

THERMOGRAVIMETRIC ANALYSIS OF PRETREATED GÖYNÜK OIL SHALE AND ŞIRNAK ASPHALTITE

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To investigate the effect of mineral matrix on thermal degradation of Göynük oil shale and Şirnak asphaltite, their samples (initial ones and those subsequently treated with solutions of the acids: HCl, HNO₃ and HF) were studied in a thermogravimetric analyzer. Initial and HCl-washed samples showed similar degradation behavior, while HNO₃ washing affected it in both cases. Changes in organic structure, which is different for shale and asphaltite – the former being aliphatic, and the latter having aromatic character – after HNO₃ treatment affected the degradation kinetics of the samples differently, whereas the mineral matter content had no effect on it.

Introduction

The lack of appreciable oil reserves obliges some countries to develop alternative energy sources, e.g. synthetic oil from low-grade solid fuels, such as oil shale, asphaltite and biomass. Oil shales are the second largest solid fuel reserve in Turkey with reserves totaling approximately five billion tons [1]. The Göynük field is a good example of Turkish oil shale fields.

Generally asphaltic materials are formed by migration of petroleum into cracks during tectonic movements. During and after migration, petroleum loses its light components and undergoes a series of complex chemical and physical changes. Depending on their extent, the formation may end up as natural asphalts, asphaltites or asphaltic pyrobitumen.

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Asphaltites are the other important hydrocarbon-based energy source in Turkey, amounting over 60 million tons (in Avgamasya, Silopi and Şırnak). In contrast to similar world deposits, whose asphaltic substance generally has a very low ash content (1%), it is very high in the case of Turkish asphaltite [2]. The latter is mostly classified between asphaltite and asphaltic pyrobitumen [3]. At present both the oil shales and asphaltites are occasionally used for domestic purposes. However, because of their properties and reserves they can be considered valuable potential source of liquid hydrocarbons.

Pyrolysis is one of the oldest liquefaction techniques used to produce liquid fuels from solid fossils. Oil shale pyrolysis is a very complex process and it involves numerous reactions because the shale is a complex mixture of kerogen and wide range of minerals. Numerous studies were made to determine the optimal conditions of oil shale pyrolysis according to such parameters as heating rate, particle size, temperature and pyrolysis atmosphere.

Thermogravimetric analysis (TGA) has been extensively used to determine devolatilization characteristics and kinetic parameters, in particular to investigate the effect of pyrolysis temperature and heating rate on oil shale decomposition. Non-isothermal thermogravimetric studies of various oil shales confirmed an increase in total weight loss with increasing temperature because the evolution of CO₂ due to carbonate decomposition occurs at temperatures above 600 °C, whereas at medium temperatures (between 200–600 °C) the weight loss due to the loss of hydrocarbons takes place. The studies also showed that increasing heating rate shifts degradation to higher temperatures. Some researchers observed the decrease of weight loss with decreasing particle size [4–6], others reported only a slight effect [7–9].

As the organic matter (kerogen) is finely distributed in oil shale inorganic matrix, mineral matter plays an important role in kerogen decomposition [10]. Karabakan *et al.* found that pyrolysis reactions were catalyzed by alkaline earth metal cations present in carbonates and inhibited by silicates [11], and suggested that the alkali M²⁺-O surface groups formed due to the interaction of alkali earth metal cations with -COOH and -OH functional groups act as the active sites on the oil shale surface.

To investigate the liquid-fuel potential of asphaltites of southeastern Turkey, liquefaction (pyrolysis, extraction) of Avgamasya asphaltite was studied, most detailed pyrolysis research made by the Mining Research and Development Institute. The optimum product distributions determined are, %: coke 64.6, gas 19.1, synthetic crude oil 11.8, liquor 2.9, hydrogen sulphide 0.5 and ammonia 0.13 [12].

Ekinçi *et al.* studied the Avgamasya asphaltite pyrolysis at different temperatures in a bench-scale Gray-King apparatus [13]. Tar yield was 10.8 and 11.1% and that of coke 83.1 and 80.7% at pyrolysis temperatures 525 and 840 °C, respectively. To investigate the possibilities of increasing the

liquefaction, supercritical gas extraction and hydrogen-donor solvent extraction were carried out [14].

In this study, a series of TG experiments was performed to investigate the effect of ash content on thermal behavior of Göynük oil shale and Şırnak asphaltite samples. The terms 'mineral matter' and 'ash' are used synonymously in this paper.

Materials and Methods

An oil shale sample (GOS) was taken from the upper 0.8–1-m layer of the Göynük Himmetoğlu deposit. The sample characteristics are as follows, wt.% (air-dry basis): proximate analysis: moisture 11.3, ash 18.0, fixed carbon 16.7, volatile matter 54.0; ultimate analysis: organic C 46.3, inorganic C 0.9, H 4.8, S 2.2, N 1.3; Fischer assay, wt.%: shale oil 22.8, gas 25.6, water 6.0, residue 45.6.

An asphaltite sample (SA) was taken from the deposit in the Şırnak Province. The sample characteristics are as follows, wt.% (air-dry basis): proximate analysis: moisture 1.4, ash 38.4, fixed carbon 25.1, volatile matter 35.1; ultimate analysis: organic C 39.0, inorganic C 1.2, H 3.2, S 4.8, N 0.5.

Both samples were ground and sieved to -0.5 mm.

Their demineralization was carried out by washing with HCl, HNO₃ and HF. The samples were first stirred at room temperature with HCl (10%) until no carbon dioxide evolved, then washed with water (until no Cl⁻ ions could be detected) and dried. Carbonate-free samples (GOS1 and SA1) were treated with HNO₃ at 40 °C; 40- and 12.5-percent HNO₃ solutions were used for AS1 and GOS1, respectively. After HNO₃ treatment, the samples (GOS2 and SA2) were stirred with HF solution (50%) for 8 h at 40 °C. The silicate-free samples (GOS3 and SA3) were washed with water and dried. Elemental analysis was performed at the Engler-Bunte Institute, Karlsruhe (Germany).

Thermogravimetric experiments were carried out with a DuPont model-951 series TG analyzer. Approximately 10-mg samples were non-isothermally pyrolyzed to 600 °C with pure helium as purge gas (flow rate ca 100 cm³ min⁻¹) at different heating rates (5, 10 or 15 °C/min) in order to investigate their degradation kinetics.

The percentage of weight loss was calculated according to the equation

$$\text{Weight loss} = ((m_i - m_a)/m) \times 100 (\%)$$

where m_i is initial mass, g;

m_a is actual mass, g;

m is initial mass on dry and mineral-matter free basis, g.

As samples tested had different mineral content, weight loss values were calculated on organic matter for each sample, and, as a result, their percentage also shows the organic matter conversion level.

Results

Elemental Analysis

The data on elemental analysis and ash content of initial and acid-washed Göynük oil shale (further: oil shale) and Şırnak asphaltite (further: asphaltite) samples are presented in Table 1. Decrease in oil-shale ash content after HCl washing is 21%. Considering CaO content (Table 2), we concluded that oil shale carbonates mainly consist of calcium carbonate. Also, HCl partly dissolved oil shale organic compounds containing sulphur and nitrogen, whereas in the case of asphaltite, sulphur content increase was 54%. We reasoned it to be aromatic sulphur, as organic sulphur compounds are very resistant against HCl solution.

Table 1. Elemental Analysis of Initial and Acid-Treated Samples, wt. %

	GOS	GOS1	GOS2	GOS3	SA	SA1	SA2	SA3
C	55.7	59.2	56.5	65.1	39.0	53.6	50.1	67.5
H	8.2	7.2	6.8	7.7	3.2	4.3	3.6	4.6
N	1.6	0.7	2.0	2.1	0.5	0.4	3.0	3.8
S	4.4	3.3	3.1	7.4	4.8	7.39	4.3	6.3
Ash	15.7	12.4	11.7	0.3	38.4	31.0	24.3	–

Table 2. XRF Analysis of GOS and SA Ashes

Compound	GOS	SA
SiO ₂	37.47	31.28
Al ₂ O ₃	–	12.21
Fe ₂ O ₃	17.21	5.16
CaO	22.94	21.73
MgO	0.69	3.37
K ₂ O	1.07	3.76
TiO ₂	0.90	0.71
MnO	0.41	–
CuO	0.23	–
ZnO	0.18	0.43
SO ₃	18.11	17.86
P ₂ O ₅	1.59	0.86

HNO₃ washing was carried out to dissolve pyrite and elemental sulphur. About 6.5-percent decrease of asphaltite ash content shows that its inorganic sulphur occurs mostly in pyritic or/and elemental form. Oil shale ash content changed negligibly. In general, under HNO₃ treatment oxidation and/or nitration are expected, depending on treatment conditions, such as acid concentration, temperature, and organic matter content [15]. In the present study, the mildest reaction conditions possible were examined. The increase in nitrogen content of both oil shale and asphaltite was attributed to nitration and the slight decrease in carbon content may be due to oxidation.

Residual mineral matter from HCl–HNO₃ washing could be removed by HF washing. H/C ratios of organic matter were 1.4 and 0.8 for oil shale and asphaltite samples, respectively.

Thermogravimetric Analysis of Göynük Oil Shale

As kerogen decomposes below 600 °C, this value was chosen to be final. Decomposition occurs in one step in the temperature range 300–550 °C (Fig. 1). As expected, the maximum rate shifts to higher temperatures at the

increased heating rate. It is in agreement with the results of other studies [16–20]. It was assumed that the above shift is attributed to the heat transfer. Jaber *et al.* [8] and Williams [16] suggested that at higher heating rates the temperature on the particle external surface is higher than in its core. This gradient leads to reactions occurring inside the particle at lower temperatures and producing oil and gas, which, passing through the higher-temperature region, undergo secondary reactions.

In spite of the fact that the temperature of the maximum decomposition rate depends on the heating rate, the residue percent is not considerably influenced by it.

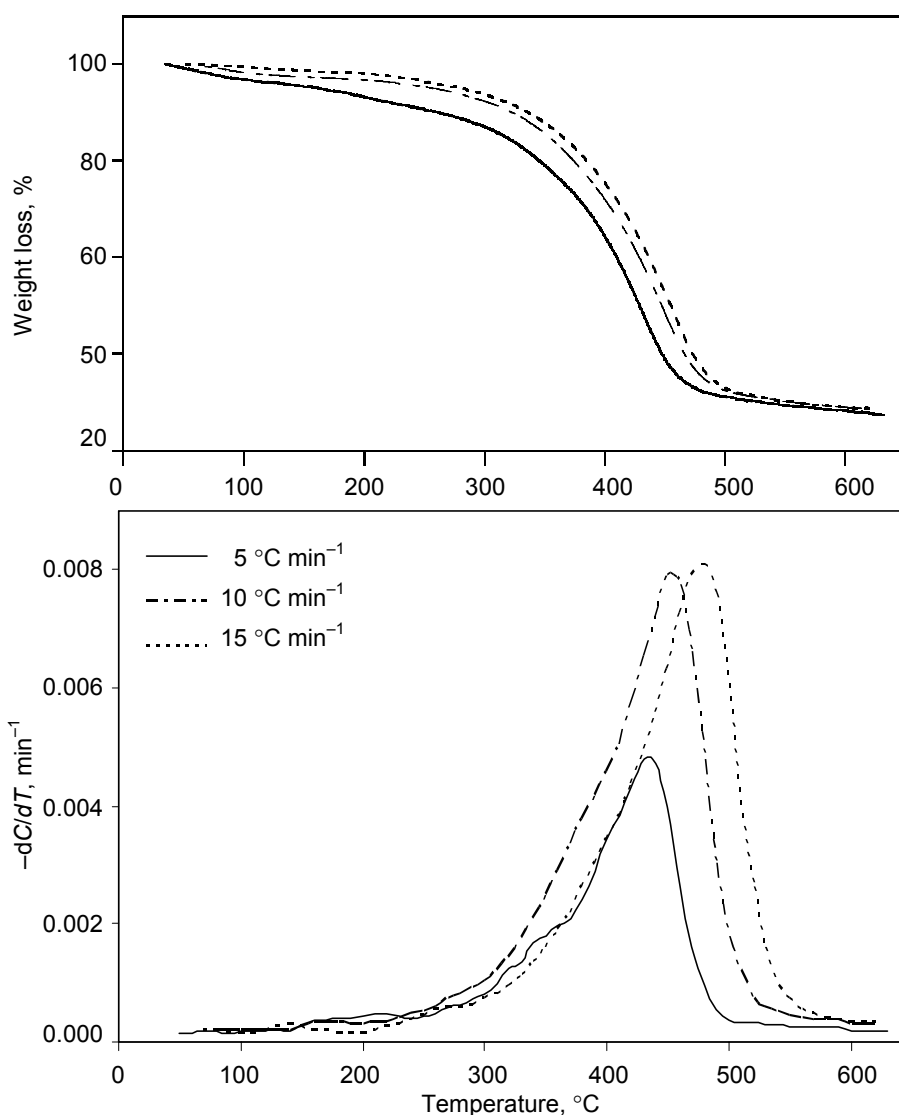


Fig. 1. TGA and DTG of Göynük oil shale at different heating rates

Obviously, HCl-washing did not influence the degree and rate of oil shale decomposition (Fig. 2).

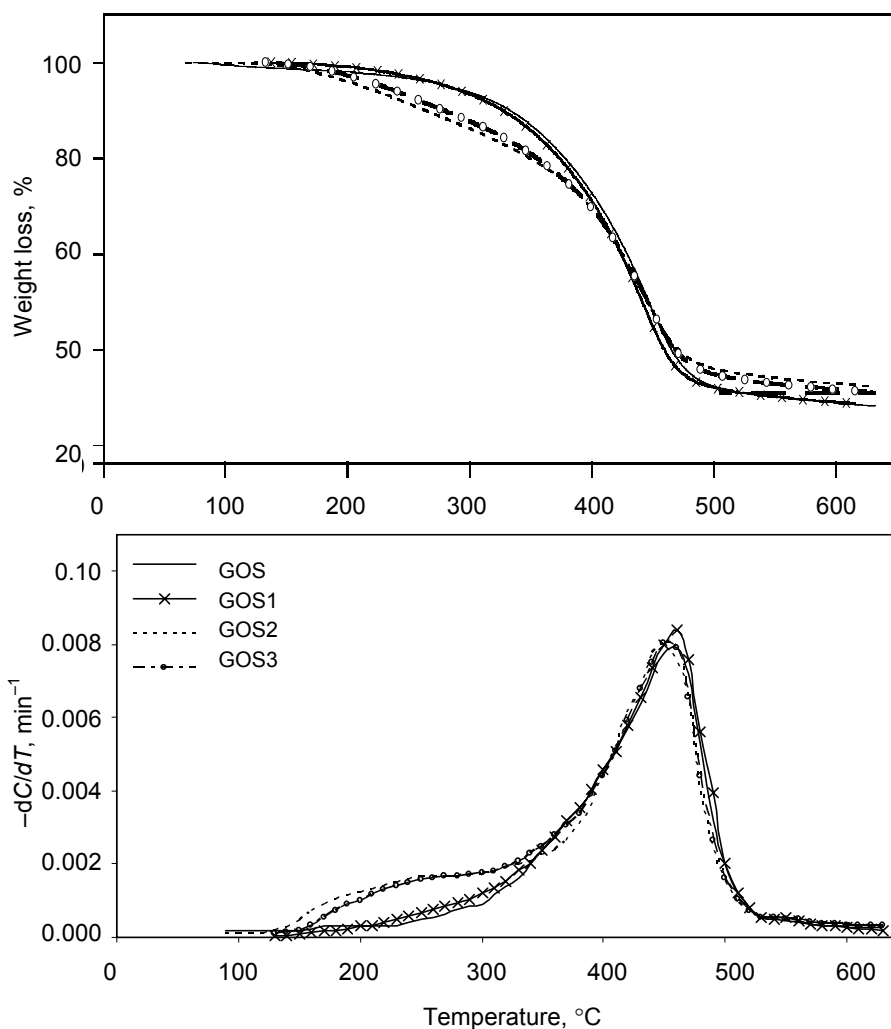


Fig. 2. TGA and DTG of the untreated and treated oil shale samples at a heating rate of 10 °C min⁻¹

Decomposition of carbonate-free sample GOS1 starts at 300 °C like in the case of original GOS, and that of HNO₃- and HF-washed GOS2 and GOS3 at lower temperature. The difference in degradation behavior between GOS and GOS2 or GOS3 is more apparent in the DTG graph. For both GOS2 and GOS3 it is similar, although their ash contents are different. Evidently, the weight loss at lower temperatures is attributed to the decomposition of oxidized and/or nitrated organic compounds in shale.

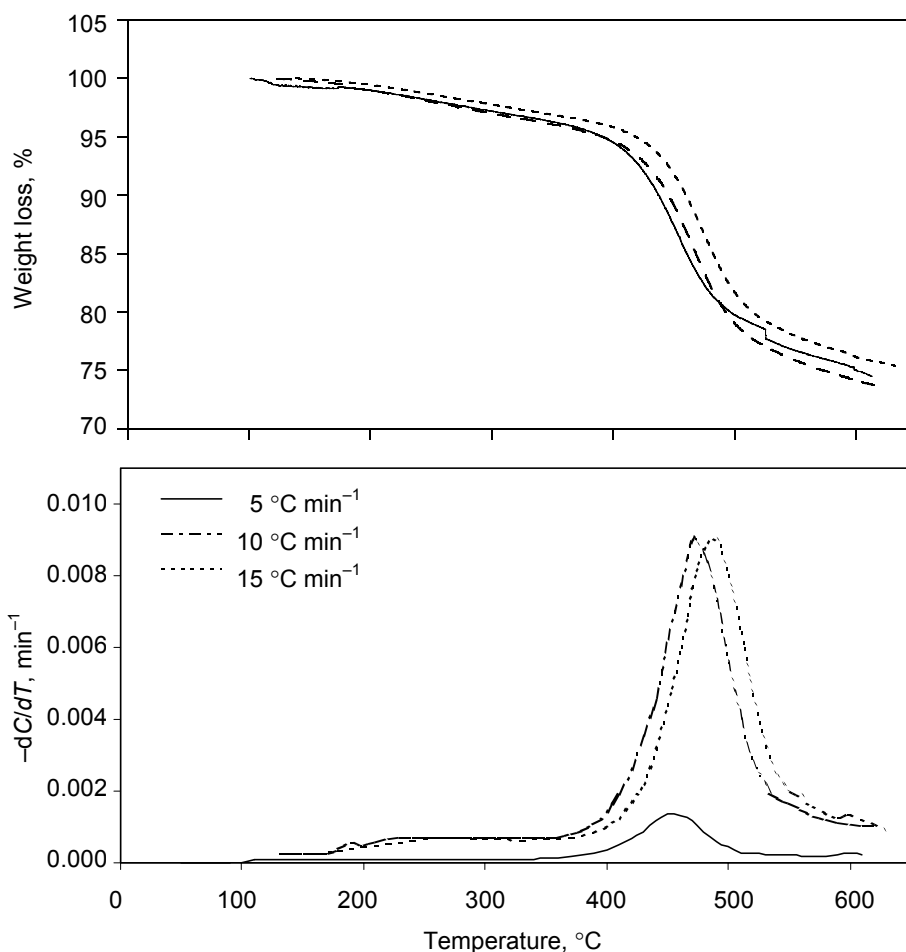


Fig. 3. TGA and DTG of Şırnak asphaltite at different heating rates

Although HNO_3 and HF washings affected the degradation pathway of GOS, total weight loss in TGA, relating to the conversion of kerogen to oil and gas products, did not considerably vary with the ash content change being 71% for GOS and GOS1, and 68% for GOS2 and GOS3. It disagrees with the results of Karabakan *et al.* [11]. They investigated the effect of GOS mineral matrix on the conversion of kerogen using Fischer assay and found that the percentage of volatiles from HF-washed samples was about 20% more than that from original GOS. This confusion, most probably, is due to different degradation conditions. Their results concerning kinetic parameters are also discussed in the present study.

Thermogravimetric Analysis of Şırnak Asphaltite

It has been suggested that this asphaltite has arisen from aromatic intermediate oil by alteration during migration. Although there is no

appropriate reference on kinetic studies of its degradation, some studies on its pyrolysis and co-pyrolysis with coal and oil shale are known [21–23].

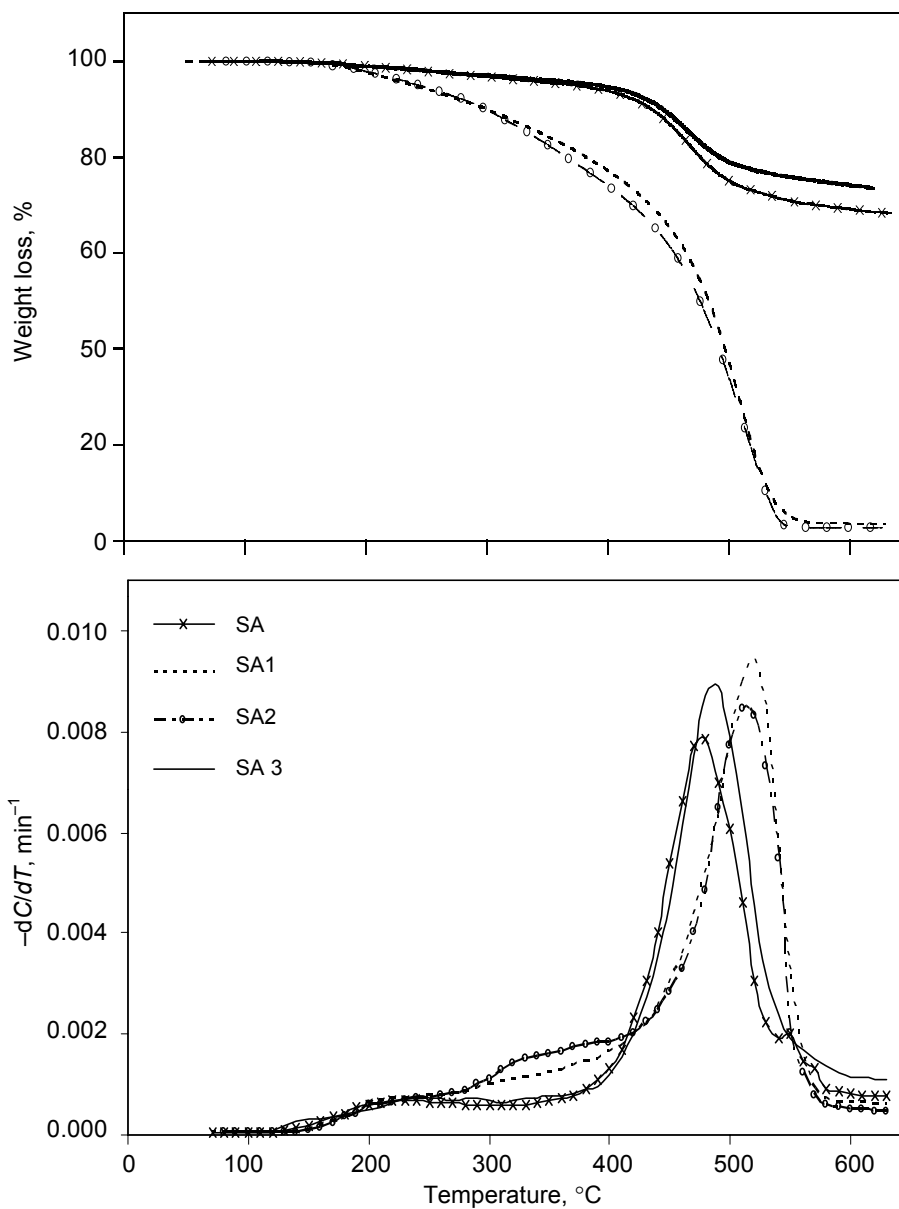


Fig. 4. TGA and DTG of the untreated and treated asphaltite at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$

Ballice *et al.* studied temperature-programmed co-pyrolysis of Şırnak asphaltite with Göynük oil shale and Soma lignites [21, 22] and found the temperature of maximum release of volatile products to be approximately

430 °C. In both co-pyrolysis studies increasing asphaltite ratios yielded more C₁–C₁₅ *n*-paraffins and coke. It was suggested that co-processing of coal or oil shale and asphaltite actually makes use of coking reactions on mineral matter of the latter to produce lower-boiling hydrocarbon fractions.

The effect of heating rate and mineral content on the pyrolysis of asphaltite was investigated under non-isothermal conditions (Fig. 3). Up to 200 °C, moisture and weight loss due to molecular rearrangement by the gas release occurred. The main weight loss was observed within the temperature range of 200–550 °C, with maximum rate occurring at about 450 °C. Similarly to oil shale pyrolysis, increasing heating rate shifted the peak temperature for maximum weight loss rate to higher temperatures, and minimum one was observed at the lowest heating rate (5 °C/min).

The level of asphaltite organic matter conversion into volatiles was less: approximately 25% for asphaltite against 70% for oil shale. This is probably due to the difference in organic structures of the samples tested. Oil shale organic matter is classified as Type I and consists mainly of aliphatic hydrocarbons, whereas that of asphaltite is mostly aromatic. In general, during pyrolysis, most of the aliphatic carbon is converted to oil, while most of the aromatic one is converted to carbon residue [23].

As seen from Fig. 4, thermal degradation behavior of HCl-washed asphaltite (SA1) was similar to that of untreated asphaltite (SA), only the percentage of volatiles from SA1 was 4% more.

Analogously to oil shale, asphaltite washing with HNO₃ and HF changed the degradation process. It starts at a very low temperature because oxidized and/or nitrated organic compounds easily decompose. Degradation of hydrocarbons reaches its maximum within the peak temperature range, while maximum weight loss takes place at a higher temperature than in the case of SA1 and SA.

In contrast to oil shale, HNO₃ and HF washing significantly increased asphaltite conversion. Its level for HNO₃- or HF-washed samples and initial asphaltite was 97 and 26%, respectively, while the conversion of all oil shale samples tested was approximately 70%. Most likely, in that case the hydrocarbons, which normally degrade in the temperature range of 300–550 °C, were partly nitrated/oxidized to form compounds degradable below 300 °C by HNO₃ treatment. On the other hand, asphaltite hydrocarbons, which are mainly aromatic and normally form coke during pyrolysis, could be converted into compounds forming volatile compounds.

It is impossible to conclude that asphaltite mineral matter affected the conversion of its hydrocarbons. Although mineral matter content of the SA2 and SA3 differs, their conversion level values were almost the same.

Kinetics

Decomposition rate was calculated according to the following formula:

$$d\alpha/dt = k(1 - \alpha)^n \quad (1)$$

where α is conversion level defined as $\alpha = (m_0 - m)/(m_0 - m_\infty)$ with m_0 being the initial mass, m actual mass and m_∞ final mass of a sample;

k is rate coefficient;

n is reaction order;

$k(T) = k_0 \cdot e^{-E_a/RT}$, where k_0 is pre-exponential factor and E_a activation energy.

Introducing the heating rate, $\beta = dT/dt$, Eq. (1) is transformed into

$$d\alpha/dT = (k_0/\beta) \cdot e^{-E_d/RT}(1 - \alpha)^n \quad (2)$$

and

$$d\alpha/dt = k_0 v z \cdot e^{-E_d/RT}(1 - \alpha) \quad (3)$$

To evaluate the overall kinetic parameters k_0 , E_a and n , Eq. (3) was integrated using a fourth-order Runge–Kutta method for the given sets of parameters. Then the minimum sum of squares of deviations between the conversion level from the integral rate expression ($\alpha_{1,cat}$) and the thermogravimetrically measured ones ($\alpha_{1,exp}$) were directly searched by calculating the sum of square in the parameter space with very high accuracy:

$$SSQ = 1/N \sum [\alpha_{1,exp} - \alpha_{1,cat}]^2 = \min$$

The kinetics parameters obtained using the Runge–Kutta method are listed in Table 3. Reaction order and activation energy were calculated for the main decomposition stage.

Table 3. Kinetic Parameters of GOS and SA Samples

Sample	n	E_a , kJ/mol
GOS	0.72	56.9
GOS1	0.96	50.6
GOS2	1.16	80.3
GOS3	1.24	84.6
SA	2.03	137.7
SA1	1.32	110.5
SA2	0.69	68.8
SA3	0.79	67.9

The reaction orders were in the range of 0.7–1.2 for all shale samples tested. One may say that the pyrolysis reactions of the initial and acid-washed oil shale were first-order ones. Elimination of carbonates did not change its pyrolysis activation energy. However, for HNO₃- and HF-washed samples it was approximately 54% higher than for initial one, since nitration changed the oil shale composition and resulting nitro-compounds decomposed at a lower temperature and, consequently, the remainder required higher activation energy.

In contrast to oil shale, the activation energies for pyrolysis of HNO₃- and HF-washed asphaltites were approximately 45% lower than those for initial samples. Apparently, HNO₃ treatment led to formation of very weak organic structures within asphaltite. This conclusion is also supported by the TGA analysis, demonstrating 97-percent conversion of HNO₃- and HF-washed asphaltites.

Conclusions

Non-isothermal thermogravimetric analysis of Göynük oil shale and Şırnak asphaltite was carried out and the effect of mineral matter content on their degradation kinetics was investigated using a selected model. An attempt was made to correlate the TGA and the kinetic parameters.

For both samples, the amount of residue did not depend on heating rate, whereas its increase shifted the maximum weight loss to higher temperature. HCl washing had no effect on the extent and rate of decomposition. However, degradation of HNO₃-washed samples started at lower temperature than that for raw ones, because of formation of oxidized and nitrated compounds after the HNO₃ treatment. Also, it led to a significant increase in asphaltite weight loss.

Although HF-washed samples contained no mineral matter, their degradation behavior was similar to that of HNO₃-washed ones. This shows that the change in organic structure plays a more important role in degradation than that in the mineral part.

Activation energies of pyrolysis reactions of HNO₃- or HF-washed oil shale were similar and higher than those for both the initial and HCl-washed oil shale. In contrast, at asphaltite pyrolysis, the activation energies of HNO₃- or HF-washed samples were lower than those of the original asphaltite.

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