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Characterization of fuel properties for coal and torrefied biomass mixtures

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ABSTRACT

Recently, there has been growing interest in co-liquefaction of coal with biomass because biomass has potential to substitute as a cheap hydrogen-donor and enhance liquid yields during direct coal liquefaction. In addition, inclusion of biomass can reduce greenhouse gas emission compared to solely coal-based processes. This paper presents characterization of coal, biomass, torrefied biomass and mixtures of coal with biomass and torrefied biomass to be used for direct liquefaction for the production of liquid fuels. Samples of yellow-poplar (YP) and red maple (RM) biomass collected from Appalachian logging residue and West Virginia Kingwood bituminous coal (C) were used in this study. The red maple and yellow-poplar samples were torrefied at 300 °C to produce torrefied red maple (TRM) and torrefied yellow-poplar (TYP), respectively. The untorrefied and torrefied samples were mixed with coal in a 1:1 ratio (by weight) creating coal-biomass and coal-torrefied biomass mixtures to be used as feed for co-liquefaction. In addition, untreated yellow-poplar and coal samples were tested as controls. All samples and mixtures were characterized for calorific value and underwent proximate, ultimate, and thermo-gravimetric analyses. The volatiles produced during thermo-gravimetric analysis were tested for chemical functional groups present in the products.

1. Introduction

Coal liquefaction is a promising technology for synthesis of liquid fuels. Direct liquefaction of coal is done by heating coal in the presence of some hydrogen-donor solvent (such as tetralin), an iron-based catalyst and hydrogen gas at a temperature ranging from 300 °C to 500 °C in a pressurized reactor. During the liquefaction process, thermal fragmentation of the coal structure produces organic free radicals, which combine with hydrogen supplied by either the hydrogen donating solvent, gaseous hydrogen, or the coal itself [1]. The process produces preasphaltene, asphaltene, and oil fractions along with other residual solid hydrocarbons. Commercial applications of the coal liquefaction process are limited due to the high initial capital cost, the low reactivity of coal, the high cost of hydrogen-donor species, and high greenhouse gas emissions.

Several attempts have been made to enhance coal liquefaction by adding biomass or agricultural waste during the process. Matsumura et al. [2] observed that the hydrogen-to-carbon ratio in the water-soluble fraction of the liquefaction product increased when coal was co-processed with cellulose. Rafiqul et al. [3] observed that co-liquefaction of bagasse with coal increased the oil yield from 10.9% to 47.8%. Karaca and Bolat [4] observed that the combined oil and gas yield for co-processing was higher than the average arithmetical value of yields obtained from the individual feeds. While co-liquefaction of biomass and coal increased overall total conversion, no synergy was observed between coal and biomass during co-liquefaction because biomass has high H/C (hydrogen-to-carbon) and O/C (oxygen-to-carbon) ratios [4]. Only cellulose and hemi-cellulose present in the biomass degrade under liquefaction temperatures (up to 350 °C) [5]. The cellulose and hemi-cellulose molecules in biomass (at 5%–10% moisture content) have molecularly bound water attached via high-energy hydrogen

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bonds. In addition, water bound by low-energy capillary and macroscopic forces is also present in the biomass. At high temperatures, between 200 °C and 350 °C, the high-energy hydrogen bonds break and molecularly bound water leaves the cellulose molecule forming the glucosan radical [6]. These glucosan radicals recombine with free oxygen present in cellulose molecules and form anhydrocellulose. If the glucosan radical does not get a chance to bridge with oxygen, it forms levoglucosan [6]. Stiller et al. [7] used sawdust, horse and cow manure and a commercial manure as an additive during co-liquefaction. They report that addition of cow manure produced the highest oil yields due to its very high lignin content [7]. One way to reduce oxygen and hydrogen content and increase reactivity and lignin content of the biomass is to perform thermal pretreatment of the biomass, for example torrefaction or pyrolysis.

Torrefaction is a pretreatment method where biomass is subjected to moderate heating (200 °C–300 °C) in a low-oxygen environment [8] to decompose hemi-cellulose, completely, and cellulose, partially, thereby producing torrefied biomass [9]. Torrefied biomass has reactive and unstable cellulose and lignin molecules with broken hydrogen bonds. Torrefaction retains not only 79%–95% of the original biomass energy but also produces a more reactive torrefied biomass with lower H/C and O/C atomic ratios than the original biomass [9]. Additionally, the torrefaction process improves the fuel and physical characteristics of biomass (high carbon content [10]; low H/C and O/C atomic ratios [11]; and brittleness [12]). Characteristics of torrefied biomass not only depend on temperature but also on its residence time at that temperature [13,14]. The combination of 260 °C and 1.0 h residence time seems sufficient to produce good quality torrefied biomass from woody feedstock [13]. Another pretreatment process, pyrolysis, also produces a reactive product: biochar. Pyrolysis involves heating the biomass in the absence of oxygen above 400 °C to produce bio-oil, biochar, and gases [15]. The biochar produced between 400 °C–550 °C is highly reactive and prone to chemisorb oxygen and moisture because most of the chemical bonds of the carbon atoms are left dangling or unbalanced and it still contains volatile matter [15].

The present study focuses on utilization of raw biomass and torrefied biomass during coal liquefaction to produce liquid fuel. The objective of this paper was to characterize coal, torrefied biomass, forest residue, coal-biomass residue, and coal-torrefied biomass mixtures for fuel properties and thermo-gravimetric analysis using the Thermogravimetric Analyzer- Fourier Transform Infrared Spectroscopy (TGA-FTIR) system.

2. Experimental procedure

2.1. Materials

West Virginia bituminous coal (C) from Kingwood, WV was selected for co-liquefaction of coal and biomass. Samples of freshly cut yellow-poplar (YP) and red maple (RM) were collected from the West Virginia University Research Forest. The biomass samples were chipped and dried at 103 °C for 24 h and then ground to less than 1 mm particle size. The ground samples were torrefied at 300 °C for 1 h under a nitrogen atmosphere to produce torrefied red maple (TRM) and torrefied yellow-poplar (TYP). A temperature of 300 °C was selected for maximizing lignin content [16] while obtaining high reactivity biomass and a residence time of 1-h was chosen based on previous studies [7,11,14,16]. Torrefaction of YP at 300 °C yielded 52.66% TYP. Similarly, torrefaction of RM yielded 52.97% TRM. Torrefied and untorrefied forest residues were mixed with coal (1:1 basis by wt) to prepare coal-biomass (C + RM and C + YP) and coal-torrefied biomass (C + TRM and C + TYP) mixtures.

2.2. Sample characterization

Samples of C, RM, YP, TYP, TRM, C + TYP, C + TRM, C + YP, and C + RM were characterized for calorific value, proximate, ultimate, chemical analysis and thermal decomposition behavior.

Calorific value was measured using a bomb calorimeter (Model: 6300 Calorimeter, Parr Instrument Company, IL) according to ASTM D 5865 [17] standard at the WVU-Bioenergy Lab. Chemical composition, which includes cellulose, hemi-cellulose, lignin and extractives, was determined by the Agriculture and Environmental Sciences Lab, University of Georgia, Athens, GA. Neutral Detergent Fiber (NDF), Acid Detergent Fiber (ADF) and Acid Detergent Lignin (ADL) measurements were used to determine the content of cellulose, hemi-cellulose, lignin, extractives and ash. NDF, ADF and ADL were measured using an Ankom 200/220 Fiber Analyzer (Model: ANKOM Technology, NY). The residue that remains after digesting the samples in neutral detergent solution is called NDF. Usually the NDF residues are hemi-cellulose, cellulose and lignin. The residue that remains after digesting the sample with an acid detergent solution is called ADF. The ADF is usually cellulose and lignin. Finally, ADL is the residue, mainly lignin and ash, after ADF is dissolved in strong sulfuric acid. The formulas used for the determination of hemi-cellulose and cellulose mass fractions are:

$$\text{Hemi-Cellulose}\ (\%) = \text{NDF}\ (\%) - \text{ADF}\ (\%) \tag{1}$$

$$\text{Cellulose}\ (\%) = \text{ADF}\ (\%) - (\text{Ash}\ (\%) + \text{ADL}\ (\%)) \tag{2}$$

where Ash (%) was determined from proximate composition.

Proximate composition was measured according to ASTM D3174 [18] using a proximate analyzer (Model: TGA 701, Leco Corporation, St Joseph, MI). The proximate composition is comprised of moisture, volatile matter, fixed carbon, and ash mass fractions in the sample. In addition, the elemental composition was measured according to ASTM D3176 [19] standard using a dedicated CHNS analyzer (Model: Flash EA 1112, CE Elantech, Inc, Lakewood, NJ).

Thermo-gravimetric analyses (TGA) of the samples were done to assess their reactivity and thermal decomposition behavior using a TGA-FTIR system (Model: Q50, TA Instruments, Schaumburg, IL). The temperature range during TGA was 30 °C–950 °C with a heating rate of 10 °C/min. Nitrogen gas was passed at a flow rate of 50 ml/min to maintain an inert atmosphere. The volatiles evolved during the TGA tests were analyzed using on-line FTIR to determine functional groups in the chemical compounds produced during thermal decomposition.

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