



Research paper

Effects of hot water extraction pretreatment on pyrolysis of shrub willow[☆]

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ABSTRACT

In this study, we tested the effect of hot water extraction (HWE) as a biomass pretreatment on the pyrolysis of three cultivars of shrub willow via both conventional heating (using a micropyrolyzer, Py-GC/MS) and microwave-assisted heating (using a laboratory scale microwave reactor and activated charcoal as an added microwave absorber). The py-GC/MS experiments revealed that there was little difference in pyrolysis behavior among the cultivars for raw or HWE pretreated samples. Using either heating method, pyrolysis of the HWE pretreated samples produced less acetic acid and CO₂ than did the untreated biomass; conversely there was an increase in levoglucosan yield with HWE pretreatment. The difference in levoglucosan yield was particularly large (4 fold increase) for the py-GC/MS experiments and was attributable in large part to the demineralization of the HWE samples. The decreased mineral content appeared to have a larger effect on conventional heating than in the microwave assisted heating. The pyrolysis of HWE pretreated biomass also led to more rapid temperature increases during microwave-assisted pyrolysis performed at 1000 W. Therefore the microwave-assisted pyrolysis of HWE was studied at two different microwave power settings to compare the effect of HWE on both processes at similar temperatures. At similar temperature conditions the yield of bio-oil, bio-char and non-condensable gases from microwave-assisted pyrolysis were similar between the pretreated and raw willow but the bio-oil contained higher concentrations of aromatic hydrocarbons and less acetic acid and levoglucosan. Overall, the HWE pretreatment had a greater effect on bio-oil composition than bio-oil yield.

1. Introduction

Biomass preprocessing or pretreatment is used to reduce recalcitrance of the lignocellulosic cell wall. For biochemical conversion processing many pretreatment technologies, such as torrefaction, steam explosion, dilute acid, ammonia fiber explosion (AFX), and hot water extraction (HWE), have all been explored to improve sugar release through enzymatic hydrolysis for the production of bioethanol via fermentation [1,2]. However, such practices have not found widespread application in thermochemical conversion processes geared toward the production of drop-in renewable fuels and chemicals although many of these could also be impactful. Fast pyrolysis is a thermochemical conversion process whose outcome could potentially benefit from selected pretreatment technologies as bio-oil, the liquid product from biomass fast pyrolysis, has compositional traits and properties that are directly relatable to the composition of the biomass feedstock used in creating it. Bio-oil is usually highly oxygenated, acidic, and viscous with a rather

limited shelf-life. Higher quality bio-oil could be obtained from biomass with altered cell wall composition and/or mineral content. The aforementioned pretreatment technologies could be advantageous for modifying the biomass to obtain more desirable properties in the bio-oil produced through fast pyrolysis.

Pretreatment by hot-water extraction can alter biomass quality and composition. Under moderate pressure hot water pretreatment can solubilize the majority of the hemicellulose and a small portion of the lignin present in the biomass, leaving behind a water-resistant solid residue consisting of higher lignin and cellulose [3,4]. The lignin remaining in the solid residue (~75-90% of initial lignin present) has been shown to be chemically altered following the pretreatment process [5,6]. Minerals are also lost into the aqueous stream during this process, thus reducing the overall inorganic content of the biomass [7]. Metal components of ash, particularly alkali metals such as potassium, are known to have a major effect on pyrolysis chemistry, catalyzing reactions that produce char, gas and result in bio-oil that is more

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concentrated with small highly and reactive oxygenated components [8–13]. As part of the integrated biorefinery system, the State University of New York College of Environmental Science and Forestry (SUNY-ESF) has developed a hot-water extraction pretreatment method that maximizes production of high-value products (wood products, ethanol, and chemicals) from hardwood materials [14,15].

The goal of the current study was to determine if and how the hot-water extraction pretreatment method impacts the biomass composition of shrub willow (*Salix* spp.) biomass crops and how these changes affect downstream thermochemical conversion particularly fast pyrolysis. Prior studies have shown that the loss of hemicellulose and alkaline minerals from the biomass that results from hot water extraction can have a significant effect on the products obtained from fast pyrolysis [7,16,17]. However, these studies were limited to microscale pyrolysis reactors (Py-GC/MS) only, and did not report isolated bio-oil, bio-char and non-condensable gas yields.

In this study, biomass from three different cultivars of shrub willow were subjected to HWE and characterized for biomass compositional changes. Both untreated biomass and HWE biomass were then evaluated for their response to pyrolysis using both conventional fast pyrolysis regime heating (as studied via Py-GC/MS), and microwave-assisted heating, which allowed for the isolation, quantification, and characterization of all pyrolysis products generated, albeit with a less rapid heating rate. The effect of the HWE on the products produced from both heating methods are compared and contrasted to explore thermochemical conversion effects.

2. Materials and methods

2.1. Hot water extraction of willow biomass and compositional analysis

Three cultivars Owasco (*Salix viminalis* x *S. miyabeana*), SV1 (*S. x dasyclados*), SX61 (*S. miyabeana*) of shrub willow biomass represent three different diversity groups. Three year old willow stems growing in a yield trial near Contableville, NY were harvested and chipped. Fresh chips were dried at 60 °C to a constant weight and ground using a Wiley mill with a 1 mm mesh screen and pulverized using a SPEX 8000M Mixer/Mill. Chips used for HWE were air dried prior to processing. Hot water extraction was performed in a 4.7 liter M/K digester using 500 g oven dried chips and 4:1 water to wood ratio at 160 °C for 120 min [18]. At the completion of the extraction, the chips were washed with water to remove dissolved substances, dried at 60 °C to a constant weight, then ground and pulverized in the same manner as the raw biomass. Both raw and hot water extracted samples were provided for each cultivar. Willow biomass samples (10 mg of oven-dry tissue for each sample) were analyzed for cell wall polymer content (hemicellulose, cellulose, and lignin) using a Thermogravimetric Analyzer 2950 (TA Instruments, New Castle, DE) with the TA Universal Analysis 2000 software. Samples were analyzed according to methods developed previously for willow biomass [19,20].

Ultimate analysis was performed on 2 mg of biomass using a ThermoFlash EA1112 CHNS/O analyzer (Thermo Fisher Scientific, Waltham, MA). GC quantification followed complete combustion of the sample. Oxygen was determined by difference on a dry-ash free basis. Moisture and ash content were determined by drying samples in a muffle furnace at 105 °C for four hours followed by combustion of the biomass at 600 °C for four hours. The BET specific surface area analysis was performed by Particle Technology Labs using a static volumetric method.

2.2. Trace metal analysis

Acid digestions were performed on 300 mg of oven-dried biomass using a modified closed tube method according to Wheal, Fowles [21]. In short, 2 cc³ of concentrated nitric acid (70%) and 500 mm³ of 30% hydrogen peroxide were added to each sample tube, capped and well

mixed using a vortexer. Samples were then stored at room temperature overnight. Next, the samples were vortexed again and then placed in a digestion block and heated to 80 °C for 30 min, followed by 120 °C for 120 min. After digestion, samples were cooled and diluted with double-distilled water to a volume of 25 cc³. After the settling of particulates, 10 cc³ of sample was transferred to autosampler tubes for analysis by inductively-coupled plasma optical emission spectroscopy (ICP-OES) on a Thermo Scientific iCAP 6300 (Waltham, MA). Quantitation of Ca, Cu, Fe, K, Mg, Na, P, S, and Zn in the biomass was determined by external standards using the instrument software.

2.3. Pyrolysis-GC/MS

Micro-pyrolysis of all biomass samples was performed as previously described [22] using a Frontier Lab (Koriyama, Japan) Double-Shot micro pyrolyzer PY-3030iD with the Frontier Lab Auto-Shot Sampler AS-1020E attached to a gas chromatograph, Shimadzu GC-2010 (Columbia, MD) coupled with a Shimadzu GCMS-QP2010S mass spectrometer. Pyrolysis was performed on 350–450 µg of sample at 500 °C.

2.4. Microwave-assisted pyrolysis

Due to sample size limitations, the three cultivars of the willow samples provided were combined for microwave-assisted pyrolysis analysis. Microwave-assisted pyrolysis experiments were performed as previously described [23] using a bench scale Milestone RotoSYNTH microwave reactor, fitted with a 2000 L quartz vessel charged with 100 g of the willow sample and 10 g of activated charcoal (Darco, 20–40 mesh particle size, granular). A schematic of the system is provided in the supporting information (Figure S1). The standard microwave power program consisted of applying 900 W for 1 min, and then increasing to 1000 W for the remainder of the experiment. A modification of the reference procedure was made in the case of the low temperature (low T) experiments performed with HWE willow feedstock during which the microwave power was increased incrementally from 900 to 980 W over the course of 15 min in order to obtain temperatures closer to experiments performed with the untreated willow feedstock (*vide infra*). The solid, liquid (bio-oil and H₂O), and gaseous products were quantified and subsequently characterized. The liquid products were collected using a cold water trap (CW) and a liquid nitrogen trap (LN₂), and the gaseous products were collected using a gas reservoir. Experiments were repeated in triplicate.

2.5. Characterization of microwave-assisted pyrolysis products

Moisture and ash content of the biochar was determined by drying samples in a muffle furnace at 105 °C for ~16 h followed by combustion at 650 °C for four hours. Elemental analysis of LN₂ oils and biochars were performed on a Thermo EA1112 CHNS/O analyzer and the oxygen content was calculated by difference. Gas chromatography with mass spectroscopic (GC–MS) analysis of liquid products was performed on a Shimadzu GCMS QC-2010. The column used was a DB-1701, 60 m × 0.25 mm, 0.25 µm film thickness. The oven temperature was programmed to hold at 45 °C for 4 min, ramp at 3 K min⁻¹ to 280 °C, and hold at 280 °C for 20 min. The injector temperature was 250 °C, and the injector split ratio was set to 30:1. Helium carrier gas flowed at 1 mL min⁻¹. The GC–MS samples of pyrolysis oils were prepared in acetone and filtered through a 0.45 µm PTFE filter prior to injection. Quantification of individual compounds was determined using response factors for authentic standards relative to an internal standard (fluoranthene). The composition of gaseous products was determined using an Agilent 3000 MicroGC.

2.6. Statistical analysis

For the Py-GC/MS data, a three-way analysis of variance was

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