

Contribution of thermal analysis and kinetics of Siberian and Tatarstan regions crude oils for in situ combustion process

Mikhail A. Varfolomeev¹ · Ruslan N. Nagrimanov¹ · Andrey V. Galukhin^{1,2} · Alexey V. Vakhin² · Boris N. Solomonov¹ · Danis K. Nurgaliev² · Mustafa V. Kok³

Received: 28 January 2015 / Accepted: 21 June 2015 / Published online: 8 July 2015
© Akadémiai Kiadó, Budapest, Hungary 2015

Abstract This research focused on the characterization and kinetics of Siberian and Tatarstan crude oils by gas chromatography, combustion calorimetry, and thermogravimetry (TG–DTG) techniques. Calorimetric experiments show that crude oil with higher saturate content and low resin fraction has higher heating value. TG–DTG curves indicates that the crude oils undergoes two major transitions when subjected to an oxidizing and constant rate environment known as low- and high-temperature oxidations at each heating rate studied. Kinetic analysis in the low- and high-temperature oxidation regions was performed using *model-free methods known as* Ozawa–Flynn–Wall and Kissinger–Akahira–Sunose. Throughout the study, it was observed that the activation energy values of the crude oil samples are varied between 41–72 and 145–198 kJ mol⁻¹ in low- and high-temperature oxidation regions, respectively.

Keywords Crude oil · Thermal analysis · TG · Calorimetry · Kinetics · In situ combustion

Introduction

Thermal analysis characterizes the physical and chemical properties of substances, depending on the temperature at a defined heating rate or on the time at a constant temperature. Thermal analysis techniques used in crude oil characterization was directed toward correlation between thermal behavior of the samples and kinetic studies.

Kok [1–4] studied combustion properties of crude oils using thermogravimetry (TG–DTG) and differential scanning calorimeter (DSC). On combustion in air, different reaction regions were identified, for different origin crude oils. Thermal analysis curves have also been used to determine the heat flow rate, reaction regions, peak and burnout temperatures and kinetic parameters of crude oils. It was observed that activation energy values of crude oils are increased as the °API gravity decreased. Effect of clay content and metallic additives on the thermal behavior and kinetics of the crude oil were also studied. Sonibare et al. [5] studied the thermal behavior of the Nigerian oil sand bitumen in an oxidizing environment using non-isothermal thermogravimetric analysis (TG) and DTA. It was observed that, increasing the heating rate caused a shift in the reaction regions and peak temperatures to higher temperatures. Castro and Vazquez [6] analyzed the four different Mexican crude oils and their SARA fractions with different densities ranging from 9 to 39 °API using TG–DTG and DSC techniques. TG–DTG technique was used to characterize the volatilization and decomposition temperature of crude oils and observed that the decomposition temperature was increased with the increasing average molecular mass of crude oil. 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

✉ Mustafa V. Kok
kok@metu.edu.tr

¹ Department of Physical Chemistry, Kazan Federal University, Kremlevskaya str. 18, 420008 Kazan, Russia
² Institute of Geology and Petroleum Technologies, Kazan Federal University, Kremlevskaya str. 18, 420008 Kazan, Russia
³ Department of Petroleum and Natural Gas Engineering, Middle East Technical University, 06800 Ankara, Turkey

under controlled conditions by thermogravimetry, 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. Ni et al. [8] studied the oxidation behavior of crude oils in the presence and absence of rock cuttings by thermogravimetry (TG–DTG) techniques. Three obvious reaction regions were observed from the TG–DTG curves which are recognized as low-temperature oxidation (LTO), fuel deposition (FD), and high-temperature oxidation. Results show that high content of C_{7-15} hydrocarbons can provide negative effect on the LTO behavior of crude oil. On the contrary, the high content of unsaturated heavy hydrocarbons including asphaltene, paraffin, and resin are benefit for the oxidation performance. Pereira and Trevisan [9] studied the fingerprinting the oxidation behavior of a Brazilian crude oil through classical thermal analysis techniques such as thermogravimetry (TG–DTG) and differential scanning calorimetry (DSC). The reaction data are treated following distinct conventional and iso-conversional non-isothermal models, using integral and differential approaches based on Arrhenius model. It was observed that by all kinetic models, HTO values are higher than those for LTO, and observation is also valid for the results of oil sand samples. Li et al. [10] studied the effect of different metallic additive on the combustion and kinetic behavior of Dagang crude oil. For this purpose, the thermal behavior of the oil-only and oil–metallic salts mixtures was studied by the thermogravimetry (TG–DTG) and differential scanning calorimetry (DSC). The result shows that Dagang crude oil exhibited apparent low-temperature oxidation (LTO), fuel deposition (FD), and high-temperature oxidation (HTO) processes. Based on the Arrhenius model, metallic additives were proven to have obvious influence on the combustion activation energy.

The present study was carried out to investigate the non-isothermal thermal behavior of high-molecular hydrocarbons in the absence of rock matrix by thermogravimetry (TG–DTG). A detailed kinetic study was conducted to understand the mechanism of crude oils and determine the main reaction parameters by different mathematical approaches. This research also intended to reveal the heating

rate effect on combustion properties and kinetics of crude oils for a possible in situ combustion process.

Experimental

Materials

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. Organic solvents, such as toluene, hexane, methanol, and dichloromethane, were purchased from Sigma-Aldrich (mass fraction was no less than 0.99). They were used in this work without additional purification.

Density and viscosity measurements

Density and viscosity of studied oils at different temperatures were measured using Stabinger SVM-3000 viscometer (Anton Paar). The apparatus was calibrated before the experiments following the instructions and requirements of the manufacturer. Measurements were carried out in accordance with ASTM D7042 for density and in accordance with ASTM D445 for viscosity. The temperature was controlled by built-in Peltier thermostat to within ± 0.02 K. Reproducibility for viscosity data is ± 0.35 % and for density data is ± 0.0005 g cm⁻³. Obtained values of physical properties of studied crude oils are given in Table 1.

SARA analysis

SARA analysis was carried out in full accordance with ASTM-recommended procedure [11]. The oil samples were initially topped to constant mass by heating. Amount of volatile organic compounds (VOC) for Samples 1 and 2 were 32.8 and 5.4 %, respectively. Compositional analyses of petroleum samples were conducted according to the common technique [12], which included asphaltene precipitation from hexane and further chromatographic separation of the non-asphaltic oil components through column filled with alumina. Hexane, toluene and a mixture of

Table 1 Physical properties of crude oils

Crude oil	°API gravity/288.45 K	Viscosity		
		cP/293.15 K	cP/313.15 K	cP/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

Table 2 Fractions of crude oils determined by SARA analysis

Crude oil	Saturate/%	Aromatics/%	Resins/%	Asphaltenes/%
Bazhenov shale (Sample 1)	64.1	28.2	7.7	0.0
Ashal'cha field (Sample 2)	24.2	43.0	28.8	4.0

methanol and dichloromethane (1:1) were used for the chromatographic elution of saturates, aromatics, and resins. Each oil sample was analyzed three times, and the repeatability of the analysis for saturate, aromatic, resin and asphaltene fractions was ± 2.1 , ± 3.1 , ± 2.5 and ± 0.5 mass%, respectively (Table 2).

Elemental analysis

CHNS elemental analysis of crude oils was carried out on PerkinElmer 2400 Series II elemental analyzer based on dynamic flash combustion of the sample. Studied objects were weighed in a tin capsule and introduced into the combustion reactor via the autosampler together with a proper amount of oxygen. After combustion, the resultant gases were transferred by a helium flow to a layer filled with copper, then swept through a GC column, and finally was detected by a thermal conductivity detector (TCD). Total run time of analysis was 10 min. The dedicated software automatically calculates the minimum formula. Before the measurements are taken, instrument calibration was performed with BBOT standard (6.51 % N, 72.53 % C, 6.09 % H, 7.44 % S) using linear regression as calibration method (Table 3).

Gas chromatography

Analysis of saturate fraction of crude oils was carried out using gas chromatography method. Preliminarily, fraction of saturated aliphatic hydrocarbons was separated from the crude oil with *n*-heptane on the chromatographic column packed with aluminum oxide. Gas chromatograph "Krytall 2000 M" with flame ionization detector was used for measurements. Temperature of column varied in each experiment from 100 to 300 °C followed by a heating rate of 10 °C min⁻¹ from 100 to 150 °C and 3 °C min⁻¹ from 150 to 300 °C, respectively. Hydrogen was used as a carrier gas. Temperatures of injector and detector were 310 and 250 °C, respectively.

Table 3 Elemental analysis of crude oils

Crude oil	C/%	H/%	N/%	S/%
Bazhenov shale (Sample 1)	78.6	13.0	0.4	3.0
Ashal'cha field (Sample 2)	81.3	12.3	0.5	3.0

Combustion calorimetry

Higher heating value of crude oils was determined on the IKA 6000 global standards combustion calorimeter in isoperibol mode at temperature 298.15 K. Before the measurements of studied objects energy equivalent of calorimetric bomb, $\varepsilon_{\text{calor}}$ was obtained from the combustion experiments of standard benzoic acid (C723 IKA) with heat of combustion $\Delta_c U = 26,460 \pm 8 \text{ J g}^{-1}$. This procedure was carried out in accordance with DIN 51900. Mass of benzoic acid in each experiment was about 1 g. Samples were burned in oxygen at a pressure of 3.04 MPa with 1.00 g of water added to the bomb. Filling the bomb with oxygen was carried out automatically. The bomb was placed in a calorimeter with a constant amount of water. Ignition was produced by the discharge of the capacitor on the steel wire connected to the sample of benzoic acid by a cotton thread with certain energy of combustion $\Delta_c U = 16,670 \pm 4.2 \text{ J g}^{-1}$. Temperature rise during the experiment was measured by platinum resistance thermometer with a resolution of 0.0001 K. The combustion products were examined for carbon monoxide and unburned carbon, but practically none was detected. Correction for nitric acid formation was based on the titration with 0.1 mol dm⁻³ NaOH (aq). Based on twenty-two experiments, $\varepsilon_{\text{calor}}$ was determined to be $8007.26 \pm 0.78 \text{ J K}^{-1}$. After the calibration of calorimeter, studied objects were measured. Samples of crude oils were encapsulated in the polyethylene containers with energy of combustion $\Delta_c U = 46,357.3 \pm 7.2 \text{ J g}^{-1}$. Combustion experiments of studied systems were carried out at the same conditions as for benzoic acid. Every sample was burned at least five times. Masses of crude oil, cotton thread, and polyethylene container used in each experiment are presented in Table 4 for crude oil from Bazhenov shale and in Table 5 for crude from Ashal'cha field.

TG-DTG analysis

The experiments were performed by using TG Q-500 models of TA Instruments system. As stated previously, TG-DTG measures the mass change of samples as a function of temperature/time in a controlled atmosphere. In TG-DTG system, mass and temperature calibrations were performed periodically using standard masses and nickel, respectively.

Table 4 Results for combustion experiments of crude oil 1 from Bazhenov shale ($T = 298.15$ K, $p^\circ = 0.1$ MPa)

Parameters ^a	Experiments number				
	1	2	3	4	5
m (crude oil)/g	0.36501	0.33231	0.38876	0.27745	0.28741
m' (cotton thread)/g	0.00284	0.00307	0.00273	0.00266	0.00271
m'' (polyethylene)/g	0.29514	0.30174	0.28997	0.28146	0.30180
ΔT_c /K	3.78930	3.6415	3.8942	3.2124	3.3834
$(\varepsilon_{\text{calor}}) \cdot (-\Delta T_c)$ /J	-30,323.9	-29,141.1	-31,163.3	-25,707.2	-27,075.7
$(\varepsilon_{\text{cont}}) \cdot (-\Delta T_c)$ /J	-64.62	-61.59	-67.18	-52.04	-55.82
$\Delta U_{\text{decomp}} \text{HNO}_3$ /J	32.85	35.84	33.45	33.45	34.04
ΔU_{corr} /J	8.68	8.28	8.95	7.13	7.62
$-m' \cdot \Delta_c u'/J$	47.34	51.18	45.51	44.34	45.18
$-m'' \cdot \Delta_c u''/J$	13,681.89	13,987.85	13,442.23	13,047.73	13,990.63
$\Delta_c u^\circ$ (cr)/J g ⁻¹	-45,526.8	-45,498.3	-45,530.4	-45,509.6	-45,419.4
$-\Delta_c u^\circ$ (cr)/J g ⁻¹	$-45,496.2 \pm 55.6^b$				

^a m —mass of crude oil sample; m' —mass of cotton thread; m'' —mass of polyethylene container; ΔT_c —corrected temperature increase adjusted for heat transfer; $(\varepsilon_{\text{calor}}) \cdot (-\Delta T_c)$ —energy used for heating the calorimetric vessel and bomb; $(\varepsilon_{\text{cont}}) \cdot (-\Delta T_c)$ —energy used for heating the contents of the calorimeter bomb in experiment; $\Delta U_{\text{decomp}} \text{HNO}_3$ —the energy released due to formation of nitric acid; $-m' \cdot \Delta_c u'$ —combustion energy of cotton thread; $-m'' \cdot \Delta_c u''$ —combustion energy of polyethylene container; ΔU_{corr} —sum of corrections for adjustment of combustion energy to the standard state; $\Delta_c u^\circ$ —combustion energy of crude oil

^b Uncertainties in this table correspond to expanded uncertainties of the mean (0.95 level of confidence)

Table 5 Results for combustion experiments of crude oil 2 from Ashal'cha field ($T = 298.15$ K, $p^\circ = 0.1$ MPa)

Parameters ^a	Experiments number				
	1	2	3	4	5
m (crude oil)/g	0.42019	0.56115	0.32006	0.24082	0.33445
m' (cotton thread)/g	0.00272	0.00266	0.00319	0.00271	0.00278
m'' (polyethylene)/g	0.28271	0.29487	0.30030	0.30028	0.30304
ΔT_c /K	3.9020	4.7321	3.4688	3.0427	3.5583
$(\varepsilon_{\text{calor}}) \cdot (-\Delta T_c)$ /J	-31,225.8	-37,868.6	-27,759.1	-24,349.2	-28,475.3
$(\varepsilon_{\text{cont}}) \cdot (-\Delta T_c)$ /J	-66.49	-85.22	-57.92	-49.67	-60.03
$\Delta U_{\text{decomp}} \text{HNO}_3$ /J	32.85	32.85	32.85	32.85	32.85
ΔU_{corr} /J	9.42	8.28	8.16	6.97	8.43
$-m' \cdot \Delta_c u'/J$	45.34	44.34	53.18	45.18	46.34
$-m'' \cdot \Delta_c u''/J$	13,105.67	13,669.38	13,921.1	13,920.2	14,048.12
$\Delta_c u^\circ$ (cr)/J g ⁻¹	-43,073.3	-43,117.2	-43,122.3	-43,159.7	-43,054.5
$-\Delta_c u^\circ$ (cr)/J g ⁻¹	$-43,089.7 \pm 51.9^b$				

^a m —mass of crude oil sample; m' —mass of cotton thread; m'' —mass of polyethylene container; ΔT_c —corrected temperature increase adjusted for heat transfer; $(\varepsilon_{\text{calor}}) \cdot (-\Delta T_c)$ —energy used for heating the calorimetric vessel and bomb; $(\varepsilon_{\text{cont}}) \cdot (-\Delta T_c)$ —energy used for heating the contents of the calorimeter bomb in experiment; $\Delta U_{\text{decomp}} \text{HNO}_3$ —the energy released due to formation of nitric acid; $-m' \cdot \Delta_c u'$ —combustion energy of cotton thread; $-m'' \cdot \Delta_c u''$ —combustion energy of polyethylene container; ΔU_{corr} —sum of corrections for adjustment of combustion energy to the standard state; $\Delta_c u^\circ$ —combustion energy of crude oil

^b Uncertainties in this table correspond to expanded uncertainties of the mean (0.95 level of confidence)

The experiments were conducted at linear heating rates of 10, 20, and 30 °C min⁻¹ under atmospheric air. The samples were heated from ambient to 900 °C for TG–DTG experiments. A sample size of ~10 mg was used for each

run. Some of the experiments were performed twice to test the repeatability, and experiments showed good consistency with standard errors of ±1 °C belonging to the same conversion degree.

Results and discussion

Almost all hydrocarbon compounds of oil undergo a permanent change when exposed to heat. In combustion experiments, theoretically fuel can be initiated whenever oxygen comes in contact with fuel. The extent of this change depends on the complexity of molecular structure and the reaction environment. Although crude oils are complex mixtures involving numerous compounds with varying physical properties, they experience similar reactions when heated. In this work, we have studied two crude oils which have different physical properties and composition (Tables 1, 2, 3). These samples have practically the same content of nitrogen and sulfur based on the results of elemental analysis (Table 3). Therefore, the C/H atoms ratio is different, in case of crude oil 1 it is about 2.0, for crude oil 2 this value is 1.8. Difference in C/H ratio is due to higher mass fraction of saturates and lower content of resins in Sample 1 than in Sample 2. Also Sample 1 has higher °API gravity and lower viscosity than Sample 2. These differences should affect the in situ combustion parameters of crude oils.

Combustion calorimetry results

From the combustion calorimetry measurements, we have determined higher heating value (HHV) of studied samples. Despite complex nature of crude oil, results from several experiments are in good agreement between each other (Tables 4, 5). Higher heating value is equal to the standard thermodynamic heat of combustion. This value indicates the maximum amount of energy that can be obtained by burning the sample at the reference temperature 298.15 K in excess of oxygen. Higher heating value

includes not only energy release due to combustion process, but also contribution from the condensation of all products to the initial temperature 298.15 K. It is usually used as a relative measure of overall energy efficiency of fuels and crude oils. It was observed that Sample 1 (Bazhenov shale) has larger HHV than Sample 2 (Ashal'cha field). This difference is caused by the higher content of paraffin's and lower content of resins in Sample 1 in comparison with Sample 2. Consequently, application of in situ combustion for recovery of crude oil 1 should be more effective thermodynamically.

Gas chromatography results

Gas chromatographic analysis helps to analyze the content of saturates fractions of studied crude oils. Obtained chromatograms of two samples from Bazhenov shale and Ashal'cha field are presented on Figs. 1 and 2. Peaks in the chromatogram were assigned to certain paraffins based on the retention time's data. Sample 1 contains a large number of different structure paraffins. The highest peaks on the Fig. 1 correspond to the linear alkanes *n*-pentadecane and *n*-hexadecane. Further, alkane content decreases monotonically with increasing alkyl group length. The most high-molecular components of saturates fraction of Sample 1 are alkanes with an alkyl group length *n*-C₃₆ and *n*-C₃₇, but their chromatographic intensity is very low. Both crude oils contain appreciable amounts of the two terpenoid-type alkanes pristane (Pr) and phytane (Ph). In case of Sample 2 (Fig. 2), they are essential components of saturates fraction. The high content of pristane and phytane and low total content of *n*-alkanes with a minor manifestation of bimodal distribution are typical for heavy oils.

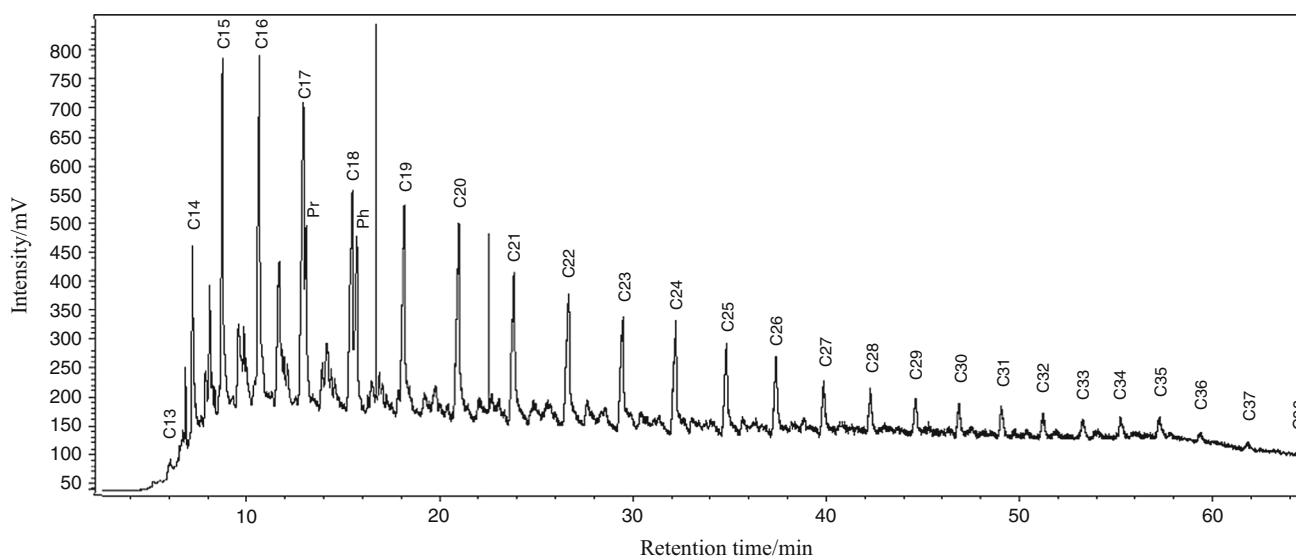


Fig. 1 GC analysis of saturate part of Sample 1 (Bazhenov field oil)

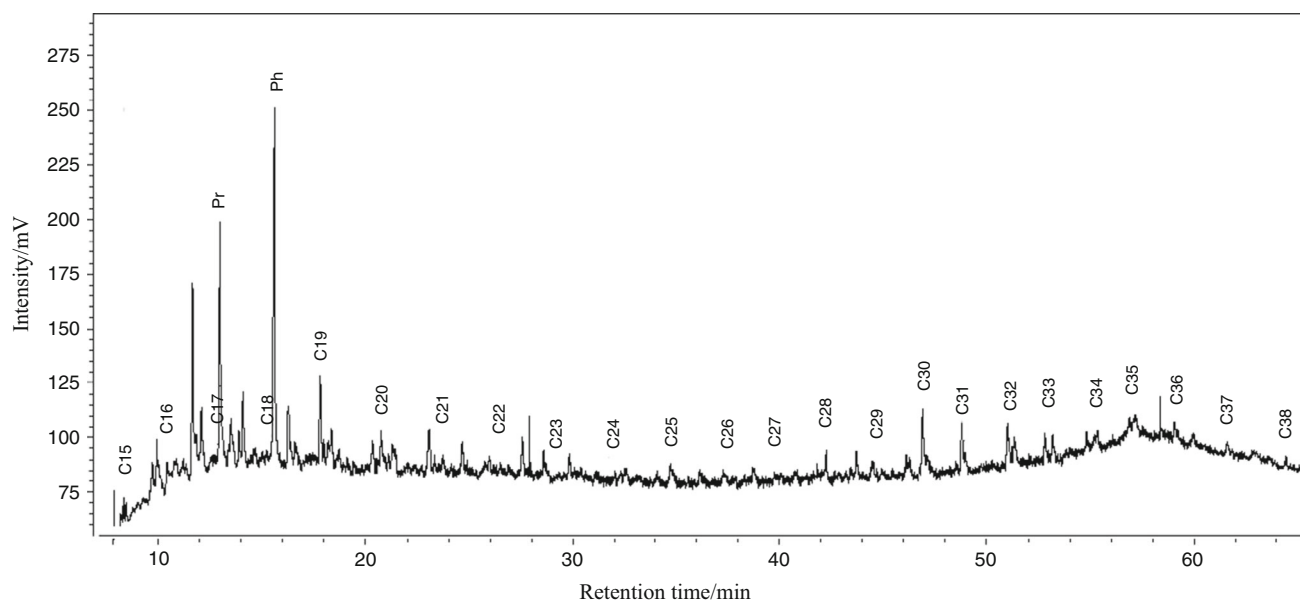


Fig. 2 GC analysis of saturate part of Sample 2 (Ashal'cha field oil)

Thermogravimetry (TG–DTG) results

In thermogravimetry (TG–DTG) experiments, crude oil samples were heated in the absence of sand grains, and two distinct regions of oxidative degradation were identified on the resulting curves (Figs. 3, 4). In the first region, after a wide distillation period, LTO reactions took place and then combustion process completed with HTO (fuel combustion) reactions in the second region. From the resulting TG–DTG curves, it was observed that both crude oils experienced the

same reactions (distillation, LTO and HTO) with different extents. Both crude oils showed huge mass loss (78–86 % for Sample 1 and 56–60 % for Sample 2) until the end of LTO region, whereas they had a lower mass loss in HTO region (14–22 % for Sample 1 and 40–46 % for Sample 2) with narrower temperature ranges (Figs. 1, 2). DTG curves indicated the effect of both distillation and LTO on reactions between oxygen and hydrocarbons in the temperature range from ambient to nearly 340–400 °C for crude oil samples studied. This region showed itself with a hump trace on DTG

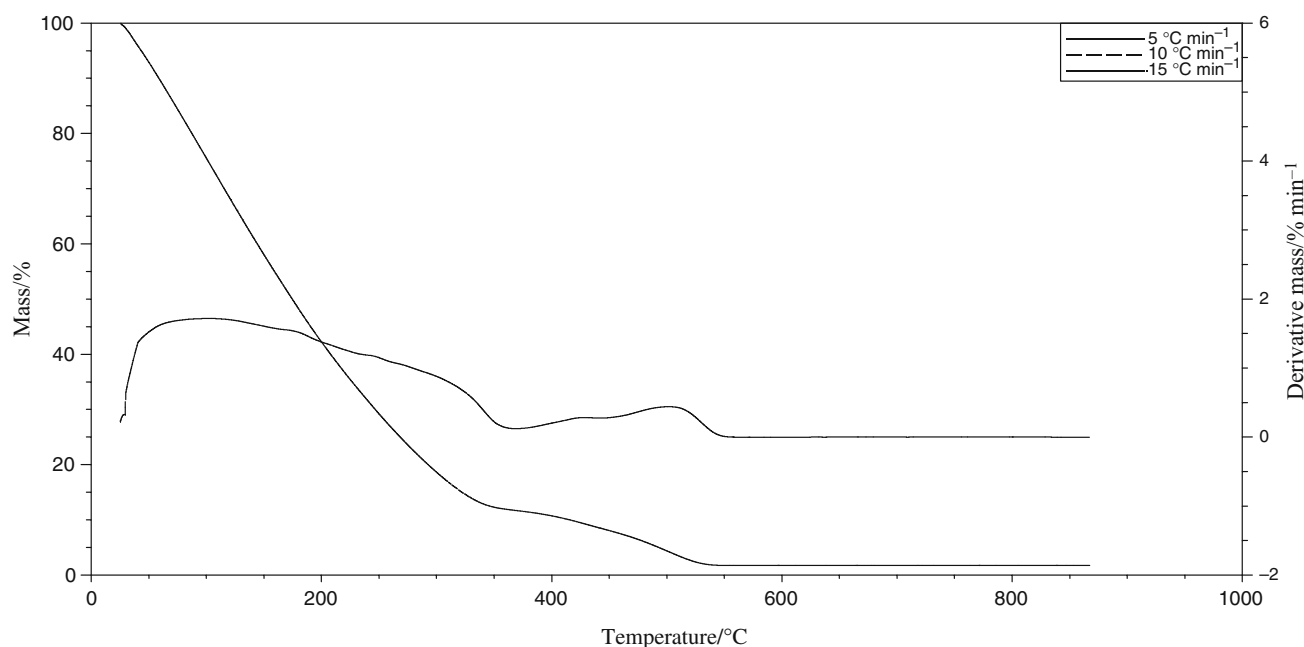


Fig. 3 TG–DTG figures of Sample 1 (Bazhenov field oil) at three different heating rates

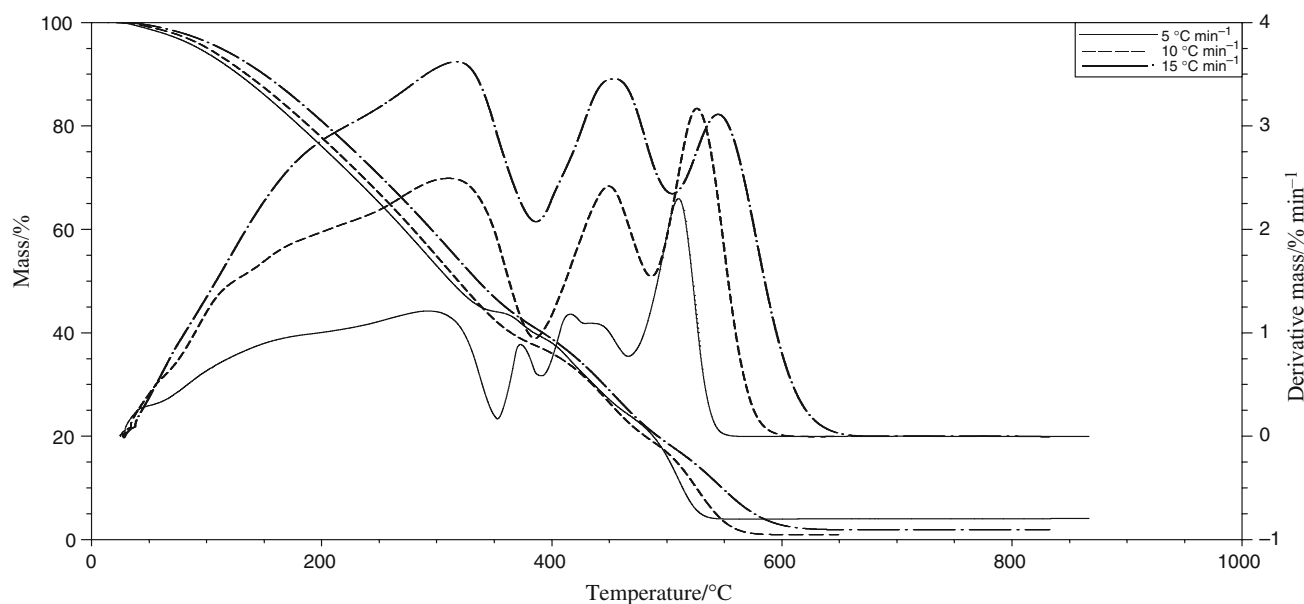


Fig. 4 TG–DTG figures of Sample 2 (Ashal'cha field oil) at three different heating rates

and a rapid mass loss on TG curves. On DTG curves, a slope difference is detected after the first region peak. Soon after this point, reactions become severe and LTO reactions begin after distillation.

Reaction intervals and peak temperatures where the maximum rate of decomposition occurs were established from DTG curves and are tabulated in Table 6. The table shows that low °API gravity oil (Sample 2) exhibited noticeably higher thermal stability. Its LTO and HTO reactions started earlier at each heating rate and took longer time to be completed. Accordingly, their burnout temperatures, the point where oxidation is completed, were lower than the other, too.

In distillation and LTO regions, mass loss is resulted from free moisture and volatile hydrocarbons. Under the same conditions, high °API gravity crude oil is more susceptible to LTO due to their relatively rich hydrogen

content. Significant amount of oxygen is consumed in LTO region. Mainly small and weak chains of hydrocarbons are broken and oxidized to give partially oxygenated hydrocarbons. The oxygenated compounds are usually more viscous, less volatile, and denser than the original oils from which they are formed. LTO reactions are characterized by low peak temperatures and carbon dioxide levels in the effluent gas stream during combustion process. LTO has a complex set of reactions. Due to complexity of the multi-component feature of crude oil mixtures, the chemistry of these reactions has not been analyzed comprehensively. The main compositional change in LTO is the increase in asphaltene content while decreasing resin content. LTO reactions considerably increase the asphaltene content of the oil leading to higher viscosity of oxygenated products. It is known that among SARA fractions, asphaltene is the most resistant one. Asphaltene molecules are so heavy and

Table 6 Reaction intervals, peak temperatures and mass loss of crude oils (TG–DTG)

Crude oil, heating rate/ °C min ⁻¹	Reac. reg.-1 Peak temp./°C	Mass loss Reac. reg.-1/%	Reac. reg.-2 Peak temp./°C	Mass loss Reac. reg.-2/%	Burnout temp./°C
<i>Sample 1^a</i>					
5	100–360/110	78	360–545/505	22	560
10	100–380/130	80	380–580/530	20	590
15	100–400/150	86	400–600/545	14	600
<i>Sample 2^b</i>					
5	100–340/290	56	340–550/520	44	540
10	100–360/310	60	360–580/540	40	560
15	100–380/320	60	380–600/560	40	590

^a Bazhenov shale, ^b Ashal'cha field

resistant that oxygen does not affect this fraction until very high temperatures. Saturates are distilled at high amounts until LTO region. In LTO, aromatics and resins contribute at the highest amounts. In distillation and LTO regions, asphaltenes react negligibly and expose to very low mass loss. They lost almost the rest of their mass in HTO region.

The heating rate is another factor affecting the TG–DTG curves of crude oils. The reaction intervals, the corresponding peak, and burnout temperatures were shifted to higher degrees with heating rate, whereas mass loss percentages remained nearly the same (Table 6).

Kinetic analysis

Non-isothermal kinetics of crude oil combustion is a complex phenomenon since numerous reactions proceed simultaneously. A variety of mathematical techniques have been developed for the evaluation of kinetic parameters such as activation energy (E), Arrhenius constant (A), and reaction order (n). The calculated kinetic parameters are accepted as apparent values representing complex and consecutive reactions.

In general, the rate of reaction is assumed to be dependent on temperature and conversion degree, α which is the rate of sample undergoing the reaction up to that temperature [13]. The rate constant, $k(T)$, is assumed to obey the Arrhenius law. Combining all these relations, equation is obtained as follows

$$\beta(d\alpha/dT) = A \exp(-E/RT)f(\alpha) \quad (1)$$

where $d\alpha/dT$ is the conversion rate of reaction, A the Arrhenius constant (min^{-1}), E the activation energy (J mol^{-1}), R the gas constant ($8.314 \text{ J mol K}^{-1}$), $f(\alpha)$ the reaction model, and β the linear heating rate ($^{\circ}\text{C min}^{-1}$).

By different arrangements of Eq. (1), many differential-based computations of kinetic parameters can be obtained. As a second option, integral of both sides is taken and the methods derived after integration is called integral methods. After the rearrangement of the terms in Eq. (1), integrals of both sides are taken, ' E/RT ' term is replaced by ' x ,' and the integration limits are transformed, and then it turns into

$$g(\alpha) = (AE/\beta R)p(x) \quad (2)$$

where $g(\alpha)$ is the integral form of reaction model and $p(x)$ is the temperature integral,

$$p(x) = \int_x^{\infty} \frac{\exp(-x)}{x^2} dx \quad (3)$$

The integral of exponential term, $p(x)$, in Arrhenius equation has no analytical solution, but has many linear approximations. There are two ways to calculate the kinetic

parameters from TG–DTG data which are model-free and model-fitting methods.

Model-free (iso-conversional) methods (TG–DTG)

Multiheating rate model-free methods allow the calculation of kinetic parameters at progressive degrees without any reaction model estimation [14]. In this study, Ozawa–Flynn–Wall (OFW) and Kissinger–Akahira–Sunose (KAS) methods were applied to TG–DTG data. OFW used Doyle's linear integral approximation for $x > 20$ [15–18]. Since Doyle's approximation is not exact for $x < 20$, a new $p(x)$ approximation is introduced by Flynn combining many previously suggested linear approaches. In KAS method [19, 20], $(1 - 2/x)(1 - m/x^2)$ term of this approximation is neglected.

Before the application of model-free methods, the corresponding temperature values of fixed conversion degrees, α , were determined for each heating rate by curve-fitting method. In this study, both reaction regions were subjected to kinetic analysis. The resulting curves were shifted to higher temperatures with the increment of heating rate, i.e., a higher heating rate gave a lower conversion degree for the same temperature.

After assigning temperature values for constant conversion degrees, OFW and KAS curves were plotted providing a series of straight lines whose slopes gave apparent activation energies. A significant variation in E with α was noted for all samples which is an indication of complex reaction mechanism of oil combustion.

There are some reasons of possible errors resulted from model-free methods. As mentioned previously, the model-free methods are derived with the assumption of reaction rate dependency on temperature and conversion degree only, without any reaction model estimation. In OFW and KAS methods, E is accepted as constant all over the reaction, but in our case this suggestion is not far to be true. In between, KAS method is more accurate due to its better approximation of temperature integral. The differences in calculated E values are due to the error of improper integration in OFW and KAS equations.

For Ozawa–Flynn–Wall method, several TG–DTG curves are used simultaneously to determine the activation energy values of crude oil samples. The TG–DTG curves move to higher temperatures with increasing heating rates. At the same conversion levels, the following relationship is used where activation energy is obtained from the slope of the plot $\log(\beta)$ versus $1/T$ at given conversion levels.

$$[d(\log \beta)/d(1/T)] = 0.4565 (E/R) \quad (4)$$

where T is the peak temperature (K), R is the gas constant ($8.314 \text{ J mol K}^{-1}$), E is the activation energy (J mol^{-1}), and β is the linear heating rate ($^{\circ}\text{C min}^{-1}$).

Table 7 Activation energy values of crude oils, OFW method ($\alpha = 0.1-0.9$)

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	09
<i>Sample 1^a</i>									
I. Region									
<i>E/kJ mol⁻¹</i>	28	31	35	39	44	49	55	63	73
<i>R²</i>	0.7229	0.8024	0.8339	0.8558	0.8733	0.8863	0.8961	0.9004	0.9166
II. Region									
<i>E/kJ mol⁻¹</i>	138	234	217	213	159	108	98	94	88
<i>R²</i>	0.7252	0.9990	0.8281	0.6633	0.4899	0.4155	0.4561	0.4878	0.4769
<i>Sample 2^b</i>									
I. Region									
<i>E/kJ mol⁻¹</i>	58	59	63	58	73	78	83	87	88
<i>R²</i>	0.9769	0.9606	0.9797	0.9905	0.9565	0.9983	0.9991	0.9993	0.9988
II. Region									
<i>E/kJ mol⁻¹</i>	144	201	203	231	290	273	186	143	113
<i>R²</i>	0.9895	0.9954	0.9866	0.9968	0.9989	0.9929	0.9958	0.9824	0.9740

^a Bazhenov shale, ^b Ashal'cha field

Table 8 Activation energy values of crude oils, KAS method ($\alpha = 0.1-0.9$)

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	09
<i>Sample 1^a</i>									
I. Region									
<i>E/kJ mol⁻¹</i>	24	26	30	34	39	44	50	57	67
<i>R²</i>	0.6299	0.7271	0.7717	0.8042	0.8302	0.8488	0.8636	0.8713	0.8939
II. Region									
<i>E/kJ mol⁻¹</i>	134	236	217	212	155	100	90	85	79
<i>R²</i>	0.6916	0.9989	0.8123	0.6378	0.4511	0.3583	0.3894	0.4156	0.3984
<i>Sample 2^b</i>									
I. Region									
<i>E/kJ mol⁻¹</i>	55	55	59	63	68	74	79	82	83
<i>R²</i>	0.9711	0.9501	0.9740	0.9878	0.9843	0.9978	0.9988	0.9992	0.9985
II. Region									
<i>E/kJ mol⁻¹</i>	140	200	202	231	293	274	183	137	105
<i>R²</i>	0.9877	0.9949	0.9850	0.9965	0.9989	0.9923	0.9951	0.9988	0.9666

^a Bazhenov shale, ^b Ashal'cha field

Table 9 Mean activation energy values of crude oils (kJ mol⁻¹)

Crude oil	I. Region (OFW)	II. Region (OFW)	I. Region (KAS)	II. Region (KAS)
Sample 1 ^a	46	150	41	145
Sample 2 ^b	72	198	68	196

^a Bazhenov shale, ^b Ashal'cha field

Kissinger–Akahira–Sunose (KAS) method is iso-conversional method to analyze the TG–DTG data of oil shale samples. Iso-conversional methods use the certain degree of conversion and a narrow temperature range related to this conversion degree. The final form of the equation is:

$$\ln(\beta/T^2) = \ln(AR/Eg(\alpha)) - E/RT \tag{5}$$

where α is the amount of sample undergoing the reaction, T is the peak temperature (K), A is the Arrhenius constant (min⁻¹), E the activation energy (J mol⁻¹), R the gas

constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and β the linear heating rate ($^{\circ}\text{C min}^{-1}$).

Before the application of model-free methods, the corresponding temperature values of fixed conversion degrees, α , were determined for each heating rate by curve-fitting method. After assigning temperature values for constant conversion degrees, Ozawa–Flynn–Wall (OFW) and Kissinger–Akahira–Sunose (KAS) curves were plotted providing a series of straight lines whose slopes gave apparent activation energies (Tables 7, 8). On the other hand, mean activation energy values of the samples are given in Table 9. It was observed that the activation values of crude oils were in the range of $41\text{--}72 \text{ kJ mol}^{-1}$ in LTO and $145\text{--}198 \text{ kJ mol}^{-1}$ in HTO region, respectively. A significant variation in E with α was noted for all samples which is an indication of complex reaction mechanism of oil combustion.

As mentioned previously, the model-free methods are derived with the assumption of reaction rate dependency on temperature and conversion degree only, without any reaction model estimation. In between, KAS method is more accurate due to its better approximation of temperature integral. The differences in calculated E values can also be caused due to the error of improper integration in OFW and KAS equations.

Conclusions

This study is performed for better understanding of the combustion behavior of Siberian and Tatarstan regions crude oils and their respective kinetic analyses. The most remarkable points of the research are summarized in the following.

- Calorimetric experiments show that in situ combustion process is more effective thermodynamically for Sample 1 with higher fraction of paraffin's and lowers content of resins due to larger HHV than Sample 2 (heavier oil).
- It was observed that Sample 1 was more susceptible to LTO reactions. Due to its higher asphaltene content, Sample 2 (heavier oil) completed its oxidation reactions at higher temperatures at each different heating rate.
- According to the kinetic results, apparent activation energies in HTO region were considerably higher than those in LTO. Heavier oil with higher asphaltene amount had higher activation energy values in HTO region.

Acknowledgements The work has been performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

References

1. Kok MV. Characterization of medium and heavy crude oils using thermal analysis techniques. *Fuel Process Technol.* 2011;92:1026–2031.
2. Kok MV. Effect of pressure and particle size on the thermal cracking of light crude oils in sandstone matrix. *J Therm Anal Calorim.* 2009;97–2:403–7.
3. Kok MV. Effect of clay on crude oil combustion by thermal analysis techniques. *J Therm Anal Calorim.* 2006;96:123–7.
4. Kok MV, Iscan AG. Catalytic affects of metallic additives on the combustion properties of crude oils by thermal analysis techniques. *J Therm Anal Calorim.* 2011;64:1311–8.
5. Sonibare OO, Egashira R, Adedosu TA. Thermo-oxidative reactions of Nigerian bitumen. *Thermochim Acta.* 2003;405–2:195–205.
6. Castro LV, Vazquez F. Fraction and characterization of Mexican crude oils. *Energy Fuel.* 2009;23:1603–9.
7. Goncalves MLA, Teixeira MAG, Pereira RCL, Mercury RLP, Matos JR. Contribution of thermal analysis for characterization of asphaltenes from Brazilian crude oil. *J Therm Anal Calorim.* 2001;64–2:697–706.
8. Ni JH, Jia H, Pu WF, Jiang H, Jang JJ, Ren Q. Thermal kinetics study of light oil oxidation using TG/DTG techniques. *J Therm Anal Calorim.* 2014;17–3:1349–55.
9. Pereira AN, Trevisan OV. Thermoanalysis and reaction kinetics of heavy oil combustion. *J Braz Soc Mech Eng.* 2014;36–2:393–401.
10. Li YB, Zhao JZ, Pu WF, Jia H, Peng H, Zhong D, Wang SK. Catalytic effect analysis of metallic additives on light crude oil by TG and DSC tests. *J Therm Anal Calorim.* 2013;113–2:579–87.
11. ASTM D-2007, Standard test method for characteristic groups in rubber extender and processing oils and other petroleum-derived oils by the clay-gel absorption chromatographic method. Annual Book of ASTM Standards. 2002.
12. Kharrat A, Zacharia J, Cherian V, Anyatonwu A. *Energy Fuels.* 2007;2:3618–21.
13. Vyazovkin S. Model-free kinetics. *J Therm Anal Calorim.* 2006;83:45–51.
14. Vyazovkin S, Wight CA. Model-free and model-fitting approaches to kinetic analysis of isothermal and non-isothermal data. *Thermochim Acta.* 1999;53:340–1.
15. Ozawa T. A new method of analyzing thermogravimetric data. *Bull Chem Soc Jpn.* 1965;38:1881–6.
16. Flynn JH, Wall LA. General treatment of the thermogravimetry of polymers. *J Res Natl Bur Stan.* 1966;70A:487–523.
17. Flynn JH. The iso-conversional method for determination of energy of activation at constant heating rates: corrections for the Doyle approx. *J Therm Anal Calorim.* 1983;27:95–102.
18. Doyle CD. Estimating isothermal life from thermogravimetric data. *J Appl Polym Sci.* 1962;6:639–42.
19. Akahira T, Sunose T. Joint convention of four electrical institutes. *Res Sci Technol.* 1971;16:22–31.
20. Friedman HL. Kinetics of thermal degradation of char forming plastics from thermogravimetry. *J Polym Sci.* 1964;6:183–95.