INVESTIGATION OF COMBUSTION KINETICS OF BEYSEHIR COAL BY THERMOGRAVIMETRIC ANALYSIS

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Abstract

Some properties of material such as mass, reaction rate, and volume can be measured as a function of increasing temperature, with controllably burning. These type of analysis are called 'thermal analysis methods'. Generally, thermogravimetric (TG) analysis, differential thermal (DT) analysis, and differential thermogravimetric (DTG) analysis techniques are used to determine the combustion characteristics of combustible materials. Thermogravimetric analyse (TGA) is one of the most common techniques used to determine the combustion properties of materials and to investigate their kinetics rapidly.

In this study, the TG analyses were carried out to investigate the combustion characteristics of Beysehir coal. Three different reaction regions were observed in TGA and DTGA curves. The burning profile of the coal sample was investigated by determining the peak temperatures and ignition temperatures. In the kinetic analyses, activation energies were calculated separately for four different reaction orders by using the Coats-Redfern method. It was observed that the moisture of the Beysehir coal moved away between at 25-130 °C, the thermal degradation took place between at 235-540 °C, and the final combustion temperature was 570-690 °C. Weight loss of coal was determined as 28% for the first region, 48% for the second region and 6% for the third region. The ignition temperature and peak temperature were found to be 196 °C and 376 °C, respectively. The activation energies were varied from 8.25 to 18.79 kJ/mol.

Keywords: *coal, combustion, combustion kinetics, TGA, DTGA*

1. INTRODUCTION

Coal is known as a heterogeneous fossil fuel consisting of both inorganic and inorganic components, with high carbon matter and low sulfur and nitrogen content. (Hessley et al., 1986). The organic matter of coal contains different hydrocarbons which ultimately define the calorific value and quality (Stach et al., 1981). These organic contents are defined as macerals and show the burning feature. Assessment of coal resources plays an important role in fulfilling energy demands of countries (Vasireddy et al., 2011). Therefore, the conversion of coal into valuable products by heat treatment should be determined with the physical and chemical behavior of coal, thermal degradation and combustion kinetics. Some material properties, such as mass, reaction rate, and volume can be measured as a function of increased temperature, with controllable combustion. One of the thermal analysis, TGA, is a method of measuring the changes in the materials as a function of time. (Coats and Redfern, 1963). The combustion characteristics of coal depend on both the specific properties of itself such as rank, type, grain size as well as the measurement parameters such as temperature, heating rate, gas flow rate and volume. (Benfell et al., 1997; Benfell et al., 1999; Morgan et al., 1987; Jayaweera et al., 1989; Kok et al., 1997; Milligan et al., 1997).

In this study, the combustion characteristics of lignite coal obtained from Konya-Beysehir region were investigated through thermogravimetric analyses. The burning profile of coal was interpreted from the TG and DTG curves and the reaction regions, peak temperatures and ignition temperatures were determined.

2. MATERIALS AND METHODS

2.1. Materials

Approximately 50 kg of coal sample obtained from coal mine was stored in airtight containers and prevented from oxidation. The amount of coal was decreased by the coning and quartering method after the mixing of the sample homogeneously. A jaw crusher and a ball mill available in the laboratory were used for size reduction. All of the grinded sample was sieved to a size of -106 µm. The prepared sample was kept in the bag for using to the calorific and thermogravimetric analysis. The proximate analysis of the coal sample was performed and obtained results were given in Table 1. The coal sample had a high ash content with low fixed carbon (FC) values. Therefore the lower heating value (LHV) of sample was determined as 3747 kcal/kg.

Table 1. Proximate Analysis of Coal Sample

Coal Sample	Ash, (%)	VM, (%)	FC, (%)	UHV, (kcal/kg)	LHV, (kcal/kg)
Beysehir	37.60	44.11	18.29	3957	3747

2.2. Methods

The calorific value of coal was determined by using the LECO brand AC-350 model of adiabatic oxygen bomb calorimetry at the ASTM D 5865-11a standard (ASTM D 5865-11a 2011). Approximately 1 g of sample was placed into the calorific bomb called the high pressure atmospheric combustion bomb. The bomb was surrounded by water. After the necessary regulations the sample in the bomb was ignited and then, the coal sample in the bomb was burned in the oxygen environment. The calorific value of sample was determined from the temperature difference of water surrounding the combustion bomb.

Thermogravimetric analyses were performed under the dry air atmosphere and a PL (Polymer Laboratories) brand TGA 1500 model instrument was used to determine the TG analyses of the coal sample. Approximately 10 mg of the coal sample was placed into the crucible of device and heated at 25 °C to 900 °C with a heating rate of 10 °C/min. The air flow was 5 ml/min. E_a (activation energies, kJ/mol) values were calculated by applying the Coats-Redfern method to the reached data.

3. RESULTS AND DISCUSSION

Thermogravimetric analysis (TG) provides a rapid assessment of the combustion characteristics of a burnable sample. However, this analyse also determines the important parameters such as combustion temperature, total mass loss and combustion period. There are three different reaction zones in the TG curves. The moisture removes in the first region, the volatiles are moved away and the burning of the carbon takes place in the second region. In the third region, the coal is exposed to decomposition. The TG and DTG curves of the coal sample were given in Fig. 1.

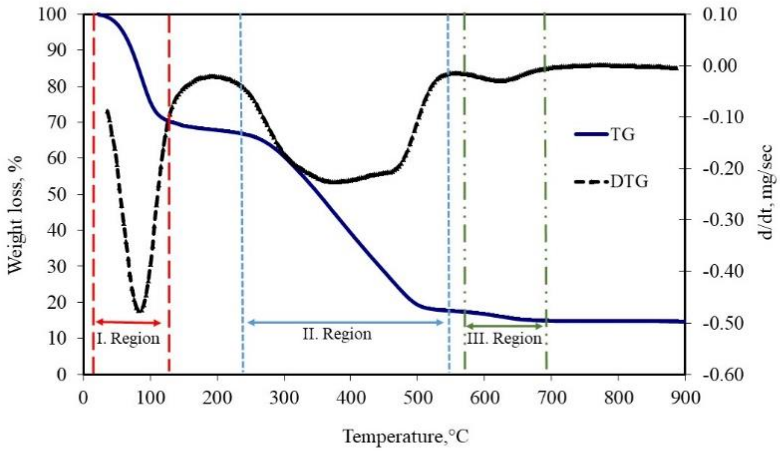

Fig. 1. TG and DTG curve of coal sample.

The maximum mass loss was observed in the second region from the TG curve (Fig. 3). That is, the burning of the carbonaceous part of the coal was taken place in this region. The temperature intervals of each reaction regions and the observed mass losses of the coal were summarized in Table 2.

Table 2. Temperature interval for reaction regions and mass loss.

	I. Region	II. Region	III. Region
Temperature interval, °C	25-130	235-540	570-690
Mass loss, %	30	50	7

DTG curve was obtained from them by taking the derivative of the weight change of sample against to time by using Equation 1. This curve shows the change in mass loss rates with increasing temperature. In this study, the ignition temperature and peak temperature for the coal sample were calculated by using DTG results.

$$\frac{(T_{final}-T_{inital})}{(t_{final}-t_{inital})} = \frac{dW}{dt} \quad (1)$$

Where, T is temperature (°C), t is time (min), W is the weight of the sample (mg).

The ignition temperature, peak temperature, final combustion temperature and total mass loss of the coal sample were determined and given in Table 3.

It is stated from the literature that the lignite coal could be ignited at temperatures between 200-300 °C depending on their volatile matter contents (Moon et al., 2013; Idris et al., 2012; Toptas et al., 2015; Atibeh and Yozgatligil, 2013; Pintana and Tippayawong, 2013). The ignition temperature of Beysehir coal was determined as very close to the literature to be 196 °C. The peak and burnout temperatures were determined as 376 °C and 690 °C, respectively. Total mass loss of coal was also ascertained as 87%. The Tp is considered as a measure of the reactivity of a coal. The lower the maximum peak temperature, the more reactive a coal may be regarded (Cumming, 1984; Kneller, 1986).

Table 3. Combustion characteristics of the coal sample.

Combustion characteristics	**Values**
Ignition temperature, °C (T_i)	196
Peak temperature, °C (T_p)	376
Burnout temperature, °C (T_b)	690
Total mass loss, %	87

Generally, Coats - Redfern (1964) method is used to investigate the thermal decomposition of coal. In this study, Equation 1 and 2 were used to assay the TGA data obtained from experiments.

$$\ln\left[-\left(\frac{\ln(1-\alpha)}{T^2}\right)\right] = \ln\left[\left(\frac{A_r R}{\beta E}\right)\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad \text{for } (n=1) \qquad (1)$$

$$\ln\left[-\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\left(\frac{A_r R}{\beta E}\right)\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad \text{for } (n\neq 1) \qquad (2)$$

where; T is absolute temperature (K), n is reaction order, A_r is Arrhenius constant, (1/min), β rate of heating (K/min), R is gas constant (J/mol, K), E is activation energy (kJ/mol). α is weight loss degrees and calculated by following Equation (3).

$$\alpha = \frac{(m_0-m_t)}{(m_0-m_f)} \qquad (3)$$

Where; m_0, m_t and m_f are initial weight of coal (g), weight of coal at *t* time (g) and final weight of coal burnt down (g), respectively.

Plots of $\ln\left[-\left(\frac{\ln(1-\alpha)}{T^2}\right)\right]$ against $\frac{1}{T}$ for n=1 or plots of $\ln\left[-\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ against $\frac{1}{T}$ for n≠1 is equal to $-\frac{E}{RT}$. The activation energy (E_a) can be obtained from the slope of the line, –E/R.

The activation energies of Beysehir coal for four different reaction orders (0.5, 0.67, 1, 1.5) were separately calculated and given in Table 4. A sample for reaction order of 1 was also given in Fig. 2. It was determined that the activation energies of the Beysehir coal varied between 8.25 and 18.79 kJ/mol depending on the order of reaction. Different activation energies were obtained against different reaction orders at constant-heating-rate conditions in this model. The obtained activation energy was increased as the reaction order increased.

Table 4. Activation energies of coal sample for different reaction orders

Reaction order, n	**Slope of curves**	**Activation energy, E_a kJ/mol**
0.5	0.9918	8.25
0.67	1.2284	10.21
1.0	1.7267	14.36
1.5	2.2603	18.79

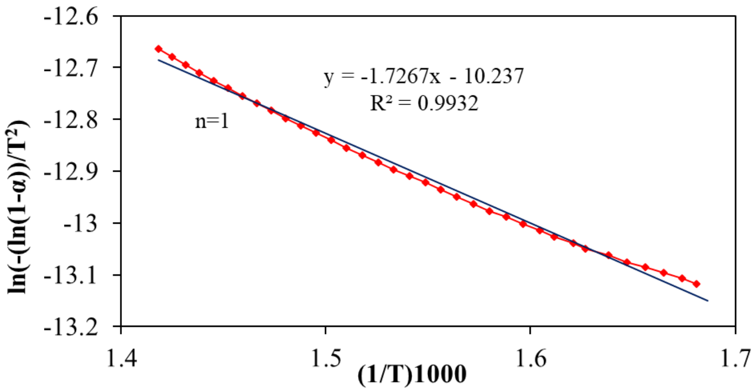

Fig. 2. Plots of ln(-ln(1α)/T^2) versus (1/T)1000 of the coal sample **(**for n=1)

4. CONCLUSIONS

The TG and DTG analyses were carried out to determine the combustion behavior of Beysehir coal. The following results were reached.

- Three different reaction regions were observed in the TG and DTG profiles of coal.
- The ignition temperature, peak temperature and burnout temperature of Beysehir coal were ascertained as 196 °C, 376 °C and 690 °C, respectively.
- Total mass loss of coal was determined as to be 87%. It was observed that the 30% of mass loss was in the first region, 50% of mass loss was in the second region and 7% of it was in the third region.
- The activation energies of Beysehir coal were varied between 8.25 and 18.79 kJ/mol depending on the order of reaction.

ACKNOWLEDGMENTS

The authors greatly acknowledge the financial support provided by Scientific Research Project Fund of Selcuk University.

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