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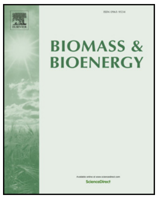

Research paper

Effects of warm water washing on the fast pyrolysis of *Arundo Donax*

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ABSTRACT

This work reports how warm water washing of biomass affects fast pyrolysis. Specifically, we applied this concept to *Arundo donax*, a common herbaceous biomass, and studied the washing effects on fast pyrolysis yields in a Py-GC/MS and a fluidized bed reactor. We stir-washed samples in water at 20 °C, 40 °C and 60 °C, and found that water at 60 °C led to an 18% increase in the removal of ash and an 11% increase in the removal of potassium compared to a room temperature wash. We pyrolyzed these samples via Py-GC/MS-FID and found that the reduction in ash increased the pyrolysis yields of acetol, furanone and levoglucosan relative to the unwashed samples. Additionally, we pyrolyzed washed *A. donax* in a fluidized bed reactor and compared the results to those of unwashed *A. donax*. We found that *A. donax* washed at 60 °C produced 9.7 wt% more bio-oil than unwashed, with increases in glycolaldehyde and levoglucosan yields of 0.78 wt% and 1.24 wt%, respectively. The yield of olefinic gases increased by 0.22 wt% and yields of carbon dioxide and alkane gases decreased 2.40 wt% and 0.11 wt% respectively. Char and water yields decreased 4.32 wt% and 10.08 wt% respectively. The gas produced from pyrolysis of washed *A. donax* has a greater HHV than that from unwashed *A. donax* (7.77 MJ/kg vs. 6.81 MJ/kg). We believe these results are a consequence of differences in the extent of secondary reactions catalyzed by the inorganic species present in herbaceous biomass.

1. Introduction

Biomass fast pyrolysis is a conversion technique with potential to produce fuels and chemicals in a more sustainable way than the current petrochemical route from which most fuels and chemicals are sourced [1]. Fast pyrolysis is the rapid heating of particles to temperatures between 400 °C and 600 °C – typical reaction times are around 1 s – in an oxygen-free environment [2]. Fast pyrolysis mainly produces a liquid oil, referred to as bio-oil. It also produces char and permanent gases as by-products [3].

Arundo donax, also known as Giant Reed, is a fast growing herbaceous reed native to India, but pervasive throughout the tropics and subtropics. It grows faster than bamboo, miscanthus and switchgrass at a rate of 30 dry tons/acre/year [4]. The fresh water requirements of *A. donax* are much lower than those of many other potential bio-energy crops. Moreover, fast pyrolysis of an herbaceous weed such as *A. donax* can mitigate problems such as agricultural displacement associated with the use of other forms of biomass [5].

A major hurdle in fast pyrolysis of herbaceous biomass is its high inorganic content, specifically the very high content of alkali salts. The problems associated with pyrolysis of materials that contain inorganics are cracking of volatiles, char formation, and catalyst poisoning [6–10]. Many of these inorganic compounds act as unintended catalysts that crack the volatile pyrolysis products into smaller compounds, mainly permanent gases like CO_2, CO, and CH_4. They also promote the formation of char, though it is unclear if this takes place by increasing the rates of condensation reactions or by reducing the heat transfer rate to the particles [7,8,11]. The effects have been thoroughly discussed previously in studies in which cellulose is doped with potassium chloride and other inorganic salts [7,11]. Potassium chloride was shown to crack levoglucosan into formic acid, glycolaldehyde, acetol, and permanent gases [12]. Similar results have been reported for cellulose and poplar wood impregnated with potassium carbonate, showing that the potassium is the culprit of these secondary reactions. The levels of potassium in biomass greatly affect the conversion of cellulose to liquid organics and shift the reactions toward the production of gas and char. The potassium carbonate loading decreases the levoglucosan content in the oil obtained from cellulose. It also increases acids and 5-HMF content [8,13].

A reduction in the potassium content of *A. donax* would likely decrease the yields of fast pyrolysis for char and gas and greatly increase the yield of levoglucosan and total organic yields. The effects on products such as acetol, acetic acid, 5-HMF, and other products would depend on the extent of potassium removal. In addition, this removal of potassium can also reduce slagging and fouling associated with the combustion of the produced char for energy applications [6].

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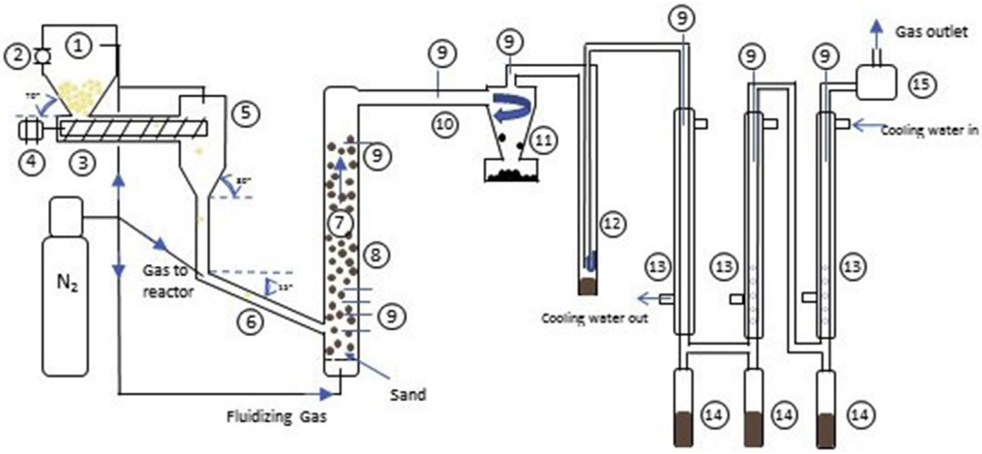

Fig. 1. Fluidized Bed Pyrolysis System. 1) Hopper, 2) Vibrating tab, 3) Auger, 4) Motor and magnetic coupling, 5) Funnel, 6) Feed tube, 7) Fluidized bed reactor, 8) Furnace, 9) Thermocouples, 10) Transfer line, 11) Cyclone and char collector, 12) Impinger, 13) Double-pipe condensers, 14) Oil collectors, 15) Filter.

Attempts to eliminate the inorganic content of over twenty biomass feedstocks have been reported and the implications for torrefaction and combustion of biomass have been shown [6]. Room temperature washes of miscanthus, wheat straw, short rotation willow, and eucalyptus reduced the ash content of these feedstocks [14]. As the water temperature of stir washing increased for the washing of wheat straw, corn stalk, rice straw, cotton stalk, and candlenut wood, the inorganic content decreased [15]. Other reports have also demonstrated the effects of using an acid to wash biomass prior to fast pyrolysis [16]. To the best of our knowledge, however, the implications of warm water washing on fast pyrolysis have not been previously studied. The present paper attempts to elucidate this. In particular, we report for the first time how washing affects the composition of bio-oil and gases: other similar papers have either focused entirely on organic liquid composition [17] and yields [18], or did not report the effect of water temperature [18,19].

In this study, we show the effects of particle size and water temperature on the removal of inorganic species from *A. donax*. Then, we report the effects of warm water washing of *A. donax* on its pyrolysis products. We carried out screening experiments in a pyroprobe to gather preliminary information, such as volatile yields, and to determine the most appropriate reaction conditions. We then performed pyrolysis in a fluidized bed reactor in order to close the mass balance and gather more detailed information, such as gas, water, organic liquid, and char yields.

2. Materials and methods

Percentages reported in this text are always relative to the original biomass unless otherwise noted.

2.1. Washing

For the washing procedure, we varied the temperature of the water and the particle size of the *A. donax*. Initially, we reduced the particle size of the *A. donax* (Thomas-Wiley, Philadelphia, PA). The particle sizes were 0.25, 1.5, and 10 mm. For the largest particle size of 10 mm, we cut the biomass with a sharp blade. For the others, we used a hammer mill (Thomas-Wiley, Philadelphia, PA). We then dried the biomass in an oven (Blue M, Blue Island, IL) at 105 °C overnight to measure its moisture content (5.81 wt%). After drying, we washed it in a beaker with a magnetic stirrer on a hot plate (VWR, Radnor, PA) for 1 h (shown previously to be the appropriate duration of a stir-wash for maximizing inorganic reduction [18,20]) at the desired temperature using 10 mL of water per gram of dry biomass. This loosened the salts within the biomass, and to avoid resettling of the inorganic compounds, we placed it onto a 200 mesh sieve and rinsed it with room temperature deionized water for 1 min. Finally, we placed the biomass back in the oven at 105 °C overnight to re-dry. We removed the samples from the oven and allowed them to cool in ambient air so that they would have a moisture content similar to the unwashed *A. donax*. Further moisture tests confirmed that the moisture content of the biomass was 5.35 wt%.

We obtained the ash content by placing samples in a muffle furnace (Thermo Fisher Scientific, Waltham, MA) at 600 °C for 24 h, according to ASTM E1755-01, and reported it on a dry biomass basis [21]. We quantified the inorganic elements by ICP-AES analysis (Thermo Fisher Scientific, Waltham, MA) according to EPA 200.7 and reported them on a dry biomass basis.

2.2. Micropyrolysis

After washing the biomass, we investigated how the washing process affected pyrolysis yields in a micropyrolysis unit, using a procedure identical to that of previous reports [22,23].

We used gas chromatography/mass spectrometry with a flame ionization detector (GC/MS-FID) (Shimadzu, Kyoto, JP) to identify and quantify the volatile pyrolysis products, using the same method as previously described [22,23].

We calibrated the GC/MS-FID for 32 products in total, with at least four different concentrations of the major products. In some instances, we used a single calibration curve to represent multiple compounds with similar molecular structures, as is reported in other works [7,22,23]. We defined the yield of "total identified volatile compounds" as the sum of all the yields of individual compounds identified and calibrated for in the GC/MS-FID. These do not include minor peaks, unidentified peaks, or volatiles which did not generate an FID peak.

2.3. Fluidized bed

Following the screening study of washed and unwashed *A. donax* in the micropyrolyzer, we performed pyrolysis in the lab scale fluidized bed (Fig. 1). We ground *A. donax* to an average diameter of 373 μm, ranging from 0 to 1 mm. We then pyrolyzed unwashed *A. donax* in the fluidized bed reactor. The sample size for each run was 200 g.

We washed and dried another 200 g sample of ground *A. donax* (same particle size as the unwashed samples) as described previously in 60 °C water.

Fig. 1 shows a schematic of the fluidized bed reactor system, described elsewhere [23]. The biomass was fed at a rate from 0.1 to 1.5 kg/hr. Nitrogen gas pneumatically feeds the particles from the funnel to the fluidized bed reactor at a flow rate of 3 SLPM from the top of the funnel and 6 SLPM from the side of the feed tube. The reactor bed