

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



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ARTICLE INFO

Article history:

Received 2 December 2013

Accepted 27 April 2014

Available online 5 May 2014

Keywords:

Biomass-coal blends

Co-pyrolysis

Activation energy

Derivative thermogravimetry

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.

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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 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 PSHN 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

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

	WV coal ^a	Cherry pits ^b
<i>Proximate analysis, wt% dry</i>		
Volatile matter	38.74	81.00
Fixed carbon	53.40	16.30
Ash	7.86	2.70
<i>Ultimate analysis, wt% dry</i>		
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 PSHN 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].

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.

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 sampleblend 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.

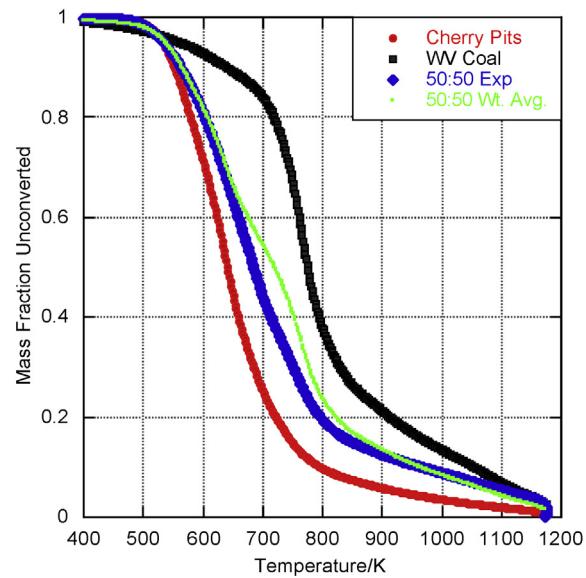
To analyze the peak mass loss rate(s), and temperature(s) at which pyrolysis occurs, we use derivative thermogravimetric (DTG) curves. First, we determine the extent of conversion, *x*, as a function of: initial mass (*m*₀), mass at any time *t* (*m*_{*t*}), and the final mass (*m*_{*f*}).

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

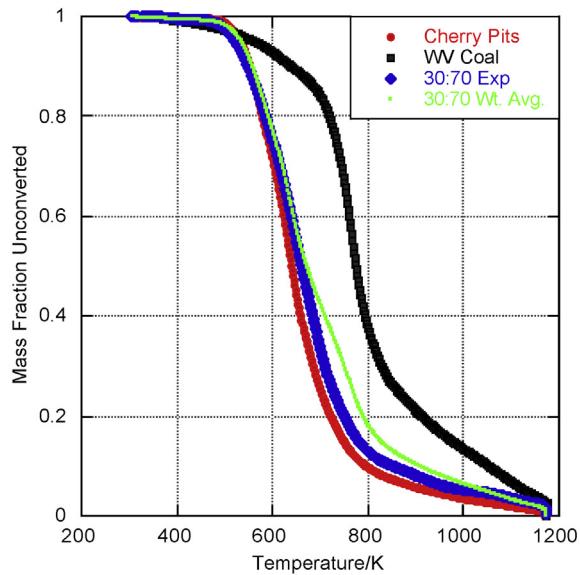
The maximum rate of decomposition is obtained by plotting *dx/dt* versus *T* (absolute temperature), occurring as a peak where the slope equals zero.

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:

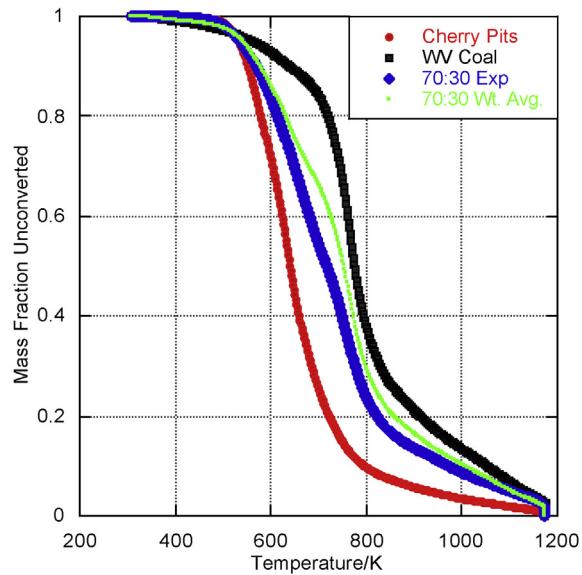
$$\frac{dx(t)}{dt} = k(1 - x(t)) \quad (2)$$



a. WV coal (•); CP (■); 50:50 blend, measured (◆); 50:50 blend, weighted average (○)



b. WV coal (•); CP (■); 30:70 blend, measured (◆); 30:70 blend, weighted average (○)



c. WV coal (•); CP (■); 70:30 blend, measured (◆); 70:30 blend, weighted average (○)

Fig. 1. Residual mass compared to weighted average value as a function of temperature for WV and CP blends.

As we conduct the experiments nonisothermally, the sample temperature is expressed at any point, t , as a function of initial temperature (T_0) and heating rate (β).

$$T = T_0 + \beta t \quad (3)$$

Combining Eqs. (2) and (3), the reaction rate constant may be solved for as:

$$k = \beta \frac{dx(T)/dT}{1 - x(T)} \quad (4)$$

The reaction rate constant, k , is modeled using a first order reaction rate application of the Arrhenius equation, whereby:

$$k = Ae^{-\frac{E_a}{RT}} \quad (5)$$

R is the universal gas constant, E_a the activation energy and A the pre-exponential (or frequency) factor, a gauge of the collision frequency of molecules during a reaction related to the number of molecules present in a given volume [27]. The apparent (or global) activation energy is found by plotting the logarithmic conversion rate, $\ln k$, versus inverse absolute temperature, $1/T$. The slope of the curve is equal to $-E_a/R$. We note that the pre-exponential factor, A ,

found from the Arrhenius equation is assumed to be constant over the temperature range for which the Arrhenius plot is linear. While there are some limitations to the reaction rate constant method (RRCM), such as needing to account for multiple mass loss regimes over different temperature ranges accounting for the stage-wise decomposition of the primary biomass constituents, and the mild dependence of the activation energy on the temperature ramp rate, there are several reasons why we employ this method here. Hundreds of biomass pyrolysis studies in the literature show a reaction order of approximately 1 using the RRCM to account for simultaneous reactions and show a high degree of linearity of the Arrhenius plots [4,28,29]. For this reason, the RRCM provides a reasonable basis for comparison to other literature studies while preserving the goal of determining the approximate effect of on coal–biomass blend ratio on pyrolysis kinetics.

3. Results and discussion

It is often asserted that the kinetic behavior of coal–biomass blends is well represented by an additive scheme; that is, each individual fuel would contribute to the mass loss or activation energy as a weighted fraction of its value, according to Eq. (6)

$$E_{a,\text{blend,predict}} = y_{\text{WV}}E_{a,\text{WV}} + y_{\text{CP}}E_{a,\text{CP}} \quad (6a)$$

$$x_{\text{blend,predict}} = y_{\text{WV}}x_{\text{WV}} + y_{\text{CP}}x_{\text{CP}} \quad (6b)$$

where y is the mass fraction of WV and CP (respectively) and E_a is the activation energy [8,9,30]. We find that this model roughly approximates the behavior observed for the peak mass loss rates and global activation energies of pyrolysis of the West Virginia coal and cherry pit blends.

In Fig. 1, the residual mass as a function of temperature for WV, CP, and blends as compared to weighted average value for the blends, we see reasonable agreement for the 50:50 blend between ~400 and 650 K (conversions less than 40%), and again at temperatures greater than ~825 K (conversions greater than 80%). In the 70:30 WV:CP blend, we see disagreement between the weighted average and experimental data over a much broader temperature range – from ~625 to 900 K, where the blend appears to be pyrolyzing at lower temperatures than would be predicted. For the 30:70 WV:CP blend, there is strong agreement between ~400 and 675 K, and above ~875 K; again we see the conversion of the blend occurring at slightly lower temperatures than that predicted by the weighted average. For the 70:30 WP:CP blend, we find a root mean square (RMS) value of relative error between the predicted value and experimental of 0.034; for the 50:50 blend 0.032, and for the 30:70 blend of 0.038. Sadhukhan et al. find good agreement between experimental TG curves and weighted average curves for the pyrolysis of an Indian lignite coal and wood waste, though their slight predictive errors are in the same direction as those noted here [21]. Using their parallel-series reaction model, Sadhukhan et al. find overall RMS values of relative error of 0.023.

Fig. 2 helps to illustrate this behavior further – here we see the total sample converted as a function of mass fraction CP in the blend. The pure coal sample reaches a maximum total conversion of about 40% over the entire temperature range, and the pure cherry pits devolatilize to loose approximately 70%, by mass, of the total sample. Like Kubacki et al., Vamvuka et al. and Zhang et al. find, as the percentage of biomass present increases, the volatiles increase and char yield decreases [31,5,32]. That is, char yields are lower than predicted on a basis of each individual fuel in the mixture ratio. Conversely, Moghtaderi et al. find that the amounts of volatiles generated from the co-pyrolysis of Drayton coal and pine saw dust are proportional to their blending ratio, at heating rates of 10 °C/min and 10⁴ °C/s with particles 0.45–0.63 mm of coal and 0.09–0.125 mm for biomass [33]. In the present study, as the

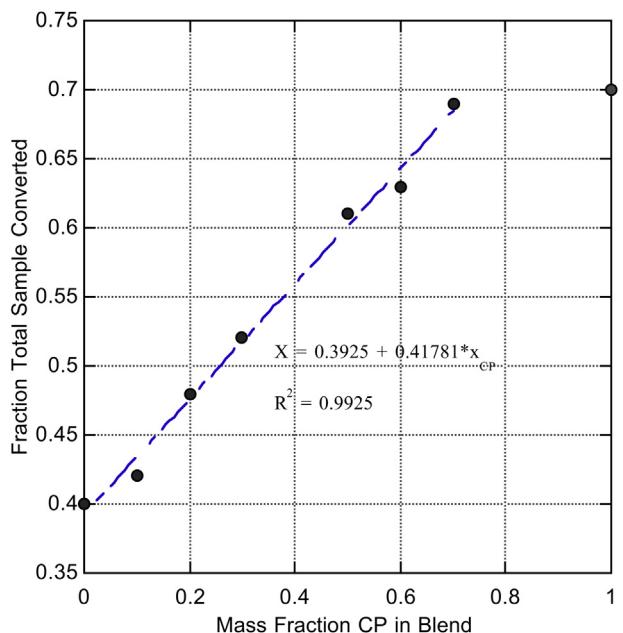


Fig. 2. Total sample conversion of CP, WV and blends pyrolyzed at 100 K/min up to 1173 K as a function of mass fraction cherry pits present in blend.

amount of CP in the blends increases, the conversion of the blend increases linearly ($R^2 = 0.9925$) up to a conversion of ~70% for the 30:70 WV:CP blend. If the maximum conversion possible for pure CP is 70%, and 30% of the blend is WV, which has a maximum conversion of only 40%, then if the mixture obeyed an additive scheme, we would expect a total conversion of 61% according to Eq. (6). As such, it seems possible that the contribution of the volatilizing biomass to the coal promotes devolatilization of the coal that might not otherwise occur during pyrolysis. We explore this further by looking at the derivative thermogravimetric (DTG) curves.

3.1. Derivative thermogravimetric curves: peak mass loss rates

DTG curves (Fig. 3) highlight the inherent complexity in analyzing coal–biomass blends; for each of the pure fuels there is a single peak for devolatilization, for the blends there are two distinct peaks (with the exception of the 30:70 WV:CP blend, for which there is one primary peak with a slight depression). Not surprisingly, the biomass DTG curve shows a fairly broad peak with a shoulder; this behavior is often noted with such heterogeneous solids as biomass, where a variety of its components pyrolyze at different rates and temperatures. Like Idris et al. [34] find, in this data there is an increase in the peak height (mass loss rate) as the weight percent of biomass increases for the first peak (lower temperature) and a higher mass loss rate for the second peak as the coal fraction increases, as shown in Fig. 3. By applying Eq. (6b) to predict the DTG peak as a function of biomass composition for both peaks, Fig. 4 shows that the peak mass loss rate is not quite an additive function of composition. In this case, Eq. (6) under-predicts the peak DTG for the low-temperature peak, indicating again that the mass loss rate is faster at lower temperatures than predicted. Conversely, the DTG peak is lower than predicted for the second (high temperature) peak. This trend appears to be coal and biomass specific. For example, Idris et al. find a fairly tight linear relationship for the pyrolysis of oil palm biomass and low rank Malaysian coal [34]. However, in the case of the cherry pit-coal blends, the fuels are considerably more disparate in terms of composition than the aforementioned study; the carbon content of the coal used by Idris et al. was 54%, and the biomass around 41–43% and oxygen content for coal and

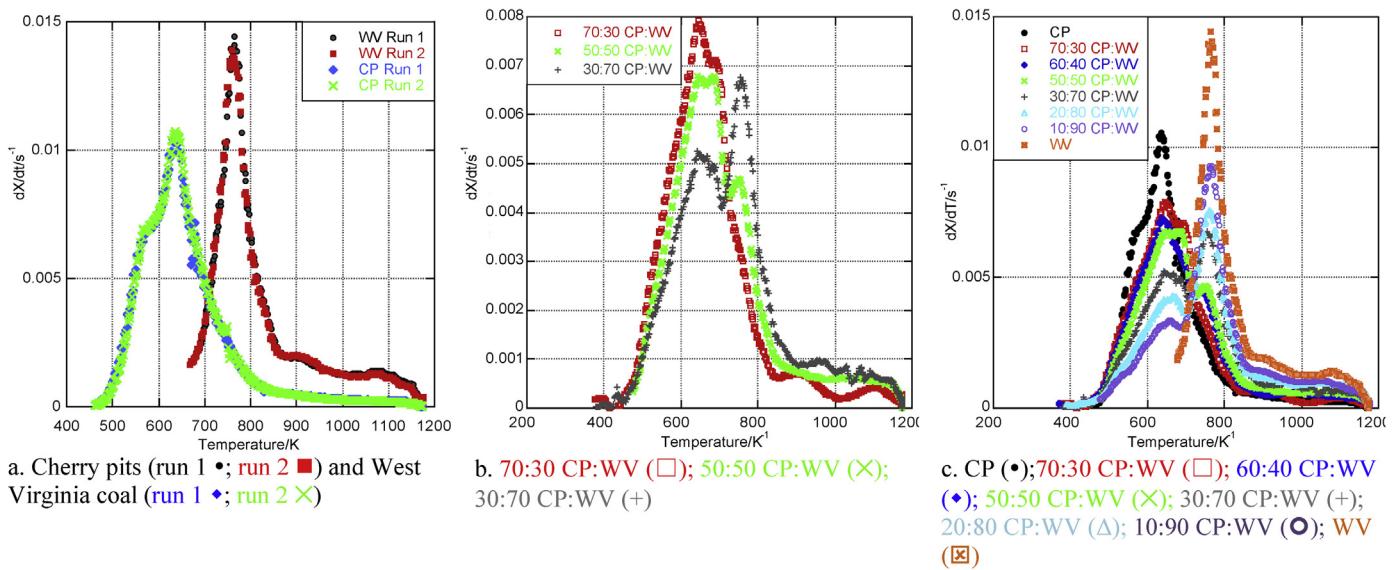


Fig. 3. DTG curves for cherry pits, West Virginia coal, and their blends pyrolyzed at 100 K/min.

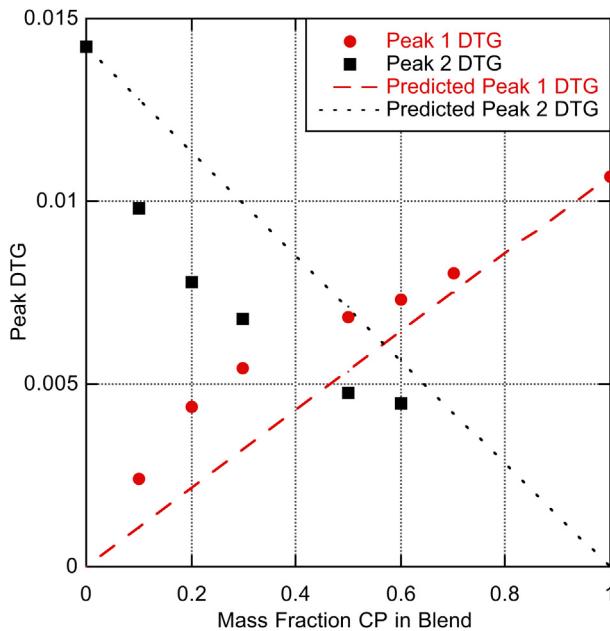


Fig. 4. Peak DTG for lower temperature peak (635–664 K) (●) and higher temperature peak (753–763 K) (■) as a function of mass fraction cherry pits present in blend compared to predicted DTG determined via Eq. (6).

palm biomass of 38% and 50–53%, respectively; in the present study the coal contained approximately 75% carbon, 6% oxygen and the cherry pits 53% carbon and 38% oxygen. In addition, the volatile content of the coal used in the present study (39%) is similar to that used by Idris et al. (42%), though the biomasses are quite different. Using the TGA, we measured a volatile content (up to 600 °C in air) of 81% for the cherry pits, whereas the oil palm biomasses ranged from 69 to 71% volatile matter. Thus in this study the biomass is considerably more reactive with a higher volatile content than the coal, likely contributing to the behavior noted in terms of the biomass promoting pyrolysis of the coal (Table 2).

3.2. Global activation energies of pyrolysis

Fig. 5 shows an Arrhenius plot for the 50:50 WV:CP blend pyrolyzed at 100 °C/min. There is high linearity over four distinct thermal decomposition mass loss regimes. That is, there exist four separate activation energies based on a first order reaction assumption for each blend; only three separate regimes are noted for each of the pure fuels (and only three for the 90:10 WV:CP blend). As seen in Table 3, thermal conversion begins between 153 and 221 °C for the pure fuels and blends. The regimes are defined by abrupt changes in slope on the Arrhenius plots. Table 3 also reports the mass fraction of each fuelblend converted over each mass loss regime, the associated activation energy and pre-exponential factor for each regime, as well as the total or overall conversion of each fuel across the entire temperature range of pyrolysis. The first mass loss regime for all the fuels and blends sees the lowest fractional conversion; this is likely attributed to an energy-intensive reaction

Table 2

Peak DTG rates and temperatures and total mass fraction sample converted during pyrolysis of West Virginia coal and cherry pit blends.

Fraction cherry pit (by mass)	DTG peak 1		DTG peak 2	
	Temperature (K)	Conversion rate (s⁻¹)	Temperature (K)	Conversion rate (s⁻¹)
1	635.5	1.07E-02		
0.7	644.2	8.06E-03		
0.6	637.5	7.30E-03	748.5	4.45E-03
0.5	664.0	6.85E-03	753.0	4.74E-03
0.3	648.0	5.42E-03	757.0	6.77E-03
0.2	657.5	4.38E-03	760.0	7.81E-03
0.1	646.0	2.43E-03	762.0	980E-03
0			763.5	1.42E-02

Table 3

Apparent activation energies of pyrolysis of West Virginia coal and cherry pit blends determined via reaction rate constant method over temperature-dependent mass loss regimes.

		Mass loss regime 1					Mass loss regime 2						
Mass fraction		Onset T	Endset T	Fraction converted	E_a	A	Onset T	Endset T	Fraction converted	E_a	A		
WV	CP	K	K		kJ/mol	s ⁻¹	K	K		kJ/mol	s ⁻¹		
1	0	484	603	0.019	22.1 ± 0.7	9.32E-02							
0.9	0.1	460	622	0.037	27.9 ± 0.6	7.59E-01							
0.8	0.2	426	507	0.009	47.3 ± 0.9	6.84E+01	537	644	0.087	31.7 ± 0.3	2.02		
0.7	0.3	467	519	0.013	63.9 ± 1.4	5.00E+03	532	639	0.12	32.1 ± 0.2	2.92		
0.5	0.5	446	514	0.014	78.4 ± 0.9	1.67E+05	525	688	0.29	33.9 ± 0.2	5.33		
0.4	0.6	455	504	0.018	66.0 ± 1.0	1.02E+04	533	642	0.20	35.5 ± 0.2	8.86		
0.3	0.7	443	530	0.030	76.5 ± 1.1	2.39E+05	528	636	0.23	35.2 ± 0.3	9.00		
0	1	481	554	0.076	92.8 ± 1.4	4.63E+06	567	642	0.25	42.3 ± 2.7	35.1		
Mass loss regime 3													
Mass fraction		Onset T	Endset T	Fraction converted	E_a	A	Mass loss regime 4					Total conversion	
WV	CP	K	K		kJ/mol	s ⁻¹	Onset T	Endset T	Fraction converted	E_a	A		
1	0	671	770	0.14	123.6 ± 1.4	5.86E+06	1009	1092	0.022	71.0 ± 2.0	43.6	0.40	
0.9	0.1	685	770	0.13	112.9 ± 1.6	2.78E+06	979	1102	0.030	52.3 ± 1.1	4.37	0.42	
0.8	0.2	700	766	0.11	88.3 ± 1.6	2.09E+04	970	1132	0.040	44.0 ± 0.5	1.54	0.48	
0.7	0.3	712	757	0.078	85.5 ± 1.4	1.42E+04	1001	1143	0.029	40.6 ± 1.5	1.05	0.52	
0.5	0.5	718	749	0.060	45.8 ± 1.9	26.2	969	1145	0.036	38.8 ± 0.5	0.74	0.61	
0.4	0.6	721	753	0.058	41.9 ± 1.0	13.7	1035	1142	0.018	39.4 ± 0.7	0.82	0.63	
0.3	0.7	666	701	0.11	34.6 ± 0.8	7.50	870	921	0.013	36.8 ± 0.9	1.46	0.69	
0	1						987	1125	0.014	30.4 ± 0.9	0.20	0.70	

initiation more so than a high degree of devolatilization [35]. The largest mass loss occurs in regimes 2 and 3. Similar series of thermal events are noted throughout the co-pyrolysis literature. Zhou et al. find four distinct thermal regions for the pyrolysis of a low-volatile coal and plastic (low and high density polyethylene, polypropylene) blends at 20 °C/min [36]. Vuthaluru notes three separate thermal events for pyrolysis of a Collie subbituminous coal with wood waste and wheat straw pyrolyzed at 20 °C/min. Their reported activation energies for 50:50 blends ranged from 46.7 to 68.7 kJ/mol in the first regime (281–327 °C) [13]. Our first thermal regime for the 50:50 WV:CP blend occurred between 173 and 241 °C and resulted in an activation energy of 78.4 kJ/mol. Our second regime for the 50:50 blend occurred between 252 and 414 °C, resulting in an activation

energy of 35.5 kJ/mol. Vuthaluru does not tabulate the amount of mass lost in each regime so it is not possible to compare results on that basis. During the second thermal event that Vuthaluru finds, the activation energy for 90% coal, 10% wood waste is 115.3 kJ/mol between 430 and 485 °C, and for the same proportion of wheat straw and coal, 124.3 kJ/mol between 414 and 488 °C. In our third mass loss regime we find for 90:10 WV:CP 112.9 kJ/mol between a temperature range of 412 to 497 °C.

It is difficult to posit specific mechanisms for the mass loss over each regime after the initiation of pyrolysis given the highly heterogeneous nature of biomass and coal resulting in multiple heterogeneous chemical reactions. The reaction dynamics of these processes are influenced by three factors: (1) breaking and redistribution of chemical bonds; (2) changing reaction geometry; (3) interfacial diffusion of reactants and products [37]. A general consensus in the literature exists for an overall biomass pyrolysis scheme. The free moisture of the solid evaporates (not indicated here, as we have dried the samples beforehand for consistency), followed by unstable polymer degradation. As temperature increases the more stable components begin to decompose, releasing volatiles from the solid matrix [38]. A solid char residue forms during primary decomposition (between 200 and 400 °C) and undergoes subsequent aromatization at temperatures above 400 °C [39]. The pyrolysis of coal is often thought to proceed via a series of first-order heterogeneous reactions [40]. Similarly to biomass, the raw coal undergoes a series of stages whereby primary gases are evolved, forming tar and char, followed by devolatilization of secondary gases, with multiple intermediate pathways where tar and primary gases form soot [41].

Fig. 5 demonstrates a frequently encountered pattern in the biomass-co-firing and co-pyrolysis literature. That is, as the percent cherry pits increase, the activation energy also increases in the low temperature regime. This corresponds to the observations noted above in terms of mass loss rates, explained by the higher percentage of lignocellulosic materials present in the biomass that can decompose at substantially lower temperatures than coal. At higher temperature regimes (mass loss regimes 3 and 4) the opposite trend is noted. The largest fraction of coal is converted in mass

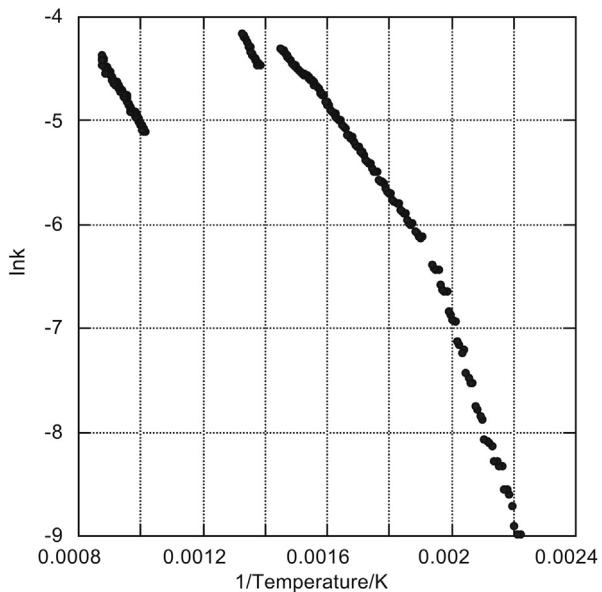


Fig. 5. Arrhenius plot for 50:50 WV:CP blend pyrolyzed at 100 K/min showing four distinct mass loss regimes.

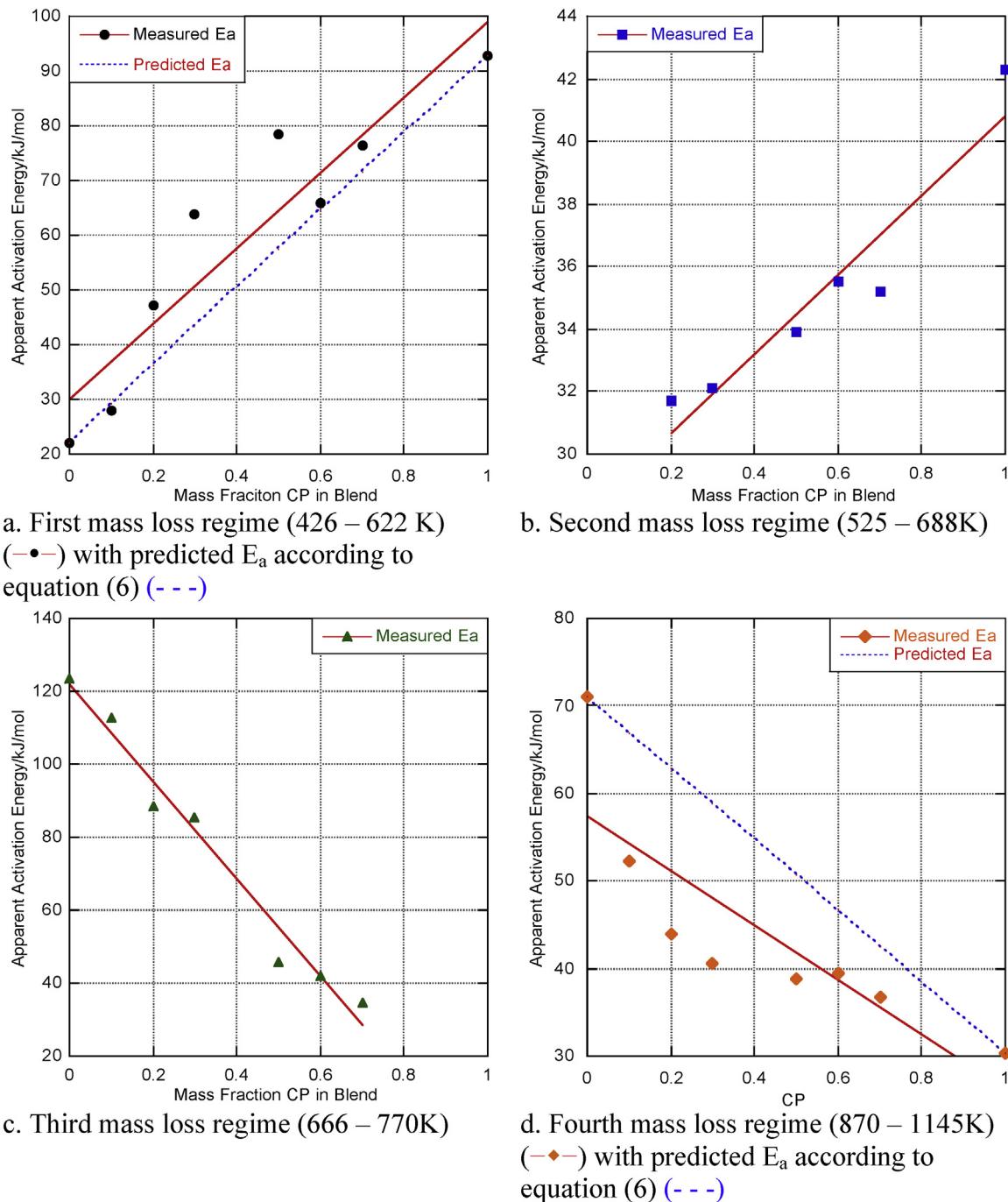


Fig. 6. Apparent activation energy as a function of mass fraction cherry pits present in blend for each temperature regime.

loss regime 3 between 398 and 497 °C (14%) with the highest activation energy (123.6 kJ/mol); the percent converted in this range, and the associated activation energies, decreases as the percent of cherry pits present in the blend increases.

Fig. 6(a) and (d) shows a predicted activation energy according to the weighted averages of Eq. (6). In mass loss regime 1, Eq. (6) tends to under-predict the activation energy of the blend by approximately 7.22 ± 9.23 kJ/mol. A linear trend line fit to the data ($R^2 = 0.92944$) estimates the activation energy within a range of -9.08 to 13.84 kJ/mol, with a standard deviation (σ) of 9.21 kJ/mol. In mass loss regime 4, Eq. (6) over-predicts the activation energy of the blend by -12.77 ± 5.49 kJ/mol, whereas a linear trend line fit ($R^2 = 0.83889$) is accurate to within -7.45

to 13.61 kJ/mol, $\sigma = 6.81$ kJ/mol. Eq. (6) under-predicts the activation energy in regime 1 and over-predicts the activation energy in regime 4 for likely the same reason. If the biomass promotes the devolatilization of coal at lower temperatures, then the mass loss of coal is higher at lower temperatures than predicted, thereby leaving less solid to pyrolyze at higher temperatures. If the biomass were to preferentially devolatilize we would expect to see higher activation energies than predicted at higher temperatures, yet the opposite is observed, leading to the assertion that the coal devolatilizes at lower temperatures with the incorporation of biomass into the mix. Vulthaluru posits a similar explanation, in that the thermal degradation of coal occurs at lower temperatures as biomass content increases, attributed to the “massive decomposition of biomass”

[19]. The author suggests that the TGA data show a linear relationship between char yield and biomass present, suggesting a lack of synergistic effects. However, there among the blend ratios tested, Vuthaluru finds that 20:80 blends of coal:biomass show the lowest activation energies, and therefore we suggest that it would be unlikely that a linear relationship exists between activation energy and blend ratio, indicating potential synergistic effects.

We cannot offer a similar prediction for mass loss regimes 2 and 3 (figures (b) and (c)) as there is not observed mass loss over similar temperatures for regime 2 for coal, and likewise for biomass in regime 3. It is noted, though, that the relationship between activation energies for the coal and blends in the second and third mass loss regimes are fairly linear ($R^2 = 0.95183$ and $R^2 = 0.98633$, respectively) and increases with increasing biomass in regime 2 and decreases with increasing biomass in regime 3. Interestingly, Vamvuka et al. find that such an additive scheme offers a “satisfactory prediction” of the behavior of mixtures of lignite coal and biomasses such as forest residue and olive kernels. However, while they present activation energies for each individual component, they do not tabulate such kinetic values for the blends, though DTG curves of blends appear to agree well with the additive predictive scheme [5]. Kubacki et al. summarize such behavior succinctly through the investigation of co-pyrolysis of coal and wheat straw blends [31], in that decomposition steps between fuel and blend components may be clearly delineated, non-additive behavior is often noted in the kinetics of biomass-coal co-pyrolysis, and is specific to a given biomass and coal.

3.3. Summary

The literature abounds with assertions of both synergistic and additive behavior of the kinetics of the pyrolytic conversion of coal-biomass blends. Through the data presented here on cherry pit and West Virginia coal blends, we find global activation energies to be functions of the blend compositions, though not perfectly additive in nature, suggesting some level of reaction synergism. The energy required to initiate pyrolysis (regime 1) is fairly dependent on the percentage of biomass present, though it appears as though the biomass may encourage pyrolysis of the coal at lower temperatures. Examination of derivative thermogravimetric curves furthers this conclusion; higher rates of reaction are observed at lower temperatures, and vice versa.

4. Conclusions

The present work investigates the pyrolysis behavior of blends of cherry pits and West Virginia coal using thermogravimetric analysis under nitrogen gas at heating rate of 100 K/min. Derivative thermogravimetric curves of the blends suggest that the rates of pyrolysis are an amalgam of the behavior of the pure fuels, though are not purely additive in nature. DTG curves of the blends show two peaks corresponding to the biomass and coal, though the height of these peaks are not directly proportional to the amount of each fuel present. That is, the rate of devolatilization is higher than expected at lower temperatures, and lower than expected at higher temperatures if one assumes an additive scenario. Using a first order reaction Arrhenius plot, it is observed that the global activation energies echo this idea. At lower temperatures, the activation energies are higher than that predicted by an additive reaction scheme, suggesting a higher amount of coal is devolatilizing than predicted at lower temperatures. At higher temperatures, the mass loss rates found through the DTG curves are lower than predicted using an additive scheme. On its own, this suggests that either the biomass preferentially devolatilized at lower temperatures, or that the coal did as such. Given that the apparent activation energies

at high temperatures are also lower than predicted, it does not seem likely that the biomass preferentially devolatilized, as this would lead to higher activation energies than predicted given the lower E_a of pure biomass compared to pure coal. As such, it appears that though simple “back-of-the-envelope” calculations to predict pyrolysis behavior of coal-biomass blends as a function of composition are likely to under-predict or over-predict the energy required to initiate pyrolysis, depending on the temperature regime, and should be applied with caution. The findings support the idea that co-firing coal and biomass may indeed increase the efficiency of industrial boilers. Co-firing is known to decrease SO_x and net CO_2 emissions, and to stabilize flame temperature. The data gathered herein suggest that incorporating biomass such as cherry pits may well promote the pyrolysis of coal, which would lead to a larger volatile profile and likely a better overall conversion during combustion.

Acknowledgements

The authors thank Richard Despins of Public Service of New Hampshire for providing the coal sample. This material is based upon work supported by the National Science Foundation under Grant No. NSF CBET-1127774.

References

- [1] M. Sami, K. Annamalai, M. Wooldridge, Co-firing of coal and biomass fuel blends, *Prog. Energy Combust. Sci.* 27 (2001) 171–214.
- [2] U.S. Energy Information Administration (US EIA), Net Generation and Fuel Consumption for Power Plants Consuming Coal and Biomass, 2010, Released August 2010. Available at: http://www.eia.gov/cneaf/solar.renewables/page/re_data/table9.html (accessed 7.09.13).
- [3] M.A. Serio, D.G. Hamblen, J.R. Markham, P.R. Solomon, Kinetics of volatile product evolution in coal pyrolysis: experiment and theory, *Energy Fuels* 1 (1987) 138–152.
- [4] L. Buessing, J.L. Goldfarb, Energy along I-95: pyrolysis kinetics of Floridian cabbage palm (*Sabal palmetto*), *J. Anal. Appl. Pyrol.* 96 (2012) 78–85.
- [5] D. Vamvuka, E. Kakaras, P. Grammelis, Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite, *Fuel* 82 (2003) 1949–1960.
- [6] D. Vamvuka, N. Pasadakis, E. Kastanaki, Kinetic modeling of coal/agricultural by-product blends, *Energy Fuels* 17 (2003) 549–558.
- [7] J.M. Heikkilä, J.C. Hordijk, W. de Jong, H. Splithoff, Thermogravimetry as a tool to classify waste components to be used for energy generation, *J. Anal. Appl. Pyrol.* 71 (2004) 883–900.
- [8] E. Kastanaki, D. Vamvuka, P. Grammelis, E. Kakaras, Thermogravimetric studies of the behavior of lignite-biomass blends during devolatilization, *Fuel Process. Technol.* 77–78 (77) (2002) 159–160.
- [9] T. Sonobe, N. Worasuwannarak, Kinetic analyses of biomass pyrolysis using the distributed activation energy model, *Fuel* 87 (2008) 414–421.
- [10] S. Krerkkaiwan, C. Fushimi, A. Tsutsumi, P. Kuchonthara, Synergistic effect during co-pyrolysis/gasification of biomass and sub-bituminous coal, *Fuel Process. Technol.* 115 (2013) 11–18.
- [11] H. Haykiri-Acma, S. Yaman, Synergy in devolatilization characteristics of lignite and hazelnut shell during co-pyrolysis, *Fuel* 86 (2007) 373–380.
- [12] C.A. Ulloa, A.L. Gordon, X.A. García, Thermogravimetric study of interactions in the pyrolysis of blends of coal with radiata pine sawdust, *Fuel Process. Technol.* 90 (2009) 583–590.
- [13] J. Aboyade, M. Gorgens, E.L. Carrier, J.H. Meyer, Knoetze, Thermogravimetric study of the devolatilization characteristics and kinetics of coal blends with corn and sugarcane residues, *Fuel Process. Technol.* 106 (2013) 310–320.
- [14] T. Sonobe, N. Worasuwannarak, S. Pipatmanomai, Synergies in co-pyrolysis of Thai lignite and corn cob, *Fuel Process. Technol.* 89 (2008) 1371–1378.
- [15] D.K. Park, S.D. Kim, S.H. Lee, J.G. Lee, Co-pyrolysis characteristics of sawdust and coal blend in TGA and a fixed bed reactor, *Bioresour. Technol.* 101 (2010) 6151–6156.
- [16] A.O. Aboyade, M. Carrier, E.L. Meyer, J.H. Knoetze, J.F. Görgens, Model fitting kinetic analysis and characterization of the devolatilization of coal blends with corn and sugarcane residues, *Thermochim. Acta* 530 (2012) 95–106.
- [17] P. Grammelis, P. Basinas, A. Malliopoulos, G. Sakellaropoulos, Pyrolysis kinetics and combustion characteristics of waste recovered fuels, *Fuel* 88 (2009) 195–205.
- [18] J.M. Jones, M. Kubacki, K. Kubica, A.B. Ross, A. Williams, Devolatilisation characteristics of coal and biomass blends, *J. Anal. Appl. Pyrol.* 74 (2005) 502–511.
- [19] H.B. Vuthaluru, Thermal behaviour of coal/biomass blends during co-pyrolysis, *Fuel Process. Technol.* 85 (2003) 141–155.

- [20] C. Wang, F. Wang, Q. Yang, R. Liang, Thermogravimetric studies of the behavior of wheat straw with added coal during combustion, *Biomass Bioenergy* 33 (2009) 50.
- [21] A.K. Sadhukhan, P. Gupta, T. Goyal, R.K. Saha, Modelling of pyrolysis of coal-biomass blends using thermogravimetric analysis, *Bioresour. Technol.* 99 (2008) 8022–8026.
- [22] C.A. Koufopoulos, N. Papayannakos, Modeling of the pyrolysis of biomass particles: studies on the kinetics thermal and heat transfer effects, *Can. J. Chem. Eng.* 69 (1991) 907–915.
- [23] Cherry Industry Administrative Board, Weekly Raw Product Report: Week 8 – 2013, 2013, <http://www.cherryboard.org/Week82013.pdf> (accessed 17.11.13).
- [24] Agricultural Marketing Resource Center (AgMRC), Cherries, 2013, http://www.agmrc.org/commodities_products/cherries/ (accessed 17.11.13).
- [25] M. Van de Velden, J. Baeyens, A. Brems, R. Dewil, Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction, *Renew. Energy* 35 (2010) 232–242.
- [26] J.F. González, J.M. Encinar, J.L. Canito, E. Sabio, M. Chacón, Pyrolysis of cherry stones: energy uses of the different fractions and kinetic study, *J. Anal. Appl. Pyrol.* 67 (2003) 165–190.
- [27] S.Y. Yorulmaz, A.T. Atimtay, Investigation of combustion kinetics of treated and untreated waste wood samples with thermogravimetric analysis, *Fuel Process. Technol.* 90 (2009) 939–946.
- [28] C. Branca, Di Blasi, Kinetics of the isothermal degradation of wood in the temperature range 528–708 K, *J. Anal. Appl. Pyrol.* 67 (2003) 207–219.
- [29] P. Parasuraman, R. Singh, T. Bolton, S. Omori, R. Francis, Estimation of hardwood lignin concentrations by UV spectroscopy and chlorine demethylation, *BioResources* 2 (2007) 459–471.
- [30] E. Biagini, F. Barontini, L. Tognotti, Devolatilization of biomass components studied by TG/FTIR technique, *Ind. Eng. Chem. Res.* 45 (2006) 4486–4493.
- [31] M.L. Kubacki, A.B. Ross, J.M. Jones, A. Williams, Small-scale co-utilisation of coal and biomass, *Fuel* 101 (2012) 84–89.
- [32] L. Zhang, S. Xu, W. Zhao, S. Liu, Co-pyrolysis of biomass and coal in a free fall reactor, *Fuel* 86 (2007) 353–359.
- [33] B. Moghtaderi, C. Meesri, T.F. Wall, Pyrolytic characteristics of blended coal and woody biomass, *Fuel* 83 (2004) 745–750.
- [34] S.S. Idris, N.A. Rahman, K. Ismail, A.B. Alias, X.A. Rashid, M.J. Aris, Investigation on thermochemical behavior of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA), *Bioresour. Technol.* 101 (2010) 4584–4592.
- [35] M.J. Antal Jr., G. Varhegyi, Cellulose pyrolysis kinetics: the current state of knowledge, *Ind. Eng. Chem. Res.* 34 (1995) 703–717.
- [36] L. Zhou, T. Luo, Q. Huang, Co-pyrolysis characteristics and kinetics of coal and plastic blends, *Energy Convers. Manage.* 50 (2009) 705–710.
- [37] A.K. Galwey, M.E. Brown, Kinetic background to thermal analysis and calorimetry, in: *Handbook of Thermal Analysis and Calorimetry*, Vol. 1: Principles and Practice, 1st ed., Elsevier Science, The Netherlands, 1998, pp. 147–224.
- [38] D.F. Arseneau, Competitive reactions in the thermal decomposition of cellulose, *Can. J. Chem. Eng.* 49 (1971) 632–638.
- [39] T. Fisher, M. Hajaligol, B. Waymack, D. Kellogg, Pyrolysis behavior and kinetics of biomass derived materials, *J. Anal. Appl. Pyrol.* 62 (2002) 331–349.
- [40] H. Jüntgen, Review of the kinetics of pyrolysis and hydrolysis in relation to the chemical constitution of coal, *Fuel* 63 (1984) 731–737.
- [41] H.A.G. Chermin, D.W. van Krevelen, Chemical structure and properties of coal IX. A mathematical model of coal pyrolysis, *Fuel* 36 (1957) 85–104.
- [42] N. Petrov, T. Budinova, M. Razvigorova, V. Minkova, Preparation of activated carbon from cherry stones, apricot stones and grape seeds for removal of metal ions from water, in: Proceedings of the 2nd Olle Lindström Symp. on Renewable Energy-Bioenergy, 1999, <https://www.ecn.nl/phyllis2/Biomass/View/1670> (accessed 18.11.13).