

PYROLYSIS KINETICS OF ASPHALTITES DETERMINED BY THERMAL ANALYSIS

Y. TONBUL^{*(a)}, A. SAYDUT^(b), C. HAMAMCI^(a)

^(a) Department of Chemistry
Faculty of Science and Art, Dicle University
TR-21280 Diyarbakir, Turkey

^(b) Department of Mining Engineering
Faculty of Engineering and Architecture, Dicle University
TR-21280 Diyarbakir, Turkey

Thermal behavior of Harbul asphaltites (SE Anatolia, Turkey) has been studied using thermogravimetric analysis at atmospheric pressure and with nitrogen as the ambient gas. Asphaltite samples were ground and separated according to their size by sieving. Particle size distribution and chemical composition of asphaltite fractions are given.

TG/DTG data of samples demonstrated two stages of mass loss. The first stage, called primary volatilization, occurs in the range of 200–600 °C, and the second stage, called secondary gasification, in the range of 600–800 °C.

Kinetic parameters of pyrolysis of asphaltite samples (activation energy, Arrhenius constant and reaction rate constant) were determined separately for both two stages using Coats-Redfern kinetic model.

Introduction

Supply of energy has become a worldwide problem during recent decades. The world reserves of petroleum and natural gas are finite, although the years of oil and gas depletion project well into the future. There is much research into alternative sources of liquid and solid hydrocarbons [1–11]. Asphaltites are known as solid fossil fuels. The initial matter passes gradual stages of metamorphism transforming into soft native asphalts, asphaltites, and finally into asphaltic pyrobitumens.

In Turkey, asphaltite is one of the large sources of energy in the south-eastern part of the country, in the provinces of Siirt, Şırnak and Mardin. Some of the resources are asphaltic pyrobitumens, some others are close to

* Corresponding author: E-mail ytonbul@dicle.edu.tr

them by characteristics, but their metamorphism has not reached the stage of asphaltic pyrobitumens [1].

The total reserve of asphaltic substances which are found in southeastern Turkey is approximately $8 \cdot 10^7$ tonnes, with *Silopi* and *Şirnak* reserves together comprising the major part of the asphaltite deposits [2, 3]. *Silopi* asphaltite is classified as a substance between asphaltite and asphaltic pyrobitumen, whereas *Şirnak* asphaltite as asphaltic pyrobitumen associated with mineral matter [2, 4–6]. The *Harbul* vein is the major part (approximately $2.5 \cdot 10^7$ tonnes) of the *Silopi* reserves [1].

Synthetic gas, liquid fuel, metallurgical coke, ammonia and sulphur have been produced from asphaltites using conversion processes. Asphaltite pyrolysis is a very complicated process including a large number of chemical reactions occurring in conjunction with structural changes in the solid fuel matrix. During pyrolysis asphaltites are thermally cracked to gas, oil and carbon [11–21].

The oils produced from retorting of asphaltites and oil shales are of a more complex composition than crude petroleum. These oils consist of complex mixtures of aliphatic, polycyclic aromatic and polar aromatic compounds containing N, O and S heteroatoms [12].

In recent years the application of thermogravimetry, differential scanning calorimetry and derivative thermogravimetry to study the combustion and pyrolysis behavior of fossil fuels has gained a wide acceptance among researchers, which is of exceptional significance for industry and for the economy [8–24]. The pyrolysis studies provide important quantitative information on the identity, composition and structure of asphaltites [13].

This paper presents the data on thermal pyrolysis kinetics of Harbul asphaltite calculated basing on thermogravimetric analysis of fractions of different particle size and applying Coats and Redfern method.

Experimental

The *Silopi* (*Harbul*) asphaltite from SE Anatolia region of Turkey was used in this study. After drying in an oven at 105 °C the samples were crushed by a jaw breaker (Retsch BB 1/A) and ground in a rotor beater mill (Retsch SRZ).

The Retsch 3B model test-sieving machine (Tyler series sieves: 3360–71 µm) was used, and the grain-size classes were weighed using an analytical balance.

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

Pyrolysis experiments were carried out by non-isothermal thermogravimetry using Shimadzu TGA-50 analyzer. The experimental procedure involved placing the sample (max. amount 20 mg) into a platinum crucible

and heating to 800 °C at a linear heating rate of 10 °C min⁻¹ in the nitrogen flow of 15 mL min⁻¹. The weight losses occurring in correspondence to the temperature rise 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.

Results and Discussion

Heating value, ash content, and sulphur distribution of the asphaltite samples were determined according to ASTM procedures. Analysis data are presented in Table 1 and Table 2.

TG/DTG data of samples demonstrated two stages of mass loss. Below 200 °C there was no mass loss. Primary volatilization of the sample occurred in the range of 200–600 °C. At the initial stage of volatilization of low-molecular-mass species takes place. Owing to the temperature rise, large molecules are cracked into small fragments. During this phase of pyrolysis, volatiles are transported to the external surfaces of the asphaltite particles. Then, the volatile fragments are removed from the surface of the asphaltite into the bulk gas phase [2].

Table 1. Proximate and ultimate analysis of Harbul asphaltite

Parameter	Asphaltite
Proximate analysis (wt. %)	
Ash	32.50
Volatile matter	46.70
Moisture	0.63
Heating value (kcal kg ⁻¹)	6965
Elemental analysis (wt. %)	
Carbon	64.30
Nitrogen	1.02
Hydrogen	4.71
Sulphur	7.74

Table 2. Elemental composition of asphaltite fractions of different particle size, wt. %

Particle size, mm	C	S	H	N
3.360–0.600	65.045	8.336	6.314	0.471
0.600–0.250	63.925	7.012	6.295	0.202
0.250–0.125	64.550	6.970	6.937	0.684
0.125–0.071	62.671	8.090	7.483	0.330
0.071–0.053	67.622	7.060	8.191	0.71

In the range of 600–800 °C the second mass loss region was observed. During this stage, called secondary gasification region, mainly decomposition of primary volatile fragments takes place, and very low amounts of CO and CO₂ are also formed as a result of carbonization of the residual solid under the effect of excess heat. The amounts of solid residues and peak temperatures in studied pyrolysis conditions characteristic of different-size fractions of Harbul asphaltite are presented in Table 3.

Five different reaction orders were proposed to describe the kinetics of the main pyrolysis processes for both the individual feedstock and their blends. Activation energies and frequency factors were determined.

Modeling of a reaction for the combustion process of coal is extremely complicated because several components are oxidized simultaneously. In the present work, thermogravimetric data were analyzed according to the Coats and Redfern kinetic model [25–33]. The calculation of the kinetic data is based on the formal kinetic equation

$$d\alpha/dt = k\alpha^n,$$

where α is the amount of sample undergoing the reaction, n is reaction order, and k is specific rate constant.

Coats and Redfern developed an integral method, which can be applied to thermogravimetric data assuming reaction order. 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 the analysis, is as follows:

$$\log \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \log \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad \text{for } n \neq 1 \quad (2)$$

$$\log \left[\frac{-\log(1 - \alpha)}{T^2} \right] = \log \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \quad \text{for } n=1, \quad (3)$$

where β is heating rate (K min⁻¹).

Table 3. The amounts of residues and peak temperatures in studied pyrolysis conditions characteristic of different-size fractions of Harbul asphaltite

Particle size, mm	Primary volatilization region		Secondary gasification region	
	Peak temp., °C	Residue, %	Peak temp., °C	Residue, %
3.360–0.600	467	28.64	724	9.58
0.600–0.250	470	35.79	756	8.40
0.250–0.125	462	27.15	741	11.11
0.125–0.071	456	25.77	738	15.53
0.071–0.053	456	29.67	707	8.40

By plotting the appropriate left-hand side of the equations versus $1/T$, the slope equals $-E/2.303R$. The values of activation energy (E), Arrhenius constant (A) and reaction rate constant (k) can be calculated from these equations [28]. Calculated parameters determined from the straight-line plots for samples are cited in Table 3 and Table 4. It can be seen from the tables that the maximum correlation coefficients were obtained proposing reaction order 0.5 for the primary volatilization region and 0.67 for the secondary gasification region. The values of activation energy varied from $4.98 \cdot 10^4$ to $6.67 \cdot 10^4$ kJ mol^{-1} and of Arrhenius constants from $3.09 \cdot 10^{-1}$ to $3.93 \cdot 10^3$ $\text{mg}^{1-n} \text{min}^{-1}$ for the primary volatilization region. For the secondary gasification region, the values of activation energy varied from $1.33 \cdot 10^5$ to $1.57 \cdot 10^5$ kJ mol^{-1} , and Arrhenius constants from $1.47 \cdot 10^6$ to $4.37 \cdot 10^7$ $\text{mg}^{1-n} \text{min}^{-1}$.

Table 4. Kinetic parameters of asphaltite pyrolysis in the primary volatilization region

Reaction order	Particle size, mm	Activation energy, kJ mol^{-1}	Arrhenius constant, $\text{mg}^{1-n} \text{min}^{-1}$	Reaction rate constant, min^{-1}	R^2
0.5	3.36–0.60	4.98E+04	4.46E+01	1.35E-02	0.9819
	0.60–0.25	6.67E+04	2.93E+03	5.97E-02	0.9553
	0.25–0.125	4.73E+04	2.32E+01	1.02E-02	0.9874
	0.125–0.071	3.55E+04	3.09E-01	8.84E-04	0.9717
	0.071–0.053	4.95E+04	4.70E+01	1.35E-02	0.9848
0.67	3.36–0.60	5.32E+04	1.25E+02	2.21E-02	0.9792
	0.60–0.25	7.08E+04	8.05E+03	8.48E-02	0.9476
	0.25–0.125	5.05E+04	6.63E+01	1.72E-02	0.9858
	0.125–0.071	3.83E+04	1.12E+00	2.03E-03	0.9821
	0.071–0.053	5.28E+04	1.33E+02	2.19E-02	0.9837
1	3.36–0.60	6.03E+04	3.31E+02	1.85E-02	0.9694
	0.60–0.25	7.95E+04	2.33E+04	6.04E-02	0.9293
	0.25–0.125	5.73E+04	1.76E+02	1.49E-02	0.9779
	0.125–0.071	4.42E+04	3.65E+00	2.51E-03	0.9949
	0.071–0.053	6.00E+04	3.58E+02	1.82E-02	0.9768
1.25	3.36–0.60	7.29E+04	2.35E+04	1.69E-01	0.9473
	0.60–0.25	9.49E+04	6.89E+03	1.48E-03	0.8976
	0.25–0.125	6.95E+04	1.26E+04	1.46E-01	0.9579
	0.125–0.071	5.46E+04	3.32E+02	4.08E-02	0.9982
	0.071–0.053	7.26E+04	2.60E+04	1.64E-01	0.9582
1.5	3.36–0.60	7.26E+04	2.23E+04	1.67E-01	0.9459
	0.60–0.25	9.45E+04	1.78E+06	4.04E-01	0.8957
	0.25–0.125	6.93E+04	1.20E+04	1.44E-01	0.9566
	0.125–0.071	5.44E+04	3.19E+02	4.02E-02	0.9979
	0.071–0.053	7.24E+04	2.47E+04	1.62E-01	0.9569

Table 5. Kinetic parameters of asphaltite pyrolysis in the secondary gasification region

Reaction order	Particle size, mm	Activation energy, kJ mol ⁻¹	Arrhenius constant, mg ¹⁻ⁿ min ⁻¹	Reaction rate constant, min ⁻¹	R ²
0.5	3.36–0.60	1.25E+05	4.10E+05	1.19E-01	0.988
	0.60–0.25	1.29E+05	5.93E+05	1.63E-01	0.9996
	0.25–0.125	1.48E+05	1.13E+07	2.65E-01	0.9998
	0.125–0.071	1.25E+05	4.69E+05	1.60E-01	0.9955
	0.071–0.053	1.44E+05	9.71E+06	2.01E-01	0.9583
0.67	3.36–0.60	1.33E+05	1.47E+06	1.60E-01	0.9934
	0.60–0.25	1.37E+05	2.05E+06	2.20E-01	0.9989
	0.25–0.125	1.57E+05	4.37E+07	3.48E-01	0.9993
	0.125–0.071	1.33E+05	1.63E+06	2.16E-01	0.9963
	0.071–0.053	1.54E+05	4.13E+07	2.64E-01	0.9682
1	3.36–0.60	1.50E+05	8.15E+06	1.09E-01	0.999
	0.60–0.25	1.55E+05	1.05E+07	1.52E-01	0.9931
	0.25–0.125	1.77E+05	2.94E+08	2.35E-01	0.994
	0.125–0.071	1.50E+05	8.38E+06	1.51E-01	0.9931
	0.071–0.053	1.74E+05	3.43E+08	1.76E-01	0.9829
1.25	3.36–0.60	1.81E+05	1.91E+09	6.15E-01	0.9963
	0.60–0.25	1.85E+05	2.16E+09	9.01E-01	0.9753
	0.25–0.125	2.11E+05	9.53E+10	1.30E+00	0.9772
	0.125–0.071	1.80E+05	1.73E+09	9.00E-01	0.9786
	0.071–0.053	2.11E+05	1.63E+11	9.43E-01	0.994
1.5	3.36–0.60	1.81E+05	1.79E+09	6.12E-01	0.9961
	0.60–0.25	1.84E+05	2.01E+09	8.94E-01	0.9747
	0.25–0.125	2.10E+05	8.81E+10	1.29E+00	0.9765
	0.125–0.071	1.79E+05	1.61E+09	8.94E-01	0.9782
	0.071–0.053	2.10E+05	1.52E+11	9.38E-01	0.994

Because asphaltite is a complex fossil fuel, when pyrolysed, it decomposes through several simultaneous reactions. Also the TGA records only the weight loss of the sample. Therefore, calculated kinetic data will provide only general information about the overall reaction kinetics. Finally, it can be said that particle size does not have any significant effect on kinetic parameters and maximum peak temperatures.

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