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Second-generation sustainability: Application of the distributed activation energy model to the pyrolysis of locally sourced biomass-coal blends for use in co-firing scenarios

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HIGHLIGHTS

• Distributed Activation Energy Model applicable to coal-biomass blend pyrolysis.

• Peak reaction rate at low temperatures linearly correlated with percent biomass.

• As biomass in blend decreases, additive prediction of activation energy less applicable.

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ABSTRACT

While first generation biofuels paved the way for a vision of a renewable energy future, their competition for arable land limited widespread applicability. Second generation fuels, made from a variety of carbonaceous wastes, are considerably more "sustainable" in a land competition sense, but require a higher degree of processing to extract energy. Here we extend the idea of second-generation sustainability by investigating blends of coal and biomasses found within 20 miles of coal-fired power stations in the Northeast United States for use in co-firing scenarios that would limit long-range transport of biomass. A commercial high volatile bituminous Pennsylvanian coal was blended at 90. 80. and 50 wt% with one of three biomasses: feed corn stover from a local farm, brewer's spent grains from Redhook Brewery, or cocoa shells from the Lindt chocolate factory. The Distributed Activation Energy Model was applied to analyze the pyrolysis kinetics of the solid fuels and blends, yielding activation energies as a function of mass fraction conversion ranging from 304 to 522 kJ/mol for coal, 164 to 304 kJ/mol for the biomasses, and 218 to 530 kJ/mol for the coal-biomass blends. Overall, the peak reaction rates and temperatures for the primarily biomass decomposition stages were linearly correlated with the percent biomass in the blend. Such an additive scheme did not represent the blends' kinetics, instead over-predicting the activation energies. Synergy was noted between the fuels, in that the biomass does appear to be promoting the devolatilization of the coal at lower temperatures.

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1. Introduction

Bringing our society to a carbon-neutral, clean-energy future is an evolutionary process combining scientific advances with available infrastructure to overcome economic, policy and technological barriers. Second-generation biomass feedstocks – agricultural waste and organic byproducts – may be blended with other solid fuels or utilized as separate fuel. Given the high percentage of electricity produced from coal, and an infrastructure already in place, a

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http://dx.doi.org/10.1016/j.fuel.2015.07.071 0016-2361/© 2015 Elsevier Ltd. All rights reserved. viable avenue in the immediate future for drop-in biomass utilization is as a blended feedstock in coal-fired boilers [1]. According to PSNH (Public Service of New Hampshire), 15% of New England's electricity is generated from coal [2]. This number jumps to 42% in Pennsylvania and 93% in West Virginia, where coal mining is a primary engine of that state's economy [3]. By blending in locally available biomass sources, we reduce long-range transport of fuels (further reducing net CO₂ emissions), overall coal consumption, and the amount of organic waste sent to landfills. However, much of the work on coal-biomass blending to date originates outside of the United States on biomass sources not widely cultivated in the U.S. (palm oil in Malaysia [4], olive kernels in Greece [5]) or coals





not available in the country [6]; our focus here is specifically to look at biomass waste available in the Northeastern United States combined with a domestic coal, and, more broadly, to gauge the applicability of the Distributed Activation Energy Model to describe the activation energies required to initiate the pyrolysis of blended coal-biomass streams, and the potential presence of synergistic behavior between the solid fuels.

At the PSNH Merrimack Station coal-fired power plant, the wet flue gas desulfurization system is not sufficient to scrub the SO_{x} emitted from burning only U.S. East Coast coal. To reduce overall sulfur emissions, PSNH imports up to \$79 million (of the \$133 million spent on coal in 2008) worth of low-sulfur coal from Columbia and Venezuela. While 59.4% of the state's coal budget was spent on these international coals, this represented only 50.5% of the total 956.1 tons burned in the state. In Massachusetts. \$42 million was spent in 2008 on domestic coal, compared to \$206 million on coal from Columbia [7]. For many, this importation represents a politically unattractive, economically inefficient allocation of resources, and one that could be offset by using blended biomass-coal streams in co-fired boilers. As Sami et al. remind us, "The potential for successful application of co-firing is site-specific. It depends upon the characteristics of the power plant being considered, the availability and price of biofuel within 50–100 miles[s] of the plant and the economic value of environmental benefits" [8]. By seeking out local sources of biomass - cocoa shells from the Lindt Chocolate factory in Stratham, NH, spent barley from Redhook Brewery in Portsmouth, NH, and feed corn stover from the Coppal House Farm in Lee, NH, all within 20 miles of a PSNH coal-fired electricity generation facility - we can improve the economic viability of biomass by reducing transportation costs as well as fuel costs. Investigating a variety of sources at different co-firing ratios is critical to mitigate seasonal availability and shifts in industrial production of biomass wastes. Blending this biomass with domestic coal could reduce SO_x emissions and curtail reliance on foreign coal sources while bringing electricity generation closer to a carbon-neutral future.

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 different temperature profiles than those for coal. The design of an effective thermochemical conversion unit requires knowledge of the chemical composition, thermal behavior, and reactivity of the fuel. Solid devolatilization, or pyrolysis, is the first step in thermochemical conversion [5]. Pyrolysis temperatures vary according to fuel composition, but overall are considerably lower for biomass than for coal. As a solid fuel is pyrolyzed, the volatiles released undergo oxidation within the gas layer surrounding the particles. The char remaining after pyrolysis is essentially fixed carbon; when the volatiles are exhausted, oxygen will diffuse toward the char surface and combustion ensues. In coal conversion, devolatilization can account for up to 70% of a coal's weight loss and is highly dependent on the organic constituents of the coal itself [9]; this increases beyond 80% for biomass [10]. In this study we focus on the pyrolysis of biomass-coal blends, as pyrolysis is often a rate-limiting step in the volatiles oxidation of solid carbonaceous fuels and determines the lag time for char oxidation to commence, as char oxidation cannot occur until pyrolysis is virtually complete [11].

A large body of work from the last century focused on developing kinetics models for the pyrolysis of coal, and the early 2000s brought a surge in our understanding of the behavior of alternative fuels, including a variety of biomass. While there are a number of studies on the kinetics of biomass materials, relatively few studies exist on coal-biomass blends [5]. The limited body of literature does agree on several points, specifically that coal-biomass blends display increasing derivative weight loss peaks for thermal evolution profiles as the percentage biomass increases, and that increasing the biomass content in a given blend decreases the fixed carbon content. However, debate exists over whether or not the thermal devolatilization curves of coal-biomass blends can be constructed as the sum of individual contributions [12]. Many suggest that the pyrolysis behavior of coal-biomass blends is well represented by a linear addition of the biomass and coal components [13–15], whereas others show evidence for synergistic reactions between the fuel components, making simple linear addition models of activation energies inaccurate to predict blend behavior [16,17].

Blending biomass with coal presents fiscal and environmental advantages, including the overall reduction of fossil fuel consumption, greenhouse gas emissions, and the amount of organic matter landfilled. Biomass is often used to achieve a better control of the burning process: in co-combustion it increases the volatile matter content, providing a more stable flame, and many sources have ash contents lower than coal, reducing waste and increasing efficiency [18,19]. While the overall trends that our worldwide counterparts have found are reasonably applicable to our energy generation systems, the U.S. uses different coals and produces different agricultural waste streams than those used in the literature to date, potentially leading to differences in activation energies, optimal heating rates, and peak devolatilization temperatures. In addition, few of the studies done on coal-biomass blending (to date) analyze the applicability of the oft-used Distributed Activation Energy Model as it applies to mixed coal-biomass streams.

2. Materials and methods

2.1. Materials

To test the applicability of the DAEM to describe coal-biomass blend pyrolysis, we obtained three different biomass samples and one domestic coal sample. To maintain the second-generation sustainability goal, the biomass sources were all within 20 miles of power stations.

2.1.1. Pennsylvania coal

We obtained a commercial U.S. high-volatile bituminous coal sample from PSNH (from Pennsylvania, PA). The PA coal was used by PSNH Merrimack Station.

2.1.2. Cocoa bean shells (CBS), Lindt Chocolate, Stratham, NH

In 2009, PSNH test-fired cocoa bean shells (CBS) from the nearby Lindt USA factory in their 50 MW pulverized coal boilers; they are now permitted to co-fire up to 8 wt% CBS. The CBS exit the chocolate process as a fairly dry stream – samples obtained from Lindt Chocolate after removal of the cocoa nib showed moisture content between 8 and 11 wt% – and as such can be co-fired as received. According to the World Cocoa Foundation, total cocoa production was up 8.73% from 2008 to 2012, with 400 tons of cocoa beans ground and processed in the United States in 2011–2012, representing approximately 10% of the world's grindings [20].

2.1.3. Brewer's spent grain (BSG), Redhook Brewery, Portsmouth, NH

In New Hampshire, there are 16 commercial breweries; the majority of them are located within 50 miles of a power plant. Though brewer's spent grain (BSG) is initially entrained in a wet stream, the water may not be discarded; many breweries (including Redhook and Anheuser-Busch Brewery in Merrimack, NH) anaerobically digest the water to produce methane, which can be used as a heat source to dry the solid BSG on-site prior to transport, year-round. According to the Beer Institute, U.S. brewers purchase approximately 4.8 billion pounds of U.S.-grown barley malt, 15

million pounds of hops, and 1.8 billion pounds of rice, corn and other grains, used in breweries across the country [21]. The BSG used in this investigation is a blend of only barley and hops, retrieved immediately after brewing from the lauter tin at Redhook Brewery in Portsmouth, NH. The samples were brought back to the laboratory and oven-dried overnight to remove moisture.

2.1.4. Feed corn stover (FCS), Coppal House Farm, Lee, NH

Feed corn stover is a seasonally available feedstock that is grown across the United States. Using a seasonal feedstock requires adaptability in processing, however for coal-biomass blending in existing coal-fired power plants, the variation in feedstock availability can be offset by the ability to fire more or less coal, or other biomass, at a given point in time. FCS samples were collected early October 2011 from the Coppal House Farm in Lee, NH, and dried in a laboratory oven. To account for heterogeneity in this biomass, four (post-harvested) corn stalks from varying locations on the farm were collected. The entire stem, including stalk, leaves and tassel, were broken into 1-2'' pieces and mixed in a large bucket. A sampling of this mixture was ground and sieved for use. It is estimated that there is approximately 1 dry ton of harvestable stover per acre of planted corn [22]. According to the National Corn Grower's Association, 97.2 million acres of corn were planted in 2012, almost 4 million of which were in the Northeast and Mid-Atlantic states [23].

Table 1 gives the proximate and ultimate analyses of each raw fuel used in this investigation and the higher heating values, as determined in-house on a Parr Model 6100 Oxygen Bomb Calorimeter, standardized with NIST-traceable Benzoic acid. All samples were ground and sieved to a particle size of 125-250 µm; it was shown by van de Velden et al. that mass transfer limitations occur in the pyrolysis of larger particles because of temperature gradients within the particle [24]. Previous work from our laboratory show no apparent effect of particle size (between 125–250, 250–300, and 300–500 µm) on activation energy of palm biomass [10]. Carbon content was determined using a thermogravimetric analyzer. Volatile matter was determined from sample mass loss from 110 °C to 910 °C in nitrogen, and fixed carbon between 910 and 950 °C in dry air; balance as ash, on a dry basis. Blends of the coal with each biomass were prepared by weighing the desired amount of each solid fuel into a glass vial on a Shimadzu semi-microbalance (±0.1 mg) followed by vortexing on a Scilogex Vortex Mixer for 5 min.

Table 1									
Ultimate ^{a,b} ,	proximate ^c ,	and	combustion	enthalpy ^c	analyses	of	biomass	and	coal
samples.									

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	wt% (dry basis)	Pennsylvania coal ^a	Brewer's spent grain ^b	Cocoa bean shells ^b	Feed corn stover ^b
	С	76.28	49.70	47.04	46.55
	Н	5.33	6.54	5.43	5.66
	Ν	1.42	3.86	2.79	0.95
	S	1.73	0.33	0.16	0.13
	0	7.65	34.87	35.59	39.59
	Moisture	6.55	5.68	3.59	4.54
	Volatile matter	32.18	71.72	71.33	75.77
	Fixed carbon	60.88	25.05	21.08	16.16
	Ash	6.93	3.23	7.59	8.07
	HHV (MJ/kg)	30.934	15.374	15.624	11.596

^a PA coal provided by PSNH suppliers.

^b Biomass performed by Hazen Research, Golden, CO.

^c Determined in house

2.2. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

Each pure fuel and blend was pyrolyzed in high purity nitrogen at a total flow of 70 mLmin^{-1} (reactive gas flow at 50 mL min⁻¹ + balance protective flow at 20 mL min⁻¹) in a 70 μ L alumina crucible in a Mettler Toledo TGA/DSC1. The mass is measured every second to the 10^{-8} g, along with temperature to ± 0.1 K. No more than 10 mg was used in each experiment to minimize potential transport limitations within the crucible; this filled the crucible to approximately 2-2.5 mm high (crucible height is 5.1 mm). Ollero et al. demonstrate, using the same TGA, that by limiting internal diffusion effects (which appeared with char sample heights greater than 3 mm) the external diffusion effects (both heat and mass) were almost negligible below 850 °C [25]. All samples were heated to 373 K and held for 30 min to insure moisture removal. The temperature was ramped back down to 298 K at -10 K/min and held for 5 min. Then the sample was heated at 10, 50 or 100 K/min up to 1173 K and held for 60 min to obtain a stable mass reading. Each sample was run at each temperature ramp rate three times each to insure reproducibility. The DSC component was calibrated using pure indium at rates of 5, 10 and 20 °C/min.

2.3. Distributed Activation Energy Model

The Distributed Activation Energy Model (DAEM) is often applied to pure solid fuel pyrolysis, including that of various biomass, coal and other carbonaceous fuels (see, for example: [26–32]). The distribution function routinely assumes the form [33,34]:

$$X(t) = 1 - \int_0^\infty \exp\left(-A \int_0^t \exp\left(-\frac{E}{RT}\right) dt\right) f(E) dE$$
(1)

where *A* is the frequency (or pre-exponential) factor, *E* the activation energy, *T* the absolute temperature, *R* the universal gas constant. *X*(*t*) represents the extent of conversion at any time, *t*, calculated by the ratio of the mass of volatiles produced at any given time, equal to the initial mass, m_0 , minus the mass at time *t*, m_t , to the total volatiles produced at the end of the pyrolysis reaction, $(m_f - m_0)$, where m_f is the sample mass remaining after pyrolysis.

$$X(t) = \frac{m_0 - m_t}{m_0 - m_f}$$
(2)

If the experiment is conducted non-isothermally at a constant temperature ramp rate, $\beta = dT/dt$, Eq. (1) can be rewritten as:

$$X(T) = 1 - \int_0^\infty \exp\left(-\frac{A}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right)dT\right)f(E)dE$$
(3)

Non-Gaussian distributions are sometimes used to represent f(E), including Weibull [35], Gamma [36], and Maxwell-Boltzmann [37] distributions. The frequency factor is often considered a constant for all reactions. However, Miura and Maki [38] allow for a compensation effect between *A* and *E* through their Integral method applied to the DAEM, used here.

3. Results and discussion

The pure coal, biomasses and their blends were subjected to thermogravimetric analysis at three heating rates to determine the nature of pyrolysis. We begin with a straightforward analysis of the thermogravimetric data to determine if any obvious synergistic behavior occurs between the two solid fuels, moving to an analysis of peak devolatilization temperatures and rates, and finally determination of activation energies using the DAEM.

3.1. Thermogravimetric curves

Often, a simple reading of the thermogravimetric data sheds incredible insight into the behavior of fuels and their blends. In Fig. 1 we see the mass fraction conversion for PA, BSG and their blends as a function of temperature vs. a "predicted" conversion, calculated as the sum of each individual fuels' weighted conversion at that temperature at 100 K/min. That is:

$$X_{\text{Blend}} = x_{\text{coal}} X_{\text{coal}} + x_{\text{biomass}} X_{\text{biomass}} \tag{4}$$

where x represents the mass fraction of coal or biomass in the blend, respectively, and X the total conversion of the sample. Fig. 1 shows DSC data (normalized by sample mass) as a function of temperature for PA, BSG and blends against a similarly predicted normalized heat flow. (CBS and FCS blends in Fig. S1 of Supplemental Information.) For all samples and blends, the blends' sample conversion is overall higher at lower temperatures (T < 500 °C), especially between 200 and 375 °C, than predicted by the simple linear addition scheme of Eq. (4). For the 50:50 blends. the predicted values agree fairly well at lower temperatures, with - especially in the case of CBS and BSG - higher deviations at higher conversion. Conversely, when the percent coal in the blend is higher, it appears that the biomass is preferentially devolatilizing and/or promoting the devolatilization of coal at lower temperatures. Interestingly, Idris et al. [4] find a reasonably additive relationship between 50:50 mixtures of a low rank Malaysian coal and oil palm, suggesting a lack of synergy between the fuels. Likewise, Sadhukhan et al. [39] conclude that a weighted average

of TGA data for a pure lignite coal (149–219 µm) and waste wood from saw mills (354–500 µm) heated at 40 °C/min agree well with blend data. We note that such conclusions may not be generalized across heating rates or analysis styles; if we plot the coal-biomass TGA data in the same way as Sadhukhan et al. (residual mass fraction vs. temperature) we find "good" agreement between a weighted average of the pure TGA data and the blends' decomposition for the 90:10 and 50:50 coal-biomass blends (Fig. S2 in Supplemental material). The distinction in the variables plotted in each graph must be underscored; Figs. 1 and S1 plot the fraction of mass converted at each temperature as a function of total mass possible to be converted. Fig. S2 shows the fraction of mass converted as a function of the total sample mass, including material that cannot devolatilize, or (m_t/m_0) . This underscores the need for a comprehensive analysis beyond comparison of mass loss data at a single temperature ramp rate to more accurately describe the decomposition behavior of blends.

Our supposition of enhanced devolatilization due to presence of biomass is bolstered by DSC data in Fig. 1 (and S1). If pyrolysis occurs via a linear addition of the fuels, predicted heat flow, especially for the 90:10 and 80:20 blends, would be considerably less endothermic at lower temperatures than noted. For the two majority coal blends, the heat required to convert the blends at low temperature was greater than an additive scheme predicts, and less than additive at high temperatures, suggesting that the addition of the biomass may promote devolatilization of the coal at lower temperatures. This is not necessarily evidence of chemical reaction synergism directly between the particles, but perhaps of transport



Fig. 1. Conversion, *X*(*T*) (TG data) and heat flow (DSC data) as a function of temperature for pyrolysis of PA, BSG and blends at 100 K/min: (•) PA coal; (■) BSG; (△) blend; (•) predicted blend. (Note: conversion from Eq. (2), *X*(*T*) = 0 for all samples; graph only shows initial *X*(900) to enable visual inspection of data at each initial temperature.)

phenomena, where evolving gases from the biomass promote transport of volatiles throughout the solid fuel particle mixture and promote reaction of the coal. Especially at lower temperatures, surface area is thought to develop at a rate proportional to the reaction, such that the gas concentration inside a particle is the same as the surrounding gas concentration [40]. It has been shown that char surface area is of critical importance in determining reaction rates by altering the rate of diffusion of reactant gases [41]. While the biomass devolatilizes at lower temperatures, the devolving gases can contact the coal particles. As the gases diffuse through the coal's boundary layer, they are available to react within the pores and at the surface. Such pyrolysis gases are not necessarily inert (i.e. CO, CO₂, H₂O, CH₄), and may well react with the coal particles, promoting degradation. The increased quantity of gas in and of itself will promote heat transfer as it devolatilizes from the solids, further increases the possibility of coal devolatilization at lower temperatures.

3.2. Peak devolatilization temperatures & rates

Throughout the literature we note a common trend among the devolatilization behavior of coal-biomass blends: the peak mass loss rates, as determined through derivative thermogravimetric (DTG) curves, are often correlated to the amount of biomass present. We also note the oft-described compensation effect of heating rate on peak temperature, in that the peak devolatilization temperature(s) of each pure fuel and blend and rates of conversion tend to be higher at higher heating rates. Haykiri-Acma and co-authors [42] posit that this is due to the heterogeneous nature of biomass, whereby each constituent displays an individual decomposition peak. They suggest that at low pyrolytic heating rates, these peaks are "seen as small broken lines or vibrations", but that at high heating rates multiple discrete peaks are not found because the constituents simultaneous decompose, such that "several adjacent peaks are united to form overlapping broader and higher peaks". At one time, a general consensus existed in the literature that this was also (at least partially) due to the thermal lag between the thermocouple measurement point and the temperature of the sample enhancing this so-called compensation effect [43]. However, in recent years this compensation effect has been reduced to the suggestion that thermal lag is in fact the underlying cause of any "compensation effect" in biomass pyrolysis, and it is otherwise the result of random experimental error [44–47]. We mention this merely to show that our data do follow trends noted by previous researchers in terms of peak rates and temperatures, and to point readers to relevant sources that have investigated such phenomena.

As illustrated in Fig. 2 for PA coal and BSG biomass blends pyrolyzed at three heating rates (all DTG curves provided in Supplemental Information, Fig. S3) we see peaks occur at different temperatures for the biomass and coal separately, and that the DTG curves for the biomass-coal blends display two distinct peaks, each at approximately the pure fuel peak DTG temperature. (Location of each peak detailed Table S1.) We find that peak rates for the first peak are highly correlated with the fraction of biomass present, as seen by Idris et al. [4]. Table 2 presents the results of linear regression of peak DTG rates as a function of percent biomass; for Peak 1 (the primarily biomass decomposition) we find that the Peak rate and percent biomass are highly correlated, with all *R*² values greater than 0.91. We found a similar linear relationship between the peak mass loss rate of BSG and Illinois No. 6 coal pyrolyzed at 100 K/min [48]. The linearity is not as consistent in the analysis of Peak 2 DTG rate as a function of biomass composition, as illustrated in Fig. 3. Here the second peak – associated with primarily coal decomposition - is linearly related to biomass composition for both BSG and FCS at 10 and 50 K/min, though this trend breaks down at 100 K/min. For CBS, the relationship between peak rate and biomass fraction holds at 50 K/min; at 10 K/min the presence of the CBS increases the peak mass loss rate over what we would expect from pure coal. Fig. 3 also shows that the peak DTG temperatures are fairly consistent for Peak 1 and 2, closely approximating the pure biomass (Peak 1) and pure coal (Peak 2), with a slight increase in temperature for Peak 1 as the fraction of coal increases for the 50 and 100 K/min samples, though this trend does not hold for the 10 K/min samples. As de Jong et al. [49] found in their pyrolysis of coal and biomasses, simulating peak pyrolysis rate temperatures from individual precursors is possible, though simulating the secondary fuels released from coal-biomass blends as a function of precursors is considerably more erroneous. We continue probing the behavior of blending fuels using the DAEM.

3.3. Activation energies via the Distributed Activation Energy Model (DAEM)

Table 3 presents the activation energies for each pure fuel and blend as a function of conversion from 0.10 to 0.80 using a DAEM model applied to the thermogravimetric data obtained at 3 heating rates for each sample, as illustrated in Fig. 4 for PA coal and 80:20 PA:BSG blend. (Table S2 in Supplemental Information provides fitted equations with associated errors and correlation coefficients for the DAEM analysis.) The activation energies of the pure fuels range from 164.4 ± 7.8 to 324.5 ± 16.7 kJ/mol for the biomasses, and 304.2 ± 2.8 to 522.5 ± 42.6 kJ/mol for the coal, as shown in Fig. 5. The overall fit of the data was quite good; correlation coefficients (R^2) were greater than 0.95 for all samples with only one experiment at each heating rate, with most greater than 0.99, indicating a strong applicability of the DAEM to describe the pyrolysis kinetics of the solid fuels and their blends. To insure a 95% confidence in the Arrhenius parameters, if correlation coefficients, R², were below 0.994, additional runs were performed at each ramp rate, and the data added to the plot to insure this statistical limit, put forth by the ICTAC Kinetics Committee, was met [50].

The values obtained here are in good accord with activation energies of pyrolysis determined via the DAEM for similar samples across the literature. The activation energies determined via the DAEM for the Pennsylvania coal are in good accord with Li et al.'s [29] values of 313 and 383 kJ/mol at a conversion of 0.4 for a Datong bituminous and Jindongnan lean coal, respectively, as compared to our value of 314.7 ± 2.4 kJ/mol at the same conversion level. In terms of the biomass samples, Li et al. [51] find activation energies ranging from 146 to 233 kJ/mole with an average of 171.6 kJ/mol for the pyrolysis of Jerusalem artichoke using heating rates of 5, 10, 20 and 30 °C/min. Cai et al. [52] use the DAEM to describe the pyrolysis of corn stover, cotton stalk, palm oil husk, pine wood, red oak, sugarcane bagasse, switchgrass and wheat straw, finding activation energies on the order of magnitude of 180–272 kJ/mol. Likewise, de Jong et al. [53] report activation energies calculated via the DAEM ranging from 136 to 299 kJ/mol for wood pellets at Miscanthus sinesis, [54,55] find a range of 176-195 kJ/mol for corn stalk, rice husk, and wheat straw, and 167-232 kJ/mol for cereal straws and Ethiopian mustard. We note that some of our activation energies are on the higher side of these values. This is likely an artifact of the temperature ramp rates used in investigation. We selected a broad range of heating rates to enable a more representative description of industrial processes (including "fast" pyrolysis), whereas many studies focus on heating rates within 5–25 °C/min, perhaps up to 50 °C/min. However, by pushing the boundaries while maintaining linearity of the Arrhenius plots, we believe that the findings are perhaps more applicable to a range of co-firing scenarios, and are within the



(a) DTG curves forpure BSG pyrolyzed at (**O**) 10 K/min; (\Box) 50 K/min; (Δ) 100 K/min and pure PA pyrolyzed at (=) 10 K/min; (•) 50 K/min; (•) 100 K/min





Fig. 2. DTG curves for BSG and PA coal pure and blend pyrolysis at three heating rates.

Table 2

Linear regression analysis of peak DTG rates as a function of mass fraction biomass, x_, in blends.

dX/dt (s⁻¹)

	Peak 1		Peak 2			
	Linear regression equation	R^2	Linear regression equation	R^2		
10 K/min						
BSG:PA	$[dX/dt]_{\text{neak}} = 0.00040755 + 0.0012438 * x_{BSG}$	0.9770	$[dX/dt]_{peak} = 0.0013475 - 0.001445 * x_{BSG}$	0.9989		
CBS:PA	$[dX/dt]_{peak} = 0.00020979 + 0.00064879 * x_{CBS}$	0.9982	$[dX/dt]_{peak} = 0.0013125 - 5.00E - 5 * x_{CBS}$	0.0085		
FCS:PA	$[dX/dt]_{peak} = 0.00039273 + 0.001332 * x_{FCS}$	0.9133	$[dX/dt]_{peak} = 0.0015174 - 0.00078878 * x_{FCS}$	0.9164		
50 K/min						
BSG:PA	$[dX/dt]_{neak} = 0.0015738 + 0.0059932 * x_{RSG}$	0.9864	$[dX/dt]_{neak} = 0.0063421 - 0.0072857 * x_{BSG}$	0.9802		
CBS:PA	$[dX/dt]_{peak} = 0.001072 + 0.0030427 * x_{CBS}$	0.9513	$[dX/dt]_{peak} = 0.0067388 - 0.0077739 * x_{CBS}$	0.9520		
FCS:PA	$[dX/dt]_{peak} = 0.001534 + 0.0059481 * x_{FCS}$	0.9330	$[dX/dt]_{peak} = 0.006744 - 0.0072463 * x_{FCS}$	0.8650		
100 K/min						
BSG:PA	$[dX/dt]_{peak} = 0.0030413 + 0.010418 * x_{BSC}$	0.9796	$[dX/dt]_{neak} = 0.0099518 - 0.0082714 * X_{BSG}$	0.4424		
CBS:PA	$[dX/dt]_{peak} = 0.0020265 + 0.0056244 * \chi_{CBS}$	0.9733	$\left[\frac{dX}{dt}\right]_{\text{neak}} = 0.010929 - 0.0079929 * x_{CBS}$	0.2809		
FCS:PA	$[dX/dt]_{peak} = 0.0023533 + 0.013574 * x_{FCS}$	0.9771	$[dX/dt]_{peak} = 0.010542 - 0.0074343 * x_{FCS}$	0.2824		
	*		*			

ICTAC's recommendation of at least one order of magnitude apart [50].

The DAEM was successfully applied to the pyrolysis of the coalbiomass blends within this expanded heating rate range. Generally speaking, as the percent of coal in a mixture increases, so does the

activation energy at each conversion level, as would be expected given coal's considerably higher activation energy than biomass. As the fraction converted for the coal and coal-biomass blends reaches beyond 50% of the total, the activation energy increases. This is likely attributed to both the nature of the chemical reactions



Fig. 3. Peak DTG mass loss rates and temperatures as a function of blend composition at three heating rates for (•) BSG Blends at 10 K/min; (■) FCS Blends at 10 K/min; (△) CBS Blends at 10 K/min; for (◆) BSG Blends at 50 K/min; (+) FCS Blends at 50 K/min; (×) CBS Blends at 50 K/min; for (◆) BSG Blends at 100 K/min; (□) FCS Blends at

occurring as temperature increases and the changes in physical structure of the solids. The solids' compositions change throughout pyrolysis, from loss of acidic groups around 300 °C to breaking of long chain aliphatics, followed by aryl–alkyl ether and ethylene bonds, to anhydride groups and aryl-aryl there and methylene bonds between 400 and 500 °C. Each successive bond cleaving requires considerably higher activation energy, as the "easily broken" compounds are lost faster during pyrolysis. Continuing higher, at temperatures above tar evolution, hydroaromatic structures are compromised, and radicals participate in cross-linking [56]. As temperatures increase, char swelling leads to expansion of the coal's porous network. However, as temperatures increase the pores may collapse, impeding devolatilization of the more condensed carbonaceous compounds, requiring a higher activation energy [57,58].

3.4. Predicting activation energies of pyrolysis of coal-biomass blends

While it is useful to understand how the DAEM can be applied to describe the activation energy of a given coal-biomass blend, a more useful application of the DAEM for coal-biomass would be to predict blend behavior of the mixture using knowledge of the activation energy of only pure components. If the fuel mixtures experience no synergistic effects in terms of reaction kinetics, we would expect that the activation energy of a blend would be the additive summation of each individual fuel's contribution, similar to the TG analysis, such that:

$$E_{\text{Blend}} = x_{\text{coal}} E_{\text{coal}} + x_{\text{biomass}} E_{\text{biomass}} \tag{5}$$

However, as Fig. 6 shows, an additive scheme may well represent the 10 and 20 wt% FCS blends, though the relationship begins to deteriorate for the other blends. In the y = x plot between measured and prediction activation energies we see that there is considerable discord between a linearly predicted activation energy according to Eq. (5) and the measured energies. This is illustrated differently in Fig. 7, where we plot the percent error in activation energy prediction as a function of mass fraction converted for each blend. In this instance, percent error was calculated as:

$$\% \text{Error} = \frac{(E_a)_{\text{measured}} - (E_a)_{\text{predicted}}}{(E_a)_{\text{measured}}} * 100\%$$
(6)

Table 3

Activation energies for coal, biomass and blend pyrolysis obtained by the Distributed Activation Energy Model (±1 standard deviation).

Conversion	Activation energy (kJ/mol					
	Barley	50:50 PA:BSG	80:20 PA:BSG	90:10 PA:BSG	PA coal	
0.10	178.5 ± 0.6	233.6 ± 19.7	246.4 ± 1.4	266.0 ± 17.8	394.1 ± 5.4	
0.15	171.7 ± 3.6	225.0 ± 8.3	251.9 ± 8.8	294.6 ± 17.1	393.4 ± 19.2	
0.20	167.9 ± 6.0	221.2 ± 17.8	259.7 ± 17.2	286.0 ± 13.8	333.9 ± 7.0	
0.25	164.4 ± 7.8	222.7 ± 12.1	291.4 ± 17.0	329.7 ± 19.1	308.8 ± 14.7	
0.30	169.5 ± 7.5	218.0 ± 2.0	313.9 ± 35.0	309.4 ± 13.6	308.6 ± 4.9	
0.35	166.1 ± 9.2	221.2 ± 3.2	306.6 ± 23.9	312.0 ± 8.4	304.2 ± 2.8	
0.40	173.1 ± 8.6	231.1 ± 2.1	328.2 ± 35.8	306.2 ± 5.2	314.7 ± 2.4	
0.45	168.5 ± 10.7	242.7 ± 8.1	345.8 ± 25.6	319.4 ± 8.4	325.4 ± 8.0	
0.50	176.3 ± 10.2	254.5 ± 7.1	312.9 ± 36.2	343.1 ± 13.8	338.9 ± 22.7	
0.55	178.4 ± 11.0	266.1 ± 6.2	377.6 ± 5.3	367.3 ± 2.8	366.0 ± 27.7	
0.60	179.6 ± 12.0	346.1 ± 4.6	343.3 ± 5.1	373.2 ± 4.1	376.0 ± 28.0	
0.65	189.7 ± 11.1	403.2 ± 92.9	336.1 ± 17.6	409.8 ± 3.3	434.5 ± 27.1	
0.70	188.9 ± 12.5	401.8 ± 12.1	341.6 ± 7.9	390.5 ± 3.5	442.8 ± 31.1	
0.75	191.9 ± 13.4	387.4 ± 29.3	353.3 ± 4.4	406.9 ± 13.3	512.6 ± 28.8	
0.80	223.7 ± 9.0	380.5 ± 30.6	386.8 ± 3.1	393.2 ± 16.1	522.5 ± 42.6	
	Cocoa bean shells	50:50 PA:CBS	80:20 PA:CBS	90:10 PA:CBS	PA coal	
0.10	227.1 ± 8.3	283.1 ± 13.4	332.0 ± 6.9	367.6 ± 10.0	394.1 ± 5.4	
0.15	263.9 ± 15.2	311.8 ± 12.6	365.3 ± 6.9	386.9 ± 18.8	393.4 ± 19.2	
0.20	315.1 ± 7.2	317.9 ± 16.7	301.4 ± 34.9	383.5 ± 28.0	333.9 ± 7.0	
0.25	324.5 ± 16.7	191.1 ± 10.1	354.1 ± 10.7	313.3 ± 26.5	308.8 ± 14.7	
0.30	291.8 ± 11.7	288.5 ± 16.4	331.3 ± 10.9	288.3 ± 6.2	308.6 ± 4.9	
0.35	271.3 ± 16.0	259.2 ± 10.4	335.9 ± 18.7	312.3 ± 16.5	304.2 ± 2.8	
0.40	276.5 ± 10.2	247.1 ± 10.9	336.0 ± 15.7	302.2 ± 28.0	314.7 ± 2.4	
0.45	254.3 ± 10.7	238.0 ± 11.3	294.2 ± 8.4	325.4 ± 28.2	325.4 ± 8.0	
0.50	275.5 ± 8.9	232.3 ± 18.1	292.3 ± 19.9	315.1 ± 22.0	338.9 ± 22.7	
0.55	238.3 ± 8.5	287.9 ± 6.6	297.7 ± 5.0	320.4 ± 21.8	366.0 ± 27.7	
0.60	282.8 ± 11.2	274.0 ± 5.9	300.8 ± 4.8	329.8 ± 20.9	376.0 ± 28.0	
0.65	282.7 ± 3.4	284.9 ± 17.9	305.3 ± 5.2	346.6 ± 27.6	434.5 ± 27.1	
0.70	290.5 ± 27.4	287.7 ± 7.6	317.0 ± 8.2	373.1 ± 23.8	442.8 ± 31.1	
0.75	271.7 ± 18.9	339.4 ± 19.1	351.5 ± 10.7	431.1 ± 0.9	512.6 ± 28.8	
0.80	260.3 ± 14.8	368.2 ± 23.4	339.7 ± 18.7	500.8 ± 12.1	522.5 ± 42.6	
	Feed corn stover	50:50 PA:FCS	80:20 PA:FCS	90:10 PA:FCS	PA coal	
0.10	218.2 ± 15.8	292.0 ± 11.1	360.0 ± 5.3	379.9 ± 11.8	394.1 ± 5.4	
0.15	202.2 ± 3.2	267.6 ± 19.1	356.5 ± 17.4	378.3 ± 18.7	393.4 ± 19.2	
0.20	215.7 ± 11.5	250.0 ± 14.7	305.9 ± 32.7	348.4 ± 24.2	333.9 ± 7.0	
0.25	225.7 ± 2.7	240.4 ± 2.4	330.2 ± 1.9	313.0 ± 19.7	308.8 ± 14.7	
0.30	240.2 ± 8.9	244.3 ± 18.2	281.7 ± 7.4	238.3 ± 5.8	308.6 ± 4.9	
0.35	244.0 ± 9.7	247.4 ± 15.1	267.3 ± 4.6	286.0 ± 8.3	304.2 ± 2.8	
0.40	251.6 ± 26.2	227.3 ± 15.8	297.9 ± 8.8	301.7 ± 8.1	314.7 ± 2.4	
0.45	258.5 ± 26.7	229.3 ± 9.3	300.4 ± 9.4	295.3 ± 8.6	325.4 ± 8.0	
0.50	232.0 ± 17.6	242.2 ± 6.2	332.4 ± 18.1	335.8 ± 37.4	338.9 ± 22.7	
0.55	26.8 ± 16.7	254.3 ± 0.5	335.9 ± 26.4	377.0 ± 37.4	366.0 ± 27.7	
0.60	274.4 ± 18.1	276.4 ± 11.1	377.5 ± 11.8	385.3 ± 25.2	376.0 ± 28.0	
0.65	287.5 ± 13.1	227.0 ± 3.0	392.2 ± 0.7	392.9 ± 19.9	434.5 ± 27.1	
0.70	261.7 ± 14.1	265.0 ± 3.1	402.5 ± 25.9	384.3 ± 5.5	442.8 ± 31.1	
0.75	270.5 ± 22.8	275.5 ± 1.9	461.2 ± 14.6	463.2 ± 0.4	512.6 ± 28.8	
0.80	250.7 ± 9.1	284.6 ± 7.6	507.8 ± 40.6	530.3 ± 14.0	522.5 ± 42.6	

Interestingly, the largest deviations are noted for the 50:50 blends of FCS and CBS. For these blends, the activation energy is significantly over-predicted by Eq. (5) for the 50:50 FCS:PA conversions. Fig. 7 illustrates that the 50:50 BSG:PA blend's activation energy is moderately under-predicted at initial conversions, over-predicted at X = 0.50 and then quite under-predicted at higher conversions.

In the case of the 50:50 BSG, CBS and FCS, the measured activation energies are predominantly lower than a simple additive scheme might predict (with the exception of the X = 0.6-0.9 BSG and 0.5 FCS). The average absolute deviation for the 50:50 blends is considerably lower for the BSG (11.3%) than the CBS (18.1%) or FCS (22.7%). This may be explained by the composition of the biomass samples; BSG has a lower ash content than the other two biomasses, with correspondingly higher C, H and N levels, and contains a large amount of protein [59]. While raw BSG may not be notably different than the other two biomasses, in this case it is an industrially processed biomass. During the brewing process it was exposed to moderately high temperature water (mashout occurs around 77 °C to halt the enzymatic

conversion of starches) and stirring. This may well explain the lower ash content, as well as the lower activation energy; the fibrous nature of the material has already been under "attack" during prolonged processing. This manifests itself as a lower overall activation energy for BSG than pure CBS and FCS, and may also lead to enhanced devolatilization of the coals. The CBS are only a moderately processed stream; a mild, rapid steam treatment is used to extract the cocoa nib from its shell, but this would not remove any entrained mineral matter. The FCS was subjected to no processing; corn ears were removed in the field before the stover was collected.

Conversely, the 80:20 and 90:10 blends experience varying degrees of negative and positive deviations from an additive activation energy scheme, as seen in Figs. 6 and 7. The FCS blends have the smallest absolute average deviations, of 4.5% and 6.9% for the 80:20 and 90:10 blends, respectively, as compared to 16.1% and 7.4% for the CBS blends and 16.1% and 11.4% for the BSG blends. In fact, many of the FCS measured activation energies are within one standard deviation of the predicted values, though this is not the case for the majority of the BSG and CBS data.



Fig. 4. Representative isoconversional plot for the Distributed Activation Energy Model calculation of activation energy for *X* = (•) 0.10; (♠) 0.15; (△) 0.20; (♠) 0.30; (ℕ) 0.35; (ℕ) 0.40; (△) 0.45; (■) 0.55; (ℕ) 0.60; (④) 0.65; (ℕ) 0.75; (ℕ) 0.75; (ℕ) 0.80.



Fig. 5. Activation energy as a function of mass fraction conversion for (•) PA coal; (**■**) biomass; and blends of (�) 50:50; (△) 80:20; (○) 90:10 by mass calculated using DAEM; error bars represent one standard deviation.



Fig. 6. Predicted (additive scheme) vs. measured activation energies for coal-biomass blends for each coal-biomass blend: (•) 50:50; (•) 20:80; (•) 10:90.



Fig. 7. Percent error in additive prediction vs. measured activation energies for coal-biomass blends as a function of mass fraction converted.



Fig. 8. Average activation energy as a function of blend composition (•) BSG:PA Blends (solid line = predicted); (•) CBS:PA Blends (dotted line = predicted); (•) FCS:PA Blends (dashed line = predicted); error bars indicate one standard deviation of average value.

The non-linearity extends to a holistic view of the overall pyrolytic decomposition of the fuel blends. In Fig. 8 we show the average activation energy as a function of mass fraction biomass in each blend, compared to the weighted prediction according to Eq. (5) of the average activation energies. The activation energies of the BSG:PA blends are slightly over-predicted at 10 and 20 wt% biomass, and spot-on for the 50:50 mixture. The CBS and FCS 50:50 mixtures were significantly over-predicted. In a previous work, we used a first-order Arrhenius equation analysis to determine the activation energies of pyrolysis of Illinois No. 6 coal and BSG. In this work we found similar trends, in that the activation energy increases relatively proportionally to the percent of biomass in the blend. However, as is often the case for an Arrhenius (also known as the Reaction Rate Constant Method) analysis, there are discrete changes in slope in the $\ln k$ vs. 1/T plots, which are often referred to a mass loss "regimes," where each regime is characterized by a straight line. We found, for IL No. 6 coal and BSG, that in the first (420-530 K) and third mass loss regimes (620-670 K) there is a fairly linear relationship between activation

energy and percent biomass in the blend, though almost an exponential increase was noted in the second mass loss regime (530– 590 K) [48]. While the first order Arrhenius analysis requires only one temperature ramp rate and breaks activation energies into regimes based on Arrhenius plot linearities, the DAEM enables the calculation of activation energy at each conversion level across temperature ramp rates. While the methods of calculation are different, overall we find similar behavior of a coal-biomass blend.

Navarro et al. [60] applied the DAEM to the devolatilization of blends of petcoke and coal to generate an algorithm to predict blend performance from reactivities - including the amount of fuel available to react and its activation energy - of the pure fuels. They find that the initial temperature predicted by DAEM model parameters is higher than measured, indicating a greater reactivity. They conclude that their model yields a "conservative prediction" for blend pyrolysis. Indeed, the use of biomass in co-firing scenarios has been demonstrated to increase reactivity, lowering initial combustion temperatures and modestly lowering reactivities [14]. Additionally, the inorganic matter in coal has been demonstrated to catalyze its pyrolysis (demonstrated by a decrease in activation energy at corresponding temperatures) [61]. A majority of the activation energies for the coal-biomass blends, especially the CBS and FCS, are over-predicted by a linearly additive scheme. Like these prior groups found, we observe that the biomass - especially the unprocessed material - does appear to lower the barrier to pyrolysis. Thus, a simple additive scheme also represents a "conservative prediction" for coal-biomass blend pyrolysis when the activation energies are determined using a Distributed Activation Energy Model.

4. Conclusions

To bridge the gap between fossil fuel dependence and a renewable energy future, we must evolve our energy production to include alternative energy sources such as biomass. However, this is a gradual shift that depends on current infrastructure, innovations in environmental and energy policy, as well as availability of suitable biomass. The overall goal of this study was to explore the use of locally sourced, second-generation biomass feedstocks as a blended fuel in coal-fired power plants in the Northeast and Mid Atlantic regions. This would curtail the importation of foreign coal by reducing overall SO_x emissions resulting from the use of high-sulfur coals commonly found along the East Coast and further lower the carbon footprint of power generation by selecting fuels of local origin to minimize long-range transport. To insure efficient conversion and optimize the blend ratio of biomass to coal used in co-firing scenarios, we must develop an understanding of the overall thermochemical conversion of such blends. However, constantly subjecting each new coal and biomass to a plethora of kinetics studies is unrealistic given the myriad of biomass samples available. As such, we undertook a study to determine (1) if the Distributed Activation Energy Model can be used to describe the pyrolysis behavior of coal-biomass blends originating from the East Coals of the United States, and (2) if the activation energies of these blends can be predicted using a weighted average of the activation energies of the blends' constituents.

The three biomasses chosen for their proximity to coal-fired power plants in the Northeast U.S. - feed corn stover sourced directly from a local farm, cocoa bean shells obtained after mild steam removal of the cocoa nib from the Lindt Chocolate factory. and spent brewer's grains obtained after the brewing process at Redhook Brewery – exhibited different pure activation energies and behavior when entrained in a blend with a Pennsylvania coal. The lower activation energies of pure BSG, and its blends with coal - are likely a function of the processing of BSG prior to use, which would remove many minerals and begin to breakdown the lignocellulose fibers. When the biomasses were blended with a high volatile bituminous coal from Pennsylvania, the resulting activation energies were overall lower than that of the pure coal, though not necessarily additive in nature. While the first peak mass loss, as determined via derivative thermogravimetric curves, for the blends are linearly correlated with the percent biomass present, this relationship does not hold for the second, high-temperature peak (representing primarily coal devolatilization). In a similar vein, the activation energies of the coal-biomass blends calculated via the Distributed Activation Energy Model cannot be exactly predicted using a linearly additive function. For FCS:PA blends the activation energies are moderately lower than predicted, for CBS:PA blends markedly lower than predicted, and for the BSG:PA blends, we see both higher and lower activation energies than would be predicted by a linear scheme at various conversion levels. The average absolute deviation from prediction was lowest for the 80:20 FCS (4.5%) and highest for the 50:50 FCS (22.7%), with the 90:10 blend having an average absolute deviation of 6.9%. The BSG blends displayed average deviations from linear predictions of 11.3%, 16.1%, and 11.4%, and for the CBS mixtures of 18.1%, 16.1%, and 7.4%, for the 50:50, 80:20, and 90:10 mixtures, respectively. For the 50:50 FCS:PA and BSG:PA blends, and all the CBS:PA blends, the majority of the deviations tend to be an over-prediction of activation energy by a linear additive scheme. This suggests that perhaps the presence of the biomass promotes devolatilization of the coal by lowering the overall activation energy barrier. Future studies to determine whether this is a result of enhanced heat and mass transfer within the coal due to the presence of devolatilizing biomass compounds, or a chemical reaction synergism, are recommended. Meanwhile, we suggest that simple additive schemes to predict activation energies of coal-biomass blends as a weighted function of pure components may over-estimate the actual barriers to devolatilization, indicating that biomass promotes reactivity of the coal in the blends.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2015.07.071.

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