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Characterization and Kinetics of Siberian and Tatarstan Regions Crude Oils Using Differential Scanning Calorimetry

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In this study, nonisothermal kinetics and thermal analysis of Siberian and Tatarstan regions crude oils is studied by differential scanning calorimetry (DSC) at different heating rates. DSC curves revealed two reaction regions in the temperature range of 20–600°C, known as low and high temperature oxidation, respectively. Three different kinetic methods (ASTM, Borchardt and Daniels, and Roger and Morris) were used to determine the kinetic parameters of the samples and it was observed that the activation energy values are varied.

Keywords: crude oil, thermal analysis, differential scanning calorimetry, kinetics, in-situ combustion

INTRODUCTION

Thermal analysis techniques constitute an important part in crude oil characterization. Numerous researchers used differential scanning calorimetry (DSC) and other thermal techniques to determine the composition and kinetics of crude oils. Crude oil is a complex mixture of different chemical species consisting mostly of hydrocarbons and combustion process involves variety of chemical reactions in the presence of air. One of the major difficulties in handling crude oils is processing since its thermal behavior is not well understood. Up to the present, there have been many studies dealing with the characterization of crude oils by various thermal analysis techniques. DSC is a precious technique commonly used on fossil fuels undergoing combustion or pyrolysis.

Kok (2006, 2009, 2011, 2012) and Kok and Gul (2013) characterized the pyrolysis and combustion properties of crude oils and their SARA (saturate, aromatic, resin, and asphaltene) fractions using thermogravimetry (TG-DTG) and DSC. On combustion in air, different reaction regions were identified for different origin crude oils and SARA fractions. DSC and TG-DTG curves have also been used to determine the heat flow rate, reaction regions, peak and burn-out temperatures and kinetic parameters of crude oils. Effect of clay content on the thermal behavior and kinetics of the crude oil were also studied. Mothé et al. (2013) applied TG/DTG and DSC to four Brazilian oils with different °API gravities (one medium, one heavy, and two extra heavy). Kinetic models showed that heavy oil had the greatest activation energy until 60% conversion. Besides, its thermal stability

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was a bit higher and also residue amount was lower than the others. Li et al. (2014) studied the effect of formation factors on the light crude oil during the high temperature air injection process. For this purpose, thermogravimetric and Fourier transform infrared spectroscopy (FTIR) techniques were combined to investigate the light crude oil and oil mixed with formation water and sand at different temperatures. The results showed that at different temperature ranges, the mass drop rate presented different trends and the formation water and sand increased the activation energy of the oxidation reaction. The formation sand exhibited the excellent catalytic effect at relative low temperature. Kok and Iscan (2011) applied DSC to the combustion of crude oils in the presence and absence of metal oxides. Three different reaction regions were observed, known as low temperature oxidation (LTO), fuel deposition (FD), and high temperature oxidation (HTO). The kinetic data indicated that the crude oils with catalyst had lower activation energy. This is attributed to the fact that catalysts lowered the energy need for commencing the reactions and provided additional pathways for the reactions. Jia et al. (2014) studied the oxidation behavior of four Chinese crude oils in the presence and absence of rock cuttings by TG/DTG techniques and oxidation tube experiments. Results show that crude oils undergo an endothermic oxidation behavior during low-temperature oxidation stage, suggesting the decomposition of hydrocarbon components. Clay can play a catalytic effect on low-temperature oil oxidation. The results of DTG-DTA tests can also better reflect oil oxidation mechanism under real condition. Mahinpey et al. (2010) studied pyrolysis and combustion characteristics of two different crude oil samples obtained from Fosterton (medium oil) and Neilburg (heavy oil) fields in Saskatchewan and compared using the results of TG/DTG analyses. The reaction region, peak, and burnout temperatures of the samples are determined. Activation energy, pre-exponential factor, and order of the reaction of the crude oils are also determined. The kinetic analysis showed similar activation energy for the combustion of coke produced from Neilburg and Fosterton oils.

The aim of this research was to determine the thermal behavior and kinetics of Siberian and Tatarstan regions crude oils under nonisothermal conditions using differential scanning calorimeter. ASTM, Borchardt and Daniels, and Roger and Morris kinetic methods are used in order to calculate the activation energy of the crude oil samples. The information obtained will be used in initial stage of the in situ combustion process.

EXPERIMENTAL

The experiments were performed by using DSC Q-200 model of TA Instruments Company. DSC monitors the differential heat flow of samples as a function of temperature/time in a controlled atmosphere and records the temperature and heat flow associated with material transitions, giving quantitative and qualitative data on heating processes.

The experiments were conducted from ambient to 600°C, at linear heating rates of 5, 10, and 15°C/min, under air atmosphere. A sample size of ~10 mg was used for each run. Experiments were performed twice to test the repeatability. Good consistency with standard error of $\pm 1^\circ\text{C}$ belonging to the same conversion degree was observed in duplicate experiments. DSC instrument was calibrated for the cell sensor resistance and temperature readings with reference materials of sapphire and indium, respectively.

Samples of crude oils studied in this work were provided by JSC "Ritek" (sample 1) from Sredne-Nazymkoe field of Bazhenov shale (West Siberian basin) and JSC "Tatneft" (sample 2) from the Ashal'cha field (Volga-Ural basin, Republic of Tatarstan). Sample of heavy oil from Ashal'cha field was recovered using SAGD (steam-assisted gravity drainage) technology. The physical properties of crude oils studied are given in Table 1. The measurements were carried out on Stabinger viscometer SVM-3000. Densities were measured in accordance with ASTM D7042 and viscosity in accordance with ASTM D445.

TABLE 1
Physical Properties of Crude Oils

Crude Oil	$^{\circ}\text{API Gravity } 288.15 \text{ K}$	Viscosity, cP		
		293.15 K	313.15 K	333.15 K
Bazhenov shale (sample 1)	34.0	7.1	4.1	2.6
Ashal'cha field (sample 2)	15.2	2249.5	423.4	119.7

RESULTS AND DISCUSSION

The combustion of crude oil is a very complex process because crude oil is a mixture of many hydrocarbons and its composition changes constantly as combustion progresses. Despite the complexity of crude oil mixtures involving numerous compounds with varying physical properties, they experience similar reactions when heated.

DSC curves of two crude oils performed at different heating rates are given in Figures 1 and 2. Under air atmosphere, after a wide distillation period with a slight endothermic peak under the base line, two main oxidation regions were clearly seen on DSC diagrams. During combustion, with the exception of endothermic distillation process, the other two main reactions showed exothermic behavior.

On DSC curves, after a large distillation period, low temperature oxidation (LTO), the first exothermic region, started nearly at 100°C and continued up to 450°C depending on the heating rate and crude oil characteristics. The second transition zone, which is known as high temperature oxidation (HTO), took place approximately between 420 and 585°C depending on the crude oil type. In the HTO region, two successive exothermic peaks were recognized on DSC curves. These reaction regions involved different chemical reactions and occurred across overlapping temperature ranges. The exothermic HTO reactions are heterogeneous and produce carbon oxides and water.

It is observed that the LTO reaction intervals of crude oils were found to be close to each other. The peak temperature of crude oil 1 in LTO and HTO reaction regions was higher probably due to

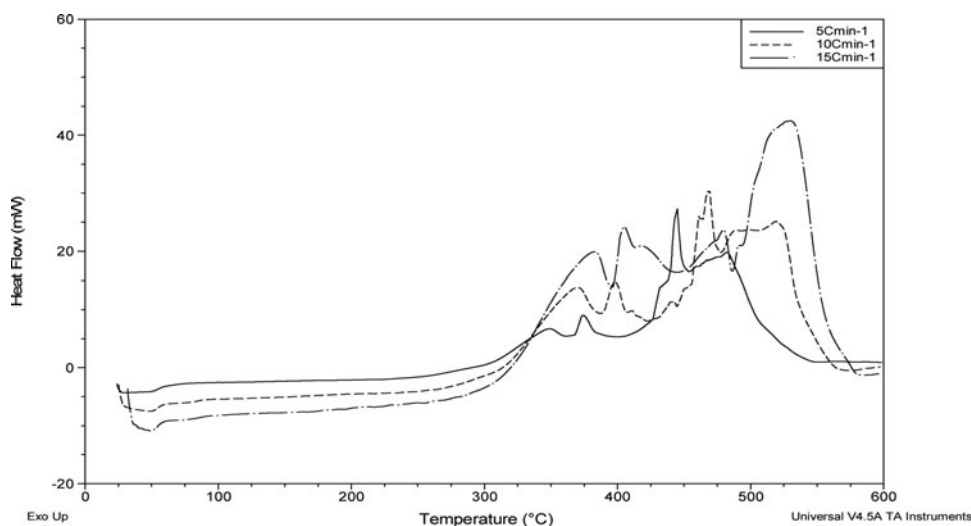


FIGURE 1 DSC Figures of crude oil 1 at three different heating rates.

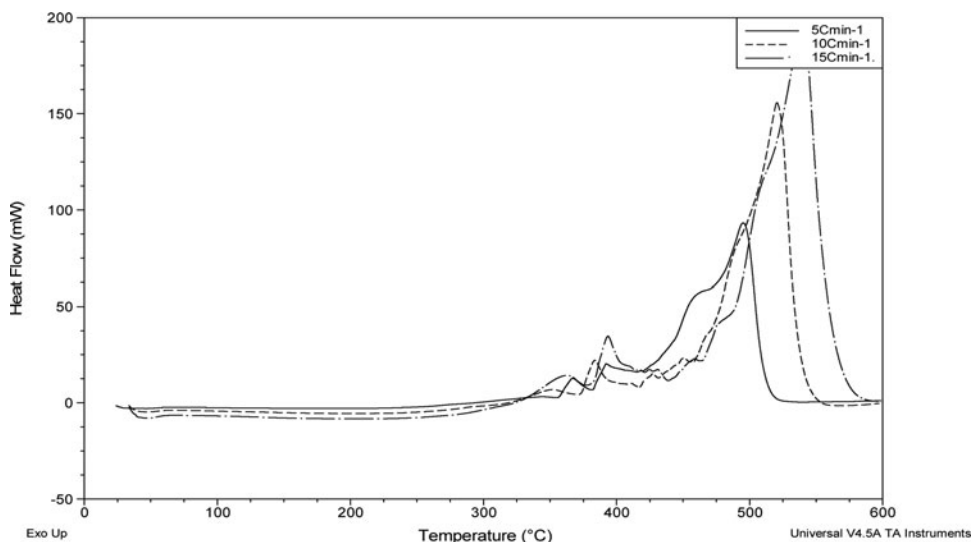


FIGURE 2 DSC figures of crude oil 2 at three different heating rates.

their higher °API gravity. It is observed that the heavier oil covered broader temperature region and completed their HTO reactions at lower temperatures. From DSC analysis, it was detected that the heavier oil released more heat during HTO reaction. For heavier crude oil, the average total heat flow rate in LTO and HTO reaction regions is 4244 J/g, whereas this value is 2443 J/g for light crude oil.

DSC experiments performed at three heating rates revealed that higher heating rates are resulted in higher peak temperatures. On the other hand, heat flow rate of crude oils are decreased gradually as the heating rate increased. This can be explained with the increment of heating rate, heat emission decreases.

The oxidation extent of crude oils strongly depends on the nature of hydrocarbons. It is known that in crude oil combustion, heat release in HTO is mostly due to the asphaltene fraction of oils. In HTO, asphaltene manage the process in terms of heat flow and sustain the continuity of combustion. As °API gravity and viscosity of crude oils are related with asphaltene amount, the oxidation behavior of low °API oil is more relevant with the oxidation behavior of its asphaltene fraction. DSC reaction intervals of regions, peak temperatures and reaction heat flow rates in HTO region are given in Table 2.

TABLE 2
Reaction Intervals, Peak Temperatures, and Heat Flow Rates of Crude Oils

Sample	Reaction Region -LTO-Peak Temp., °C	Reaction Region -HTO-Peak Temp., °C	Heat of Reaction LTO + HTO, J/g
Sample 1, 5°C/min	100–420/385	420–560/445	2681
Sample 1, 10°C/min	100–440/395	440–575/465	2320
Sample 1, 15°C/min	100–450/400	450–585/530	2328
Sample 2, 5°C/min	100–420/380	420–520/497	4671
Sample 2, 10°C/min	100–425/390	425–545/523	4169
Sample 2, 15°C/min	100–440/400	440–570/541	3892

TABLE 3
Kinetic Parameters of Crude Oils in HTO Region (ASTM I and II)

<i>Kinetic Data</i>	<i>Sample 1</i>	<i>Sample 2</i>
Activation energy, kJ/mol LTO region, ASTM I	45	63
Arrhenius constant, 1/min LTO region, ASTM I	0.00009984	0.0001986
Activation energy, kJ/mol HTO region, ASTM I	118	181
Arrhenius constant, 1/min HTO region, ASTM I	0.0003352	0.002275
Activation energy, kJ/mol LTO region, ASTM II	43	60
Arrhenius constant, 1/min LTO region, ASTM II	0.00009163	0.0001284
Activation energy, kJ/mol HTO region, ASTM-II	116	177
Arrhenius constant, 1/min HTO region, ASTM II	0.0003124	0.001986

Kinetic Analysis

The nonisothermal kinetic study during a combustion process is extremely complex, because of the presence of numerous components and their parallel and consecutive reactions.

A general approach for DSC kinetics is the ASTM E 698 method (ASTM, 1979). A means of determining activation energies using DSC data by ASTM methods (ASTM I and II) requires very precise measurement of reaction peak temperatures as a function of linear programmed heating rates. In this study, the sample temperature is increased at linear heating rates and any exothermic peaks are recorded. In ASTM method, a trial and error procedure is used and the activation energy is calculated in two different approaches.

In the first method (ASTM 1), the activation energy and the Arrhenius constant are calculated approximately from the following equations, respectively:

$$E = ((-2.303 R/D) \times (d \log \beta / d(1/T))) \quad (1)$$

$$A = \beta E e^{E/RT} / RT^2 \quad (2)$$

In the second method (ASTM-2), the activation energy is calculated approximately from the following equation.

$$E = (R \times d - \ln(\beta/T^2)/d(1/T)) \quad (3)$$

where β is heating rate, E is activation energy, R is gas constant, A is Arrhenius constant, T is peak temperature, and D is the dimensionless constant.

Two different kinetic approaches are utilized in ASTM kinetics and it was determined that the average activation energy values for sample 1 were between 43 and 45 kJ/mol for LTO and 117 and 118 kJ/mol for high temperature oxidation region. On the other hand, the average activation energy values for sample 2 were between 45 and 46 kJ/mol for reaction region 1 and 177 and 181 kJ/mol for reaction region 2, respectively (Table 3). On the other hand, the correlation coefficient values obtained from the calculation of activation energy were in the range of 0.96–0.99.

The second approach in DSC kinetics is the Borchardt and Daniels method (1957) and it is based on a single heating rate approach. In this method the DSC exotherm is divided into segments over the region from 10% peak height to 50% peak area. The kinetic parameters such as reaction order (n), activation energy (E) and Arrhenius constant (A) is obtained by multiple regression analysis of the following equation:

$$\ln(dy/dt) = \ln A - E/RT + n \ln(1 - \gamma) \quad (4)$$

TABLE 4
Kinetic Parameters of Crude Oils in HTO Region (Borchardt and Daniels Method)

<i>Kinetic Data</i>	<i>Sample 1</i>	<i>Sample 2</i>
5°C/min Heating Rate		
Activation energy, kJ/mol	98	177.4
Arrhenius constant, 1/min	6.84	11.15
Reaction order	0.54	0.50
Standard error, 1/sec	0.1348	0.0757
10°C/min Heating Rate		
Activation energy, kJ/mol	102	184.5
Arrhenius constant, 1/min	6.91	11.69
Reaction order	0.55	0.61
Standard error, 1/sec	0.1457	0.2116
15°C/min Heating Rate		
Activation energy, kJ/mol	114	195.8
Arrhenius constant, 1/min	7.13	12.34
Reaction order	0.63	0.68
Standard error, 1/sec	0.1847	0.0922

where $d\gamma/dt$ is reaction rate, γ is fractional conversion, n is reaction order, E is activation energy, A is Arrhenius constant, and T is temperature of the partial area section.

The DSC exotherm measures two basic parameters $d\gamma/dt$ and γ for each of the partial area sections. The software uses this information and a multiple linear regression routine to solve for kinetic analysis (activation energy, Arrhenius constant, and reaction order). The average activation energy value at three different heating rates for reaction region 2 (high temperature oxidation) for the crude oil samples are varied between 106 and 114 kJ/mol for sample 1 and 178 and 196 for sample 2, respectively (Table 4).

The third approach in DSC kinetics is the Rogers and Morris method (1966), which offers a graphical approach in order to determine kinetic parameters. In this model, the distance between DSC curve and its baseline with respect to the corresponding temperature is measured for each peak below the decomposition temperatures and this distance is proportional to the rate constant. Then, activation energy is calculated from the following equation:

$$-E = R(\ln D_1 - \ln D_2)/(1/T_1 - 1/T_2) \quad (5)$$

where D_1 and D_2 are distances from baseline at associated temperatures T_1 and T_2 .

Activation energies obtained by Roger and Morris method for combustion data obtained at different heating rates for sample 2 are varied between 135 and 164 kJ/mol in the HTO region.

In general, the activation energy values were close to each other in three different kinetic models studied by differential scanning calorimeter. Differences between the values can be explained with the different equation parameters and assumptions that those models are based on.

On the other hand, the results obtained in this study are in good order with the similar research studies in the literature. Goncalves et al. (2008) studied the petroleum fractions of crude oils by TG/DTG. The data were treated by a multiple heating rate methodology. The apparent activation energies for the light and middle fractions were within the range of 62–74 kJ/mol and for heavy distillation residues were within the range of 80–100 kJ/mol. Trejo et al. (2010) calculated the reaction kinetic parameters from TG analysis during asphaltene cracking and a set of activation energies ranged from 122 to 219 kcal/mol. Mahinpey et al. (2010) studied comparative kinetics and thermal behavior of Fosterton and Neilburg field's crude oils of different °API gravity. The kinetic analysis showed similar activation energy for Neilburg and Fosterton oils is 129.5 and 127 kJ/mol,

respectively. Finally, Mehta et al. (2009) studied the oxidation behavior of different crude oils. It is observed that oxidation behaviors for light and medium oils are substantially different.

CONCLUSIONS

In this research combustion characteristics and kinetics of Siberian and Tatarstan regions crude oils were investigated by DSC at different heating rates. In DSC analysis, two different reaction regions were observed, known as low and high temperature oxidation, respectively. Reaction intervals and peak temperatures are increased as the heating rate is increased. It was also observed that heating rates affected the heat of reactions of the crude oil samples studied. Different activation energy values are observed in the kinetic methods studied. The heavier oil studied has a higher activation energy and higher peak temperature.

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