater, 2002). These conditions are chosen to maximize the production of liquid products. Gasification involves the oxidation of the char with a sub-stoichiometric amount of oxygen in a reactive atmosphere containing oxygen, steam or carbon dioxide as the reactive phase (Suzuki et al., 2011).

Biomass contains various amounts of cellulose, hemicellulose and lignin as well as inorganic ash-forming elements (Fengel and Wegener, 1984). The latter ones are bound to the biomass at carboxylic and/or phenolic groups (Wilson, 1966). The chemical composition of the biomass affects the distribution and composition of the pyrolysis products. Typical yields of woody biomass pyrolysis are 60–75% bio-oil, 10–20% gases, and 15–25% solid char (Mohan et al., 2006). Pyrolysis of biomass with a higher lignin content than woody biomass tends to yield less bio-oil (Mohan et al., 2006). The ash-forming metals in the biomass affect the composition of the bio-oil (Huber et al., 2006). Pyrolysis of cellulose can produce bio-oil with up to 66% of levoglucosan (Essig et al., 1988). However, small amounts of inorganic salts change the composition of the bio-oil in a way that the levoglucosan concentration is significantly lower and higher concentrations of formic acid, glycolaldehyde and acetol are formed (Evans and Milne, 1987; Patwardhan et al., 2010; Ronsse et al., 2012).

The ash-forming elements can be removed to some extent from the biomass by using water (Davidsson et al., 2002; Eom et al., 2011; Stephanidis et al., 2011). More extensive removal of the metals can be performed in acidic medium (Davidsson et al., 2002; Granholm et al., 2009; Eom et al., 2011; Su et al., 2010, 2012).

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However, if the leaching conditions are too harsh the main chemical composition of the biomass can change. Characteristically, if too high acid concentration and/or elevated temperatures are applied some degradation of hemicellulose can occur and thereby the cellulose and lignin contents are higher (Eom et al., 2011; Stephanidis et al., 2011).

Desorption of the metals prior to pyrolysis can have a positive effect. Stephanidis et al. (2011) studied the catalytic upgrading of biomass pyrolysis vapors and the effect of hydrothermal pretreatment on beech wood. Higher bio-oil yield was obtained through pyrolysis of the treated wood compared to the untreated one. The chemical composition of the bio-oil was also affected by the pretreatment, smaller concentrations of aromatics, phenols, furans, acids, ester and ketones were detected and the concentrations of sugars were significantly affected as they increased from 0.93% to 40.47%.

The influence of different metals, mainly alkali and alkaline earth, has been previously studied in the pyrolysis of biomass (Mourant et al., 2011; Eom et al., 2012; Fuentes et al., 2008; Richards and Zheng, 1991), furthermore, metals such as iron and nickel (Bru et al., 2007; Fuentes et al., 2008) have been investigated. Mourant et al. (2011) studied the effects of alkali and alkaline earth metallic species on the yield and composition of bio-oil. They applied different washing techniques to remove different amount of the metallic species using de-ionized water and dilute nitric acid. It was found that by prolonging the washing time more efficient removal of the metals was obtained. However, some metals were still present in the biomass after 48 h washing. By applying dilute nitric acid (0.1 wt.%) more metals could be removed in only 2 h, and no sodium, potassium or magnesium were detected. The different washing methods, i.e. different metal concentrations in the biomass, showed no differences in the yield of the pyrolysis products (char, bio-oil and gases). However, the chemical composition of the bio-oil changed. Removal of the alkali and alkaline earth metals resulted in increased yield of sugars and lignin-derived oligomers in the bio-oil and simultaneously in decreased water and light organic contents.

Eom et al. (2012) used a different approach in studying the effect of essential inorganic metals on primary thermal degradation of lignocellulosic biomass compared to Mourant et al. (2011). First most of the inorganic metals were removed by leaching them out from the poplar wood with 3 wt.% hydrofluoric acid at room temperature for 1 h, followed by washing with distilled water. Thereafter, the demineralized sample was impregnated with metal-salt solutions of desired concentration at 100 °C for 1 h, in order to study the effect of potassium, magnesium and calcium. It was found that the char yield increased when the biomass was impregnated with potassium chloride. The impregnation of the different metals to the biomass sample also affected the composition of the bio-oil. The concentration of levoglucosan decreased significantly from 12.6 wt.% to 1.68 wt.% for the sample with the highest potassium content. The modification with magnesium had a positive effect on the levoglucosan yield increasing from the above mentioned concentration to 19.41 wt.% with the highest magnesium loading.

In this work the ash-forming elements of pine wood, *Pinus sylvestris*, were selectively leached away without altering the main chemical composition, namely the hemicellulose, cellulose and lignin contents. Furthermore, different metals were adsorbed to the carboxylic groups on the biomass sample. The influence of the modifications was investigated in a laboratory fluidized bed pyrolyzer and the chars from the pyrolysis were gasified in a thermogravimetric analyzer in a CO_2-containing atmosphere to compare the char reactivity of the different chars from the pyrolysis reactor. Earlier studies have been carried out studying the catalytic effects of alkaline and alkaline earth salts on biomass of char gasification (e.g., Mitsuoka et al., 2011; Dupont et al., 2011). These biomass chars are different in that the carboxylic acid sites of the original biomass were doped with the metals rather than adding metals as salts.

2. Methods

2.1. Biomass

The biomass used in this work was pine wood, *P. sylvestris*. The wood was milled and sieved into 355–500 μm particles before any other pre-treatments took place. Prior to the pyrolysis experiments all biomass samples were dried at 100 °C overnight.

2.2. Leaching of ash-forming elements

Dilute acid leaching was performed on the biomass to remove the ash forming elements. Different methods were applied for the leaching procedure.

(1) Approximately 30 g of air-dry biomass was placed in a beaker and filled with 0.5 L of ion-exchanged water. The pH was then adjusted to 2 with nitric acid and heated to approximately 60 °C. The leaching was carried out for one hour under rigorous stirring. Then the liquid was removed and the leaching procedure repeated. After the second leaching cycle the sawdust was washed carefully with ion-exchanged water and then dried at 100 °C.
(2) Leaching experiments were also carried out by using nitric acid at room temperature (RT). Approximately 15 g of air-dry biomass and 0.5 L of ion-exchanged water were utilized in the RT-leaching experiment. The pH of the mixture was adjusted to 2 and stirred for 1 h. Thereafter the liquid was filtered off and the leaching was repeated for 1 h at pH 2, followed by careful washing with ion-exchanged water and drying at 100 °C.
(3) Different acids, namely sulfuric, hydrochloric and oxalic acids were tested using the method 1, described above. However, the amount of air-dry biomass was smaller in these leaching experiments, 15 g compared to 30 g in method 1.

Leaching experiments were also carried out at pH 2, 60 °C for only 1 h. Another experiment was done where the biomass sample was leached three times for one hour with changing of the solvent in between. Furthermore, leaching was also tested at pH 1 at ambient temperature for 1 h. It was found that the procedure 1 was suitable for removing most of the ash-forming elements.

2.3. Adsorption of metals

Adsorption of various metals was performed in aqueous solutions. Different conditions were tested in the adsorption, i.e. different pH, concentrations of metals in the solution, and adsorption time. Approximately 15 g of air-dry leached biomass (prepared according the method 1, described above) was used in all adsorption methods. The five most dominant elements found in the untreated biomass sample were used in the adsorption experiments. The adsorption procedures are given in detail below.

(1) A 0.05 mol/L nitrate solution with the metal was prepared and 500 mL was poured onto the biomass. The mixture was then stirred and the pH was adjusted to 7 with a corresponding metal-hydroxide solution. The adsorption was carried out for 72 h. K^+, Na^+ and Ca^{2+} were adsorbed on the