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COMBUSTION CHARACTERISTICS OF LIGNITE AND OIL SHALE SAMPLES BY THERMAL ANALYSIS TECHNIQUES

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Abstract

In this research thermal analysis and kinetics of ten lignite's and two oil shale samples of different origin were performed using a TA 2960 thermal analysis system with thermogravimetry (TG/DTG) and differential al analysis (DTA) modules. Experiments were performed with a sample size of ~10 mg, heating rate of 10°C min^{-1}. Flow rate was kept constant (10 L h^{-1}) in the temperature range of 20–900°C. Mainly three different reaction regions were observed in most of the samples studied. The first region was due to the evaporation of moisture in the sample. The second region was due to the release of volatile matter and burning of carbon and called as primary reaction region. Third region was due to the decomposition of mineral matter in samples studied. In kinetic calculations, oxidation of lignite and oil shale is described by first-order kinetics. Depending on the characteristics of the samples, the activation energy values are varied and the results are discussed.

Keywords: activation energy, coal, kinetics, lignite, oil shale, thermal analysis

Introduction

Thermal analysis is a popular and convenient tool in studying combustion reactions of fossil fuels. The requirement of only a small amount of material coupled with the comparatively fast and easy performance of experiments makes the technique attractive. Thermal analytical instruments monitor the changes in properties caused by different processes. Thermogravimetry (TG/DTG) measures the mass loss of a sample as function of temperature or time and can be used to measure any reaction involving mass change. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are the methods widely used in characterization of fossil fuels undergoing combustion or pyrolysis.

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Ciuryla and Weimar [1] performed thermogravimetric characterization of four different coals and their chars to obtain fundamental information on pyrolysis, and coal and char reactivity for these materials. The results indicate that the temperature of the maximum rate of volatilization increases with heating rate for all coals. Cumming [2] has developed a method for describing the reactivity or combustibility of solid fuels, such as lignite, bituminous coals and petroleum coke, in terms of a weighted mean apparent activation energy, derived from simultaneous TG/DTG readings on a 20 mg sample heated at a constant rate in a flowing air atmosphere. He proposed that the mean activation energy method should be the established method, which involves recording overall temperatures on the burning profile curve. Smith and Neavel [3] carried out coal combustion experiments in the temperature range 25–900°C using air at atmospheric pressure in a derivative thermogravimetry analysis system. Sixty-six coals with high vitrinite and low inorganic contents were examined as part of a coal characterization program. The rate data were fitted to an Arrhenius equation and plots showed four distinct regions of combustion. Calculated apparent activation energies were of the correct orders of magnitude to describe combustion regions corresponding to chemical-reaction-controlled as well as diffusion-controlled processes. Morgan and Robertson [4] determined coal burning profiles by thermogravimetric analysis. They have claimed that kinetic parameters from Arrhenius plots of the profiles cannot readily be related to any specific stage of combustion. However some features of the profiles are clearly related to coal properties and a correlation exists between unburned carbon loss as predicted from high-temperature oxidation rates and a characteristic temperature of the thermogravimetric profile. Smith *et al*. [5] investigated the burning process of sixty-six coal samples, from lignite to black coal, and found that the burning temperature for half of these coal types is linearly dependent on their concentration. Haykiri *et al*. [6] investigated the behavior of some fossil fuels during thermal treatment. DTA and TG were applied to peat, lignite, bituminous coal, anthracite, oil shale and asphaltite samples under a nitrogen atmosphere and the results are discussed. They concluded that an increase of the volatile matter content causes a decrease in the maximum mass loss rate temperature. Earnest [7] analyzed the thermal behavior of Green River oil shale in a dynamic nitrogen atmosphere with TG and DTG and compared it with that in retorting processes. Using the results of this study, the pyrolysis onset temperatures and the temperatures at the maximum pyrolysis rate were related to the type of organic maceral components of the oil shale specimen. Guldogan *et al.* [8] determined the pyrolysis kinetics of lignite at different heating rates by TG/DTG. Although some differences were obtained at different heating rates, the same volatile matter yield of 40.7% of the total mass of the sample was calculated. Lower activation energies (~24.8 kJ mol^{-1}) were calculated at higher heating rates. Várhegyi *et al*. [9] discussed several techniques for the handling of the non-statistical errors during the least-squares evaluation of kinetic data. The methods were illustrated by the evaluation of oxidative thermogravimetric experiments on lignite. Altun *et al.* [10] investigated the effect of particle size and heating rate on the combustion properties of asphaltites. TG/DTG experiments were carried out at three different size fractions and five different heating rates. Weighted mean activation energies of the samples were around 47.5 kJ $\mathrm{mol^{-1}}$. As the particle size was decreased and the heating rate was increased, the activation energies of combustion of the samples also increased. Torrente and Galan [11] studied the kinetics of thermal decomposition of oil shale using TG/DTG. The rate of thermal decomposition of oil shale could be suitably described by overall first-order kinetics. No mass and heat transfer resistance was observed for the different particle sizes studied. Jaber and Mohsen [12] investigated the drying kinetics of two oil shales from different deposits over a temperature range of 70–150°C using TG/DTG. The drying rate decreases at a critical temperature (120°C) and approaches zero beyond this temperature. Li *et al.* [13] investigated the pyrolysis of oil shale kerogen using TG/DTG. An overall first-order reaction model was successfully used to simulate mass loss data. The activation energies measured for most of the oil shales studied ranged from 160 to 170 kJ $\mathrm{mol^{-1}}$. Khraisha and Shabib [14] used TG/DTG and DSC for investigation of oil shale. The mass loss data show that the pyrolysis of shale oils takes place in one regime, and that the major mass loss occurs in the range of 175–450°C. The DSC data reveal the endothermic behaviour of the decomposed samples. The results could be described by a first-order reaction and the measured activation energies varied from 21 to 30 kJ $\mathrm{mol^{-1}}$. Kok [15] analysed the combustion curves of seventeen lignite samples using TG/DTG. The relationships between peak temperature, burnout temperature, moisture content, ash, volatile matter, fixed carbon and calorific values of the samples were examined. Xie and Pan [16] reviewed the thermal characterization of materials using evolved gas analysis. TG/FTIR, TG/MS and pyrolysis/GC-MS systems and their applications in the study of several materials were discussed, including the analysis of the degradation mechanisms of originally modified clays, polymers and coal blends. Avid *et al.* [17] determined the influence of temperature, heating rates (10–50°C $\mathrm{min^{-1}}$) and purge gas (N_2 and CO_2) employed on the thermal degradation of coal samples pyrolysed non-isothermally in a thermogravimetric analyser. The coal was also investigated in a fixed-bed reactor to determine the influence of temperature and heating rate of the pyrolysis on the yield of products and composition of gases evolved. Ozbas *et al.* [18] determined the kinetic analysis of different coals and studied the effect of cleaning process on kinetic parameters of raw and cleaned coal samples using thermogravimetry (TG-DTG). Kinetic parameters of the samples are determined using different kinetic models and the results are discussed. Ozbas *et al.* [19] used DSC to determine the combustion behaviour and kinetic analysis of raw and cleaned coal samples of different size fractions. DSC curves of the samples showed two reaction regions. Kinetic parameters of the samples are determined and the results are discussed.

Experimental

Coal and oil shale experiments were performed using TA 2960 thermal analysis system with TG/DTG and DTA modules. Experiments were performed with a sample size of ~10 mg, at heating rate of 10°C $\mathrm{min^{-1}}$. Air flow rate through the sample pan was kept constant at 10 L $\mathrm{h^{-1}}$ in the temperature range of 20–900°C. Prior to the experiments, the instrument was calibrated for temperature readings, using indium as reference material. The balance was calibrated for buoyancy effect allowing the quantitative estimation of mass changes and all the experiments were performed twice for repeatability. Properties of the samples are given in Table 1.

Table 1a Properties of lignite samples

Sample	Calorific value/kJ kg^{-1}	C/%	H/%	O, N/%	S/%
Çeltek	14630	45.19	2.95	10.43	1.25
Milas	6715	32.08	2.68	12.14	3.09
Horasan	6205	16.64	1.58	12.08	1.30
Sorgun	20585	61.42	3.79	13.63	4.10
Kangal	6245	19.70	1.55	9.39	3.57
Keles	2103	28.38	2.29	9.31	4.23
Seydişehir	8790	19.96	1.50	7.77	1.66
Soma	13155	51.60	3.89	16.99	0.92
Elbistan	4390	20.60	1.82	9.88	1.46
Gülşehir	20900	38.51	3.27	6.05	6.05

Table 1b Properties of oil shale samples

Sample	Calorific value/kJ kg^{-1}	C/%	H/%	O, N/%	S/%
Beypazari	3555	8.40	1.6	4.55	0.21
Ulukişla	3845	7.96	1.4	4.22	0.24

Results and discussion

Theoretically, the combustion of fuel can be initiated whenever oxygen comes into contact with fuel. However, the temperature and composition of the fuel and air supply dictate the nature of the reactions. The first region was due to the evaporation of moisture in the sample. The second region was due to the release of volatile matter and burning of carbon and mentioned as the primary reaction region. Third region was due to the decomposition of mineral matter in the investigated samples. The main mass loss occurs in the second region, which proves the combustion of the carbonaceous part of the sample (Figs 1 and 2). The main characterization point on the TG/DTG curve is the peak temperature where the rate of mass loss is maximal. Beyond the peak temperature the derivative curve falls rapidly to the so called burn-out temperature. The burn-out temperature represents the temperature where sample oxidation is complete (Table 2). According to the TG/DTG analysis of oil shales, it was observed that the amount of the organic matter content involved in the combustion reaction varies between 16.9–46.8%. This situation supports that oil shale grade increases with the increasing content of organic matter.

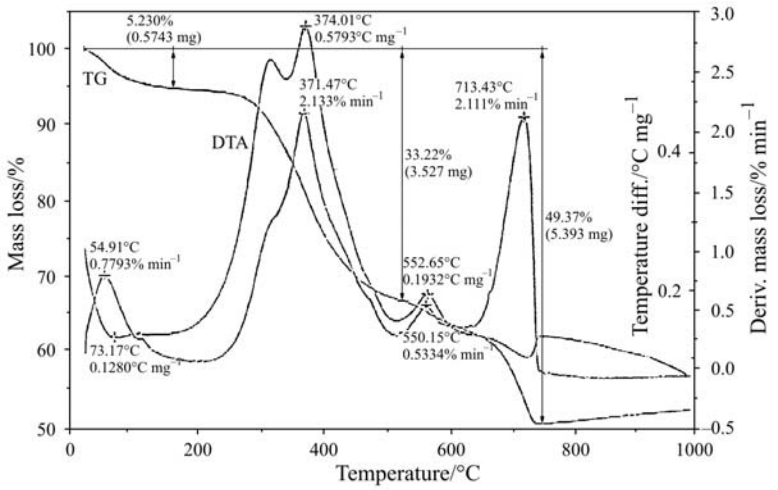

Fig. 1 TG/DTG and DTA curves of Soma lignite

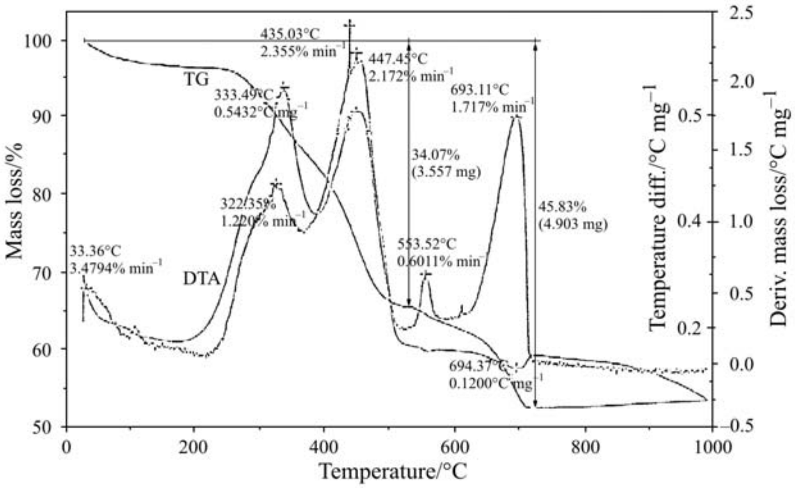

Fig. 2 TG/DTG and DTA curves of Ulukişla oil shale

Kinetic analysis

The combustion kinetics of fossil fuels is extremely complex, but if certain broad generalizations are made, certain useful information can be deduced. When the sample size is small and with an excess air supply, the progress of the reaction is independent of the oxygen concentration. It is therefore reasonable to assume that the oxidation can be described by first-order kinetics (Arrhenius method). In this method [20–22], the model assumes that the rate of mass loss of the total sample only depends on the rate constant, the remaining sample mass and the temperature with first-order kinetics. Ap-

Table 2a Results of DTA and TG/DTG curve analysis of lignite samples

Sample	Peak temperature I/°C	Peak temperature II/°C	Mass loss/%
Çeltek	414.1	438.1	95.91
Milas	418.3	490.5	86.91
Horasan	377.8	429.1	67.58
Sorgun	361.3	428.6	40.03
Kangal	327.5	401.8	48.39
Keles	382.8	482.9	49.80
Seydişehir	477.5	–	80.18
Soma	371.5	–	49.39
Elbistan	308.3	371.1	79.53
Gülşehir	428.7	463.2	81.25

Table 2b Results of DTA and TG/DTG curve analysis of oil shale samples

Sample	Peak temp. I/°C	Peak temp. II/°C	Burn-out temp./°C	Mass loss/%
Beypazari	400.6	642.5	702.4	16.9
Ulukişla	447.4	693.1	710.8	46.8

plication of this model to the TG/DTG curves is easy and fast. So the equation of the Arrhenius-type kinetic model takes the following form.

$$\mathrm{d}W/\mathrm{d}t = kW^{n} \tag{1}$$

$$k = A_{\mathrm{r}}\exp(-E/RT) \tag{2}$$

where $\mathrm{d}W/\mathrm{d}t$ is the rate of mass change, E is the activation energy, T is the temperature, A_{r} is Arrhenius constant and n is the reaction order.

Assuming first-order kinetics,

$$\mathrm{d}W/\mathrm{d}t = A_{\mathrm{r}}\exp(-E/RT)W \tag{3}$$

$$\frac{1}{W}\frac{\mathrm{d}W}{\mathrm{d}t} = A_{\mathrm{r}}\exp\left(-\frac{E}{RT}\right) \tag{4}$$

Taking the logarithm of both sides,

$$\lg\left(\frac{1}{W}\frac{\mathrm{d}W}{\mathrm{d}t}\right) = \log A_{\mathrm{r}} - \frac{E}{2.303RT} \tag{5}$$

When $\lg[(\mathrm{d}W/\mathrm{d}t)/W]$ is plotted *vs.* $1/T$, a straight line is obtained which will have a slope equal to $E/2.303R$ and from the intercept the Arrhenius constant can be estimated.

Modeling of reaction kinetics for combustion process of lignite and oil shale is extremely complicated, because several components are simultaneously oxidized. In kinetic calculations oxidation of samples is described by first-order kinetics. Therefore the data reported here were obtained by taking the reaction order as unity. Activation energies of the samples were determined for all the reaction regions. The individual activation energies for each reaction region can be attributed to different reaction mechanisms, but they do not give any indication of the contribution of each region to the overall reactivity of the lignite. Depending on the characteristics of lignite and oil shale samples, higher activation energy values are obtained at higher reaction temperatures (Table 3).

Table 3a Activation energy values of the lignite samples

Sample	Activation energy/kJ mol^{-1}		
	I. Region	II. Region	III. Region
Çeltek	31.7	128.8	273.5
Mials	37.6	62.9	157.8
Horasan	26.5	–	59.7
Sorgun	26.7	–	77.1
Kangal	26.7	51.3	105.3
Keles	33.7	–	56.9
Seydişehir	26.6	65.3	174.6
Soma	35.3	82.9	188.5
Elbistan	25.2	60.1	274.8
Gülşehir	51.5	–	264.5

Table 3b Activation energy values of the oil shale samples

Sample	Activation energy/kJ mol^{-1}		
	I. Region	II. Region	III. Region
Beypazari	32.3	–	47.7
Ulukişla	36.1	58.7	176.3

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