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Thermal characterization, combustion and kinetics of different origin crude oils

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HIGHLIGHTS

- Heavier oils with higher thermal stability.
- Increasing heating rate, higher reaction interval, peak temperature, same mass loss.
- With the increment of heating rate, decrease in heat emission of crude oils.
- Higher activation energy and Arrhenius constant of oils with greater asphaltene content.
- Not a remarkable change in activation energy with heating rate.

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ABSTRACT

In this research, the combustion behavior of six Turkish crude oils (light and medium type) was investigated by thermogravimetry/derivative thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) methods under atmospheric air in the absence of rock matrix. Two main reaction intervals were observed on all thermograms known as low temperature oxidation (LTO) and high temperature oxidation (HTO) regions. The resulting curves showed that the mass loss under combustion is accompanied by exothermic peaks due to the oxidative degradation of crude oil components. Heavier oils with greater asphaltene content were exposed to more heat release during oxidation reactions. By the increment of heating rate, not a remarkable variation was observed in apparent activation energies whereas the heat emission of crude oils decreased. Based on the model free and model fitting kinetic approaches, heavier oils had higher apparent activation energy and Arrhenius constant values for all oxidation regions.

1. Introduction

In the last few decades, all sectors of modern economies have been tightly bounded to energy and most of the energy has been supplied from fossil fuel products such as coal, oil, and natural gas. Hence, there is an urgent need to improve the knowledge of thermal analysis and kinetics for the full understanding of crude oil combustion.

TG/DTG and DSC are two popular techniques widely used in the evaluation of thermal characteristics of fossil fuels. TG measures the mass change in a specified temperature interval and DTG gives the rate of mass change as a function of time. DTG is beneficial for the resolution of individual stages of more complex TG curves in the overlapping processes [1]. DSC measures the difference in heat flow associated with material transitions between sample and reference while they are subjected to a pre-controlled temperature program and provides quantitative and qualitative information on thermal processes [2].

Application of thermal analysis techniques to crude oil combustion is not a recent approach. There have been many studies in literature focused mainly on different phases of oil combustion process. Tadema [3] was the first investigator who attempt to apply DTA (differential thermal analysis) for crude oil combustion and distinguished two exothermic reaction regions. Bae [4] used TG and DTA to examine the thermooxidative behavior and fuel forming properties of various crude oils. Vossoughi and El-Shoubary [5] investigated the effects of specific surface area, oxygen partial pressure, and oil content yet to be burned on the crude oil coke combustion. Kok [6,7] made major contributions on the characterization of combustion properties of fossil fuels using TG/DTG, DTA and DSC. During combustion, three reaction regions were observed, known as LTO, FD (fuel deposition) and HTO. Li et al. [8] used TG/DTG to investigate the oxidation behavior of crude oil fractions using thermal fingerprinting effects on pure paraffin samples and mixtures of pure components with crude oil. Ambalae et al. [9] investigated thermal behaviors of both crude oils and their asphaltene fractions, each mixed with reservoir sand. Of

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all the SARA (saturate, aromatic, resin and asphaltene) fractions, asphaltene contribute the most to the coke formation. Kuppe et al. [10] examined the heat of combustion (HOC) of crude oils and their SARA fractions. They observed that only asphaltene HOC of crude oils was dissimilar between all four fractions. Mahinpey et al. [11] conducted a comparative study on thermal characteristics of asphaltene and whole oil from Fosterton (medium) and Neilburg (heavy) fields. Asphaltene fraction of oils had a lower volatile and ash content as well as higher fixed carbon values than whole oil which made it more suitable as a fuel source. Jia et al. [12] studied the effect of different clay minerals on oxidation kinetics of Keke Ya oil. Based on Arrhenius method, a significant reduction in activation energy was observed due to catalytic and surface area effect of clays and reservoir cuttings. This brief review discloses the wide application area of thermal analysis methods in combustion characterization of crude oils.

The present study was carried out to investigate the non-isothermal thermal behavior of light and medium gravity crude oils in the absence of rock matrix by TG/DTG and DSC methods. A detailed kinetic study was conducted to understand the mechanism 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.

2. Experimental set-up and procedure

The experiments were performed by using TG Q500 and DSC Q200 models of TA Instruments system. As stated previously, TG/DTG measures the mass change while DSC monitors the differential heat flow 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 weights and nickel, respectively. DSC instrument was calibrated for the cell sensor resistance and temperature readings with reference materials of sapphire and indium, respectively.

The experiments were conducted at linear heating rates of 5, 10 and 15 °C/min under atmospheric air. The samples were heated from ambient to 600 °C (873 K) for DSC and to 900 °C (1173 K) for TG/DTG experiments. A sample size of ~2 mg was used for each run. 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.

The crude oils used in this research were taken from the southeastern region of Turkey namely from Beykan, Karaali, Kastel, Kurkan, Piyanko and Yalankoz fields. The physical properties and ultimate analysis of crude oils are given in Table 1. The analyses were performed by Turkish Petroleum Corporation (TPAO) Research Center.

3. Results and discussion

Despite the complexity of crude oil mixtures involving numerous compounds with varying physical properties, they experience similar reactions when heated [13].

3.1. TG/DTG combustion results

TG/DTG curves of six crude oils heated at 10 °C/min are given in Fig. 1. In earlier studies, crude oils mixed with reservoir sand were subjected to TG/DTG and the resulting curves revealed three major transitional stages known as LTO, FD and HTO regions [6,14]. Yet, in the case of present study, oil samples were heated in the absence of sand grains and two distinct regions of oxidative degradation were identified on the resulting curves. In the first region, after a wide distillation period continuing utmost ~550 K, LTO reactions took place and then combustion process completed with HTO (fuel combustion) reactions in the second region.

From the resulting TG/DTG curves, all crude oils experienced the same reactions (distillation, LTO and HTO) with different extents. As shown in Fig. 1, crude oils showed huge mass loss (70–85%) until the end of LTO region, whereas they had a weak HTO region (9–28%) with narrower temperature ranges. DTG curves indicated the effect of both distillation and LTO on reactions between oxygen and hydrocarbons in the temperature range from ambient to nearly 650 K for all samples. This region showed itself with a hump trace on DTG 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 [15].

Reaction intervals and peak temperatures where the maximum rate of decomposition occurs were established from DTG curves and tabulated in Table 2. The table shows that low gravity oils (Karaali and Yalankoz) exhibited noticeably higher thermal stability. Their LTO and HTO reactions started later and spent longer time to be completed. Accordingly, their burn-out temperatures, the point where oxidation is completed, were higher than the others, too.

The heating rate is another factor affecting the TG/DTG curves of crude oils. The reaction intervals, the corresponding peak and burn-out temperatures were shifted to higher degrees with heating rate whereas mass loss percentages remained nearly the same (Table 2).

As reported by other researchers [4,5,15–17], in distillation and LTO regions, mass loss is resulted from free moisture and volatile hydrocarbons. Under the same conditions, high °API gravity crudes are more susceptible to LTO due to their relatively rich hydrogen content [17]. 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 [18,19]. LTO reactions are characterized by low peak temperatures and carbon oxide levels in the effluent gas stream during combustion process [20].

LTO has a complex set of reactions. Due to complexity of the multicomponent feature of crude oil mixtures, the chemistry of these reactions has not been analyzed comprehensively [21]. 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

Table 1
Physical properties and ultimate analysis of crude oils.

Crude oil	°API	Viscosity	Asphaltene	Ultimate analysis (wt%)			
	(°/15 °C)	(cP/60 °C)	(wt%)	C	H	N	S
Beykan	32.8	4.65	1.96	87.21	12.05	2.03	0.69
Karaali	23.6	19.70	4.58	86.61	11.81	1.67	1.49
Kastel	34.8	3.82	2.27	86.28	11.96	3.18	1.22
Kurkan	31.5	5.45	2.24	83.48	11.63	3.63	0.87
Piyanko	34.1	3.90	1.58	87.48	12.34	3.84	1.27
Yalankoz	21.1	45.90	9.00	85.40	11.53	1.53	2.92