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Impact of blend ratio on the co-firing of a commercial torrefied biomass and coal via analysis of oxidation kinetics



^a Department of Mechanical Engineering, Division of Materials Science & Engineering, Boston University, 15 St. Mary's St., Brookline, MA 02446, United States ^b Department of Chemistry, University of New Hampshire, 23 Academic Way, Durham, NH 03824, United States

HIGHLIGHTS

• Peak mass loss rate linearly proportional to torrefied biomass present in blend.

• Activation energy to start decomposition decreases as torrefied biomass increases.

• Combustion enthalpies linearly related to percent torrefied biomass present.

• Percent torrefied biomass has no noticeable impact on extent of char oxidation.

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ABSTRACT

Incorporation of torrefied biomass into coal-fired power plants could potentially lower the SO_x and net CO_2 emissions resulting from electricity generation. However, concerns over lower heating values and slightly higher ash content of torrefied biomass suggest that blending it with coal in industrial boilers may be preferable to complete fuel transition. By studying the oxidation kinetics of coal-torrefied biomass blends in a thermogravimetric analyzer at a heating rate of 100 °C/min, we find an additive nature among the fuels for peak mass loss rates and enthalpies of combustion. The activation energy required to initiate decomposition decreases from 132.6 to 77.6 kJ/mol as the torrefied biomass increases from 0 to 100 wt%, with a sharp decrease between 0 and 40 wt%. Data suggest that incorporation of torrefied biomass into coal-fired boilers is dependent on the ability to sacrifice heating value for the lower emissions of SO_x and net CO_2 garnered using bio-coal.

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1. Introduction

In 2008 coal accounted for almost 50% of the electricity generated in the United States, while other renewables – wind, solar, wood and wood derived fuels, geothermal and other biomass – accounted for a mere 3.1% of the total. While coal-fired power plants are often charged with being the world's primary anthropogenic source of carbon emissions to the environment (Gao et al., 2010), biomass has negligible sulfur content, is essentially CO₂ neutral, and can reduce the overall greenhouse gas emissions of an existing power plant (Baxter, 2005).

While the potential to lower SO_x and net CO_2 emissions via coalbiomass blending is an attractive quality of biomass (Al-Mansour and Zuwala, 2010), its higher proportion of oxygen and hydrogen to carbon atoms does lower the heating value of the fuel, as

* Corresponding author. Current address: Department of Mechanical Engineering, Division of Materials Science & Engineering, Boston University, 15 St. Mary's St., Brookline, MA 02446, United States. Tel.: +1 617 353 3883.

E-mail addresses: JillianLGoldfarb@gmail.com, JillianG@bu.edu (J.L. Goldfarb).

breaking the C-H and C-O bonds of biomass releases less energy than the predominately C=C bonds of coal. However, the higher oxygen content of biomass does lead to a higher reactivity than coal and thus a lower activation energy barrier to devolatilization and oxidation (Haykiri-Acma and Yaman, 2008). The heterogeneous nature of biomass often leads to ash deposition and fouling problems on hot surfaces with the combustion of pure biomass streams (de Jong et al., 2007). This, combined with the inherent problems of raw biomass (low bulk density, high moisture content, hydrophilic nature), issues with mill performance, and an infrastructure currently designed for coal, limits the complete changeover of all coal to biomass (Tumuluru et al., 2011). These issues can be reduced by co-firing coal-biomass blends (Haykiri-Acma and Yaman, 2008), and further mitigated by the blending of socalled bio-coal (torrefied biomass) with fossil coal (Agar and Wihersaari, 2012). Incorporation of torrefied biomass into coalfired power plant fuel streams may likely be done at higher blend ratios than raw biomass given the coal-like characteristics of torrefied biomass that lead to negligible decreases in energy efficiency and fluctuations in boiler load (Li et al., 2012).







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This paper presents an investigation of the oxidation kinetics of blending a commercial Venezuelan coal, currently used by PSNH (Public Service of New Hampshire; A Northeast Utilities Company), with a commercially available torrefied biomass from HM³ Energy, as part of a study to determine the feasibility of large-scale cofiring of a "typical" commercial torrefied product with a currently used coal. Torrefaction is a low-temperature (200-300 °C) pyrolysis process that, chemically speaking, reduces the oxygen and hydrogen to carbon ratios of a solid fuel to increase its energy density, grindability and hydrophobicity, while simultaneously reducing or eliminating biological activity, degradation, and spontaneous combustion (Rousset et al., 2011). By heating biomass in an inert atmosphere at low temperature, the solid fuel that results has physical and chemical properties between those of raw biomass and coal (Fisher et al., 2012). Torrefied biomass has 1–3 wt% moisture content (Bergman and Kiel, 2005), thereby reducing the costs associated with transporting water weight. and preventing biomass decomposition during transport and storage (Tumuluru et al., 2011). While a significant amount of work has been done to understand the impact of torrefaction process conditions on the products' properties, there is a relatively small body of literature available on the thermochemical behavior of torrefied biomass, and less on the blending of torrefied biomass with other solid fuels (e.g. Arias et al., 2008; Biagini et al., 2002; Bridgeman et al., 2008; Broström et al., 2012; Chen and Kuo, 2011; Couhert et al., 2009), even though biomass torrefaction is increasingly being considered as a pretreatment option for co-combustion with coal and other thermochemical energy extraction processes (Saddawi et al., 2012).

In the combustion of a solid fuel, the first step, pyrolysis, involves the release of moisture (if present) and volatiles from the solid fuel matrix. The volatiles released 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 follows. It is suggested that the torrefaction process essentially acts as a pre-combustion pyrolysis step, lowering the reactivity of higher heating rate chars (Fisher et al., 2012). Some debate exists in the literature as to whether or not the thermal decomposition curves of coal-biomass blends can be constructed as the sum of individual fuel contributions (Heikkinen et al., 2004) or if synergistic reactions occur among the fuels. Many agree that the pyrolysis behavior of coalbiomass blends is well represented by a linear addition of the biomass and coal components (Gil et al., 2010). However, this has not yet been proven to be the case for the behavior of coal-biomass blend oxidation or coal-torrefied biomass blend oxidation. Given the complex nature of combustion, some suspect that the presence of oxygen leads to gas-phase reactions with the volatiles released and combustion of char generated during solid degradation (Bilbao et al., 1997; Skodras et al., 2007). In the coal-torrefied biomass system, we have the potential for both homogeneous and heterogeneous reactions, leading to a more complete combustion (that is, the CO released via heterogeneous reactions can undergo oxidation in the gas phase) (Sami et al., 2001). As such, this investigation probes the impact of blend ratio on the global activation energies and combustion enthalpies of a series of torrefied biomass and coal blends.

Blending biomass with coal presents several fiscal and environmental advantages, including overall reductions in fossil fuel consumption, greenhouse gas emissions, and the amount of organic matter landfilled. However, designing an industrial combustion furnace and tweaking current operating conditions for blended feedstocks requires a greater understanding of the thermal characteristics and combustion kinetics driving coal-biomass blends (Munir et al., 2009; Shen et al., 2009). Though the reactivities measured in this study are at low temperatures as compared to small-particle industrial combustion applications, it is thought that the particles will be within the Zone II kinetics regime at the initial stage of char combustion, shifting to Zone I near 100% burn-out. As such, low temperature measurements are useful in studying the latter stages of burn out for industrial applications, though of course they cannot illuminate thermal annealing behavior of the char particles (Chan et al., 1999; Jones et al., 2012).

2. Methods

Like coal, biomass is a carbonaceous fuel that will undergo a series of steps from pyrolysis to oxidation. The less-condensed aromatic nature of biomass leads to vastly different temperature profiles than those for coal utilization. The design of an effective thermochemical conversion unit requires knowledge of the chemical composition, thermal behavior, and reactivity of the fuel in question. This study probes the global oxidation kinetics of Venezuelan coal, torrefied biomass, and varying blend ratios of these solid fuels using thermogravimetric analysis and bomb calorimetry.

2.1. Materials

The Venezuelan coal and the torrefied biomass (TB) pellets (produced by HM³ Energy; Gresham, OR, USA) samples were provided by PSNH in May 2012. HM³ Energy has demonstrated pilot plant scale operation to produce a commercial "TorrB" torrefied biomass sourced from urban wood waste, forest thinning, logging slash, and agriculture residue, in pellet and briquette form. Table 1 details the Venezuelan coal analysis as provided by PSNH and TB analysis as performed by Hazen Research (Golden, CO, USA). The coal and TB were each ground and sieved to a particle size less than 125 µm to insure that the Biot number was less than one, such that there are no transport limitations imposed by a large particle size. Varying mass ratio blends of the two fuels were fabricated by weighing each fuel directly into a glass vial on a Shimadzu semi-micro balance (±0.001 mg), followed by vortexing each vial for five minutes to insure a homogeneous distribution.

2.2. Activation energy measurements via thermogravimetric analysis (TGA)

The apparent, or global activation energies of oxidation were determined using a Mettler Toledo DSC/TGA-1; TGA is commonly used to assess the thermal decomposition profiles of coal and other solid fuels (Kök, 2001). Between 3 and 5 mg of each fuel or fuel blend were added to a 70 μ L alumina crucible to achieve a thin layer on the bottom of the pan to prevent mass transfer limitations from impeding activation energy calculations. All samples were heated to 110 °C and held for 20 min (until a constant mass at this

Table 1

Fuel analysis of Venezuelan coal (performed by PSNH supplier) and torrefied biomass (performed by Hazen Research, Inc., Golden, CO).

	Coal	Torrefied biomass			
Ultimate analysis (wt% dry basis)					
С	76.90	69.23			
Н	5.36	4.49			
Ν	1.35	0.32			
0	8.74	23.32			
S	0.64	0.08			
Cl	0.041	Not Reported			
Ash	7.01	2.56			
Total moisture (ar)	wt%				
	7.84	4.12			

temperature was obtained) to insure water removal. The fuels were subjected to heat treatment at a ramp rate of 100 °C/min up to 900 °C to mimic fast oxidation while maintaining experimental reproducibility under a constant flow of dry air at 50 cc/min. Given the dependence of the kinetic evaluation on terminal mass, samples were held at 900 °C until a stable mass was obtained to mimic the complete oxidation of the solid fuel to ash (including mineral decomposition that occurs at temperatures above 620 °C.) The sample mass was logged every second to the 10^{-8} grams, along with time and temperature to 0.01 °C. Each fuel and fuel blend was measured at least twice; if activation energies differed by more than 5%, a third sample was run.

When a solid fuel is oxidized it undergoes a complex series of chemical reactions, and as such its kinetics are represented by an apparent, or global, kinetic analysis (Burnham and Braun, 1999). This global reaction model accounts for not only multiple reactions occurring simultaneously, but also any transport limitations present, which were minimized by the small particle size and sample size used. The apparent oxidation energies of biomass and coal are often calculated by the Arrhenius equation under the assumption of overall first order reaction kinetics.

Using the mass loss as a function of time data obtained from the TGA, the extent of conversion, *x*, at time, *t*, *is given* as follows:

$$x = \frac{m_i - m_t}{m_i - m_c} \tag{1}$$

where m_i is the initial mass of the semicoke (following water removal), m_t is the mass at time t, and m_c is the mass of the semicoke following complete loss of the organic char portion of the semicoke. The rate of reacted material with respect to time is:

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

The rate constant k can obtained from the Arrhenius expression under the assumption that the oxidation of char is an overall first order reaction (Chen and Kuo, 2011):

$$k = Ae^{\frac{-2a}{RT}} \tag{3}$$

where *A* is the pre-exponential factor, E_a the activation energy, *R* the universal gas constant, and *T* the absolute temperature. The apparent activation energy of oxidation can be obtained by plotting the logarithmic conversion rate versus the inverse temperature, 1/T. The slope of the curve equals $-E_a/R$. Of course, the pre-exponential factor determined from the Arrhenius equation is assumed to be constant over the temperature range for which the Arrhenius plot is linear.

2.3. Heats of combustion determination via bomb calorimetry

The massic energies of combustion of TB, coal, and blends were measured using an adiabatic jacket static bomb calorimeter equipped with a twin-valve combustion bomb (Type 1108, Parr Instrument Company) with an internal volume of 0.340 dm³. The energy equivalent of the calorimeter was determined by standard procedure as described by Garland et al. (2003) from the combustion of benzoic acid (National Institute of Standards and Technology Standard Reference Material 39j). For all combustion experiments, samples in pellet form were ignited in oxygen at a pressure between 25 and 30 atm. The calorimeter temperatures were measured to $\pm(5 \cdot 10^{-4})$ K at time intervals of 10 s by a stainless steel temperature probe (Vernier) that is interfaced to a PC to acquire data through a Logger Pro program.

3. Results and discussion

Presented below is an analysis of the mass loss conversion profiles, global activation energies as determined by the Arrhenius equation, and combustion enthalpies of the torrefied biomass-Venezuelan coal blends. It is apparent that the conversion rates, energy required for conversion, and energy released from combustion of these blends are strong functions of the amount of each fuel present in a given blend. However, the nature of the relationship between different reaction descriptors and blend ratios is not the same.

3.1. Analysis of derivative thermogravimetric curves

From the TGA data, the conversion rates of the oxidation of torrefied biomass (TB) and coal blends are relatively proportional to the weight percent of each solid fuel present. Looking first at the derivative mass loss curves (DTG curves, Fig. 1), there are two primary stages of decomposition. From Fig. 1a, the TB decomposes at the highest rate around 355-360 °C, whereas coal decomposes at the highest rate around 595-600 °C. The peak mass loss rates of the first stage of decomposition of each blend are within ± 10 °C of that for the torrefied biomass. The shape of the torrefied biomass DTG curve agrees well with that found by Arias et al. (2008) for the oxidation at a heating rate of 15 °C/min of torrefied eucalyptus that had undergone full devolatilization of hemicellulosic components. Like Arias et al., the TB data presented here show a second stage of decomposition for the TB around 470-480 °C (Fig. 1a) whose mass loss rate is depressed when the coal is added into the blend (Fig. 1b).

With the incorporation of coal into the TB, the shape of the DTG curves reflect an amalgam of both fuels; maximum DTG values for the first stage are linearly proportional to the amount of TB present in the blend, as seen in Fig. 2, a plot of the peak mass loss rate between 340 and 355 °C as a function of fraction TB. The y-axis of Fig. 2 is the point at which dx/dt is at a maximum during the first stage of decomposition, representing the highest rate of conversion.

Combustion and co-combustion DTG curves for coal, manure, and their blends at 5 °C/min presented by Otero et al., (2011) show considerably sharper, smoother peaks with higher peak conversion rates, likely a factor of the slower heating rate. Though the characteristic shape of the DTG curves for the manure/coal blends are different, Otero et al., also see two oxidation zones for biomass. In Fig. 1b it appears that this second stage exists between 575 and 590 °C for the coal and coal-TB blends; it is attributed primarily to char and coal oxidation. The first derivative peak for solid fuel oxidation is often attributed to the devolatilization and subsequent oxidation of the light organic volatiles, followed by a second stage for oxidation of the char (Zheng and Koziński, 2000), which in this case overlaps with the primary coal oxidation peak. This overlap underscores the inherent complexity in analyzing the kinetics of thermal decomposition of torrefied biomass-coal blends: though TB is similar in heating value, moisture content, energy density and other physical properties to coal, thermogravimetric experiments alone can only describe the global reaction kinetics; they cannot differentiate between specific reactions occurring simultaneously. However, thermogravimetric analysis is useful for determining an overall activation energy, and for assessing the impact of blend ratio on global oxidation behavior to assist in specifying blend ratios for industrial boilers.

3.2. Determination of global activation energies

Gil et al. (2010) use a two-stage reaction kinetics model for the thermal decomposition of coal-biomass blends in oxygen,



Fig. 1. (a) Derivative mass loss peaks for (•) coal, (×) torrefied biomass; (b) derivative mass loss peaks for (•) coal, (×) torrefied biomass, and blends of (°) 9.5, (♦) 29.9, (□) 61.4 wt% torrefied biomass in coal.



Fig. 2. Peak mass loss oxidation rate of first decomposition stage (between 340–355 $^{\circ}\text{C})$ as a function of percent, by mass, torrefied biomass in coal.

consisting of two independent reactions. In the first reaction, the solids react with oxygen to form char and gas, followed by a second stage where the char undergoes further oxidation to yield gas and ash. The authors suggest that the two separate reactions are governed jointly by a first-order Arrhenius equation. Using a high-volatile bituminous coal and pine sawdust blend, they find three stages of decomposition at distinct temperature regions corresponding first to the oxidative degeneration of the biomass (release and burning of volatiles), then to the combustion of char, and then to the final stage attributable to coal combustion. The peak temperature was equal for each stage no matter the blend ratio, though as the percentage of biomass increases, the maximum rate of mass loss increases for the first stage and decreases for the second and third stages (Gil et al., 2010). As discussed above, these

experiments yield similar results in the DTG curves, though the second and third stages described by Gil et al., are somewhat indistinguishable in Fig. 1, perhaps because of the condensed coal-like structure of the torrefied biomass as compared to the pine sawdust biomass used by Gil et al., However, it is through the Arrhenius plots of the coal-TB blends that distinct thermal decomposition regimes occurring over discrete temperature ranges are noted.

Fig. 3a presents the Arrhenius plot for 23.4% TB in coal oxidized at 100 °C/min, with each mass loss regime clearly identified in Figures 3b-e. For each pure fuel and blend used in this work, at least two experiments were run to generate at least two Arrhenius plots for each sample. The Arrhenius plots generated (and hence the mass loss rates and corresponding temperatures) were virtually identical across each repetition; activation energies calculated from the slopes of the mass loss regimes were repeatable within ± 5%. Table 2 reports the temperate range, fraction of sample converted, activation energy and pre-exponential factor over each mass loss regime. A 95% confidence interval was calculated for the activation energy. Each fuel or fuel blend was held at 900 °C until a steady final mass was reached; this resulted in an overall sample loss of between 83 and 93 wt% for all samples, as detailed in Table 2. Samples visually examined after oxidation were graybrown in color with no evidence of residual carbon remaining. There is no overall trend in total sample oxidized as a function of TB, suggesting that the extent of char oxidation for these two fuels is not dependent on blend ratio.

There are three separate mass loss regimes for the oxidation of coal and four each for the oxidation of torrefied biomass and TB + coal blends, as determined by the discrete changes in slopes of the Arrhenius plots as shown in Fig. 3. The first two of these regimes for every sample shows that no more than 8 wt% of the total sample mass is lost across these two regimes combined. And indeed, the first mass loss regime has, on average, the highest activation energy of all regimes, suggesting that these initial stages are a barrier to initiating devolatilization, rather than oxidation of volatiles or char. As noted by Haykiri-Acma and Yaman (2008) biomass has lower activation energy to initiate pyrolysis, on average, than coal; the data on TB and coal agree and go a step further, showing a sharp decrease in activation energy in the first mass loss



Fig. 3. Arrhenius plot for oxidation of 23.4% TB in coal at 100 °C/min (a = full temperature range; b = mass loss regime 1; c = mass loss regime 2; d = mass loss regime 3; e = mass loss regime 4).

Table 2

Apparent activation energies (with 95% confidence interval) of oxidation for coal-torrefied biomass blends as determined by the Arrhenius equation with associated mass loss fractions over each mass loss regime.

Mass loss regime 1					Mass loss regime 2						
wt% TB in coal	Fraction mas loss	ss Temp range/°C	Activation energy/ kJ/mol	Pre-exponent factor/s ⁻¹	ntial	Fraction mass loss	Temp range/°C	Activation kJ/mol	energy/	Pre-expo factor/s	nential
0.0	0.01	157-176	132.6 ± 5.9	3.1E + 13		0.02	178-246	33.4 ± 2.8		61.6	
8.5	0.01	164-196	112.3 ± 6.4	4.5E + 10		0.02	206-276	23.9 ± 0.4		5.3	
9.5	0.02	152-198	107.5 ± 4.7	1.9E + 10		0.02	211-286	22.8 ± 0.5		5.1	
23.4	0.01	153-188	96.3 ± 4.1	3.9E + 09		0.03	196-297	23.2 ± 1.5		5.0	
25.8	0.03	156-193	95.3 ± 3.5	7.2E + 08		0.04	205-301	25.4 ± 0.2		7.7	
29.9	0.01	159-198	90.1 ± 3.5	2.0E + 08		0.04	205-295	24.9 ± 1.1		9.8	
37.7	0.01	161-198	85.5 ± 3.4	3.6E + 07		0.02	203-301	26.0 ± 0.2		10.5	
45.2	0.01	152-185	81.8 ± 2.7	1.3E + 07		0.02	209-282	23.5 ± 0.5		3.7	
61.4	0.01	169-192	78.8 ± 1.7	8.8E + 06		0.02	204-287	30.8 ± 0.1		37.8	
100.0	0.04	154-222	77.6 ± 2.6	8.0E + 06		0.10	227-315	32.5 ± 1.2		74.3	
Mass loss re	egime 3			Mass loss re	gime 4				Total sam	ple mass	wt% TB in
Fraction mass loss	Temp range/°C	Activation energy/kJ/mol	Pre-exponential factor/s ⁻¹	Fraction mass loss	Temp range/°C	Activation Energy/kJ/n	Pre-e nol Facto	exponential or/s ⁻¹	loss/wt% co		coal
0.89	291-689	44.9 ± 2.1	2.9E + 02						93		0.0
0.03	307-332	50.0 ± 0.7	1.1E + 03	0.81	346-681	39.0 ± 0.2	131.	3	86		8.5
0.07	290-366	55.0 ± 2.4	3.4E + 03	0.74	368-699	38.2 ± 1.7	131.	1	84		9.5
0.08	299-354	68.8 ± 1.3	6.9E + 04	0.82	361-702	30.3 ± 0.4	44.	1	93		23.4
0.14	302-356	69.7 ± 3.1	8.3E + 04	0.70	354-706	29.3 ± 0.5	38.	2	90		25.8
0.11	299-360	69.2 ± 2.1	7.5E + 04	0.65	364-641	29.0 ± 0.5	40.)	83		29.9
0.09	307-357	72.5 ± 5.5	2.9E + 05	0.75	364-638	24.8 ± 2.2	29.)	90		37.7
0.14	299-329	63.4 ± 0.7	1.5E + 04	0.73	366-679	38.0 ± 0.1	100.)	91		45.2
0.22	308-360	84.6 ± 0.9	2.5E + 06	0.68	356-623	20.9 ± 0.1	15.	7	86		61.4
0.31	319-370	85.9 ± 1.3	4.1E + 06	0.51	377-538	18.8 ± 1.4	16.	4	93		100.0

regime as the weight percent of TB increases, leveling off after the majority of the blend consists of TB, as shown in Fig. 4. As noted by Gil et al. (2010), the addition of biomass to coal lowers barriers to devolatilization. As biomass combustion often ensues in the gas phase, its activation energies are lower because of the propensity for the predominantly heterogeneous C-H and C-O bonds of biomass (versus C=C bonds of coal) to devolatilize from the more porous nature of biomass. Gil et al., find that blends of 50 and 80 wt% biomass in coal show similar E_a and A values to pure biomass (103.2, 102.0, 102.3 kJ/mol for 50, 80 at 100 wt% biomass, respectively over stage 1, and 224.1, 217.4, 236.1 kJ/mol in stage 2), similar to the trend in activation energies encountered here for torrefied biomass and coal blends.

The majority of each sample's total mass loss occurs in the final mass loss regime (3rd for coal, 4th for TB and blends). Chao et al. (2008) use thermogravimetric and differential thermal analysis of coal, rice husk and bamboo oxidized at 5 °C/min to show that the energy resulting from biomass combustion results from the reaction of volatile matter, whereas the energy from coal comes from char oxidation. However, in the case of torrefied biomass, it appears plausible that a higher proportion of energy released from oxidation results from the oxidation of the solid char. Given that torrefied biomass has a higher energy density, a more condensed structure, and overall more coal-like characteristics than raw biomass, this is not surprising.

There is much debate in the literature as to whether or not solid fuel blending results in "additive" or "synergistic" effects in terms of activation energies and enthalpies of combustion. An additive nature – where the blend's thermodynamic or kinetic property is a sum of the individual fuels' contributions – clearly describes the peak mass loss rates, which are a linear function of weight percent of torrefied biomass (Fig. 1) and approximates the heats of combustion (Fig. 5). In a recent paper, Lu et al. (2013) find little evidence of synergistic reactions in the co-pyrolysis of their own torrefied wood (TW) and anthracite coal blends. Interestingly, their pyrolytic activiation energies of wood torrefied at 250 °C and coal blends decrease (from 108.68 to 80.50 kJ/mol) as the percent TW decreases from 100 to 25 wt% in the second stage reaction and increase in the third stage reaction from 5.62 kJ/mol at 75 wt% to 23.72 kJ/mol at 25 wt%. Conversely, in the co-oxidation of the Venezuelan coal with torrefied biomass, in the first reaction stage the activation energy decreases from 132.6 to 77.6 kJ/mol as the fraction of coal goes from 100 to 0 wt%, without a clear trend observed in the second reaction stage.



Fig. 4. Activation energy of oxidation as a function of percent, by mass, torrefied biomass in coal over mass loss regime 1 (\bullet); mass loss regime 2 (\blacksquare); mass loss regime 3 (\blacklozenge); mass loss regime 4 (\Box).



Fig. 5. Heat of combustion as a function of percent, by mass, torrefied biomass in coal as determined by bomb calorimetry.

Such a linear relationship is not observed for the activation energies of each fuel and blend observed in this paper. As mentioned above, there is a sharp decrease in the activation energy for the first mass loss regime as the percent TB increases, indicative perhaps of a "synergistic" scheme in which the volatiles of the torrefied biomass are likely releasing first, which may promote pyrolysis of the coal. The activation energies of the second and fourth mass loss regimes are within 20 kJ/gram of each other, with no distinct trend related to TB content. The activation energies of mass loss regime three increase sharply as the TB content exceeds 20 wt%, and level off (in a similar fashion to mass loss regime one) after TB content exceeds 60%, suggesting perhaps a slight synergism in terms of TB's impact on the oxidation of volatiles in this mass loss regime. Overall, though there is not an "additive" scheme present in terms of activation energies, the mechanisms behind a global reaction synergism remain elusive.

The pre-exponential factor (frequency factor, A) depends on the collision frequency of molecules during a reaction and is therefore tied to a material's structure; *i.e.* the number of molecules present in a given volume (Yorulmaz and Atimtay, 2009). In Table 2, it is noted that A decreases sharply as the percent TB increases in mass loss regimes one and four, while increasing in mass loss regime three as TB percent increases. There is no clear trend in A over mass loss regime two. The frequency factors are greatest (by several orders of magnitude) in mass loss regime one, corresponding to the highest activation energies for every sample, but the lowest overall mass loss. A is (according to Collision Theory) strongly dependent on the concentration of reactants while only mildly dependent on temperature. This suggests that one should see

Table 3			
Heats of combustion	for torrefied	biomass-coal	blends

Mass fraction TB in coal	m _{sample} / g	m _{fuse} / g	T _i /K	$T_{\rm f}/{ m K}$	$\Delta T/K$	$\Delta U_{\rm fuse}/J$	$\Delta_c U/$ (kJ g ⁻¹)
0	0.6118	0.0050	295.625	297.393	1.768	29.29	28.85
0.388	0.7735	0.0127	294.106 294.668	296.231 296.487	2.125 1.819	74.39 70.88	27.38 24.74
0.625	0.6946	0.0107	295.299	296.975	1.676	62.68	24.04
1	0.6802	0.0117	294.574 294.925	296.184	1.306	68.53	24.28

decreasing pre-exponential factors as the fuels go from mass loss regime one to four as the concentration of potential reactants continuously decreases. However, A is orders of magnitude higher in mass loss regime three than in two or four, yet the majority of mass is lost (for TB and blends) in regime four (Table 3).

4. Results summary

Though the total mass loss across each sample in the low temperature mass loss regime is quite small - no more than 4 wt% - the activation energies and pre-exponential factors for each fuel and blend are the highest of all mass loss regimes. This high initial barrier to oxidation of the dry fuels is likely due to the initiation of pyrolysis, whereby degradation of the solid matrix and aromatic ring rupture lead to high activation energies. Because coal has a more condensed structure than torrefied biomass, there are higher activation energies as the percent coal in the blend increases. Mass loss regimes three and four (two and three for pure coal) likely represent the oxidation of volatiles released previously, and finally oxidation of the resulting char over a broad temperature range of \sim 300–700 °C. Overall, the percent TB in a blend reduces the activation energy to initiate thermal decomposition. Since the total mass lost during oxidation at 900 °C for each blend is not a function of TB content, the fraction of TB that can be cocombusted with coal is more a function of the decreased amount of energy available as TB content increases than kinetic parameters.

5. Implications of results

The incorporation of solid renewable fuels into conventional coal-fired boilers requires the ability to accurately predict the impact of co-firing on reaction rates and temperatures and thus overall process efficiency. Models for the co-firing of coal-biomass and coal-torrefied biomass blends abound in the literature; many assume a scenario whereby the coal and biomass contribute to the thermodynamics and kinetic properties in a manner directly proportional to each fuel present. The present results suggest that, at a global reaction level, this assumption is likely valid, such that the energy garnered and rate of production may be modeled as a function of the individual contributions of each fuel in the blend comprising the boiler load. Furthermore, evidence of potential reaction synergisms - as noted through disproportionate changes in activation energies across the blends - lead to questions surrounding the reaction mechanisms of solid fuel blending, which could have potential implications in the amount of CO, NO_x, and VOCs produced during co-firing.

6. Conclusions

Oxidation of a commercial torrefied biomass, Venezuelan coal, and their blends was carried out in a TGA at 100 °C/min. Peak mass loss oxidation rates (between 340 and 355 °C) increase linearly as the percent, by mass, of torrefied biomass in the blend increases. The activation energy required to initiate thermal decomposition decreases sharply as the percent TB increases until ~40 wt%, when the activation energies level off around 80 kJ/mol. Activation energies for char oxidation are not strongly dependent on the percent TB present. Heats of combustion decrease somewhat linearly as the percent of TB in blends increases.

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