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Thermal decomposition of *Tatarstan Ashal'cha* heavy crude oil and its SARA fractions

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HIGHLIGHTS

- One main region in heavy crude oil and its fractions.
- Higher heat of reaction in asphaltenes and resins fractions.
- Lowest mass loss in asphaltene fraction.
- Highest activation energies in asphaltene fraction.

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ABSTRACT

In this research, heavy crude oil from Ashal'cha field, Republic of Tatarstan, and its SARA (saturate, aromatic, resin and asphaltene) fractions were analyzed by differential scanning calorimetry (DSC) and thermogravimetry (TGA) methods. The experiments were performed at three different heating rates (10, 20, 30 °C/min) for DSC and at single heating rate for TGA analysis, all under the air atmosphere. In DSC experiments, two main reaction regions were detected at each heating rate known as low and high temperature oxidation reactions. On the other hand, in TGA experiments, one main region was observed. For all the SARA fractions studied, highest heat of reaction was observed in lowest heating rate. The kinetic analysis of the crude oils and their fractions was also performed using ASTM E-698 and Arrhenius methods, respectively. Activation energy values of the crude oil sample and the fractions varied between 69.2 and 201.8 kJ/mol in LTO region and 82.9–182.1 kJ/mol in HTO regions, respectively. In Arrhenius method, the activation energy values were in the range of 33.1–108.9 kJ/mol.

1. Introduction

Crude oil is mainly composed by hydrocarbons and derived organic sulfur, nitrogen, oxygen and metal-containing compounds. Generally, hydrocarbons and its derivatives in oil sample can be classified into four fractions, known as *S*aturated (alkanes and cyclo-paraffins), *A*romatics (hydrocarbons, mono, di and poly-aromatic), *R*esins (polar molecules with heteroatoms N, O and S) and *A*sphaltenes (higher molecular weight and polyaromatic core), shortly *SARA* fractions. The distinction between the asphaltenes and resins is that asphaltenes are insoluble in an excess of heptane or pentane, whereas resins are miscible with heptane or pentane [1].

Thermal analysis techniques such as thermogravimetry (TGA), and differential scanning calorimetry (DSC) became highly important research tools and constitute an important part from the point view of correlation between thermal behavior and kinetic studies of crude oils and their fractions.

Different °API gravity crude oils and their SARA fractions were studied by DSC to characterize the volatilization and decomposition temperature of crude oils. It was observed that the decomposition temperature was increased with the increasing average molecular mass of crude oil [2–4]. In DSC analysis of different origin crude oils and their SARA fractions, reaction intervals and corresponding peak temperatures, burn-out temperatures, heat flow rates and kinetics were also studied. The kinetic analysis showed similar activation energy for the combustion of coke produced [5–7]. Effect of catalyst and metal oxides on the thermal behavior and kinetics of crude oils was also studied [8]. The kinetic analysis using different methods showed similar activation energy values

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for different origin of crude oils based on their °API gravities [9,10]. On the other hand, TGA was used to determine the thermo-oxidative behavior of the crude oils those correlated with the viscosity and density [11]. TGA technique was also 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. Heat of combustion of different origin crude oils and their respective SARA fraction was also studied by DS and it was observed that heating values of saturates and aromatics were higher than the heating values of the resins and asphaltenes [12].

In this research, the aim was to determine the initial parameters for a typical in-situ combustion process. For this reason, thermal characteristics and kinetics of heavy crude oil from Ashal'cha field (Republic of Tatarstan) and its *SARA* fractions were studied using DSC and TGA techniques under non-isothermal heating conditions. ASTM kinetic methods (ASTM I and II) and different model free kinetics were applied in order to determine the activation energy and Arrhenius constant of the samples studied.

2. Experimental set-up and procedure

The heavy crude oil sample studied in this research was from Ashal'cha field (Volga-Ural basin, Republic of Tatarstan). In this research, experiments were performed under air atmosphere in the temperature range of 20–750 °C for DSC at three different heating rates (10, 20 and 30 K/min) and 20–950 °C for TGA at single heating rate (20 K/min), using ~10 mg of sample.

To separate the crude oil into its SARA fractions, ASTM procedure was used. The ASTM procedure was a chromatographic separation of the non-asphaltic oil components through two columns: an attapulgite clay-packed column adsorbs the resins and a second column packed with activated silica gel separates aromatics from the saturate fraction. A 50:50 mixture of toluene and acetone was used to recover the resin fraction from the clay packing. The aromatics can be recovered by Soxhlet extraction of the silica gel in hot toluene. Volatile components lost during the process are calculated by mass difference [13].

All the experiments were performed twice to test the repeatability. Good consistency with standard error of ±1 °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. On the other hand, prior to the experiments, it was essential to calibrate the thermo-balance (TG-DTG) for buoyancy effects in order to allow quantitative estimation of mass changes. SARA fractions, density, °API gravity and elemental analysis of the crude oil were given in Table 1.

3. Results and discussion

Although, several oxidation studies have been conducted on the thermal properties of crude oils and its fractions, kinetics and heat of combustion studies have not been well documented. Since the crude oil is a complex mixture of many hydrocarbons, combustion of crude is complex process and depending on the progress of combustion, the composition crude oil changes constantly. In the case of *SARA* (*saturate-aromatics-resin and asphaltene*) fractions, it is known that saturate fraction consist on *n*-paraffins, iso-paraffins, cyclo-paraffins, and other materials, aromatic fraction is a very complex mixture of hydrocarbon containing both paraffin and aromatic parts and resin structure consists of paraffinic chains and naphthenic rings.

3.1. DSC combustion results

DSC monitors heat effects associated to phase transitions and/or chemical reactions as a function of temperature. In DSC combustion curves, thermal effects for the heavy crude oil were observed in different temperature ranges. For the heavy crude oil studied, in the temperature range of 310–540 K, an endothermic effect was observed. Following this endothermic effect, two successive exothermic regions were observed, known as low temperature oxidation (LTO) and high temperature oxidation (HTO) in each heating rate, respectively (Figs. 1–5).

In the case of *SARA* fractions (*saturate-aromatics-resin and asphaltene*), DSC curves represented the same behavior. Initially, an endothermic effect was observed in the temperature range of

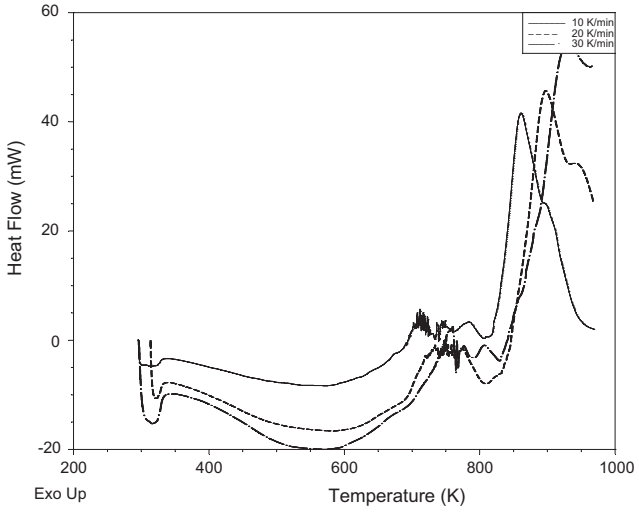

Fig. 1. DSC curves of crude oil at different heating rates.

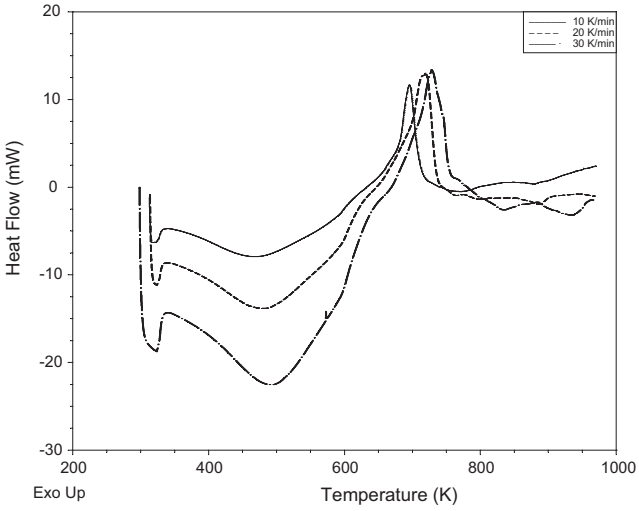

Fig. 2. DSC curves of saturate fraction at different heating rates.

Table 1
Properties of crude oils.

°API Grav. (°API)	Viscosity (mPa s)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Saturate (%)	Aromatic (%)	Resin (%)	Asphaltene (%)
13.9	1106.6	82.09	10.12	0.63	2.65	26.2	40.6	28.5	4.2