



Research paper

Optimization of bio-oil yields by demineralization of low quality biomass



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ABSTRACT

Lignocellulosic biomass contains inorganic elements (ash) that are known to act catalytically during fast pyrolysis and result in a decrease of the process' selectivity towards the desired liquid product. In this work, the removal of inorganic elements from two forestry residues, two agricultural residues and two energy crops was studied with the aim to maximize the liquid product yield from the fast pyrolysis process. The biomass samples were washed with water and solutions of nitric or acetic acid and the effects of time, temperature, acid type and acid concentration in the washing solution were studied. The original and the pretreated biomass samples were then pyrolyzed in a bench-scale fixed bed reactor in order to investigate the effects of the demineralization on the yields and composition of the pyrolysis products. Washing with water was effective for the removal of up to 42% of the inorganics in the biomass samples, whereas washing with acidic solutions achieved inorganics removal higher than 90%. The most important factor during the biomass pretreatment proved to be the washing temperature; higher temperatures (50 °C) were more effective for the removal of the inorganics than room temperature. The type of acid used in the washing solution was also an important factor, as nitric acid proved to be more effective than acetic acid. In the pyrolysis experiments, the demineralized biomass samples yielded less gas products and solid residue, while the selectivity towards the liquid product was substantially increased in all cases.

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1. Introduction

Renewable energy has been the focus of research efforts in the past years due to the increasing world energy demand, finite oil/natural gas reserves and concerns over energy security and the protection of the environment. Biomass is an abundant renewable carbon source that can help mitigate the dependence on fossil fuels and the emission of greenhouse gases. Among the various types of biomass, lignocellulosic biomass is attractive for energy production because it is a low-cost, widely available feedstock that does not compete with the food chain.

A variety of process options are available for the conversion of lignocellulosic biomass to high added value products. Fast pyrolysis is a low-cost thermochemical process that takes place at

atmospheric pressure and moderate temperatures (usually 450–550 °C) and converts biomass to a liquid product known as bio-oil. Gas (mainly CO₂ and CO) and solid (char) products are also produced. Another advantage of fast pyrolysis is that it is feedstock-flexible and can utilize low-quality, high-ash feedstocks, such as agricultural residues and energy grasses that would be unsuitable for other processes. Low-quality biomass is more readily available compared to waste wood (high-quality, low ash content), as the latter is already being utilized for heat generation and pelletization and has increased in value over the past years.

The minerals (ash) in biomass are known to act catalytically during fast pyrolysis and shift the selectivity away from the desired bio-oil, to char and gases [1]. It has been suggested that the minerals affect both the initial degradation pathways of the biomass constituents [2–5], as well as the cracking of the volatiles as they come in contact with mineral-rich charred biomass particles [6]. Therefore, an efficient strategy for minimizing char and gas

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formation and optimizing the bio-oil yield from ash-rich feedstocks is to remove the inorganics from the biomass prior to pyrolysis. Demineralization can be beneficial for other reasons as well; inorganic matter in bio-oil, originating from the biomass feedstock, catalyzes deleterious chemical reactions during storage, resulting in reduced stability [7–9]. In addition, in the case of fast pyrolysis processes with in-situ catalytic upgrading of the pyrolysis vapors, inorganic matter from the biomass feedstock is deposited on the catalyst, leading to deactivation [10,11].

Inorganics can be removed from biomass by water washing, acid washing and size reduction. Various groups have reported moderate ash removal levels after water washing of biomass [12–21]. The use of tap versus distilled water does not seem to influence ash removal [12,16,19]. However, tap water with high inorganics content may affect the ash composition of the treated feedstock [16]. Water washing achieves reduction of potassium, chlorine, sulfur and sodium from biomass, while some groups have also reported the removal of phosphorous [12,17] and silicon [13]. Ash removal benefits from increased treatment temperature [15,19,21] and washing time [13,14,19,21], although the rate of ash removal was very slow after a certain time [13]. The pretreatment of biomass feedstocks with water washing has been reported to result in increased bio-oil yields during pyrolysis [13–15].

Acid washing is more effective than water washing for the removal of inorganics [14,16,18,21]. In addition to increased ash removal, acid washing is effective for the removal of inorganics that cannot be removed by water washing, such as magnesium [14,18,22], calcium [14,18], aluminum [14], iron [18,22] and zinc [22]. Ash removal has been found to increase with increased treatment temperature and duration, with the temperature being the most critical parameter [23]. The strength of the acid used was also an important parameter, as stronger acids were more effective [18]. The pyrolysis of acid washed feedstocks has been reported to result in increased bio-oil yields [16,23,24] and reduced char [14,18,22,23] and gas [14,18,24] yields. However, feeds high in lignin and potassium were found to be an exception by Raveendran et al. [24] who observed increased char yields from acid washed coir pith, groundnut shell and rice husk.

Size reduction, i.e. milling of biomass and removal of the finer particles, has also been found to be effective for the reduction of mineral matter. Jenkins et al. [12] observed that finer biomass particles of rice straw had substantially higher ash content. Pattiya et al. [21] investigated size reduction as a means of ash content reduction and observed that the fractions with particles larger than 250 μm had much lower ash content than the finer particles. It was therefore concluded that milling and fine particle removal can be applied for removing ash from biomass.

In this work, we report a systematic parametric study for the demineralization of six different biomasses, including low-, medium- and high-ash feedstocks, and more specifically two wood residues (oak and pine), two agricultural residues (wheat and barley straws) and two energy crops (eucalyptus and miscanthus). Water washing and acid washing were first carried out with a reference lignocellulosic feedstock from beech wood. The effect of treatment duration, temperature and acid type (acetic or nitric acid) was investigated. Optimal conditions were established and then applied for the demineralization of the six different biomass feedstocks. The effect of deashing on not only the yield, but also the quality of bio-oil, analyzed by two-dimensional chromatography time-of-flight mass spectroscopy (GCxGC-ToFMS), was studied in detail.

Process-wise, we envisage this additional pre-treatment not to significantly affect the configuration of a fast biomass pyrolysis plant. Drying of the demineralized biomass will be integrated in the already existing biomass drying pretreatment step in the plant,

which is necessary for lowering the moisture content of the feedstock that arrives at the gate from about 30–40 to 8–10 wt.%. The heat demand for this pre-drying step is usually covered by the combustion of the produced char in existing biomass pyrolysis plants. Of course, the water content of the biomass after demineralization will be much higher, implying higher heat duties. This can be dealt with by initially subjecting the biomass to partial drying in open storage and by optimizing the heat integration in the plant, exploiting all available waste heat streams. Based on unpublished results of a techno-economic analysis performed in our group, we estimate that these additional steps will decrease the energy efficiency of the entire pyrolysis process by 7–10%. Other issues important to consider in terms of the process is the impact of nitric acid washing on the nitrogen content of the biomass and the disposal of the washing liquid. Concerning the first, we anticipate that some nitrogen will be absorbed by the biomass, which will end up as NH_3/NO_x in the pyrolysis gases. The amount is expected to be very low, therefore not significantly affecting the environmental performance of the overall process. The spent washing liquid should undergo biological treatment and could then be used for irrigation, as it will be rich in accumulated inorganics from the biomass.

2. Materials and methods

2.1. Biomass samples and characterization

Seven biomass samples were used in this study; a reference commercial lignocellulosic biomass from beech wood (Lignocel HBS 150-500, purchased from JRS), two forestry residues (oak and pine wood), two agricultural residues (wheat and barley straw) and two energy crops (miscanthus and eucalyptus). Carbon and hydrogen content in the biomass samples was determined with a CHN LECO-800 elemental analyzer from Leco Corporation. Oxygen content was determined by difference. The total ash content was measured by combustion via the following procedure: a sample of 2 g was placed in a furnace. In the presence of ambient air, the temperature was raised to 550 °C where it was maintained for 3 h. The ash content was calculated based on the final biomass weight, which was considered to be the ash in the biomass, compared to the initial sample weight. The moisture content was measured by drying a pre-weighed sample at 105 °C for 4 h. The calorific value was determined by burning a pre-weighed sample in an oxygen-bomb calorimeter (Parr 1261) under controlled conditions (ASTM D4809). Inductive coupled plasma-atomic emission spectroscopy (ICP-AES) was used for the determination of the ash composition of the untreated and the demineralized biomass samples, utilizing a Perkin Elmer Plasma 400 spectrometer, equipped with a Cetac6000AT + ultrasonic nebulizer.

2.2. Biomass pretreatment methods

2.2.1. Water treatment

The biomass samples were first crushed with a cutting mill and sieved to a particle size of 90–500 μm prior to pre-treatment. The crushed and sieved biomass (4 g) was dissolved in 80 ml water and was stirred on a magnetic stirrer at constant temperature for a specific amount of time. The investigated parameters included the temperature (room temperature and 50 °C) and the residence time (2, 4, 8 and 24 h). After treatment, the pH of the solution was measured and the solution was vacuum filtered through a Whatman No1 filter paper. The solid was then dried in an oven at 80 °C for 22 h. The weight of the cooled sample was finally measured.

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