

THE EFFECTS OF ACID TREATMENT ON THE PYROLYSIS OF GÖYNÜK OIL SHALE (TURKEY) BY THERMOGRAVIMETRIC ANALYSIS

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The present study investigates pyrolysis kinetics of raw and pretreated Göynük oil shales by thermogravimetric analysis (TGA). Samples were treated with HCl, HNO₃ and HF solutions and characterized by TGA data. All experiments were carried out at a heating rate of 5 K min⁻¹, in the temperature range of 25–1000 °C under the nitrogen atmosphere. Coats-Redfern method was used to determine the kinetic parameters of the activation energy using the data from thermogravimetric analysis. From the kinetic analysis it was concluded that Göynük oil shale samples have two reaction regions and the activation energies of the first region are lower.

Introduction

Oil shales are broadly defined as petroleum source rocks containing sufficiently high content of organic matter to make their utilization feasible. Like coal, the world's reserves of oil shales are vast, being many times larger than those proven for crude oil. Oil shale utilization has attracted renewed attention as a source of transport fuels and chemical feed stocks due to the uncertainty in the long-term on the availability of the crude oil supplies. Indeed, during the last twenty years a number of innovative processes have been developed, such as fluidized-bed pyrolysis, combustion and hydro-retorting, that has enabled to obtain considerably higher oil yields compared to the classic retorting procedures [1].

Oil shale can be defined as a compact rock of sedimentary origin with ash content more than 33% and containing organic matter that yields in oil when destructively distilled, but not appreciably when extracted with ordinary solvents. Oil shales contain organic matter mostly in the form of kerogen which is defined as the fraction of the organic matter in a sedimentary rock

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that is insoluble in common petroleum solvents. The other fraction called bitumen is soluble in organic solvents, but represents only a small amount of the organic matter in an oil shale. The oil shale deposits in Turkey are widely distributed, in the middle and western Anatolian [2]. Oil shales are the second largest solid fuel reserve in Turkey with approximately five billion tonnes [3].

There are different technologies in use or under development for oil shale treatment to valuable products, including surface retorting, energy production in power plants, and in-situ retorting. Therefore, changes in the structure of the organic matter at a temperature region of oil shale thermobitumen formation (up to 350–400 °C) or in the active pyrolysis region (375–600 °C) are of interest in oil shale conversion into liquid fuels or chemicals, because the macromolecular structure of kerogen needs to be broken down to obtain oil [4].

Kerogen is a complex substance with large molecules consisting mainly of carbon, hydrogen, nitrogen, sulphur and oxygen atoms. The average molecular weight is 3000 and approximate empirical formula is $C_{200}H_{300}SN_5O_{11}$. When shale particles are heated to about 350 °C, the kerogen starts to decompose and partially vaporize, leading to final products that, at room temperature, consist of gas, oil, and residual carbon. For the design of equipment to obtain oil from shale it is necessary to know the rate of decomposition [5].

Thermal analysis is a popular and convenient tool of studying the combustion and pyrolysis reactions of fossil fuels and thermogravimetric analysis (TG/DTG) of oil shale samples has been extensively used as a way of determining the kinetic parameters. Thermal methods providing information about net results of mass loss and calculation of kinetic parameters are based on simplified assumptions, which do not correspond to the complex chemical reactions in the thermal degradation of the oil shale. The study of kinetics is essential for understanding the mechanisms and mathematical modeling of the process, which may lead to improved techniques for oil shale conversion [6].

Numerous attempts addressing the mechanistic and kinetic points of view have been made to understand the processes occurring during oil shale pyrolysis.

Thakur and Nuttall [7] studied the pyrolysis kinetics of the thermal decomposition of oil shale by isothermal and non-isothermal thermogravimetry. Their results showed that the thermal decomposition of oil shale involves two consecutive reactions with bitumen as an intermediate. Both reactions follow the first-order kinetics. Karabakan and Yürüm [8] investigated the effect of mineral matrix of oil shales and air diffusion on the conversion of organic material in oxidation reactions. The overall reaction orders from the kinetic analysis were found to be pseudo-first-order. The magnitude of the activation energies of oxidation reactions at equal heating rates changed. Kök and İçcan [6] studied the pyrolysis and combustion

behavior of three different oil shale samples from Turkey, carrying out the thermal analysis (TG/DTG). They used differential methods to calculate the activation energies. The activation energies of all oil shale samples were found to be between 13.1–215.4 kJ/mol. In the study of Kök [9], thermal analysis with Seyitömer oil shale was carried out by thermogravimetry (TG/DTA) and differential scanning calorimetry (DSC). It was discovered that Seyitömer oil shale samples have more than one reaction regions where the activation energy of the first region is higher compared to the second region.

The basic principles of pyrolysis of oil shales may be understood by examining the overall pyrolysis behavior of the original oil shale and taking into account the interaction between kerogen and inorganic matrix. Pyrolysis behavior of demineralization products provides useful information about the interaction between the kerogen and inorganic matrix of the oil shale. Mineral matter present in oil shales is believed to play an important role in the thermally induced catalytic alteration of kerogen during petroleum formation [10]. Oil shale consists of complex sapropelic organic matter of high molecular weight (kerogen) that is finely distributed in an inorganic matrix. The inorganic part consists mainly of quartz, clay minerals, different types of carbonates (CaCO_3 , MgCO_3 , and dolomite), pyrite, and Fe_2O_3 , as well as trace elements (As, B, Mo, Ni, and Zn) [11].

In this article, the isolation of kerogen was mainly investigated. Among several isolation methods, chemical methods are generally applicable for obtaining good separation of the kerogen from the minerals. The conventional hydrochloric/hydrofluoric acid treatment is effective for removing most of the carbonate, oxide, and monosulphide minerals from the sedimentary rocks and it leaves kerogen and pyrite largely unaffected [12, 13]. In our previous study [14] of removing pyrite, dilute HNO_3 solution was used and the acid treatment did not significantly alter the kerogen structure during the acid leaching.

There are several approaches such as Coats-Redfern [15], Kissinger-Akahira-Sunose [16], Friedman [17], Flynn-Wall-Ozawa [18], Criado [19] methods to analyze isothermal/ nonisothermal thermogravimetric data and determine the reaction rate equation. The use of different approaches of analysis may lead to different values of the kinetic parameters. In such case comparison of the values becomes difficult.

As interaction between kerogen and the inorganic matrix during reactions is not well understood, fifteen different reaction mechanisms were proposed in this study. These models were applied to TG data and the reaction rate mechanisms. Precise activation energies were calculated for all Göynük oil shale samples.

The interesting fact that emerged during thermogravimetric analysis is that the understanding of kinetics of the thermal decomposition of oil shales is crucial for designing and operating the conversion systems. So, the purpose of the study was to investigate the effect of mineral matter on the

pyrolysis, on the reaction rate equation and on the activation energies of Göynük oil shale. A series of isothermal thermogravimetric analysis were performed to express the reaction rate mechanisms and to explain thermal behavior of the raw and pretreated oil shale samples.

Experimental study

Material

In this study, the oil shale samples were obtained from Göynük oil shale deposit near the town Bolu in northwestern Turkey. The samples were sieved for the experiments to obtain a fraction with particle size < 0.1 mm. All chemicals (HCl, HNO₃ and HF) used in this study were of analytical grade.

Demineralization

The raw oil shale sample (GOS-R) was successively demineralized with 10% HCl, 5% HNO₃ and pure HF under inert atmosphere.

1 g of sample was stirred with 20 mL of 10% HCl solution. The slurry was stirred for 48 hours under inert atmosphere. Then the sample was filtered and washed with distilled hot water until Cl⁻ ions could not be detected. Carbonate free samples (GOS-C) were treated with 20 mL of 5% HNO₃ solution. The slurry was stirred for 1 h at room temperature, after which it was filtered and washed with distilled hot water until the filtrate became neutral. The solid residue was dried under vacuum (GOS-N). Finally 20 mL of HF was added to the residue and the mixture was stirred for 8 h. After being filtered, the demineralized oil shale was washed with distilled hot water and dried under vacuum (GOS-F).

Thermogravimetric analysis

Thermogravimetric experiments were carried out with a thermogravimetric analyzer DuPont Model 951. Oil shale samples, named as GOS-R, GOS-C, GOS-N and GOS-F, were used in TG analyses. Experimental parameters: 100 mg samples were pyrolyzed to 1000 °C with nitrogen as a purge gas (15 mL/min) at a heating rate of 5 °C/min.

Results and discussion

Thermogravimetric analysis of Göynük oil shales

TG and DTG curves for thermal decomposition of the oil shale samples are given in Fig. 1. Weight loss of GOS-R in the low-temperature region, from ambient up to approximately 200 °C has been attributed to the loss of moisture, interlayer water from clay minerals and also to decomposition of mineral nahcolite (NaHCO₃), which is one of the minerals present in the raw

shale. The weight loss in the temperature region from about 300 to 520 °C occurs on account of the hydrocarbonaceous material. The main weight loss begins at about 300 °C, from then on, the rate of weight loss increases rapidly due to the formation of volatile hydrocarbons. It was concluded that acid washing causes higher weight losses. Although decomposition of original samples starts from 300 °C, the other oil shale samples decomposed at lower temperatures. Weight losses of GOS-R, GOS-C, GOS-N and GOS-F at temperatures up to 520 °C were determined to be 48 %, 70%, 75% and 82%, respectively. It was observed that decomposition process for all samples took place in two stages: 300-420 °C and 420-520 °C.

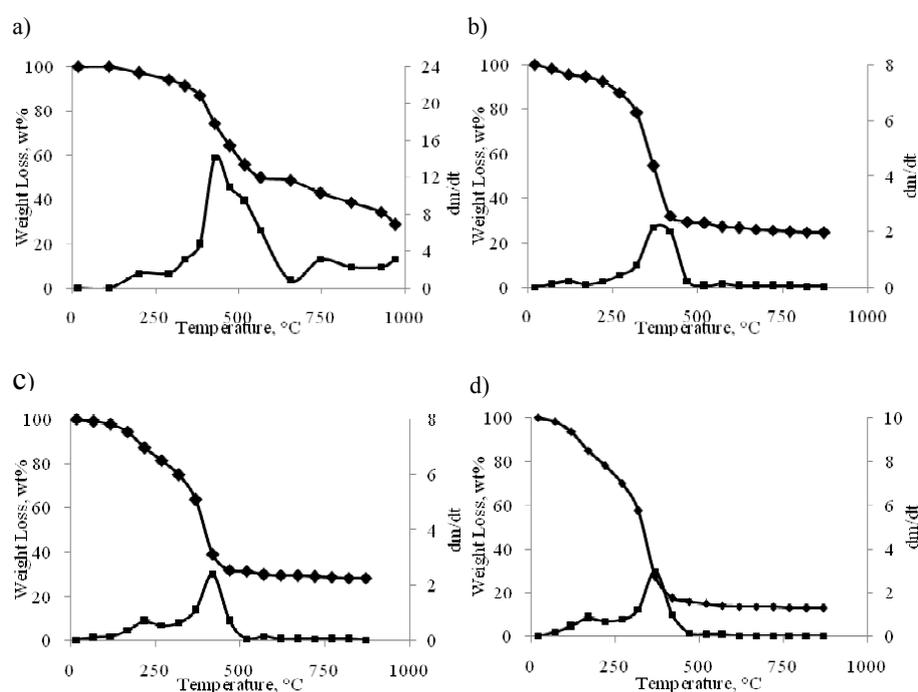


Fig. 1. TGA and DTG curves of a) GOS-R, b) GOS-C, c) GOS-N, d) GOS-F.

Between 600 °C and 900 °C, the weight loss is attributed to the decomposition of carbonate minerals such as calcite, dolomite, ankerite, and others. At the same time, CO₂ (the product of carbonate decomposition), which at high temperature reacts with residual char to form CO, also causes some weight loss.

Demineralization

Fisher assay of raw Göynük oil shale and the data on elemental analysis of initial and acid-washed Göynük oil shale samples are presented in Table 1 [20] and 2 [21], respectively. Decrease in the mineral content of the oil shale

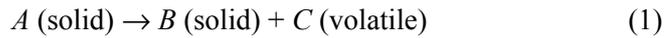
after HCl washing is 19.4 wt%. Oil shale carbonates mainly consist of calcium carbonates and HCl dissolved organic compound of the oil shale containing nitrogen and sulphur [14]. 14.0 wt% of the mineral matter was removed after HNO₃ washing, because of the dissolution of pyrite and elemental sulphur [22]. Residual mineral matter can finally be removed by HF washing. H/C ratios of the organic matter of the initial and final oil shale samples were 0.128 and 0.123, respectively.

Table 1. Fisher assay of raw Göynük oil shale sample [20]

Fisher assay, wt%	
Shale oil	31.8
Gas	9.6
Decomposition water	3.6
Residue	51.2

Kinetic study

The pyrolysis process may be represented by the following reaction scheme:



The rate of conversion, dx/dt for TG experiment at constant heating rate of temperature change, $\beta = dT/dt$ may be expressed as follows:

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x), \quad (2)$$

where

- $f(x)$ – function of conversion, such as $(1-x)$ for first-order reaction,
- E – activation energy,
- A – Arrhenius factor,
- R – gas constant,
- x – degree of advance defined by

$$x = \frac{w_0 - w}{w_0 - w_f}, \quad (3)$$

where

- w – weight of the sample at a given time t ,
- w_0, w_f – initial and final weight of the sample, respectively.

Integration of Equation 2 gives the Coats-Redfern Equation:

$$\ln\left[\frac{g(x)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT}, \quad (4)$$

where $g(x)$ – integrated form of $f(x)$.

Reaction mechanisms and their algebraic expressions $f(x)$ and $g(x)$ most commonly given in literature [23] for the description of solid state reactions are listed in Table 3.

Table 2. Elemental analysis of raw and treated oil shale samples [21]

Oil shale samples	N	C	S	H
GOS-R	0.97	56.34	4.12	7.20
GOS-C	1.19	60.00	3.96	7.63
GOS-N	1.02	59.87	4.07	7.58
GOS-F	1.30	67.59	4.38	8.31

Table 3. Set of reaction models applied to describe thermal decomposition in solid [23]

Model	Mechanism	$f(x)$	$g(x)$
1	First-order reaction (F1)	$(1-x)$	$-\ln(1-x)$
2	Second-order reaction (F2)	$(1-x)^2$	$(1-x)^{-1}-1$
3	Third-order reaction (F3)	$(1-x)^3$	$[(1-x)^{-2}-1]/2$
4	Power law (P2)	$2x^{1/2}$	$x^{1/2}$
5	Power law (P3)	$3x^{2/3}$	$x^{1/3}$
6	Power law (P4)	$4x^{3/4}$	$x^{1/4}$
7	One-dimensional diffusion (D1)	$1/2x$	x^2
8	Contracting area (R2)	$2(1-x)^{1/2}$	$[1-(1-x)^{1/2}]$
9	Contracting volume (R3)	$3(1-x)^{2/3}$	$[1-(1-x)^{1/3}]$
10	Two-dimensional diffusion (D2)	$[-\ln(1-x)]^{-1}$	$[(1-x)\ln(1-x)]+x$
11	Three-dimensional diffusion (D3)	$3(1-x)^{2/3}/[2(1-(1-x)^{1/3})]$	$[1-(1-x)^{1/3}]^2$
12	Ginstling-Brounshtein (D4)	$3/2((1-x)^{-1/3}-1)$	$(1-(2x/3)-(1-x)^{2/3})$
13	Avarami-Erofe'ev (A2)	$2(1-x)[- \ln(1-x)]^{1/2}$	$[- \ln(1-x)]^{1/2}$
14	Avarami-Erofe'ev (A3)	$3(1-x)[- \ln(1-x)]^{2/3}$	$[- \ln(1-x)]^{1/3}$
15	Avarami-Erofe'ev (A4)	$4(1-x)[- \ln(1-x)]^{3/4}$	$[- \ln(1-x)]^{1/4}$

Coats and Redfern developed a graphical method to determine the kinetic parameters for solid decomposition [13]. The Coats-Redfern analysis was performed by plotting $\ln[(g(x))/T^2]$ versus $1/T$. In order to determine the most probable model, the Coats-Redfern method was used. All reaction mechanisms given in Table 3 were fitted to the experimental data. Activation energies were found from the slope of best fitted curve.

As stated earlier, decomposition of raw oil shale and treated oil shale samples was performed in two-stages process. For this reason kinetic study was investigated for both temperature regions. For each region, regression coefficients of 15 different reaction mechanisms are given in Table 3 and were found by graphical method and tabulated in Tables 4 and 5. As seen from these tables, TGA data were fitted for the second order reaction mechanism. The plots of $\ln[(g(x))/T^2]$ versus $1/T$ for Model 2 and Region I and II are shown in Figures 2 and 3, respectively. Activation energies and Arrhenius factors for Region I and II were calculated according to this mechanism and shown in Table 6. As seen from Table 6, the

activation energy for decomposition of raw oil shale sample is 31.56 kJ/mol. Yağmur and Durusoy [24] studied the kinetics of the pyrolysis and combustion of Göynük oil shale and they found that the activation energy at a heating rate of 10 K min⁻¹ was 2.2 kJ/mol. This difference may come from the origin or deposition of sample and from the kinetic model applied.

Table 4. Regression coefficients of oil shale samples for Region I

Model	R^2			
	GOS-R	GOS-C	GOS-N	GOS-F
1	0.97	0.96	0.98	0.92
2	0.98	0.99	0.99	0.95
3	0.99	0.98	0.97	0.94
4	0.97	0.96	0.97	0.93
5	0.97	0.97	0.98	0.92
6	0.96	0.98	0.97	0.92
7	0.96	0.97	0.97	0.86
8	0.95	0.97	0.94	0.90
9	0.97	0.97	0.96	0.90
10	0.97	0.97	0.96	0.88
11	0.96	0.96	0.95	0.91
12	0.96	0.96	0.95	0.86
13	0.98	0.95	0.98	0.87
14	0.97	0.95	0.98	0.63
15	0.97	0.96	0.96	0.67

Table 5. Regression coefficients of oil shale samples for Region II

Model	R^2			
	GOS-R	GOS-C	GOS-N	GOS-F
1	0.97	0.96	0.97	0.94
2	0.98	0.99	0.99	0.96
3	0.99	0.98	0.98	0.95
4	0.96	0.96	0.97	0.94
5	0.97	0.97	0.98	0.93
6	0.98	0.97	0.96	0.93
7	0.98	0.96	0.96	0.90
8	0.95	0.96	0.94	0.90
9	0.94	0.95	0.97	0.92
10	0.95	0.95	0.97	0.92
11	0.98	0.97	0.96	0.94
12	0.96	0.94	0.96	0.90
13	0.97	0.93	0.97	0.91
14	0.96	0.93	0.97	0.91
15	0.97	0.96	0.98	0.90

Sonibare et al. [25] performed nonisothermal TGA on Lokpanta oil shales (Nigeria) and found that its activation energies vary from 73.2 to 75 kJ/mol. Doğan and Uysal [26] however, reported the activation energies for Turkish oil-shales, of approximately 25 kJ/mol for the lower temperature decomposi-

tion and up to 43 kJ/mol for the main stage of decomposition. Qing et al. [27] studied the pyrolysis characteristics of Huadian oil shales and found that the activation energies change from 47 to 80 kJ/mol at different heating rates.

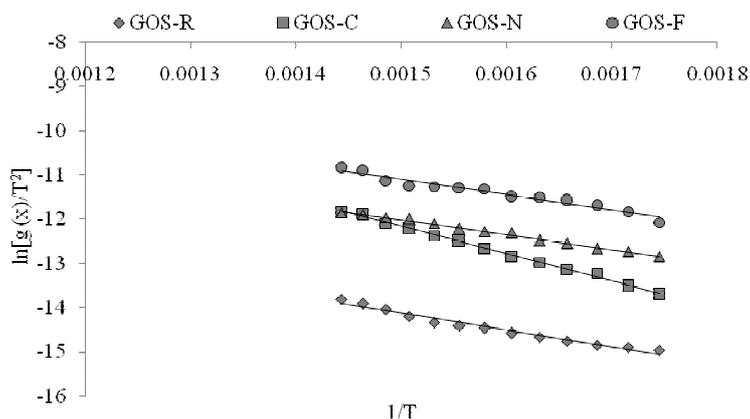


Fig. 2. The plot of $\ln[g(x)/T^2]$ vs $1/T$ for Model 2 and Region I.

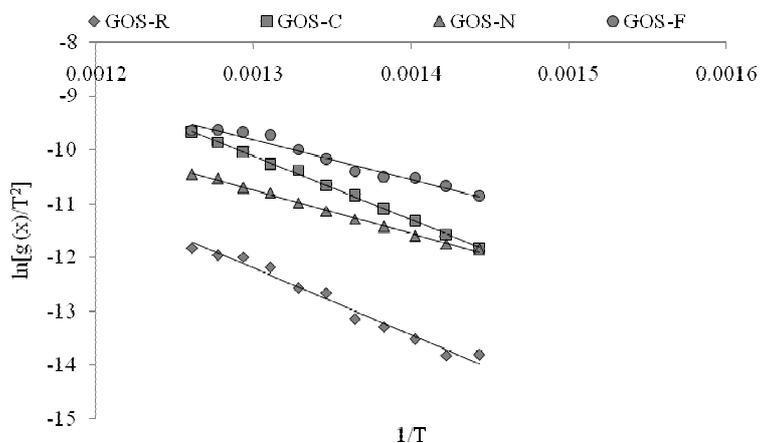


Fig. 3. The plot of $\ln[g(x)/T^2]$ vs $1/T$ for Model 2 and Region II.

Table 6. Activation energies of oil shales for Region I and II

Oil shale samples	Region I		Region II	
	E, kJ/mol	A	E, kJ/mol	A
GOS-R	31.56	8	102.62	$5.7 \cdot 10^6$
GOS-C	51.46	3487	97.84	$20.8 \cdot 10^6$
GOS-N	27.94	32	66.33	$5.4 \cdot 10^4$
GOS-F	28.86	95	61.47	$6.0 \cdot 10^4$

Calculated activation energies for decomposition of GOS-R, GOS-C, GOS-N and GOS-F were 31.56, 51.46, 27.94 and 28.85 kJ/mol, respectively.

After demineralization of GOS-R with HCl, activation energy increased from 31.56 to 51.46 kJ/mol. Removal of carbonates caused an increase in the activation energies of the pyrolysis reactions of shales. The interaction of alkaline earth metal cations in the carbonates with –COOH and –OH functional groups possibly results in the formation of the alkali M^{2+} -O surface groups. These alkali M^{2+} -O surface groups have been proposed as the active sites on the oil shale surface and therefore the alkaline earth metal cations might have some catalytic effect in the pyrolysis reactions of original Göynük oil shales [11]. Pyrolysis of demineralized oil shale was also investigated by Karabakan et al. [8] in order to obtain kinetic parameters for the decomposition process. The experiments were conducted nonisothermally at 300, 400, and 500 °C for 0, 5, 15, 30, and 60 min for both, raw and demineralized oil shale. Removal of the carbonates caused an increase in the activation energies of the pyrolysis reactions. This was in accordance with the increase in activation energy of the oil shale sample after HCl washing.

Mineral matter in the oil shale body causes heat transfer resistance and increases the required energy for decomposition. After removing minerals from the organic structure, the energy consumption decreased during obtaining gas and liquid products. Mass loss increased sharply after treating the sample with nitric acid and remainder of the sample required lower activation energy. The activation energy for the decomposition of pyrite-free oil shale sample (GOS-N) was found to be 27.94 kJ/mol. This result shows that removal of the HNO_3 -soluble material slightly affected the reactivity of pyrolysis reactions.

The removal of silicates by HF washing caused a slight decrease in the activation energy of the original oil shale sample. This indicated the inhibitive effect of silicate minerals originally present in the shales during pyrolysis [11].

In Region II, the activation energy for decomposition of GOS-R, GOS-C, GOS-N and GOS-F were found as 102.62, 97.84, 66.33 and 61.47 kJ/mol, respectively. Activation energies calculated for the pyrolysis reactions of HF-washed shales were 39% lower than those of original Göynük oil shales. This indicates the inhibitive effect of the silicate minerals originally present in the shales in the pyrolysis reactions

Conclusion

The pyrolytic behaviour of raw and treated oil shale samples has been investigated using a TGA apparatus. The conclusions drawn from the present work are as follows:

- In the kinetic study of oil shale samples, 15 kinetic models were employed to TGA data in two-stage process with temperature regions 300–420 °C and 420–520 °C.

- TGA data were represented by Model 2, which is the second-order reaction, for each temperature interval.
- In Region I, the activation energies of GOS-R, GOS-C, GOS-N and GOS-F were found as 31.56, 51.46, 27.94 and 28.85, respectively.
- After demineralization of GOS-R with HCl, the activation energy increased from 31.56 to 51.46 kJ/mol. The removal of HNO₃-soluble material slightly affected the reactivity of pyrolysis reactions. The removal of silicates by HF washing caused a slight decrease in the activation energy.
- In Region II, the activation energies of GOS-R, GOS-C, GOS-N and GOS-F were found to be 102.62, 97.84, 66.33 and 61.47, respectively. Removing minerals from organic structure decreases the required energy for decomposition of oil shales.

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