

Co-firing of biomass with coals

Part 2. Thermogravimetric kinetic analysis of co-combustion of fir (*Abies bornmulleriana*) wood with Beypazari lignite

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Abstract The combustion of coal and coal/fir (*Abies bornmulleriana*) wood blends at the proper ratio (20, 40, 50 wt%) was investigated with thermogravimetric analysis (TG). The influence of biomass blends on thermal and kinetic behavior of coal was studied under non-isothermal conditions. The activation energy of the samples was evaluated with the Ozawa–Flynn–Wall model which compares the combustion of these biowastes with coal under non-isothermal conditions. Our research found that blending influences activation energy of coal; moreover, activation energy related to 50 wt% blend was more similar to pure wood combustion than to coal combustion. Therefore, the activation energy profile shifted from 80.6 to 169.3 kJ/mol. The average reaction order of the samples ranged from 0.13 to 0.35.

Keywords Combustion · Coal–wood blends · Thermogravimetric analysis · Non-isothermal kinetics

Introduction

Burning of fossil fuels produce CO₂, a greenhouse gas, that contributes to the global warming. Unlike oil and coal combustion, however, the presence biomass provides a sizeable opportunity to reduce CO₂ emission. Biomass fuels include wood, agricultural residues, wood pulping liquor, municipal solid waste (MSW) and refuse-derived fuel. Combustion technologies convert biomass fuels into several forms of useful energy for commercial or industrial

uses: hot air, hot water, steam, and electricity. The co-firing of biomass with fossil fuels is being considered a promising energy technology for the future [1]. Because today's fossil fuel technologies do not meet environmental needs, biomass is thus becoming a major source of energy in developing countries [2].

From an economic point of view, combustion, pyrolysis, gasification, and liquefaction are the common methods for converting biomass to energy [3]. Among these methods, co-combustion has been a well-established technique for energy harvest from renewable resources. Previous research indicated that combustion of biomass, without fossil fuels led to technical problems such as corrosion and fouling on the hot surfaces [1]. Therefore, biomass as blended with coal during combustion is more advantageous to solve the problems encountered when it is burned alone.

A strong knowledge of thermal properties and kinetics of biomass and coal blends combustion is thus necessary for the efficient design and modeling of co-fired boilers [4]. Thermal gravimetric methods provide useful information in the thermal decomposition of blended samples while measuring weight loss as a function of temperature. Thus, kinetic parameters of the co-combustion process can be estimated under non-isothermal conditions.

Coal-biomass (sewage sludge, paper mill sludge, biomass chars, artificially degraded woods, seaweed, *Eucalyptus dunnii*) combustion has been investigated by many research groups recently [5–13]. In this study, thermal processes in co-combustion of a fir wood with Beypazari lignite samples were investigated and non-isothermal kinetic techniques were used to determine the kinetic parameters. The thrust of this article, therefore, is to identify the thermal behavior and activation energy of the fir wood blended coal samples by the Ozawa–Flynn–Wall model under non-isothermal conditions.

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Experimental

Materials and characterization

Coal and a bark-free fir (*Abies bornmulleriana*) sawdust were used in this study. The coal came from Beypazari, a region central Anatolia. The wood sample used in this study was obtained from Bolu Forest, also in Turkey. Prior to analysis, the coal samples were ground to 65 mesh ASTM under a nitrogen atmosphere and dried at 110 °C under a vacuum. For fir wood samples, 175 µm (–80 mesh) size was used for this study. The proximate and elemental analyses of the coal and the wood samples are given in Table 1. Proximate analysis of coal samples was made according to ASTM D3172, ASTM D3173, ASTM D3174, ASTM D3175 procedures; for wood samples, ASTM E871, ASTM D1102-84, ASTM D3172-89 procedures were used. The carbon, hydrogen, nitrogen, and sulfur content of the samples were determined with CHN-600 and S532-500 analyzers. Higher heating value (HHV) at a constant volume was measured by the Parr 6100 calorimeter.

Thermogravimetric analysis

TG measurements were performed on a Netzsch STA 449 C Jupiter differential thermogravimetric analyzer (precision of temperature measurement ± 2 °C, microbalancesensitivity < 5 µg) under air atmosphere with a flow rate 60 ml/min, at a linear heating rate of 10 °C/min. In order to obtain thermogravimetric curves (TG), each sample (coal and wood) as well as each of the blends (Coal–fir wood 20 wt%, Coal–fir wood 40 wt%, and Coal–fir wood 50 wt%), to prevent heat transfer limitations approximately 20–25 mg was heated at four different heating rates (β) of 5, 10, 20, and 30 K/min over 25–900 °C temperature range as it was also conducted in new reports [14, 15]. To assure reproducibility of satisfactory results, TG experiments were replicated at least twice.

Kinetic theory

The rate of heterogeneous solid-state reactions are defined as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α is the conversion degree, t is the time, T is the absolute temperature, $f(\alpha)$ is a function that depends on the reaction model, and $k(T)$ is the temperature dependent rate constant.

Temperature dependence of the rate constant is usually described by the Arrhenius equation. Thus the rate of the reaction is

$$\frac{d\alpha}{dt} = Ae^{-E/RT}f(\alpha) \quad (2)$$

where A is the preexponential or frequency factor, E is the activation energy, and R is the gas constant.

Non-isothermal rate expression describes reaction rates as a function of temperature at a constant heating rate ($\beta = \frac{dT}{dt} = \text{constant}$). Equation 2 can be rearranged to

$$\frac{d\alpha}{dt} = \frac{1}{\beta} Ae^{-E/RT}f(\alpha) \quad (3)$$

The integration of the Eq. 3 up to conversion α gives directly:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-E/RT} dT \quad (4)$$

According to non-isothermal isoconversional methods applied by Ozawa [16], Wall and Flynn [17] using the Doyle's approximation [18] of $p(x)$, the activation energy can be determined by measuring the temperatures corresponding to fixed values of α from experiments at different heating rates:

$$\ln(\beta) = \ln \left[\frac{AE}{Rg(\alpha)} \right] - 5.331 - 1.052 \frac{E}{RT} \quad (5)$$

By plotting $\ln(\beta)$ versus $1/T$ at different conversion values α gives E_a from the slope.

To find out reaction order, Avrami theory [19–21] employed so as to describe the non-isothermal data where the variation of the degree of conversion with temperature and heating rate can be explained as

Table 1 Analyses of the Beypazari lignite and bark-free fir (*Abies bornmulleriana*) sawdust

Sample	Moisture content/%	Volatiles ^a /%	Ashes ^a /%	C _{fixed} ^a /%	C ^b /%	H ^b /%	N ^b /%	S ^b /%	O ^c /%	HHV ^a /J/g
Coal	6.2	34.9	36.4	22.5	65.2	5.4	2.1	5.4	21.9	17190
Wood	3.7	85.5	0.3	10.5	47.2	6.1	0.3	1.6	44.8	18816

HHV high heat value

^a Dry basis

^b Dry ash free basis

^c Calculated by difference

$$\alpha(T) = 1 - \exp\left[-\frac{k(T)}{\beta^n}\right] \quad (6)$$

Taking double logarithm of both sides of Eq. 6 with substituting Arrhenius equation gives

$$\ln[-\ln(1 - \alpha(T))] = \ln A - \frac{E}{RT} - n \ln(\beta) \quad (7)$$

A plot of $\ln[-\ln(1 - \alpha(T))]$ versus $\ln \beta$, which is obtained at the same temperature from a number of isotherms taken at different heating rates, should give in straight lines whose slope will have the value of the reaction order or the Flynn–Wall–Ozawa exponent n [16, 22].

Results and discussion

Characterization of materials

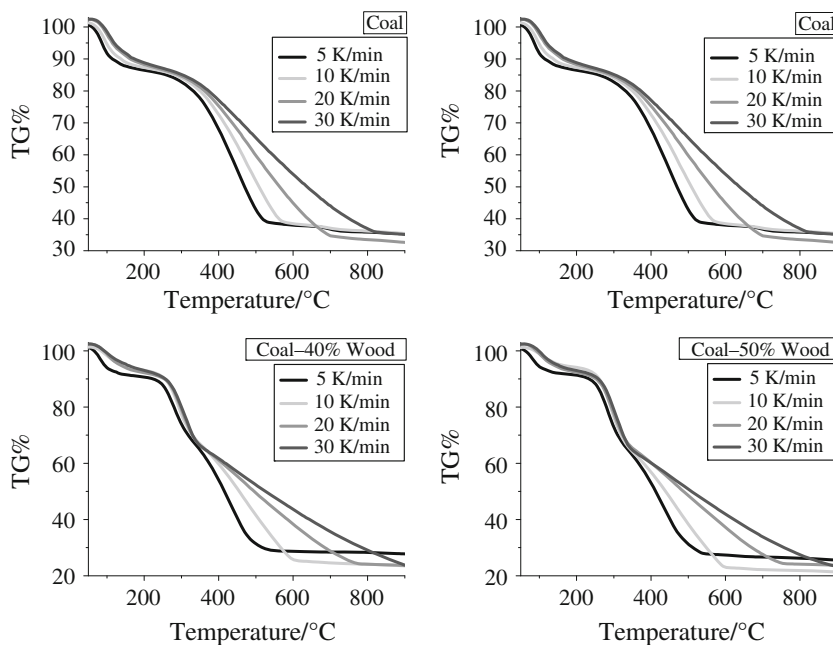
Table 1 demonstrates the elementary and proximate analysis of coal and wood samples. It was found that these two materials significantly differ from each other. The coal showed a relatively higher amount of ash yield than there was in wood. Moreover, the wood sample had much more pronounced volatiles and much lower fixed carbon when compared to coal's volatility and fixed carbon content. Comparison on the basis of HHV, revealed that, both samples show similar values, to the coal and wood samples used in other published works [23, 24]. In terms of elemental analysis, furthermore, coal displays notably higher C, H, N, and S content than does wood.

TG results

Thermal degradation behavior of coal and fir wood blended samples was determined by TG. The TG curves were obtained at 5, 10, 20, and 30 K/min heating rates (β) depicted in Fig. 1. TG results compared for coal, coal–fir wood 20 wt%, coal–fir wood 40 wt%, and coal–fir wood 50 wt% were compared, respectively. It was observed that increasing temperature resulted in weight loss due to combustion. Weight loss in coal case has one sequential zone, while blended samples have two. For all blended samples, devolatilization stage is followed by char oxidation combined with coal combustion step. Furthermore, all samples showed slight change in weight starting from 25 up to 100 °C represents water evaporation.

Coal considered for this study required higher temperatures to begin combustion. This behavior was the result of the difference in the molecular structure strength of coal as compared to that of wood. The wood and other biomass composed of cellulose, hemicellulose, and lignin polymers are linked together with very weak ester bonds. In contrast, high aromatic content of the coal with bond energy of a 1000 kJ mol^{-1} enables superior heat resistance [4, 25]. Although, TG curves of wood blended samples were similar to those of coal, it was found that blending influenced the temperature at which combustion completed, shifting it to higher temperature. Furthermore, with the increased heating rate, TG curves were very close to each other, and the weight loss started at higher temperatures. This trend was attributed to changes in the heat transfer. The increase of heating rate was expected to cause short exposure time to a

Fig. 1 TGA thermograms of the combustion of coal and wood blended samples at different heating rates (β)



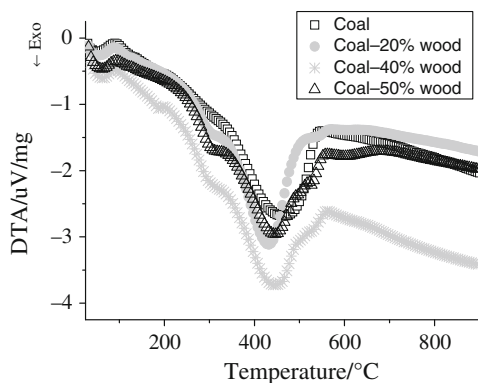


Fig. 2 Combustion DTG curves (5 K/min) for coal and fir wood blended samples

particular temperature which in turn affect combustion kinetics. In addition, residual mass decreased with an increasing amount of wood content in the blend. Because the wood contained less fixed carbon and high volatile matter which volatilized more easily under the combustive conditions prevailed thus leaving less amounts of residual matter behind.

The DTA curves for coal and its fir wood blended sample are illustrated in Fig. 2. It can be seen that between 25 and 100 °C initial mass loss occurred due to water evaporation. Among DTA curves, coal displayed one stage due to combustion. In contrast, blended samples showed two main steps. It was perviously reported that, biomass consists of two steps, first one is pyrolysis of hemicellulose and cellulose, that is followed by char oxidation [26]. In the case of blended samples, char oxidation, and coal combustion is overlapping. As the fir wood amount increase in ratio, first step becomes more significant.

Fig. 3 Curves indicating the kinetic model proposed by Ozawa–Flynn–Wall to various conversion percentages corresponding to the combustion of coal and wood blended coal at different β

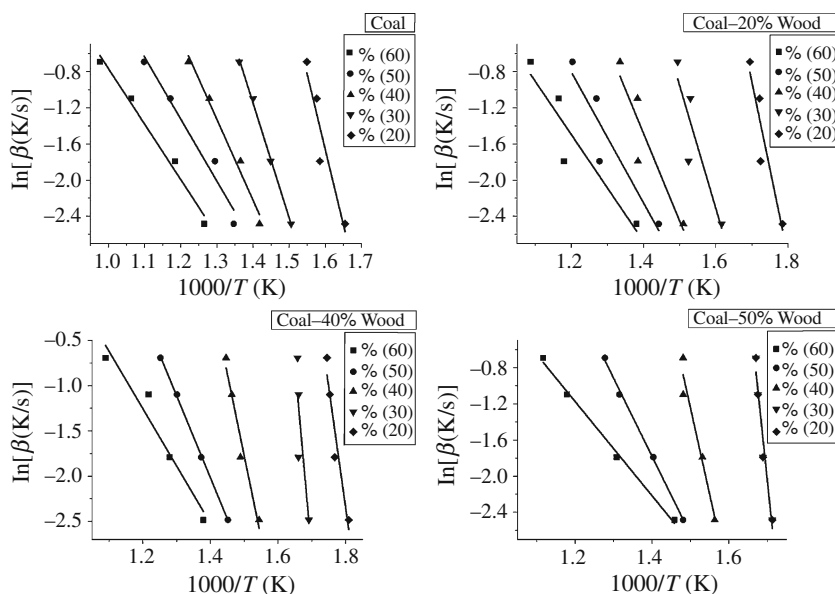


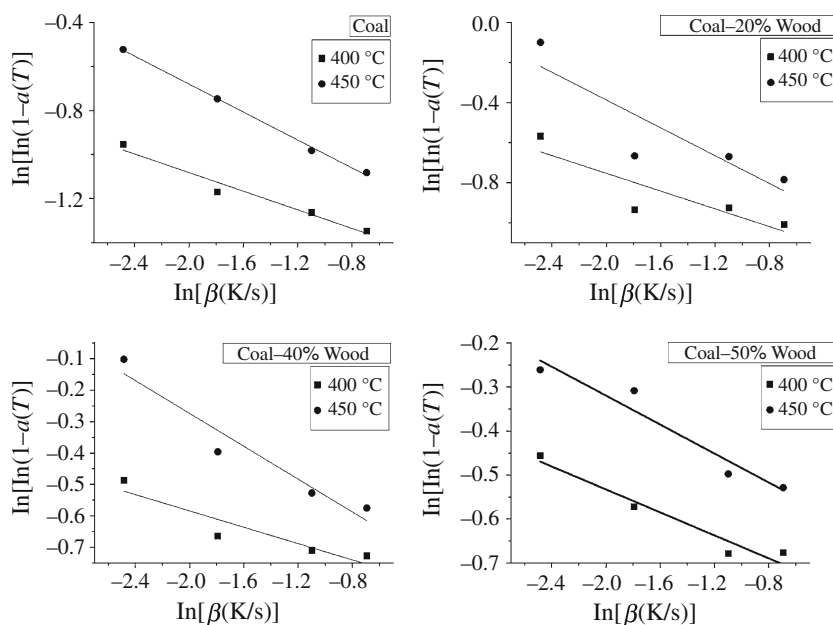
Table 2 Values of activation energy, slopes and correlation coefficients (R^2) corresponding to linear fittings in Fig. 2

Sample	Conversion/%	Slope	E/kJ/mol	R^2
Coal	60	-16.6	131.1	0.894
	50	-12.7	100.4	0.997
	40	-8.9	70.6	0.983
	30	-6.8	54.2	0.966
	20	-6.1	48.5	0.985
Coal-20% wood	60	-19.3	152.1	0.870
	50	-13.5	106.9	0.808
	40	-9.7	76.6	0.846
	30	-7.2	57.2	0.868
	20	-5.9	46.7	0.874
Coal-40% wood	60	-26.7	210.7	0.926
	50	-42.2	333.5	0.727
	40	-18.1	143.1	0.964
	30	-9.1	71.6	0.999
	20	-6.3	50.1	0.947
Coal-50% wood	60	-31.4	248.4	0.912
	50	-40.5	319.9	0.957
	40	-19.1	151.2	0.955
	30	-9.5	75.4	0.990
	20	6.5	51.5	0.986

Table 3 Values of activation energy estimated by the Ozawa–Flynn–Wall isoconversional method

Sample	Average activation energy/kJ/mol
Coal	80.9
Coal-20% wood	87.9
Coal-40% wood	161.8
Coal-50% wood	169.3

Fig. 4 Curves indicating the reaction order n for different temperatures along the combustion of coal and wood blended coal at different heating rates



The plots of $\log \beta$ versus $1/T$ with respect to several conversion degrees are depicted in Fig. 3. For each curve, five different percentages of conversion (α) 20, 30, 40, 50, and 60% were pointed out. It is noted that, there were mostly linear relations for the five different percentages of conversion. Therefore, the activation energies were calculated from the corresponding slopes according to the Ozawa–Flynn–Wall kinetic model. Tables 2 and 3 represent the activation energies at given conversion and average activation energies of the coal and wood blended samples.

The isoconversional method is considered as a good approach for the investigation of combustion kinetics of carbonaceous material, as the dependence of conversion on activation energy is crucial to explore the mechanism and kinetics of decomposition process. According to observations, calculated activation energies for wood blended samples were found consistently higher than those of coal. The wood blends with 40 and 50 wt% possessed relatively similar E values to that of pure fir wood [27]. This result was verified with repeated experiments run for 50 wt% wood blends. On the other hand, the 20 wt% blend was fairly similar to activation energy of the pure wood, but this blend was consistently analogous to activation energy of coal. Resembling the activation energy corresponding to coal was consistent with the activation energies that were reported for low rank coal [28].

Figure 4 shows $\ln[-\ln(1 - \alpha(T))]$ versus $\ln(\beta)$ plot for the comparison of reaction orders. It was expected that n values depend on temperature and type of carbonaceous material. Temperature dependence of n values for coal, and wood blended coal samples are represented in Table 3. It can be seen that the reaction order values were close to

Table 4 Reaction order (n) as a function of temperature

Temperature/°C	Coal	Coal–20% wood	Coal–40% wood	Coal–50% wood
400	0.21	0.21	0.13	0.13
450	0.32	0.35	0.26	0.16
Average n	0.26	0.28	0.19	0.15

zero and the reaction order in the range of 0.13–0.35. Coal and coal–wood 20 wt% had comparable n values and greater than 40 and 50 wt% blended samples.

Conclusions

Comprehensible thermal decomposition differences are observed during the combustion of coal and coal/wood blends. In general: (1) the thermal degradation temperature of coal is higher than that of blended coal samples due to molecular structure strength; (2) increasing the heating rate resulted in more pronounced heat transfer limitations that caused the combustion to complete at higher temperatures; (3) as blending ratio increases, residual mass decreases.

The kinetic analyses demonstrate that the activation energy and reaction order changes in the range of 80.6–169.3 kJ/mol and 0.13–0.35, respectively, depending on blending ratio. Among the tested blends, the 20 wt% blend shows the lowest activation energy (87.9 kJ/mol), while 50 wt% blend has higher activation energy (169.3 kJ/mol). The wood blends with 50 wt% possessed relatively similar E values to that of pure fir wood. This result was verified with repeated experiments run for 50 wt% wood

blends. These values are in agreement with those found in the literature in the combustion of low rank coal and wood (Table 4).

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