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Influence of pyrolysis condition on switchgrass bio-oil yield and physicochemical properties

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ABSTRACT

The poor and inconsistent physicochemical properties of bio-oil are inhibiting its industrialized production. We investigated the variability in properties of switchgrass bio-oil produced at three pyrolysis temperatures (T = 450, 500, and 550 °C) and three feedstock moisture contents (MC = 5%, 10%, and 15%) in a 3 × 3 factorial experiment in order to exploit opportunities to improve bio-oil properties through optimization of pyrolysis parameters. Results showed that even with the single type of feedstock and pyrolysis system, the two main factors and their interaction caused large variations in bio-oil yield and most of the measured physicochemical properties. Following improvements of bio-oil properties could be individually achieved by selecting an optimal pyrolysis condition (shown in parenthesis) comparing with the worst case: increase of bio-oil yield by more than twofold (MC = 10%, T = 450 °C), increase of pH by 20.4% from 2.74 to 3.3 (MC = 10%, T = 550 °C), increase of higher heating value by 18.1% from 16.6 to 19.6 MJ/kg (MC = 10%, T = 450 °C), decrease of density by 5.9% from 1.18 to 1.11 g/cm^3 (MC = 5%, T = 550 °C), decrease of water content by 36% from 31.4 to 20.1 wt.% (MC = 5%, T = 450 °C), decrease of viscosity by 40% from 28.2 to 17 centistokes (MC = 5%, T = 550 °C), decrease of solid content by 57% from 2.86 to 1.23 wt.% (MC = 15%, T = 550 °C), and decrease of ash content by 41.9% from 0.62 to 0.36 wt.% (MC = 15%, T = 550 °C). There is no single, clear-cut optimal condition that can satisfy the criteria for a bio-oil product with all the desired properties. Trade-offs should be balanced according to the usage of the end-products.

1. Introduction

Bio-oil, a liquid product of biomass pyrolysis, shows promise as a substitute for fuel oil or diesel in many static applications that use boilers, furnaces, engines, and turbines for electricity generation or chemical production (Bridgwater and Peacocke, 2000; Demirbas, 2001; Zhang et al., 2007). Many types of biomass have been tested for bio-oil production, and pilot plants have been established worldwide (Bridgwater and Peacocke, 2000; Guo et al., 2001). Researchers and industries are constantly looking for biomass resources that can be easily cultivated with high output. One of the dominant tall grass species in Central North America, switchgrass (*Panicum virgatum* L.), is thought to be a good candidate for bio-oil production because of its hardiness in poor soil and climate conditions, low fertilization and herbicide requirements, and high biomass yields (McLaughlin et al., 1999). Boateng et al. (2007) used a 2.5 kg/h bench-scale fluidized-bed reactor for switchgrass conversion to demonstrate that bio-oil yield greater than 60% by mass, with energy conversion efficiency ranging from 52% to 81% can be achieved. Investigating the efficacy of pre-treatment in switchgrass pyrolysis conversion, Bridgeman et al. (2007) found that milling could improve feedstock quality for conversion.

A significant barrier to the industrialization of bio-oil products is the lack of norms or standards for bio-oils (Elliott, 1984; Diebold et al., 1997; Oasmaa and Meier, 2005; Oasmaa et al., 2005). Comprehensive norms and standards for bio-oils have not been determined yet because of poor and inconsistent bio-oil physicochemical properties, including high viscosity, low heating value, low pH value, and unstable chemical composition in aging period. Bio-oil refining has been discussed and tried as a necessary step to improve the poor physicochemical properties for fuel applications (Oasmaa and Czernik, 1999; Zhang et al., 2005). However, refining means additional unit operations and production costs. It is reasonable to first investigate the variability of bio-oil properties caused by different pyrolysis conditions and exploit opportunities to improve bio-oil properties through optimization of pyrolysis parameters before refining. Several studies reported that some pyrolysis parameters, such as feedstock chemical composition, particle size, and moisture content, pyrolysis temperature, and heating rate significantly affect bio-oil yield and properties (Demirbas, 1998, 2005; Bonelli et al., 2001; Debdoubi et al.,

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2006; Boateng et al., 2006; Onay, 2007; Li et al., 2007). However, these studies were scattered over different biomass types and different combinations of pyrolysis systems and parameters, paying little attention to improving bio-oil properties via adjustment of pyrolysis condition in a production perspective.

Our objectives were (1) to investigate the variability of bio-oil physicochemical properties caused by two main pyrolysis parameters: feedstock moisture content and pyrolysis temperature; and (2) to explore the effects of these two parameters to determine the optimum combination of switchgrass moisture content and pyrolysis temperature for producing bio-oils.

2. Experimental

2.1. Raw material

Switchgrass were collected from mature stands of the Cave-in-Rock cultivar while dormant (early spring) at Chariton, IA. Cellulose, hemicellulose, lignin and ash are the major chemical constituents in biomass, and the first three constituents can be converted to bio-oil. To provide a starting point, chemical composition of switchgrass as mass percentage based on the dry biomass was determined as glucan (41.56%), xylan (17.29%), galactan (1.95%), arabinan (3.29%), mannan (0.83%), lignin (21.73%), and ash (2.62%), according to protocols detailed in Ye et al. (2008). Following ASTM D 240 (2002) standard, higher heating value (HHV) of dry switchgrass was also measured with an IKA C200 calorimeter as 18.82 MJ/kg. The feedstock samples were ground in a knife mill to pass through a 3.175-mm screen. Three batches of the switchgrass samples were placed in a drying oven to vaporize water till their moisture contents decreased to 15%, 10% or 5%, respectively.

2.2. Pyrolysis

Pyrolysis experiments were conducted with a 5 kg/h pilot fluidized-bed fast pyrolysis reactor located at the Iowa State University Center for Sustainable Environmental Technologies. Depicted in Daugaard (2003), this reactor system is comprised of the following: a fluidized-bed reactor and plenum; a biomass feed system with feed hopper, feed auger, and injection auger; a burner system; cyclone solid separators; and a bio-oil collection system with condenser train and packed bed; and data acquisition system. The fast pyrolysis reactor is 1 m high and 16.2 cm in diameter; the sand bed located in the inner cylinder has a depth of 32 cm and a sieved diameter of 735 μm; 225 L/min of nitrogen was used to fluidize the sand bed.

A 3 × 3 factorial experimental design was followed to perform nine treatments of pyrolysis with three levels of moisture content (5%, 10%, and 15%) and three levels of pyrolysis temperature (450, 500, and 550 °C). Three replicates, each with a feedstock weight of 5 kg, were used for each treatment. The physicochemical properties of the produced bio-oils were determined according to methods described in subsequent Sections 2.3, Section 2.4, Section 2.5, Section 2.6, and Section 2.7. The effects of treatment condition on bio-oil properties were analyzed using analysis of variance (ANOVA) and the Tukey–Kramer Multiple Comparison Test conducted in NCSS software (Kaysville, Utah).

2.3. Physical properties analysis

The bio-oil properties of density, pH, viscosity, higher heating value (HHV), water content, solid content, and ash content were measured in triplicate. Density was measured according to the standard method of ASTM D 1217 (2002), and pH was measured with an Extech pH meter (model 407228). A Schott TitroLine Karl Fischer volumetric titrator was used to measure water content according to ASTM D 4377 (2002) standard. The HHV was measured with an IKA C200 calorimeter according to ASTM D 240 (2002) standard. Viscosity was measured, according to ASTM D445 (2006) standard, at 40 °C with serialized Schott Ubbelohde capillary viscometers. Ash content was measured according to ASTM D482 (2003) standard at 575 °C.

To determine the bio-oil solid content, the ethanol insoluble materials in the sample were measured according to Boucher et al. (2000). In brief, 5 g of bio-oil was first dissolved in 50 ml of ethanol. Then the solution was filtered through Whatman glass fiber filter paper (2.7 μm pore size, 47 mm diameter) in a Buchner funnel. The filter was washed with ethanol until the filtrate was clear, then dried in an oven at 105 °C for 1 h and placed in a desiccator before weighing. The bio-oil solid content was calculated as the percentage weight of ethanol insoluble materials collected on the filter based on the weight of the bio-oil sample.

2.4. Gel permeation chromatography (GPC)

Bio-oils are made up of molecules of different sizes resulting from fragmentation of cellulose, hemicelluloses, and lignin, constituting mixtures of compounds with a range of molecular weight. We used GPC analysis to examine the influence of pyrolysis conditions on the molecular weight distribution (*MWD*) of bio-oils. The statistics such as mass average molecular weight (*Mw*), number average molecular weight (*Mn*), or *MWD* (the ratio of *Mw:Mn*) have been used to characterize the distribution of bio-oil mass (Britta, 2002). Molecular weight distributions were determined using a Waters Delta 4000 LC system with a Lambda-Max 480 UV detector at 220 nm. The separation was performed using three columns in a series – the Styragel HT 6E + HR 5E + HR 4E, each 300 mm in length and 7.8 mm in diameter with a particle diameter of 10 μm. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.8 mL/min. Bio-oil samples were dissolved in THF at a concentration of 1 g/L. To remove particles that may damage GPC columns, the sample solutions were filtered with 0.2 μm pore size microfilters and centrifuged at 10,000 rpm before being injected into the sample loop. Elution times were converted to apparent molecular weight by calibration with polystyrene standards (Shodex standard, SL-105, from Showa Denko K.K., Japan). All the samples were measured in triplicate. The *Mw*, *Mn* and *MWD* of each sample were calculated in Microsoft Excel according to Russo (2001).

2.5. Fourier transform infrared (FT-IR) analysis

The infrared (IR) spectra were acquired for bio-oil samples to find the main organic components, according to the peaks of functional groups, by an attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometer (Varian 3100 FT-IR with Varian 400 UMA), equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The oil was applied as a droplet around a germanium crystal, and 64 scans were acquired and processed.

2.6. Gas chromatography–mass spectrometry (GC–MS) analysis

A Shimadzu GC–MS (QP2010S) with a Restek Rtx-1701 capillary column (60 m × 0.25 mm × 0.25 μm) was used for the GC–MS analysis. The carrier gas was helium (purity 99.999%). The column temperature was programmed from 45 to 250 °C at 5 °C/min after an initial 5 min isothermal period and kept at the final temperature for 8 min. The inlet was set at 260 °C, and sample injection was made in split mode (1:10). The mass spectrometer was set at an ionizing voltage of 70 eV with mass range (*m*/*z*) of 30–300. The compounds were identified by comparing their mass spectra with