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NON-ISOTHERMAL DSC AND TG/DTG ANALYSIS OF THE COMBUSTION OF SİLOPİ ASPHALTITES

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In this research, non-isothermal combustion and kinetics of Silopi (Turkey) asphaltite samples were investigated by differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG). A sample size of 10 mg, heating rates of 5, 10, 15 and 20°C min^{-1} were used in the temperature range of 20–600°C, under air atmosphere. Two reaction regions were observed in DSC curves. The first region is due to the evaporation of moisture in asphaltite sample whereas, release of volatile matter and burning of carbon is called the second region.

A general computer program was developed and the results of four different kinetic models (Arrhenius, Coats–Redfern, Ingraham–Marrier and Horowitz–Metzger) are compared and discussed with regards to their accuracy and the ease of interpretation of the kinetics of thermal decomposition. In general similar activation energy values were obtained when the kinetic models are compared with each other. It was also observed that there was no general trend in the activation energy values from the point of heating rates.

Keywords: *coal, combustion, kinetics, thermal analysis*

Introduction

Turkey has very large resources of low quality lignite and asphaltite. The asphaltic substances encompass a great variety in character depending upon their locality, geological formation and the degrees of progress in metamorphosis. The characteristic properties of these substances are associated with varying amounts of mineral matter in a finely divided form.

Cumming [1] 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. He proposed that the mean activation energy method be the established method, which involves recording overall temperatures on the burning profile curve. Morgan and Robertson [2] determined coal-burning profiles by TG/DTG. They have claimed that kinetic parameters from Arrhenius plots of the profiles cannot readily be related to any specific stage of combustion. El-Akrami *et al.* [3] described different procedures for the preparation of stabilized fibers from asphaltite products. The asphaltite pitches obtained by different methods are characterized by various techniques such as elemental and thermogravimetric analysis (TG/DTG). Iordanidis *et al*. [4] carried out thermogravimetry (TG/DTG) experiments for seven lignite samples. The burning profiles of the samples studied, combined with proximate analysis and calorimetry results, contribute to a clearer identification of lignite structure and a better understanding of the coalification process. Várhegyi *et al.* [5] developed least squares criteria for the kinetic evaluation of thermal analysis experiments. They discussed several evaluation techniques for the handling of the non-statistical errors during the least squares evaluation of experimental series. The methods are illustrated by the evaluation of oxidative thermogravimetric experiments of lignite. Altun *et al*. [6] comprised the effect of particle size and heating rate on the pyrolysis of asphaltites. Results showed that there are significant differences in the pyrolysis characteristics and kinetics of the samples according to different size fractions and heating rates. Ozbas *et al*. [7] used differential scanning calorimetry (DSC) to determine the combustion behavior and kinetics analysis of raw and cleaned coal samples of different size fractions. DSC curves of the coal samples studied showed two reaction regions. Kinetic parameters of the samples are determined by different kinetic models and the results are discussed. Duz *et al.* [8] examined the relationship between particle size and chemical composition of coal samples by elemental analysis and by thermogravimetric pyrolysis. The results indicate that activation energies increase as the particle size decreases. Ballice [9] investigated the oxidation of Şırnak asphaltite samples under isothermal conditions using a fixed-bed reactor in various temperature modes. The effect of heating rate on reaching final isothermal temperatures was investigated and kinetic

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parameters of the overall oxidation reaction for each heating rate determined. Kök *et al.* [10–17] studied the pyrolysis and combustion behavior of fossil fuels. The pyrolysis and combustion characteristics of the samples were analyzed using DSC, DTA and TG/DTG. Combustion kinetics of the samples was determined using different type kinetic models. Results showed that there are significant differences in the combustion characteristics and kinetics of the samples according to origin, different size fractions and heating rates.

The aim of this work is to study the thermal behavior and combustion kinetics of asphaltite sample at different heating rate on decomposition temperatures. The importance and the main innovation of the present study is the application of different kinetic models and their interpretation.

Theory

Thermal analysis techniques are widely used in the evaluation of kinetic parameters of solid-state decomposition processes. Non-isothermal kinetic study of mass loss (TG/DTG) under combustion process is extremely complex for fossil fuels because of the numerous complex components and their parallel and consecutive reactions. A number of models have been developed to obtain kinetic parameters from the TG/DTG data in order to study the mechanisms of solid-state decomposition reactions. In this research, four different kinetic models (Arrhenius, Coats–Redfern, Ingraham–Marrier and Horowitz–Metzger) were used in order to determine the kinetic parameters of Silopi asphaltite sample. In this study, to determine the kinetic parameters for the combustion of asphaltite sample, the first order thermal decomposition model was assumed in three models, whereas different reaction orders were used in Coats and Redfern model.

The calculation of kinetic data is based on the formal kinetic equation,

$$d\alpha/dt = k\alpha^{n} \tag{1}$$

The temperature dependence of *k* is expressed by the Arrhenius equation:

$$k=A\exp(-E/RT) \tag{2}$$

In Arrhenius model [18], since the measured rate of mass loss accounts for gross changes in the system, the Arrhenius-type reaction model assumes that the rate of mass loss of the total sample dependent only on the rate constant, the mass of sample remaining and the temperature. In this model reaction order is selected as 1. The final form of the equation is as follows:

$$\log[(dw/dt)/w]=\log A-E/2.303RT \tag{3}$$

Coats and Redfern [19] developed an integral method, which can be applied to TG/DTG data, assuming different order of reactions. In this model reaction orders are assumed as 1/2, 2/3, 1, 3/2 and 2. The correct order is presumed to lead to the best linear plot, from which the activation energy is determined. The final form of the equation, which is used for analysis is as follows:

$$\log[1-(1-\alpha)^{1-n}/T^{2}(1-n)]= \log[AR/\beta E)(1-2RT/E)-(E/2.303RT)] \tag{4}$$

Ingraham and Marrier [20] developed a simplified method for the determination of a heterogeneous reaction exhibiting linear kinetics. In this model reaction order is assumed as 1. The final form of the equation, which is used for analysis, is as follows:

$$\log(dw/dT)=\log T-\log\beta+\log A-E/2.303RT \tag{5}$$

In Horowitz and Metzger model [21], a reference temperature was defined at the point of inflexion of the reaction curve and changed the variable temperature. In this model reaction order is assumed as 1. The final form of the equation, which is used for analysis, is as follows:

$$\ln[1-(1-\alpha)^{1-n}/(1-n)]=(E/RT^{2}_{\mathrm{m}})\theta \tag{6}$$

where: α=fraction of sample decomposed (%); T= temperature (K); A=pre-exponential factor (s^{-1}); R= gas constant (8.314 J mol^{-1} K^{-1}); E=activation energy (kJ mol^{-1}); β=heating rate (°C min^{-1}); T=temperature (K); dw/dt= the loss in mass from unit area in the period of time; n = reaction order; T_{m}=peak temperature (K) and $\theta=T-T_{\mathrm{m}}$.

Experimental

In this research, combustion experiments were performed with DuPont 9900 thermal analysis system with differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG) modules. DSC monitors differential heat flow of the samples whereas TG/DTG has the capability of measuring the mass loss either as a function of temperature or time in a

Table 1 Proximate and ultimate analysis of asphaltite sample

Moisture/%	Ash/%	Volatile matter/%	Fixed carbon/%	Cal.value/ kcal kg^{-1}	C/%	H/%	S/%	N,O/%
0.88	35.9	18.8	13.2	5540	54.2	5.07	8.23	0.25

varied but controlled atmosphere. Prior to the experiments DSC system was calibrated for temperature readings using indium as reference standard. The TG/DTG system was also calibrated with calcium oxalate monohydrate for temperature readings and silver was used in order to correct for buoyancy effects. The asphaltite sample used in this research had a particle size <60 mesh and prepared according to the ASTM Standards (D 2013-72). DSC and TG/DTG experiments were performed with a sample size of ~10 mg, at four different heating rates (5, 10, 15 and 20°C min^{-1}). Air flow rate through the sample pan was kept constant at 50 mL min^{-1}, in the temperature range of 20–600°C. For repeatability, some of the experiments were performed twice. The properties of the asphaltite sample [22] are given in Table 1.

Results and discussion

Theoretically, the combustion of fuel can be initiated whenever oxygen comes into contact with the sample. However, the temperature, composition of the fuel and the air supply dictate the nature of the reaction. In the temperature region of 200–350°C, coal samples start to loose small amounts of pyrolysis water from decomposing phenolic structures, and oxides of carbon from carboxylic and carbonyl groups. At around 350°C, primary carbonization starts initially with the release of carbon dioxide and hydrogen. Methane and other lower aliphatic are evolved together with hydrogen, carbon monoxide and alkyl aromatics with an increase in temperature [23].

In combustion of Silopi asphaltite, differential scanning calorimetry (DSC) curves revealed two reaction regions in the asphaltite sample studied (Fig. 1). The first region is due to the evaporation of moisture in asphaltite sample. Release of volatile matter and burning of carbon is called the second region. This is the primary reaction region where the mass loss is mainly observed in TG/DTG curves (Fig. 2). It is observed that, due to the petroleum origin of asphaltite, as the heating rate is increased, the melting of the material occurs faster and this melting results in higher burn-out temperatures. Burn-out temperature represents the temperature where sample oxidation is complete. The main characterization point in DSC and TG/DTG curves is the maximum peak temperature that represents the maximum mass loss. In this study, it was also observed that maximum peak temperatures increased as the heating rate is increased from 5 to 20°C min^{-1}. Another important point about the maximum peak temperatures is that as the heating rate increased, the mass losses occurring at the maximum peak temperatures decreased. This may be the result of longer reaction time allowed and slower combustion at lower heating rates. The temperature regions, peak and burn-out temperatures of the asphaltite sample at each heating rate are given in Tables 2 and 3 respectively.

In this research, four different kinetic models (Arrhenius, Coats–Redfern, Ingraham–Marrier and Horowitz–Metzger) were used in order to determine

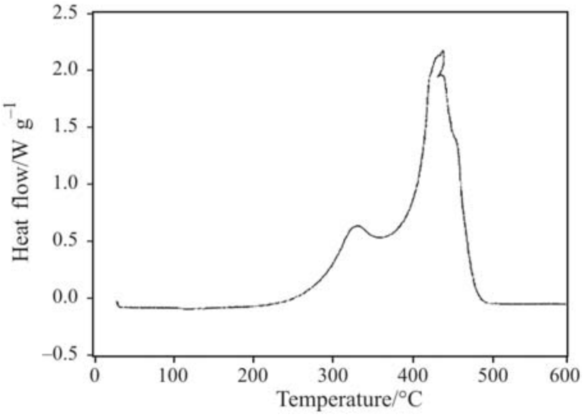

Fig. 1a DSC curve of asphaltite sample at heating rate 5°C min^{-1}

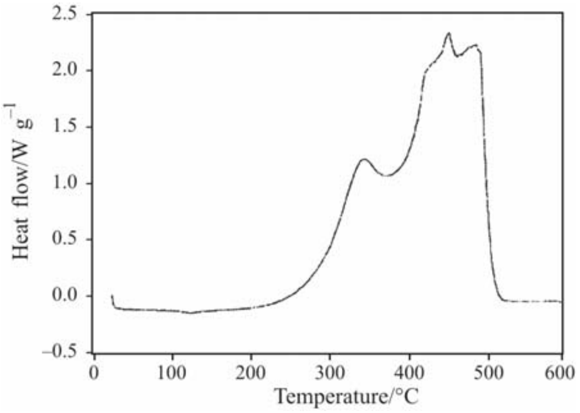

Fig. 1b DSC curve of asphaltite sample at heating rate 10°C min^{-1}

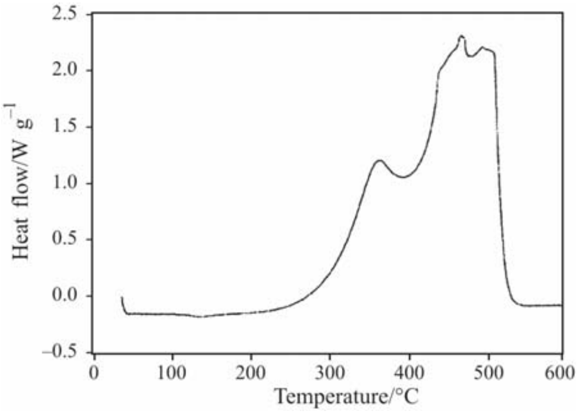

Fig. 1c DSC curve of asphaltite sample at heating rate 15°C min^{-1}

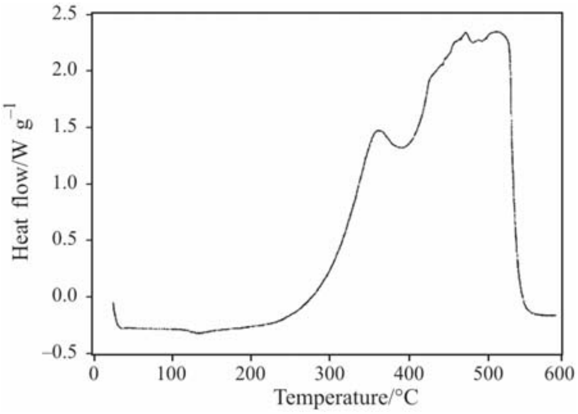

Fig. 1d DSC curve of asphaltite sample at heating rate 20°C min^{-1}

the kinetic parameters of Silopi asphaltite sample at different heating rates (Table 4). In Arrhenius model, reaction order is assumed as unity and the linear least square correlation coefficients varied between 0.95 and 0.99 at different heating rates. The activation energy values are varied between 134 and 179 kJ mol^{-1}. In Coats and Redfern model, reaction orders are assumed as 1/2, 2/3, 1, 3/2 and 2. The correct order is presumed to lead to the best linear plot, from which the activation energy is determined. The highest correlation was observed at unity reaction order. The activation energy values are varied between 164 and 194 kJ mol^{-1}. In Ingraham and Marrier model, the linear least square correlation coefficients varied between 0.93 and 0.97 at different heating rates at a unity reaction order. The activation energy values are varied between 97 and 148 kJ mol^{-1}. In Horowitz and Metzger model, the linear least square correlation coefficients varied between 0.94 and 0.98 at different heating rates. The reaction order is assumed as unity. The activation energy values are varied between 160 and 194 kJ mol^{-1}. It was observed that there was no general trend in the activation energy values from the point of heating rate. These activation energy values

Table 2 The temperature regions, peak and burn-out temperatures of the asphaltite sample at each heating rate (DSC results)

Heating rate/ °C min^{-1}	Temp. regions/°C	Peak temp./ °C	Burn-out temp./°C
5	370–515	445	515
10	375–525	475	525
15	390–550	485	550
20	400–560	495	560

Table 3 The temperature regions, peak and burn-out temperatures of the asphaltite sample at each heating rate (TG/DTG results)

Heating rate/ °C min^{-1}	Temp. regions/°C	Peak temp./ °C	Burn-out temp./°C
5	370–500	445	500
10	380–540	455	540
15	400–550	465	550
20	410–565	475	565

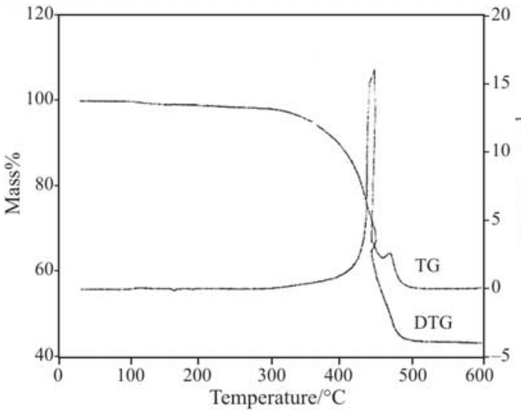

Fig. 2a TG/DTG curves of asphaltite sample at 5°C min^{-1} heating rate

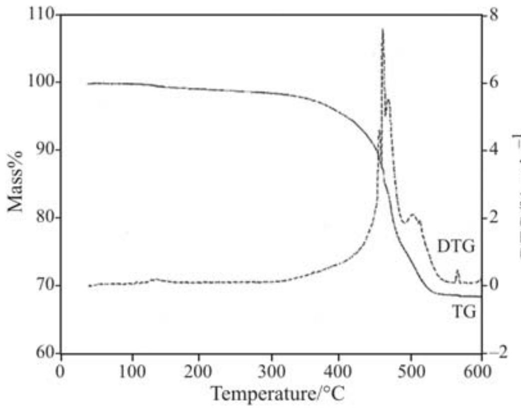

Fig. 2b TG/DTG curves of asphaltite sample at 10°C min^{-1} heating rate

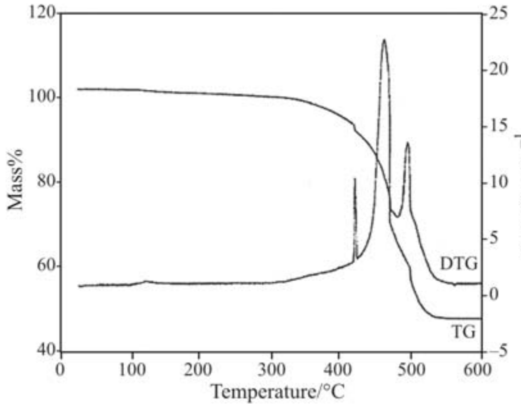

Fig. 2c TG/DTG curves of asphaltite sample at 15°C min^{-1} heating rate

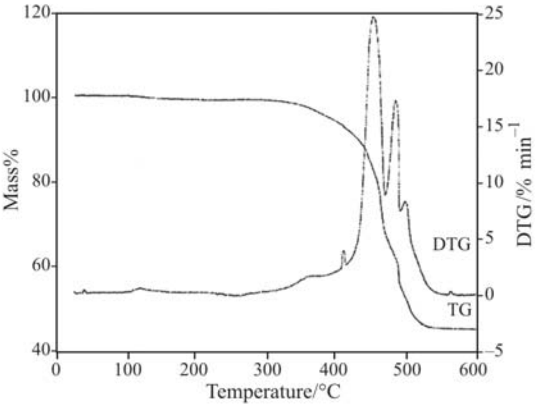

Fig. 2d TG/DTG curves of asphaltite sample at 15°C min^{-1} heating rate

Table 4 Activation energy (kJ/mol) of the asphaltite sample at different heating rates

Heat rate/ °C min^{-1}	Model 1	Model 2	Model 3	Model 4
5	179	n. a.	135	168
10	134	164	97	160
15	161	179	136	n. a.
20	169	194	148	194

n. a. – not available, Model 1 – Arrhenius model,
Model 2 – Coats –Redfern model,
Model 3 – Ingraham–Marrier model,
Model 4 – Horowitz–Metzger model

are rather different than the study performed with the same asphaltite sample [22]. The reason is that, the concept of weighted activation energy (E_{wm}) was used rather than individual activation energies.

The average activation energy values were 160 kJ mol^{-1} for Arrhenius model, 179 kJ mol^{-1} for Coats and Redfern model, 129 kJ mol^{-1} for Ingraham and Marrier model and 174 kJ mol^{-1} Horowitz and

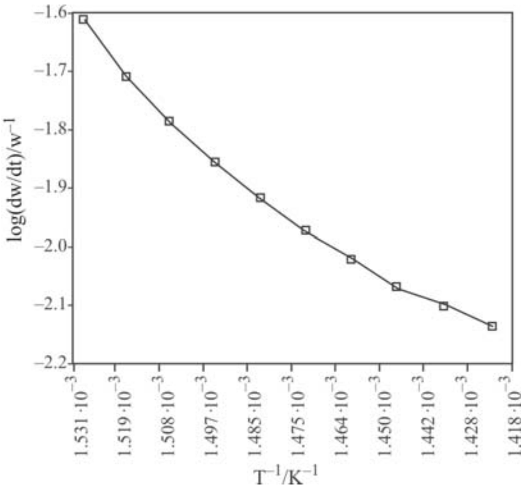

Fig. 3a Kinetic curve of asphaltite sample using (Arrhenius model)

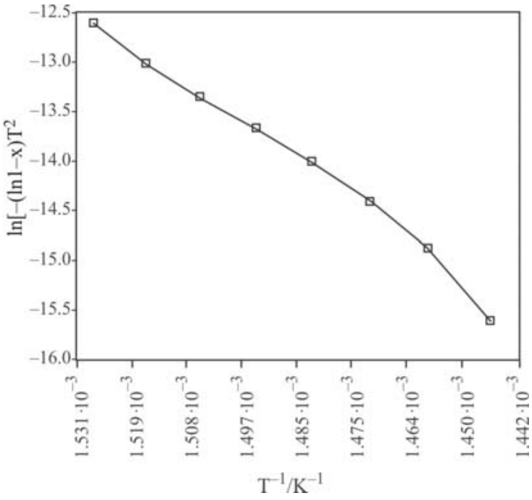

Fig. 3b Kinetic curves of asphaltite sample using Coats–Redfern model

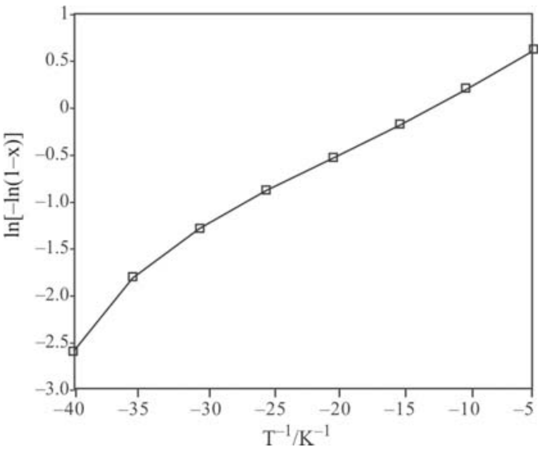

Fig. 3c Kinetic curve of asphaltite sample using Horowitz–Metzger model

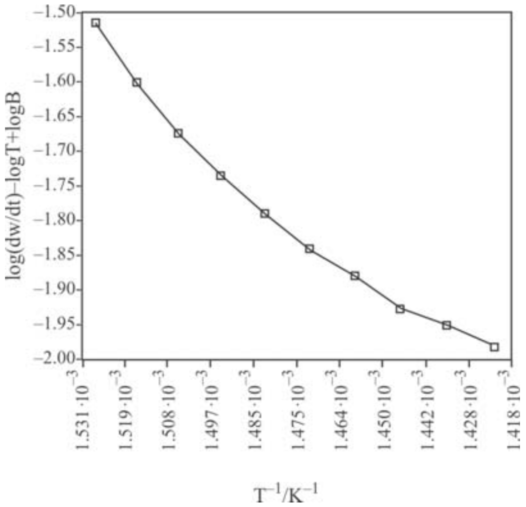

Fig. 3d Kinetic curve of asphaltite sample using Ingraham–Marrier model

Metzger model respectively. In general, similar activation energy values were obtained when the kinetic models are compared with each other. Differences between the activation energies of the samples can be explained with the different equation parameters and assumptions that those models based on.

Conclusions

The thermal decomposition of Silopi asphaltite in air occurs in two reaction regions. The first region is due to the evaporation of moisture in asphaltite sample. Release of volatile matter and burning of carbon is called the second region, in which, this is the primary reaction region where the mass loss is mainly observed in thermogravimetry curves. Also activation energy of the asphaltite sample studied was in the range of 97–194 kJ mol^{-1} depending on the heating rate and model assumptions.

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