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Co-combustion of brewer's spent grains and Illinois No. 6 coal: Impact of blend ratio on pyrolysis and oxidation behavior

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ABSTRACT

Co-combustion of locally available biomass in existing coal-fired power plants is an attractive option to increase the share of renewable fuels in the energy market with minimal capital investment. Utilizing existing coal-fired combustion equipment for blends requires knowledge of pyrolysis and combustion characteristics. This study presents thermal evolution profiles (decomposition rates, apparent activation energies and devolatilized compounds) of coal–biomass blends to probe the effect of blend ratios on pyrolysis and combustion behavior. The global rate of pyrolysis of Illinois No. 6 coal and brewer's spent grains (BSG) is a function of fuel composition, though analysis of evolved gases suggests the presence of both potential additive and synergistic interactions on a molecular level. For oxidation, a rapid decrease in peak conversion rate is seen as the percentage of BSG increases from 0% to 20%, becoming less pronounced as the percentage of BSG increases above 20%.

1. Introduction

Almost half of the electricity in the United States is generated by burning coal, a process that emits vast amounts of carbon dioxide and produces a flue gas laden with sulfur and nitrogen oxides [1]. The environmental impacts of the mining, transport, and combustion of coal, along with questions surrounding its future supply levels, have led to considerable research on alternative and renewable fuels, including biomass. Second-generation biomass feedstocks, comprised of agricultural wastes and organic byproducts, may provide a bridge between conventional fossil fuel sources and a renewable energy future. Given that much of today's electricity infrastructure is devoted to coal combustion, a likely avenue in the near future for biomass utilization is as a blended feedstock with coal.

While the low sulfur content of most biomass has the potential to reduce overall SO_x emissions, as well as net CO_2 emissions from a coal-fired power plant [1,2], the higher proportion of oxygen and hydrogen to carbon atoms in biomass does result in a lower heating value for biomass than coal [3]. However, the higher oxygen content of biomass also tends to give it a higher reactivity than coal, and thus a lower activation energy barrier to devolatilization and oxidation [4,5]. Ash deposition from the combustion of pure biomass streams results in fouling and slagging on heat exchanger surfaces in the boilers [6]. To overcome the issues associated with pure biomass combustion, existing pulverized coal-fired boilers across the world blend biomass in varying proportions with coal. Optimizing operating conditions for such fuel blending requires a greater understanding of the thermal characteristics and combustion kinetics of coal–biomass blends [7,8]. Currently, much of the research on coal–biomass blends originates from Europe and Asia on coals of regional origin with varying volatile and chemical compositions, blended with biomass specific to those regions, such as palm oil in Malaysia [9] and olive kernels in Greece [10]. In the Northeast region of the United States, readily available biomass includes forest and agricultural byproducts and industrial organic waste, including spent barley and hops from local breweries. Brewer's spent grain (BSG) is 85 wt.% of the total by-product generated in the brewing process and is produced year-round by breweries across the country [11].

Our focus on a locally available biomass source such as BSG is intended to mitigate the long-range transport of fuels (thereby decreasing both the cost and carbon footprint of the fuel). There are 16 commercial breweries in the state of New Hampshire alone, three of which are located in Portsmouth, near Schiller Station, a 150 MW station with two 50 MW coal-fired boilers. While BSG exits the brewing process as a wet stream, in many cases the wastewater produced may not be discarded. Breweries, such as Redhook Ale Brewery in Portsmouth and Anheuser-Busch Brewery in Merrimack, NH, use microbes to treat the water, producing methane. This methane could be used as a heat source to dry the solid BSG on-site for transport to a local coal-fired power plant.

Like coal, biomass is a carbonaceous fuel that will undergo a series of steps from pyrolysis to oxidation. Pyrolysis—the thermal decomposition

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of a solid in the absence of oxygen—is rapidly gaining attention itself as a thermochemical conversion process to obtain fuels from biomass [12–15]. Pyrolysis is also the first step in thermochemical conversion via oxidation [10]. The volatiles released during pyrolysis undergo oxidation within the gas layer surrounding the particles. The char remaining after the pyrolysis and ensuing volatile combustion is essentially fixed carbon; when the volatiles are exhausted, oxygen will diffuse towards the char surface and combustion ensues. Because the composition of biomass varies from source to source, a blanket reactivity profile for the pyrolysis and oxidation of a specific lignocellulosic biomass material is not applicable across all biomass types. On a dry basis, barley straw contains approximately 20% hemicellulose, 33% cellulose, 17% lignin, 2.2% ash, and the remainder of proteins and fat [16]. For comparison, wood contains 39–41% cellulose, 24–35% hemicellulose, and 20–28% lignin on a dry basis [17].

Although each type of biomass exhibits different thermal decomposition profiles, the pyrolysis of biomass generally yields global activation energies within similar ranges. When analyzed using the Arrhenius method under a first order global reaction scheme, most biomasses show three distinct devolatilization regions (suggesting three distinct activation energies) with abrupt transitions, roughly corresponding to the hemicellulose, cellulose and lignin fractions of the biomass. The pyrolysis of hemicellulose occurs approximately between 220 and 315 °C, cellulose from 315 to 400 °C, and lignin over a range of 160–900 °C [18]. Grammelis et al. [19] find activation energies of the pyrolytic decomposition of the primary components (hemicellulose, cellulose, lignin) of waste paper biomass of 107–164, 198–232, and 30–48 kJ/mol, respectively, at a heating rate of 20 °C/min under the assumption of multiple degradation reactions occurring simultaneously with a summative reaction order of one. Also under a first order reaction scheme, our laboratory found activation energies of pyrolysis of cabbage palm biomass with ranges of 64–115, 67–152 and 19–25 kJ/mol for the same three fractions under heating rates ranging from 25 to 100 °C/min [20]. Interestingly, activation energies for the pyrolysis of coal–biomass blends fall into a similar range as those of pure biomass, with the activation energies increasing as the amount of coal increases, such as those noted by Vuthaluru [3] in the pyrolysis of a Collie subbituminous coal and wheat straw.

Under oxidative conditions, many analyses using the Arrhenius method find two decomposition regimes, corresponding to a lumped pyrolysis/oxidation of volatiles, and a second step for char oxidation. Gil et al. [5] studied the co-combustion of high-volatile bituminous coal blended with pine sawdust, suggesting that biomass combustion takes place in two steps over a low temperature range (200–490 °C), while coal combusted in a single step (315–615 °C); they found the co-combustion of these solid fuels to be additive, as three steps occurred during the process. Like pyrolysis, the activation energies of oxidation increased with increasing coal content in initial stages of degradation, however, Gil et al. did find that for a greater than 80 wt.% coal content, the kinetic parameters increase dramatically—more so than perhaps an additive scheme would suggest.

There is a question of synergistic (non-additive) effects occurring with blended fuel pyrolysis and oxidation reactions. Some groups find that the kinetics of pyrolysis and oxidation of blended biomass and coal are somewhat additive in nature, whereby each fuel contributes to the activation energy and peak devolatilization rates proportionally to the blend ratios [5,9,21,22]. Other studies suggest synergistic reaction chemistry during biomass–coal co-firing, lowering overall activation energies for the combustion of blends as compared to an additive scheme of coal plus biomass activation energies [23–25]. While biomass exhibits lower heating values than coal, it tends to release volatiles more rapidly during the pyrolysis stage of combustion, [23] and as such the overall decomposition profiles are necessary to determine the optimal blend ratio(s) for a given biomass and coal in co-combustion.

2. Materials and methods

2.1. Materials

One local source of biomass in Southeastern New Hampshire is the spent barley and hops from the many commercial breweries. To measure the reaction kinetics of this biomass and coal, brewer's spent grains (BSG) were collected from Redhook Brewery immediately following the malting process, dried in an oven at 105 °C overnight, then ground and sieved to < 125 μm. Illinois No. 6 coal was available in-house with a particle size < 44 μm. Between 5 and 10 g of each blend (90:10, 80:20, 50:50 coal/BSG by mass) were made by measuring the desired mass of each fuel to the 0.1 mg on a Shimadzu semi-mircobalance into a glass vial and mechanically agitating with a Scilogex vortex mixer. Ultimate analyses of each of these materials are given in Table 1.

2.2. Thermogravimetric analysis

The pyrolysis and oxidation kinetic measurements were performed on a Mettler Toledo TGA/DSC1, with data output from Mettler STARe Default DB V10.00 software. The mass was logged every second to the 10^{-8} g, along with time and temperature to ±0.1 K. Between 7 and 12 mg of each sample (pure biomass, pure coal, and three different blends) were placed in a 70 μl alumina crucible and thermally treated in a N_2 (pyrolysis) or air (oxidative) atmosphere, flowing at approximately 50 ml/min. The biomass samples were heated from 298 K to 383 K at 50 K/min, and held at 383 K for 60 min to remove any residual water. The temperature was ramped back down to 298 K at −10 K/min and held for 5 min. For the pure biomass samples, the temperature was increased to 1023 K at 100 K/min to simulate fast pyrolysis/oxidation (while maintaining experimental reproducibility) and held for 5 min to insure that the reactions were complete (reactions were all complete before this temperature was reached) as a terminal mass is critical to determining the kinetic parameters. The coal and the biomass–coal blends were pyrolyzed/oxidized in the TGA through the same process, but up to a temperature of 1173 K to ensure complete decomposition of the coal. Each thermal treatment was repeated a minimum of three times per sample to insure reproducibility.

There are several factors to consider when describing the reaction kinetics for the combustion of biomass with coal. To overcome potential heat and mass transfer limitations, much research on biomass/coal kinetics has been performed at slow heating rates (<10 K/min). However, this does not model the rapid combustion processes in an industrial coal boiler with heating rates up to 1000 K/min. In this study we employ a fast heating rate of 100 K/min to insure reproducibility within our data but expand available literature on the kinetics of thermochemical conversion processes. This is performed for both the pyrolysis and oxidation of BSG and BSG–coal blends; pyrolysis is often a rate-limiting step in combustion during which most volatiles are released from the solid fuel. It was observed by van de Velden et al. [26] that there are mass transfer limitations in the pyrolysis of larger particles as larger particles and higher heating rates cause a temperature gradient from the outside to the center of the particle; as such we elect to use very fine particles to mitigate potential mass transfer limitations within the

Table 1
Ultimate analyses of brewer's spent grain and Illinois No. 6 coal.

wt.% (dry)	Illinois No. 6 Coal	Brewer's spent grain
C	70.2	49.70
H	4.8	6.54
N	0.9	3.86
S	3.1	0.33
O	9.9	34.87
Ash	11.1	4.70
Moisture %	4.2	5.68