Journal of Thermal Analysis and Calorimetry, Vol. 95 (2009) 1, 197–202

A KINETIC INVESTIGATION ON THE PYROLYSIS OF SEGURUK ASPHALTITE

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The pyrolysis of Seguruk asphaltite has been investigated using thermogravimetric analysis at atmospheric pressure between 293 to 1223 K at different linear heating rates of 5, 10 and 20 K min^{-1} under nitrogen as ambient gas. There was a two-stage thermal decomposition. Thermal decomposition started around 630 K for stage 1 for the slowest heating rate. On the other hand, for the same heating rate and stage 2, thermal decomposition started around 950 K. These values were shifted to higher temperatures with increasing heating rate. In this study, two different Coats–Redfern methods were applied to thermal degradation of Seguruk asphaltite.

Keywords: *asphaltite, Coats–Redfern method, kinetic, Seguruk, TG*

Introduction

Energy production is one of the most important concerns of the world. The inevitable dependence of the industrialized world on energy requires the sustainable development of energy. To develop an energy policy that can both ensure current needs and meet future expectations, a number of aspects have to be considered. These aspects include new techniques for efficient source utilization, exploration of new deposits and evaluation of potential alternatives [1]. Successive world energy crises and large increases in the prices of oil derivatives have caused renewed interest in the different possibilities offered by the valorization carbonaceous material as an energy source and in chemical exploitation of pyrolysis products. Synthetic gaseous or liquid fuels are obtained by converting a carbonaceous material to another form. The most abundant naturally occurring materials suitable for this purpose are coal, tar sand, oil shales and asphaltites [2].

Asphaltite is petroleum originated substance and formed by metamorphism associated with mineral matter containing some valuable raw metal such as molybdenum, nickel, vanadium and some radioactive metals such as uranium and thorium [3, 4]. The low oxygen content of asphaltites (<2%) is the best evidence about its origin. Even though asphaltites have the physical appearance of coal, they are derived from crude oil which migrated to inorganic formations. By the effect of catalytic activity of inorganic matrix, metamorphosis has taken place to produce condensed heavier hydrocarbon structures due to various chemical, physical and biological changes [5, 6].

With proven reserves of approximately 77.5 million tones, the southeastern region (mainly explored around Sirnak and Silopi) of Turkey has a great asphaltite potential [7, 8]. Different veins of asphaltic materials have different physical and chemical characteristics depending on the location of asphaltic material, geological formation and degree of metamorphosis [9]. Seguruk vein ($5.7 \cdot 10^5$ T) is an important asphaltite deposit in Turkey [10].

Pyrolysis is the general name of the process of production of various products in gaseous, liquid and solid phases from fossil fuels, especially from coal, in the absence of oxygen via heating. This process, which is also named as carbonization, is one of the most important conversion processes to obtain high quality fuel char or a number of gaseous and liquid by-products [7]. There are two methods of studying the pyrolysis of a fuel; the slow heating method and the fast one. Each method has its advantages and shortcomings. The fast heating method is similar to industrial situations, but the measurement of the parameters is difficult. The slow heating methods use lower heating rates than in industry, but its parameters can be measured accurately [11].

The present study aims to investigate either thermal behavior of Seguruk asphaltite in pyrolysis condition studied or to use two different Coats–Redfern methods to calculate the kinetic parameters of pyrolysis reaction and finally to compare the results with each other.

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1388–6150/$20.00

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Experimental

Seguruk asphaltite from southeastern Anatolia of Turkey was used in this study. After drying in an oven at 378 K the samples were crushed into –3.36+0.60 mm to obtain homogenous particle size by a jaw breaker (Retsch BB 1/A) and ground in a rotor beater mill (Retsch SRZ).

Sieve analysis (passing a known amount of the sample material successively through a series of standard sieves of decreasing size) is one of the oldest methods to determine size distribution of solid particles. The Retsch 3B model test-sieving machine (Tyler series sieves: 3360–71 μm) was used, and the grain-size classes were weighted an analytical balance.

Elemental analysis of the samples were done by Carlo Erba model 1108 elemental analyzer calibrated with standard compounds using the *K* factor calculation.

The pyrolysis experiments were carried out by non-isothermal thermogravimetry using Shimadzu TGA-50 analyzer connected to thermal analysis controller. Thermal gravimetric experimental procedure involves placing the sample (ca. 10 mg) into a platinum crucible and then heating 293 to 1223 K at different linear heating rates of 5, 10 and 20 K $\mathrm{min^{-1}}$ and with a nitrogen flow rate of 40 mL $\mathrm{min^{-1}}$. The mass losses occurring in correspondence to the temperature rises were continuously recorded with a computer working in coordination with the furnace and the control unit of the analyzer, in order to collect the data required to determine the pyrolysis characteristics and kinetics of the samples. All the experiments were carried out at least twice for reproducibility.

Results and discussion

The heating value, ash content, and sulfur distribution analysis of the sample were carried out according to ASTM (3174, 3175, D2492-77) procedures and results obtained were presented in Table 1.

Figures 1 and 2 show TG and DTG curves of asphaltite samples, respectively. It can be easily seen from the figures that there is a two-stage thermal decomposition. Thermal decomposition started around 630 and reached 790 K for stage 1 for the slowest heating rate. On the other hand, for the same heating rate and stage 2, thermal decomposition started at around 950 and reached 1060 K. These values were shifted to higher temperatures with increasing heating rate. These shifts can be attributed to the variations in the rate of heat transfer with the change in the heating rate and the short exposure time to a particular temperature at the higher heating rates, as well as the effect of kinetics of decomposition [12].

Table 1 Elemental and proximate analysis of Seguruk asphaltite

Proximate analysis/%		Elemental analysis/%	
Moisture	0.62	C	46.78
Ash	40.80	H	4.41
Volatile matter	33.72	N	0.76
Fixed carbon	24.86	S (total)	6.75
Calorific value/MJ $\mathrm{kg^{-1}}$	5.43		

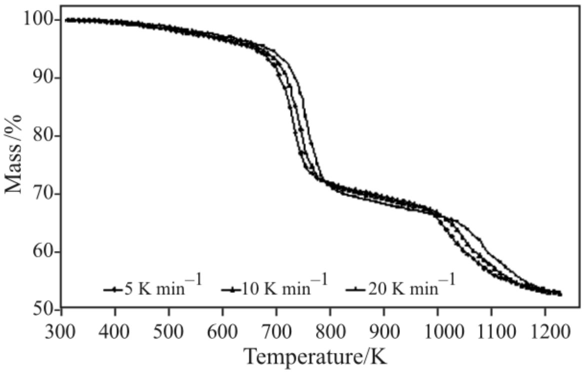

Fig. 1 TG curve of Seguruk asphaltite particle size –3.36+0.60 mm

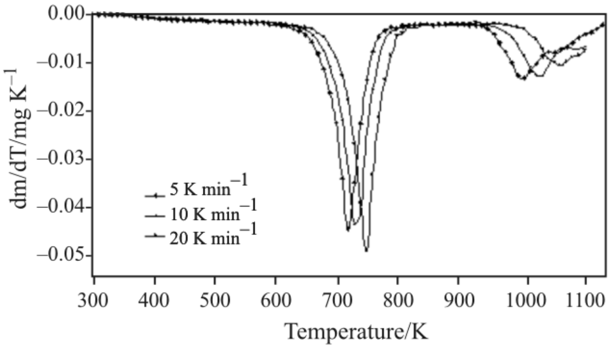

Fig. 2 DTG curve of Seguruk asphaltite particle size –3.36+0.60 mm

As mentioned before, asphaltite samples demonstrated a two-stage thermal decomposition according to TG and DTG data. First one (stage 1) occurred at lower temperatures is named primary devolatilization region and the second (stage 2) occurred at higher temperatures is named secondary gasification region [7, 8]. It is generally known that asphaltic substances contain complex large molecules, including all kinds of hydrocarbons and other compounds. During the thermal process, firstly weaker chemical bonds are destroyed and some small gaseous molecules are destroyed, then, the temperature is higher, the cracking is faster and the stronger chemical bonds are broken, so that larger molecules decompose into small molecules in the gas phase. Finally, only coke remains [11].

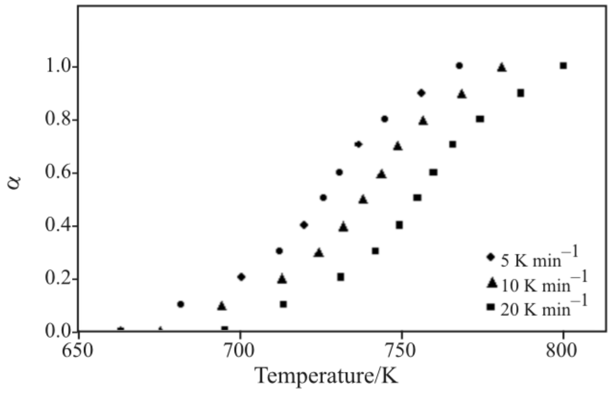

Fig. 3 α(β,*T*) graph of Seguruk asphaltite particle size –3.36+0.60 mm for stage 1

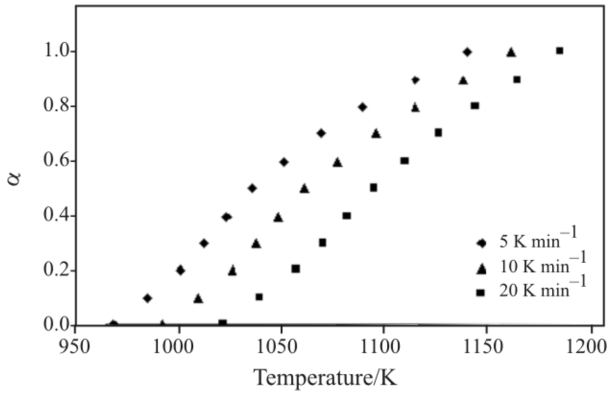

Fig. 4 α(β,*T*) graph of Seguruk asphaltite particle size –3.36+0.60 mm for stage 2

Table 2 Set of reaction models applied to describe thermal decomposition in solids

	Reaction model	*f*(α)	*g*(α)
1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion	$1/2\alpha^{-1}$	α^{2}
6	Mampel (first-order)	$1-\alpha$	$-\ln(1-\alpha)$
7	Avrami–Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
8	Avrami–Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
10	Three-dimensional diffusion	$2(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$	$[1-(1-\alpha)^{1/3}]^{2}$
11	Contracting sphere	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
12	Contracting cylinder	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13	Second-order	$(1-\alpha)^{2}$	$(1-\alpha)^{-1}-1$
14	Contracting linear	1	α
15	Contracting area	$2(1-\alpha)^{1/2}$	$[1-\ln(1-\alpha)^{1/2}]$
16	Contracting volume	$3(1-\alpha)^{2/3}$	$[1-\ln(1-\alpha)^{1/3}]$
17	Two-dimensional diffusion	$-1/\ln(1-\alpha)$	$(1-\alpha)\ln(1-\alpha)+\alpha$
18	Three-dimensional diffusion D3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$	$[1-\ln(1-\alpha)^{1/3}]^{2}$
19	Three-dimensional diffusion D4	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2/3\alpha)-(1-\alpha)^{2/3}$
20	Random nucleation with one nucleus on the individual particle	$1-\alpha$	$\ln(1-\alpha)$
21	Random nucleation with two nuclei on the individual particle F2	$(1-\alpha)^{2}$	$1/(1-\alpha)$
22	Random nucleation with two nuclei on the individual particle F3	$1/2(1-\alpha)^{3}$	$1/(1-\alpha)^{2}$

Reaction rate is defined as the derivative of conversion with respect to time. In thermogravimetric measurements, the conversion is typically calculated as:

$$\alpha=\frac{w_0-w_\mathrm{i}}{w_0-w_\mathrm{f}} \qquad (1)$$

where: w_0 – initial mass of sample in given stage, mg; w_i – current mass of sample, mg; w_f – mass of sample after completion of given stage, mg.

The dependence of conversion degree on temperature are shown in Figs 1 and 2 for stages 1 and 2, respectively. The kinetic information can be extracted from dynamic experiments by means of various methods. Kinetic studies assume that the isothermal rate of conversion, dα/dt, is a linear function of the reactant concentration loss and of the temperature-independent rate constant, k, and a temperature-independent function of the conversion, α, that is:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \tag{2}$$

where $f(\alpha)$ is the reaction model and depends on the mechanism of the degradation reaction. The reaction model may take various forms, some of which are presented in Table 2. Discussions of the form and of the validity of this approach have been the concern of many investigators. The function k is always described by the Arrhenius expression:

$$k(T)=A\exp(-E/RT) \tag{3}$$

where A, the pre-exponential factor (Arrhenius constant), is assumed to be independent of temperature, E is the activation energy, T the absolute temperature and R the gas constant. The combination of Eqs (2) and (3) gives the following relationship:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}\approx A\exp(-E/RT)f(\alpha) \tag{4}$$

If the sample temperature is changed by a controlled and constant heating rate, $\beta=\mathrm{d}T/\mathrm{d}t$, the variation in the degree of conversion can be analyzed as a function of temperature, which depends on the time of heating. Therefore, the reaction rate may be written as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{\mathrm{d}\alpha}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t}=\beta\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{5}$$

A combination of Eqs (4) and (5) leads to

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}\approx\frac{A}{\beta}\exp(-E/RT)f(\alpha) \tag{6}$$

Integration of this equation from an initial temperature, T_0, corresponding to a degree of conversion $\alpha=0$, to the peak temperature, T_p, where $\alpha=\alpha_\mathrm{p}$, gives:

$$\int_0^{\alpha_\mathrm{p}}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{\mathrm{T}_0}^{\mathrm{T}_\mathrm{p}}\mathrm{e}^{-\frac{\mathrm{E}}{\mathrm{RT}}}\mathrm{d}T \tag{7}$$

If T_0 is low, it may be reasonably assumed that $\alpha_0=0$ and considering that there is no reaction between 0 and T_0:

$$g(\alpha)=\int_0^{\alpha_\mathrm{p}}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{\mathrm{T}_0}^{\mathrm{T}_\mathrm{p}}\mathrm{e}^{-\frac{\mathrm{E}}{\mathrm{RT}}}\mathrm{d}T \tag{8}$$

where $g(\alpha)$ is the integral function of conversion [13].

Analysis of the changes in thermogravimetric data, which are brought about by variation of heating rate, are the basis of the most powerful methods for the determination of kinetic parameters.

Coats and Redfern method is a model-fitting method and uses an asymptotic approximation for resolution of Eq. (8).

$$\ln\left[\frac{g(\alpha)}{T_\mathrm{M}^2}\right]=\ln\frac{AR}{\beta E}\left[1-\frac{2RT_\mathrm{M}}{E}\right]-\frac{E}{RT_\mathrm{M}} \tag{9}$$

where T_M is the mean temperature and $g(\alpha)$ is the integral function of conversion. Inserting various $g(\alpha)$ into Eq. (9) results in a set of Arrhenius parameters determined from the plot $\ln[g(\alpha)/T^2]$ *vs.* $1/T$. The sets of Arrhenius parameters for the thermal decomposition of Seguruk asphaltite are shown in Table 3. For each model, the goodness of fit is customarily estimated by a coefficient of linear correlation, R^2. A single pair of E and $\ln A$ is the commonly chosen as that corresponding to a reaction model that gives rise to the maximum absolute value of the correlation coefficient [14–17]. This method was described as method 1. In this study, as shown in Table 2, 22 different reaction model were applied to thermogravimetric data and best correlation coefficients were observed in Mampel first order (model no.: 6) reaction model for stage 1 and second order (model no.: 13) reaction model for stage 2. Kinetic parameters calculated using method 2 for stages 1 and 2 were presented in Table 4. It can be seen from the table that all the kinetic parameters calculated using method 2 are higher in stage 2 than those of stage 1 and, on the other hand, increasing as the heating rate increases for both cases.

Table 3 Kinetic parameters for Seguruk asphaltite at 5 K min^{-1} determined using the method 1 for stage 1

Model[a]	E/kJ mol^{-1}	$\ln A$/min^{-1}	R^2
1	21.41	–13.28	0.9457
2	32.53	–2.97	0.9583
3	54.76	4.63	0.9671
4	188.14	29.63	0.9753
5	254.82	40.81	0.9761
6	172.37	27.73	0.9953
7	34.14	–1.89	0.9927
8	49.50	3.55	0.9937
9	80.22	10.72	0.9946
10	318.24	49.95	0.9938
11	153.15	22.94	0.9932
12	144.41	21.72	0.9902
13	243.88	40.76	0.9737
14	121.44	18.05	0.9736
15	909.58	156.87	0.4426
16	927.04	159.58	0.4391
17	282.68	45.13	0.9861
18	180.63	–38.52	0.2575
19	294.37	45.66	0.9875
20	–	–	–
21	110.50	17.97	0.7938
22	232.94	40.73	0.8100

Table 4 Kinetic parameters of the Seguruk asphaltite calculated from method 1

	Heating rate/K min^{-1}	Reaction model no.	E/kJ mol^{-1}	ln$A$/min^{-1}	R^2
Stage 1	5	6	172.37	27.73	0.9953
	10	6	178.72	29.00	0.9951
	20	6	191.75	31.14	0.9934
	mean		180.95	29.29	
Stage 2	5	13	276.64	31.27	0.9881
	10	13	290.51	32.79	0.9882
	20	13	317.26	35.55	0.9944
	mean		294.80	33.20	

The modified Coats–Redfern method is a multi-heating rate application of the Coats–Redfern equation, producing a model-free isoconversional approach.

$$\ln\left[\frac{\beta}{T^2(1-2RT/E_a)}\right]=-\frac{E_a}{RT}+\ln\left(-\frac{AR}{E_a\ln(1-\alpha)}\right) \quad (10)$$

At fixed conversions for each of the heating rates, the left-hand side for each heating rate is plotted *vs.* $1/T$ at that heating rate, giving a family of straight lines of slope $-E_a/R$, which is substituted into the intercept to obtain A. Since the left-hand side is a weak function of E_a, the process must be done iteratively by first assuming a value of E_a, then recalculating the left-hand side until convergence occurs. This is slightly more accurate than moving $(1-2RT/E_a)$ into the intercept and assuming it is a constant. If the value of E_a varies with the extent of conversion, the results should be interpreted in terms of multi-step reaction mechanisms [18]. This method was described as method 2 and calculated kinetic parameters for stages 1 and 2 using method 1 were presented in Tables 5 and 6, respectively. It can be seen from the tables that all the kinetic parameters are increasing when α values increase. When compare the Tables 5 and 6, it can be seen that the activation energies for stage 1 are slightly higher than those of for stage 2 but ln$A$ values for stage 2 are much higher than those of for stage 1.

Table 5 Kinetic parameters calculated from method 2 for stage 1

Conversion/%	E/ kJ mol^{-1}	ln$A$/ min^{-1}	R^2
10	164.22	25.30	0.9834
20	178.83	27.80	0.9881
30	191.84	30.00	0.9884
40	195.41	30.62	0.9889
50	204.35	32.14	0.9920
60	208.32	32.83	0.9937
70	209.46	33.02	0.9901
80	210.62	33.12	0.9878
90	207.44	32.41	0.9866
mean	196.72	30.80	

Table 6 Kinetic parameters calculated from method 2 for stage 2

Conversion/%	E/ kJ mol^{-1}	ln$A$/ min^{-1}	R^2
10	198.48	20.00	0.9980
20	199.15	20.41	0.9976
30	198.21	20.48	0.9960
40	199.28	20.70	0.9955
50	201.10	20.93	0.9930
60	210.24	21.91	0.9969
70	222.66	23.19	0.9994
80	240.66	25.04	0.9994
90	279.40	29.06	0.9992
mean	216.58	22.41	

When compared the results obtained from both methods, for the stage 1, it can be said that from the Tables 4–6 calculated the activation energies and ln$A$ values using method 2 were slightly higher than those of method 1. For the stage 2, the calculated kinetic parameters vary in a wide scale. For example, while, the activation energy calculated is 294.80 kJ mol^{-1} using method 1 and 216.58 kJ mol^{-1} using method 2. Similar results were obtained in ln$A$ values also.

Conclusions

In this study, two different Coats–Redfern methods (model-fitting and model-free) were applied to thermal degradation of Seguruk asphaltite. As a result, even if different Coats–Redfern methods are named as same, the kinetic parameters calculated using these methods were different with each other. This difference is mainly due to having different approach of studied methods to thermogravimetric data. Application of model-fitting methods to non-isothermal data may give ambiguous kinetic parameters [18]. Because, as a reaction mechanism, $f(\alpha)$ or $g(\alpha)$ models are chosen from a list of model such as that given in Table 2. There is no guarantee that it includes the appropriate model. However, any list of models will always produce some best-fit models. Kinetic analysis based on an isoconversional method is frequently referred to as 'model-free' because it allows the effective activation energy to be evaluated for different constant extents of conversion without assuming any particular form of the reaction model [19].

On the other hand, asphaltite is a mineral matter and consists of a lot of compounds. In a pyrolysis reaction, it decomposes through several simultaneous reactions. This scheme is clearly seen in the results using method 2. It is generally accepted that if the activation energies are varied with conversion degree (α), this attributes to parallel reactions occurring in same conditions.

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Received: February 8, 2008
Accepted: May 6, 2008
OnlineFirst: August 15, 2008

DOI: 10.1007/s10973-008-9054-7