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Co-pyrolysis reaction rates and activation energies of West Virginia coal and cherry pit blends

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ABSTRACT

Bringing our society to a carbon-neutral, clean-energy future is an evolutionary process that must combine technological advances with available infrastructure. By co-firing biomass in existing coal-fired power plants, we can utilize standing equipment to increase the share of renewables in energy generation portfolios. This study investigates the pyrolysis behavior of blends of sweet cherry pit stones and a West Virginia coal using thermogravimetric analysis at a heating rate of 100 K/min under nitrogen to determine mass loss rates and global activation energies as a function of blend composition. Derivative thermogravimetric curves show two distinct peaks for the fuel blends at temperatures corresponding to peaks for the pure cherry pits and coal. The peak mass loss rates for blends are higher than predicted using an additive scheme at the lower temperature peak and lower than predicted at the higher temperature peak. Global activation energies determined using a first order Arrhenius equation were higher than predicted by a linear addition scheme at lower temperatures, and lower than predicted at higher temperatures, suggesting that the incorporation of the cherry pit biomass may promote devolatilization of the coal at lower temperatures.

1. Introduction

To increase the share of renewables in their energy portfolios and reduce their pollutant emissions, coal-fired power plants worldwide are co-firing biomass in varying proportions with coal [1]. This is especially useful when it comes to abating SO_x emissions that result from burning the highly sulfurous coals mined in the United States. In West Virginia, where coal mining is a driving factor of the state's economy, over 93% of the electricity generated comes from coal [2]. While this statistic is likely to remain high for the foreseeable future, one way to increase the use of biomass for energy generation in the immediate time frame is as a blended feedstock in coal-fired boilers. In this study, we look at the pyrolytic behavior of blends of a commercial West Virginia coal and sweet cherry pits using thermogravimetric analysis.

During the thermochemical conversion of coal and biomass, devolatilization can account for the majority of the solids' weight loss, depending on the organic constituents of the fuel [3,4]. The evolution of gaseous products and tars, and the formation of carbonaceous chars during pyrolysis, result from the depolymerization, vaporization and cross-linking of the solid fuel matrix. While both coal and biomass undergo pyrolysis as an initial (and often rate-limiting) step to eventual combustion, the rates and temperatures at which the reactions occur can be significantly different [5,6]. Moreover, when two solid fuels are blended, debate exists over whether or not the thermal devolatilization of the blend occurs as the independent summation of the reactions of both fuels, or if reaction synergies exist that promote the devolatilization of the solid having the more condensed structure (in this case, coal) because of reactions occurring in the more volatile component [7]. Some conclude that the rates and activation energies of pyrolysis of coal–biomass blends are the linear addition of each component's independent behavior, that is, that no interactions exist between the biomass and coal [8,9]. Others find evidence for synergistic reactions between the solids, negating a simple linear addition model for activation energies to predict blend behavior. This evidence comes in the form of non-additive natures of the kinetic parameters such as activation energies, and also the products formed upon of co-pyrolysis. Some groups find that the yields of specific volatile products are not proportional to the yields experienced upon pyrolysis of components separately [10–15]. The mechanisms underlying this behavior are unclear; Aboyade et al. [16] provide

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an excellent summary of potential explanations from throughout the literature, ranging from the promotion of demethoxylation reactions by inorganic matter in biomass to the larger H/C ratio in biomass preventing repolymerization and cross linking of free-radicals necessary for char condensation reactions.

Though biomasses examined across the literature demonstrate different thermal decomposition profiles owing to the specific organic constituents present, the pyrolysis of biomass generally requires global activation energies within similar ranges. When analyzed using the reaction rate constant method (first order reaction assumption of the Arrhenius equation) many lignocellulosic biomasses exhibit two or three distinct devolatilization regimes – abrupt transitions at temperatures specific to a given biomass – with each region having its own activation energy. For example, the pyrolysis of waste paper biomass at 20 °C/min shows three primary decomposition regimes with activation energies between 107–164, 198–232, and 30–48 kJ/mol for each region [17]. Similarly, our laboratory found three decomposition regimes for the pyrolysis of cabbage palm biomass ranging from 64–115, 67–152 to 19–25 kJ/mol at heating rates ranging from 25 to 100 °C/min [4]. What is especially interesting is that similar activation energies have been found for the pyrolysis of coal–biomass blends, though with activation energies increasing as the amount of coal increases [18,19]. Though blending biomass with coal is fiscally and environmentally advantageous, and industrially efficient (in co-firing scenarios biomass can increase flame stability due to its higher volatile content [20]), a general consensus on the kinetic behavior of coal–biomass blends has yet to be formed in the literature. Various schemes are proposed to predict the thermal behavior of the blending of biomasses and coal, including parallel reactions and parallel–series reactions (i.e. [21,22]) and simple linear combinations of the individual components behavior (i.e. [5,6]). Here we probe if such a simple summation of the individual behavior of a coal and biomass accurately predicts such a mixture's behavior, and explore the implications of deviations from an additive scheme in terms of potential reaction synergies.

2. Materials and methods

2.1. Preparation of coal–biomass blends

A West Virginia high-volatile bituminous coal (WV) was provided by Public Service of New Hampshire (PSNH), a Northeast Utilities Company, as part of a shipment received by PSNH Merrimack Station. Proximate and ultimate analyses as performed by the supplier are given in Table 1. Sweet cherry (*Prunus avium*) pits (CP) were collected after the fruit was consumed, washed to remove residual fruit and oven-dried at 110 °C to remove moisture before storage (to prevent molding). According to the U.S. Cherry Industry Administrative Board, the total 2013 production of U.S. cherries (sweet and tart) was over 130 million metric tons [23]. Approximately 25% of sweet cherries and 99% of tart cherries grown in the U.S. are used for processing and as such there are large quantities of fruit stones available as waste by-products [24].

The coal and biomass were separately mechanically ground and sieved to a particle size of 125–250 μm; van de Velden et al. showed that mass transfer limitations occur in the pyrolysis of large particles because of temperature gradients within the particle [25]. Our laboratory previously demonstrated no apparent effect of particle size (between 125–250 μm, 250–300 μm, and 300–500 μm) on activation energy of palm biomass up to 100 °C/min [4]. González et al. showed that the particle size, up to 1.6 mm, of cherry pit stones had relatively no influence on mass loss rates, suggesting that up to this size, heat and mass transfer limitations were not relevant and the pyrolysis was kinetically limited [26]. Approximately 10 grams of each blend (i.e. 90:10, 70:30, 50:50 *etc*. WV:CP by mass) were made by measuring the required mass of each fuel to the 0.1 mg on a Shimadzu semi-microbalance into a glass vial and agitating with a Scilogex vortex mixer.

Table 1
Proximate and ultimate analyses of West Virginia coal and cherry pits.

	WV coal[a]	Cherry pits[b]
Proximate analysis, wt% dry		
Volatile matter	38.74	81.00
Fixed carbon	53.40	16.30
Ash	7.86	2.70
	WV coal[a]	Cherry pits[c]
Ultimate analysis, wt% dry		
Carbon	75.71	53.41
Hydrogen	5.33	7.04
Nitrogen	1.42	0.30
Sulfur	3.33	0.30
Oxygen	6.25	38.05
Moisture	6.30	6.00
Higher heating value, kJ/kg		
	3.27E+04	2.29E+04

[a] Provided by PSNH from coal supplier.
[b] As measured in our laboratory by TGA in air up to 610 °C (volatiles) and 950 °C (fixed carbon/ash).
[c] As measured by Petrov et al. [42].

2.2. Thermogravimetric analysis

Each fuel and blend sample was pyrolyzed at least twice (a third sample was used if results differed by more than 5%) using a Mettler Toledo TGA/DSC1. Briefly, approximately 5 mg of each sample/blend was loaded into a 70 μL alumina crucible and pyrolyzed in high purity nitrogen gas with a total flow (reactive + protective gas) of approximately 50 mL/min The samples were heated from 25 °C to 100 °C at 50 °C/min, and held for 30 min to remove any residual moisture. The samples were then heated to 900 °C at 100 °C/min and held for sufficient time such that a steady mass plateau was reached to insure all material devolatilized. An accurate final mass is required to describe the kinetic parameters.

Much of the pyrolysis literature focuses on slow heating rates (1–10 °C/min); this does not model the rapid combustion processes in industrial boilers; unfortunately, a TGA cannot be operated at heating rates upwards of 1000 °C/min to mimic this process. As such, in this study we employ a fast rate of 100 °C/min to insure reproducibility and expand the literature on the pyrolysis kinetics of coal, biomass and their blends.

To analyze the peak mass loss rate(s), and temperature(s) at which pyrolysis occurs, we use derivative thermogravimetric (DTG) curves. First, we determine the extent of conversion, x, as a function of: initial mass (m_0), mass at any time t (m_t), and the final mass (m_f).

$$x(t) = \frac{m_0 - m_t}{m_0 - m_f} \tag{1}$$

The maximum rate of decomposition is obtained by plotting dx/dt versus T (absolute temperature), occurring as a peak where the slope equals zero.

Using the reaction rate constant method, widely applied to determine the activation energy and pre-exponential factor of biomass, coal, and coal–biomass blends, we determine the rate of reacted material with respect to time via:

$$\frac{dx(t)}{dt} = k(1 - x(t)) \tag{2}$$