KINETIC STUDY OF COAL AND BIOMASS CO-PYROLYSIS USING THERMOGRAVIMETRY

Ping Wang^a, Sheila W. Hedges^a, Kiran Chaudhari^b, and Richard Turton^b

^aDOE/NETL, 626 Cochran's Mill Road, Pittsburgh, PA 15236, USA

^bDepartment of Chemical Engineering, West Virginia University, WV 26506, USA

Introduction

The major driving force for adding biomass in coal utilization is to utilize renewable energy resources and reduce net coal CO₂ emission. Co-firing (blend of biomass with coal combusted in air) as a co-utilization technology has been successfully demonstrated in numerous power plants and has shown reduction of CO₂ emission¹. A life cycle (LC) analysis concluded that co-firing of Illinois No. 6 coal and forest residue (10% heat) reduces the LC greenhouse gas (GHG) emission by 6.6%². Simulation tools that can be used to predict behaviors of coal and biomass blends in co-utilization and to optimize system designs and operation are a potentially cost effective way to assist further technology development. Kinetic models are needed for blends of coal and biomass for devolatilization/pyrolysis, gasification and combustion processes. Thermogravimetry (TGA) has been widely used to obtain kinetics parameters of solid fuel thermal processes using non-isothermal methods at one or multiple heating rates³. Biomass mainly consists of hemicelluloses, cellulose, and lignin and it has different composition with coal. Biomass pyrolysis kinetic models are mainly developed based on the mechanism of three independent parallel first order reactions of three pseudo-components⁴. Iso-conversional and multi-heating rate methods are widely used in solid thermal decomposition kinetics study³. Using the methods on the co-pyrolysis is challenging due to inherent heterogeneity of both biomass and coal, and to the complexity of co-pyrolysis of these blends. The objectives of this study are to investigate thermal behavior of coal and biomass blends in inert gas environment at low heating rates and to develop a simplified kinetic model using model fitting techniques based on TGA experimental data.

Materials and Methods

Powder River Basin (PRB) sub-bituminous coal and pelletized southern yellow pine wood sawdust with less than 1% bark and without additional chemicals were received from DOE National Carbon Capture Center managed by Southern Company in Wilsonville, Alabama. These materials were ground then sieved and the fraction between 100 to 300 μ m is used in this study. The proximate and ultimate analysis of the coal and wood samples were listed in Table 1.

Table 1. Proximate and Ultimate analysis of Powder River Basin (PRB) Sub-bituminous Coal and Wood

	Proximate analysis (% dry basis)								
	Volatile matter	Fixed carbon	Ash						
PRB coal	46.2	47.2	6.6						
Wood	85.1	14.3	0.6						
	Ultimate analysis (% dry basis)								
	C	H	N	S	ash	O (diff)			
PRB coal	66.21	4.2	1.21	0.48	6.6	21.3			
Wood	48.84	5.78	0.38	0.15	0.6	44.21			

Thermal behavior and co-pyrolysis kinetics of the coal, wood, and blends having 10 and 20% (wt) of wood were studied using a thermogravimetric analyzer (TGA) (Perkin Elmer Pyris 1). The samples (~10mg) were first heated up to 100°C and held for 20min to dry them. A non-isothermal method with low heating rates of 10, 20, and 50°C/min, respectively, was selected. The samples were heated up to 1000°C and held for 5-20 min in dry N₂ with a total flow rate of approximately 125 ml/min. The experiments were performed in triplicate (quadruplicate or more for coal and wood blends) to assess their reproducibility.

Results and Discussion

Thermal behavior of coal, wood and their blends at low heating rates in pyrolysis. Figures 1 and 2 show the weight fraction remaining ($m/m_0\%$ where m_0 is initial dry weight of the feedstock sample at 100°C) as a function of temperature (TG), and the weight loss rate (DTG) of coal, 20% wood in blend, and wood at 50°C/min heating rate during pyrolysis. Coal pyrolysis has higher final residue 58.4 $\pm$ 0.5 db% compared to wood 16.7 $\pm$ 1.3 db% (figure 1). DTG curve of coal has a broad peak with temperature of maximum weight loss rate $T_{max}=475\pm2^\circ\text{C}$ and lower maximum weight loss rate $R_{max}=0.13\%$ %/s compared to wood which has a sharp peak with a shoulder in DTG with lower $T_{max}=395\pm0.5^\circ\text{C}$, and higher $R_{max}=0.7\%$ %/s. Blend with 20% wood has two peaks with $T_{onset}=397\pm1^\circ\text{C}$ close to wood and $R_{max}=0.24\%$ %/s higher than coal.

Figure 1. Weight fraction remaining of coal, 20% wood in blend, and wood vs temperature at 50°C/min heating rate during pyrolysis.

Figure 2. Weight loss rate of coal, 20% wood in blend, and wood vs temperature at 50°C/min heating rate during pyrolysis.

Figures 3 and 4 show TG) and DTG of 20% wood in blend at heating rates of 10, 20 and 50°C/min during co-pyrolysis. As heating rates increase, weight loss rates increase (figure 4) but T_{max} and weight fraction remaining are not significantly different (figure 3 and

table 2). This absence of clear trends is likely due to the high heterogeneity of wood and coal, and the relatively small difference between heating rates.

Figure 3. Weight loss of 20% wood in blend vs temperature at heating rates of 10, 20 and 50°C/min during co-pyrolysis.

Figure 4. Weight loss rate of 20% wood in blend vs temperature at heating rates of 10, 20 and 50°C/min during co-pyrolysis.

Table 2. T_{max} , Final Residues, and Kinetic Parameters for Co-Pyrolysis of 10% Wood in Blend

Heating rate (°C/min)	10	20	50
T_{max} (°C)	406±1	380±4	399±2
Final residues (db%)	53.1±1.3	53.4±1.1	53.2±0.6
E_1 (cal/mol)	1841	9154	8341
A_1 (s ⁻¹)	0.0005±0.0001	0.101±0.016	0.116±0.019
E_2 (cal/mol)	6841	14154	13341
A_2 (s ⁻¹)	0.0486±0.0069	43.334±4.674	37.716±3.096

Modeling fitting and Kinetic Parameters of coal, wood and their blends pyrolysis. Single first order reaction (SFOR) kinetic model ^{4b} and competitive two step reaction (CTSR) model that two single first order reactions (SFOR) take place simultaneously are selected to fit the experimental data. The two kinetic models can be described as following equations of SFOR (1) and CTSR (2).

$$\frac{dV(t)}{dt} = A \exp\left(\frac{-E}{RT}\right) (V^\infty - V(t)) \quad (1)$$

where $V(t)$ is the instantaneous volatiles yield; V^∞ is the ultimate volatiles yield (obtained from experiment weight loss data); A is a frequency factor, and E is an apparent activation energy; R is the universal gas constant and T is the sample temperature in K.

$$\frac{dV(t)}{dt} = \{\alpha A_1 \exp\left(\frac{-E_1}{RT}\right) + (1-\alpha) A_2 \exp\left(\frac{-E_2}{RT}\right)\} (V^\infty - V(t)) \quad (2)$$

where A_1 and A_2 are frequency factors for reaction R_1 and R_2 respectively; E_1 and E_2 are apparent activation energy for reaction R_1 and R_2 respectively; and α is the fraction of volatile matter participating into reactions.

SFOR kinetic model was used to obtain E and A by taking natural log of equation 1 and fitting to straight line using the experimental data including the maximum weight loss rate. For CTSR, it was assumed that $E_1 = E$ from the SFOR, and $E_2 = E + 5000$ cal/mol and $\alpha = 0.5$. Then Generalized Reduced Gradient nonlinear solver that minimizes the error between the predicted and experimental weight loss with respect to A_1 and A_2 . Figure 5 shows the experimental and predicted weight losses by CTSR models with respect to temperature for 10% wood in blend. The kinetic parameters for the blend from CTSR are listed in Table 2 at 10, 20 and 50°C/min heating rates. SFOR model failed to replicate the experimental weight loss exactly in all tests of the coal and wood blends. CTSR model fits well with experiment weight loss data.

Figure 5. Weight loss vs temperature of experimental and predicted by two step reactions (CTSR) models for 10% wood in blends at the heating rate of 50°C/min.

Conclusions and Future work

Differences in thermal behavior and reactivity in co-pyrolysis of Powder River Basin (PRB) sub-bituminous coal and pelletized southern yellow pine wood sawdust blends at low heating rates are observed. Coal/wood blends have higher reactivity compared to coal alone in the lower temperature due to the high volatile matter content of wood. As heating rates increase, weight loss rates increase. The experiment data obtained from TGA has a better fit with proposed two step first order reactions model compared single first order reaction model. This is an ongoing study. Experiments at higher heating rates and different type of coal and biomass blends will be performed, and the kinetic model will be further developed.

References

- (1) (a) Hein, K. R. G.; Bemtgen, J. M., EU clean coal technology - co-combustion of coal and biomass. *Fuel Processing Technology* **1998**, *54* (1-3), 159-169; (b) Hughes, E. E.; Tillman, D. A., Biomass cofiring: status and prospects 1996. *Fuel Processing Technology* **1998**, *54* (1-3), 127-142.
- (2) Skone, T. J. Role of alternative energy sources: pulverized coal and biomass co-firing technology assessment; DOE/NETL: 2012.
- (3) Ozawa, T., Thermal analysis - review and prospect. *Thermochimica Acta* **2000**, *355* (1-2), 35-42.
- (4) (a) Antal, M. J.; Varhegyi, G., Cellulose pyrolysis kinetics - the current state knowledge. *Industrial & Engineering Chemistry Research* **1995**, *34* (3), 703-717; (b) Branca, C.; Albano, A.; Di Blasi, C., Critical valuation of global mechanisms of wood devolatilization. *Thermochimica Acta* **2005**, *429* (2), 133-141.