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Enhancing biomass + coal Co-firing scenarios via biomass torrefaction and carbonization: Case study of avocado pit biomass and Illinois No. 6 coal

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ABSTRACT

Co-firing of biomass with coal is a short-term solution to increase renewables in energy generation portfolios. Fuel blending uses existing infrastructure for coal combustion to reduce economic costs and net CO₂ and SO_x emissions. However, the lower heating value and higher reactivity (at lower temperatures) for raw biomass than coal could lead to fuel segregation, resulting in burn-out at lower temperatures, loss of steam generation efficiency, and fouling. To probe whether torrefaction/carbonization may solve issues related to fuel segregation, this study analyzed the possibility of co-firing a series of avocado biomass samples carbonized at 200, 300, 400, 500 and 600 °C, with Illinois No. 6 coal. Overall, the H/C ratio and average activation energy of oxidation of the biomass decreased as pyrolysis temperature increased, while surface area and higher heating value increased. Low temperature pyrolysis (300 °C) produced a biochar with similar characteristics to the coal, virtually eliminating fuel segregation as noted through derivative thermogravimetric curves with singular peak reactivities. As carbonization temperature increases, the energy input required to carbonize the biomass increases, and there may be issues with reverse fuel segregation, where the biomass begins to resemble a much higher rank coal than often available in the United States.

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1. Introduction

Worldwide, pulverized coal-fired boilers blend biomass in varying proportions with coal to reduce fuel costs, lower net CO₂ and overall SO_x emissions, reduce the quantity of landfilled organic waste, and increase the sustainability of electricity production. Biofuels are often used to achieve a better control of the burning process; in co-combustion they are known to increase the volatile matter content, providing a more stable flame [1,2]. At the same time, ash deposition and fouling on hot surfaces are frequently

encountered with the combustion of raw biomass [3], especially in combustors designed for pure coal combustion [4]. Biomass' higher proportion of oxygen and hydrogen to carbon atoms results in a lower heating value as compared to coal, as breaking the C–H and C–O bonds of biomass releases less energy than the predominately C–C bonds of coal. In addition, the higher oxygen content of biomass enhances its reactivity as compared to coal, lowering its activation energy barriers to devolatilization and oxidation [5]. This can lead to segregation of fuels during the co-firing process [6]. When fuels segregate, there is the potential for the creation of hot spots in the combustion reactor due to the uneven burning of volatile matter, which results in decreased combustion efficiency and increased emissions of CO and hydrocarbons [6,7].

One possible solution to the thermal mismatch between coal and raw biomass is to torrefy the biomass by heating it in a low temperature (200–300 °C) inert atmosphere [8]. However, while

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torrefied biomass does condense the carbon structure of the biomass, some torrefied samples display thermal reactivities and profiles that are quite similar to the parent biomass [9], whereas others are significantly different than the raw samples [10]. Our laboratory found that the derivative thermogravimetric curves of a commercial torrefied biomass and coal display peaks corresponding to the pure fuels' reactions, and that the initial decomposition peak was a linear function of the percent torrefied biomass in the blend. However, it was noted that the activation energy of oxidation was not a linear function of each fuel in the blend; there was a decrease in activation energy in an initial mass loss regime as the percent torrefied biomass in the blend increased, suggesting a form of synergism where the volatiles of the torrefied biomass may promote conversion of the coal [11]. As such, torrefaction likely decreases the level of fuel segregation, but may not entirely eliminate the thermal reactivity mismatch. Recent research suggests that torrefied biomasses must be optimally blended with coals to reduce the potential for slagging and fouling of boiler surfaces that occurs because of its lower ignition temperatures and thermal mismatch [12].

Carbonization of biomass – heating in an inert atmosphere (pyrolyzing) at higher temperatures (up to 600 °C) to condense the carbonaceous structure – was recently demonstrated by Haykiri-Acma et al. to reduce this segregation tendency in terms of mass loss characteristics and heat flow during oxidation [13]. Park et al. find that samples of woody biomass torrefied at 275 °C blended with coal display segregated behavior, whereas the same woody sample torrefied at 350 °C mixed with the same coal exhibit similar thermal profiles [14]. In their study, Du et al. show that burnout decreases linearly with increasing carbonization temperature of a series of biomass samples [15].

Carbonization yields a solid char residue with considerably lower reactivity, and increased higher heating value as compared to the raw biomass, more closely mimicking the structure and composition of (especially) low rank coals [5]. While there is a growing body of literature on the co-firing of torrefied biomass and coals [11,16–18], there is relatively little known about how the degree of carbonization impacts the segregation behavior of coal-biomass blends. In this study, we probe the degree to which torrefaction and carbonization improve the thermal profiles of a biomass-coal blend using thermogravimetric analysis, differential scanning calorimetry and combustion calorimetry. Torrefied and carbonized avocado pits were blended at 25, 50, and 75 wt% with Illinois No. 6 coal. Each fuel was characterized in terms of elemental and volatile/fixed carbon analysis to determine the impact of carbonization on fuel characteristics and blended fuel profile. The distributed activation energy model was applied to the raw and carbonized biomass, and biomass + coal fuel blends to determine the oxidation activation energy and the presence of any synergistic relationships between the fuels. This is one of the first systemic studies in the literature to explore how the composition (elemental and proximate analysis), heating value, and porosity of a raw biomass changes as it undergoes successively “harsher” pyrolysis conditions, going from low-temperature torrefaction to higher-temperature carbonization. We explore how these changes impact the thermal reactivity of the solid fuel and its blends with a well-characterized coal to shed light on how torrefaction/carbonization may reduce fuel segregation at certain conditions, and may well lead to reverse segregation as the biomass is increasingly carbonized.

2. Materials and methods

In 2011, the U.S. avocado production was over 220,000 tons (produced between Florida and California), and valued at

approximately \$492 million [19]. To identify biomass sources that limit long-range transport to consolidate fuel streams, we must identify sources that are concentrated in relatively small areas. The Calavo Growers of California run an avocado processing plant in Ventura County, CA, turning out more than 20 million pounds of avocado-based items a year, responsible for around 40% of worldwide commercial guacamole production [20], representing a viable source of this waste biomass material.

A sample of Illinois No.6 Coal (IL) from the Argonne Premium coal bank, particle size 47–75 μm, was available in house. It is a high volatile bituminous coal from the Illinois #6 (Herrin) seam.

2.1. Sample preparation

To insure a representative biomass sample, 20 Haas avocados (*Persea Americana*) were purchased from local grocery stores over the course of two months. The avocado pits were dried in an oven at 110 °C for 48 h then mechanically ground and sieved to yield a sample with $d_p < 125 \mu\text{m}$. Particle size is an important factor in these experiments. Basu et al. suggest that the mass and energy yields of torrefied biomass increase with particle length and are inversely related to particle diameter [21]. Peng et al. note a dependence of torrefaction rate on particle size, especially at higher temperatures [22]. Because the process of torrefaction and carbonization – and indeed pyrolysis and oxidation – are both heat and mass transport limited, we decided here to use the smallest particle size available to us to (1) reduce transport limitations, as demonstrated in prior work [23,24] and (2) to more closely mimic the co-firing scenario of pulverized coal boilers. As such, particles less than 125 μm were used, insuring that the Biot number (Bi) was considerably less than one (Equation (1)), in order to negate transport limitations caused by large particles.

$$Bi = \frac{hL}{k} \quad (1)$$

l is the particle's characteristic length (estimated here as the maximum particle diameter of 125 μm); h is the convection coefficient; and k is the thermal conductivity of the biomass. As an order of magnitude estimate, if we assume that the thermal conductivity of biomass particles range from 0.01 to even as high as 1.0 W/mK, and the convection coefficient ranges from 0.25 to 1 W/m²K [25,26], we find a Biot number in the conservative range of 3×10^{-5} to 0.1, allowing us to neglect internal transport resistances.

Torrefaction is usually considered to occur at temperatures up to 300 °C, and carbonization above that; both involve pyrolysis (heating an inert atmosphere) to initiate devolatilization of the solid sample [15]. A series of torrefied and carbonized avocado biomass samples were fabricated by placing the raw biomass in a porcelain boat and inserting the boat into a 2" tube furnace (MTI). The samples were purged in nitrogen flowing at 100 mL/min, and then heated to 110 °C at 10 °C/min, held 30 min (to drive off residual moisture) and then heated to 200 °C, 300 °C, 400 °C, 500 °C or 600 °C at 10 °C/min, and held at the maximum temperature for 30 min. Samples were cooled under nitrogen to prevent oxidation.

Fuel blends (with raw and treated biomass) were fabricated at 25:70, 50:50 and 75:50 biomass:coal ratios by weighing the solid samples to ±0.1 mg directly into glass vials to make at least 5 g of each mixture. The vials were mixed on a vortex mixer for several minutes to insure homogeneity.

2.2. Characterization of raw, torrefied and carbonized samples

Proximate analysis of all samples was performed on a Mettler-Toledo TGA-DSC-1 using 70 μL alumina crucibles. 5–10 mg of

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