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KINETICS OF CRUDE OIL COMBUSTION

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In this research, thermal characterization and kinetics of Karakus crude oil in the presence of limestone matrix is investigated. Thermogravimetry (TG/DTG) is used to characterize the crude oil in the temperature range of 20–900°C, at 10°C min^{-1} heating rate using air flow rate of 20 mL min^{-1}. In combustion with air, three distinct reaction regions were identified known as low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO). Five different kinetic methods used to analyze the TG/DTG data to identify reaction parameters as activation energy and Arrhenius constant. On the other hand different $f(\alpha)$ models from literature were also applied to make comparison. It was observed that high temperature oxidation temperature (HTO) activation energy of Karakus crude oil is varied between 54.1 and 86.1 kJ mol^{-1}, while low temperature oxidation temperature (LTO) is varied between 6.9 and 8.9 kJ mol^{-1}.

Keywords: *activation energy, crude oil, kinetics, thermal analysis*

Introduction

In recent years the application of thermal analysis to study the combustion behavior of crude oils has gained a wide acceptance among researchers. Ranjar and Pusch [1] considered the effect of the oil composition, described on the basis of light hydrocarbon, resin and asphaltene contents, on the pyrolysis kinetics of the oil and the combustion kinetics of the fuel. The results of their analysis revealed that the colloidal composition of oil has a pronounced influenced on fuel formation and composition as well as the transfer-ability and heat transfer characteristics of the pyrolysis medium. Bae [2] examined the thermooxidative behavior and fuel-forming properties of various crude oils. The results indicated that oils could be categorized according to their oxidation characteristics. No complete correlation could be established between viscosity, composition or density of the crude with the thermooxidative characteristics of the oil. Vossoughi and Bartlett [3] have developed a kinetic model of the in situ combustion process by using the data taken from thermogravimetric analysis (TG/DTG) and differential scanning calorimetry (DSC). Kinetic model is used to predict fuel deposition and combustion rate in a combustion tube in their study and they obtained good agreement between predicted and observed fuel deposition and combustion rate in a combustion tube. Kök [4] described the pyrolysis and combustion properties of two heavy crude oils. On combustion in air, three different reaction regions were identified, known as low-temperature oxidation, fuel deposition and high-temperature oxidation. DSC-TG/DTG curves have also been used to decide on the heat values and reaction parameters of crude oil. Kinetic data were obtained from the high-temperature oxidation region from the DSC and TG curves. It is observed that activation energy values increased as the API gravity of the crude oil decreased. Barkia *et al*. [5] studied organic matter evolved and kinetics of combustion of fossil fuels which has been examined by thermogravimetry (TG/DTG). An agreement was observed between both techniques where it was found that combustion of organic matter occurs in two steps. Kök [6] applied TG-DTA to light crude oil combustion both in the presence and absence of metal oxide.

Three main transitional stages were detected in crude oil-limestone mixtures as distillation, low temperature and high temperature oxidation regions. Kinetic parameters of the samples are determined using ASTM method and it was noticed that the reduction in activation energy is considered to be an indication of the catalytic activity of the additive. Goncalves *et al*. [7] investigated the thermal behavior of asphaltenes from crude oil using thermal analysis techniques. The approach involves kinetic studies of the thermal decomposition of asphaltenes under controlled conditions by thermogravimetry (TG/DTG), characterization of volatile fractions by thermogravimetry and differential thermal analysis coupled with gas chromatography/mass spectrometry and by gas chromatography/mass spectrometry in the volatile recovered. The coke formed was also studied after being decomposed into smaller molecules using selective oxidation. Kök and Keskin [8] investigated the thermal characteristics and kinetics of three crude oils using thermogravimetry (TG/DTG). In combustion with air, three distinct reaction regions were identified in

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all crude oil samples studied, known as low temperature oxidation, fuel deposition and high temperature oxidation. A computer program was developed for automatically processing the data to estimate the reaction parameters. Laux *et al.* [9] proposed that thermogravimetry proves to be an effective method for the determination of important parameters of processing of crude oil residues considering the influence of the colloidal character of these complex mixtures. Lukyaa *et al.* [10] used pressurized differential scanning calorimetry to study the effects of sand particle size, pressure and oxygen partial pressure on the heat evolution during the combustion of North Sea crude-sand mixtures. They observed that decreasing particle size of the sand and increased pressure the extent of low-temperatures oxidation and thus favored fuel lay-down. Kök *et al.* [11] studied the light crude oil combustion in the presence of limestone matrix. Three distinct reaction regions were identified. Depending on the characteristics of crude oils, the mean activation energy is varied between 50.3 and 55.8 kJ mol^{-1}. Kök *et al.* [12] identified the kinetics of ten lignite's and two oil shale samples. In kinetic calculations, oxidation of lignite and oil shale is described by first-order kinetics. Depending on the characteristics of the samples, the activation energy values are varied. Kök [13] used DSC and TG/DTG to obtain information on the temperature-controlled combustion characteristics of seventeen coals of different origin. Reaction intervals, peak and burn-out temperatures of the coal samples are determined. Two different kinetic models were used to analyze the kinetic data.

Experimental

The crude oil sample used during the experiment was from Karakus (30.1°API) oil field which is one of the major oil fields of Turkey. The crude oil sample is mixed with crushed limestone (<60 mesh) and the final oil saturation was 15% in the mixture. TG-DTG experiments were carried out using TA thermal analysis system. Prior to the experiments thermal analysis systems were calibrated with calcium oxalate monohydrate for temperature readings and silver was used in order to correct for buoyancy effects. Simultaneous TG/DTG experimental procedure involves placing sample (≈30 mg) setting the heating and gas (air) flow rate, then commencing the experiment. Experiment was performed at heating rates of 10°C min^{-1} and using air flow rate of 20 mL min^{-1} over the temperature range of 20 to 900°C. Experiments were performed twice for repeatability.

Theory

In kinetic analysis, it is found convenient to express a reaction by using a certain function [11], $f(\alpha)$ of the reaction extent, α:

$$\alpha=(W_\mathrm{i}-W)/(W_\mathrm{i}-W_\mathrm{f}) \qquad (1)$$

where W is the weight or the weight percentage of the sample at a certain time. W_i and W_f are the initial and final values of the reaction.

The most commonly used equation to describe the reaction rate is in the differential form:

$$\mathrm{d}\alpha/\mathrm{d}t=f(\alpha)k(T) \qquad (2)$$

where $f(\alpha)$ is the function of α which represents the reaction mechanism (Table 1). $k(T)$ is the rate constant at the temperature T and generally takes the Arrhenius equation form:

$$k(T)=Ar\exp(-E/RT) \qquad (3)$$

where Ar is the frequency factor, E is the activation energy, R is the gas constant and T is the absolute temperature.

If Eq. (3) is combined with Eq. (2) and rearranged, then:

$$\mathrm{d}\alpha/f(\alpha)=Ar\exp(-E/RT)\mathrm{d}T/\beta \qquad (4)$$

where β is the linear heating rate ($\mathrm{d}T/\mathrm{d}t$).

The approximate integration of the Eq. (4) gives,

$$\ln(G(\alpha)/T^{1.921503})=\ln(ArE/\beta R)+3.7720501- \\ -1.921503\ln E-E/RT \qquad (5)$$

where $G(\alpha)$ is the integral form of the reaction function shown in Table 1. On the other hand, there are several other methods to find Ar and E.

Differential method [14]

One of the well-known methods to identify kinetics of the samples is differential method. By using the Eqs (2) and (3) to give:

$$\mathrm{d}\alpha/\mathrm{d}t=Arf(\alpha)\exp(-E/RT) \qquad (6)$$

The logarithmic form of the Eq. (6) is taken to give:

$$\ln[(\mathrm{d}\alpha/\mathrm{d}t)/f(\alpha)]=\ln Ar-E/RT \qquad (7)$$

By using the experimental data from a single heating rate curve, a plot of $\ln[(\mathrm{d}\alpha/\mathrm{d}t)/f(\alpha)]$ *vs.* $1/T$ be obtained by testing all well-known functions. The linear regression is calculated and then the activation energy (E) and the frequency factor (Ar) can be calculated from the slope and intercept of the regression line.

Table 1 Reaction intervals and burn-out temperature

Sample	LTO/°C	Fuel deposition/°C	HTO/°C	Burn-out/°C
Karakus crude oil	25–390	390–655	655–880	880

Integral method [15]

Another method used for determination of Ar and E is the integral method. Using Eq. (5), the plot of $\ln[G(\alpha)/T^{1.921503}]$ *vs.* $1/T$ is plotted and all the $G(\alpha)$ functions are tested. The activation energy (E) and the frequency factor (Ar) are obtained from the slope and intercept of the linear fit line.

Coats–Redfern method [16]

Coats and Redfern developed an integral method, which can be applied to TG/DTG data, assuming the order of reactions. The correct order is presumed to lead to best linear plot, from which the activation energy is determined. The final form of the equation is:

$$\ln[1-(1-\alpha)^{1-n}]/T^2\times(1-n)=\ln[ArR/\beta E)(1-2RT)]-E/(RT) \qquad (8)$$

The plot of $\log[-\log(1-\alpha)/T^2]$ *vs.* $1/T$ is plotted. The activation energy (E) is obtained from the slope of the linear fit line which gives the $-E/2.303R$.

Ingraham–Marrier method [17]

Ingraham and Marrier developed a simplified method for the determination of a heterogeneous reaction exhibiting linear kinetics. The rate constant, k may be expressed as $\mathrm{d}w/\mathrm{d}t$, where $\mathrm{d}w$ represents the loss in mass from unit area in the period of time $\mathrm{d}t$.

$$\log(\mathrm{d}w/\mathrm{d}T)=-\log T-\log\beta+\log Ar-E/2.303RT \qquad (9)$$

The plot of $\log(\mathrm{d}w/\mathrm{d}T)+\log T+\log\beta$ *vs.* $1/T$ is plotted. The activation energy (E) is obtained from the slope of the linear fit line which gives the $-E/2.303R$.

Arrhenius method [15]

This model assumes that the oxidation rate of the total sample is dependent only on the rate constant, the mass of sample remaining (w) and the temperature. The final form of the equation is as follows:

$$\log(\mathrm{d}W/\mathrm{d}t/w)=\log Ar-(E/2.303RT) \qquad (10)$$

The plot of $\log[\mathrm{d}W/\mathrm{d}t/w]$ *vs.* $1/T$ is plotted. The activation energy (E) is obtained from the slope of the linear fit line which gives the $-E/2.303R$.

Results and discussion

In the first part of this research, three reaction regions are identified in Karakus crude oil (Fig. 1). A reaction up to 400°C is actually the first region of the crude oil and called as low-temperature oxidation (LTO). In general this oxidation reaction produces small quantities of carbon-dioxide and presumably acids, aldehydes, ketones and peroxides which are primary products of lower temperature oxidation. A second reaction region takes place between 400 and 650°C where major production of carbon-dioxide starts in this interval and called as fuel deposition (FD). The final reaction of the crude oil inferred from the curves takes place between 650 and 880°C known as high temperature oxidation (HTO). This reaction contributes most of the exothermic heat of reaction when the crude oil is heated in an oxidizing environment. On the other hand, a burn-out temperature that represents the temperature where sample oxidation is complete was also identified for Karakus crude oil. Reaction intervals and the burn-out temperature are given in Table 1.

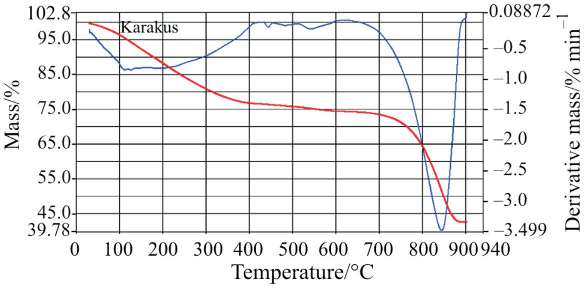

Fig. 1 Mass and derivative mass of Karakus crude oil

In the second part of the research, the activation energy (E) of Karakus crude oil is determined for low temperature and high temperature oxidation reaction regions using Coats–Redfern, Ingraham–Marrier and Arrhenius methods (Figs 2–4) and the results are given in Table 2. On the other hand, the solution of

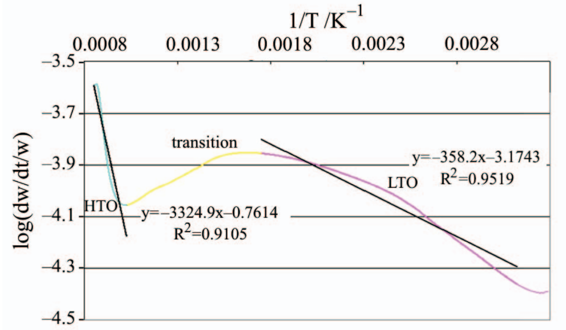

Fig. 2 Activation energy calculation by Arrhenius method

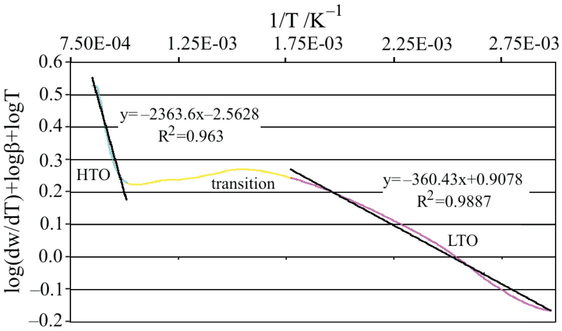

Fig. 3 Activation energy calculation by Ingraham–Marrier method

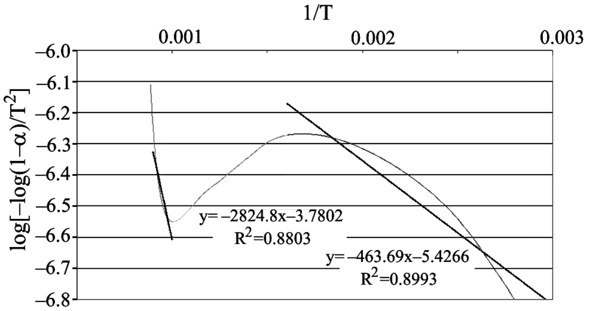

Fig. 4 Activation energy calculation by Coats–Redfern method

Table 2 Activation energy (E) values (kJ mol^{-1}) from different methods

Activation energy	Method type		
	Arrhenius	CR	IM
LTO	6.9	8.9	6.9
HTO	63.6	54.1	45.3

LTO – low temperature oxidation; HTO – high temperature oxidation; CR – Coats–Redfern method; IM – Ingraham–Marrier method

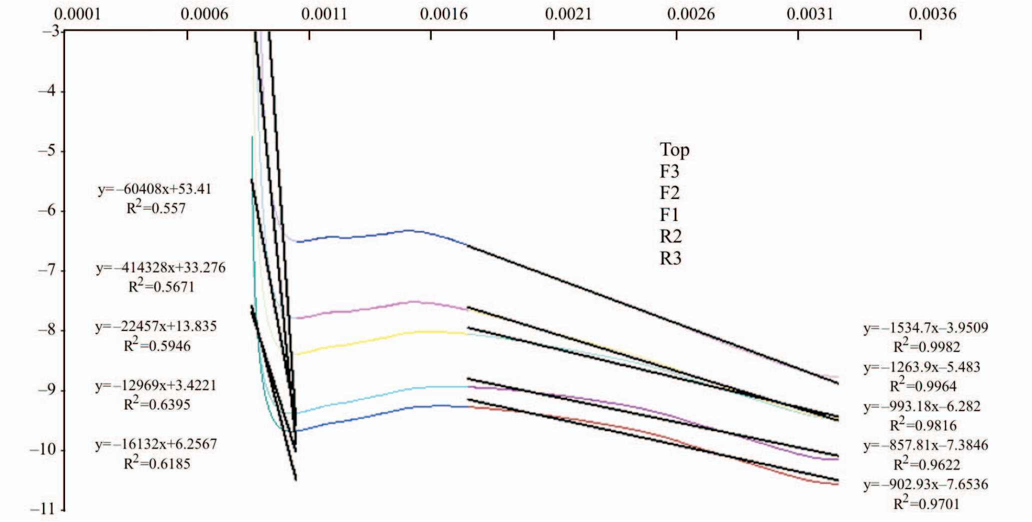

Fig. 5 Activation energy calculation by deceleratory mechanisms

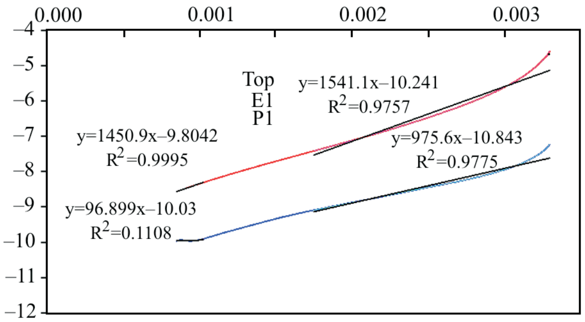

Fig. 6 Activation energy calculation by acceleratory mechanisms

Table 3 Slopes and activation energies after data reduction

	Slope of trend line		Activation energy/kJ mol^{-1}	
	HTO	LTO	HTO	LTO
R2	–6586.8	–827.81	54.7	6.9
R3	–7841.3	–902.93	65.2	7.5
F1	–10350	–993.18	86.1	8.3
F2	–17877	–1263.9	148.6	10.5
F3	–25405	–1534.7	211.9	12.8

the differential and integral method requires trial and error procedure as there exists several equations of $f(\alpha)$ and $G(\alpha)$. As it is mentioned in the theory part, α is calculated by the corresponding formula and then by using the experimental data from a single heating rate curve, a plot of $\ln[(d\alpha/dt)/f(\alpha)]$ *vs.* $1/T$ be obtained by testing all the functions. The activation energy E is obtained from the slope of the linear fit line which gives the $-E/R$ or α *vs.* t graph is plotted ac-

Table 4 Activation energies (kJ mol^{-1}) for all approaches

Activation energy	α approaches (differential method)			Arrhenius	Coats–Redfern	Ingraham–Marrier
	R2	R3	F1			
LTO	6.9	7.5	8.3	6.9	8.9	6.91
HTO	54.8	65.2	86.1	63.6	54.1	45.2

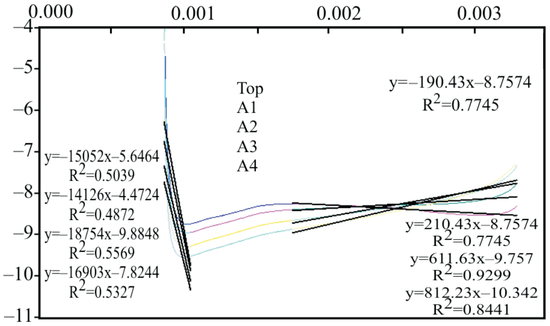

Fig. 7 Activation energy calculation by S-shaped (A1, A2, A3, A4) mechanisms

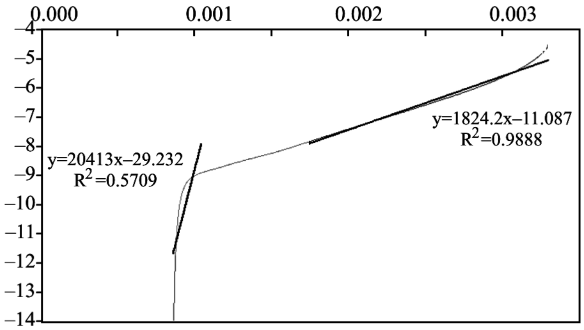

Fig. 8 Activation energy calculation by S-shaped (B1) mechanisms

cording to the shape of this graph $f(\alpha)$ chosen from Table 1. All the results are given in Table 3 and the corresponding Figs 5–8. Result of the decelerator type of equation gives very good results when compared with the above mentioned methods especially in LTO activation energy values (Table 4). It was observed that high temperature oxidation temperature (HTO) activation energy of Karakus crude oil is varied between 54.1 and 86.1 kJ mol^{-1}, while low temperature oxidation temperature (LTO) is varied between 6.9 and 8.9 kJ mol^{-1}.

Conclusions

In this research, thermal characterization and kinetics of Karakus crude oil in the presence of limestone matrix is investigated. In combustion with air, three distinct reaction regions were identified known as low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO). The activation energy of Karakus crude oil is determined by using four different approaches and the results are between 54.1 and 86.1 kJ mol^{-1} (LTO), and 6.9 and 8.9 kJ mol^{-1} (HTO). There exist some differences between these approaches. The differences between the activation energy values of the sample can be explained with the different equation parameters and assumptions that these four methods are based on.

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