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Thermo-oxidative reactions of crude oils

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Abstract In this research, thermo-oxidative reactions of crude oils of different origin are determined in limestone matrix using simultaneous thermogravimetry and differential thermal analysis (TG–DTA) systems. Two different reaction regions were identified known as low temperature (LTO) and high temperature oxidation (HTO). Kinetic parameters of the samples were determined by four different methods and the results are discussed.

Keywords Crude oil · Limestone · Combustion · Thermogravimetry · Kinetics

Introduction

Thermal analysis techniques used in crude oil characterisation was directed towards correlation between thermal behaviour of the samples and kinetic studies. Bae [1] investigated the thermo-oxidative behaviour and fuel-forming properties of various crude oils using thermogravimetry. The results indicated that oils can be classified according to their oxidation characteristics. No complete correlation could be established between viscosity, composition or density of the crude with the thermo-oxidative characteristics of the oil. Ranjbar and Pusch [2] studied the effect of the oil composition, characterised on the basis of light hydrocarbon, resin and asphaltenes contents, on the pyrolysis kinetics of the oil and the combustion kinetics of the fuel by thermogravimetry and differential scanning calorimeter. The results showed that the colloidal composition of oil as well as the transfer-ability and heat transfer characteristics of the pyrolysis medium has a pronounced influence on fuel formation and composition. Ranjbar [3] investigated the influence of reservoir rock composition on the pyrolysis and combustion behaviour of crude oils in porous media. Pyrolysis and combustion tests were performed to examine how clays affect the amount of fuel and its reactivity. From the experimental results, he concluded that clay minerals present in the matrix enhance fuel deposition during the pyrolysis process and also catalyse the oxidation of fuel. Kok [4] characterised 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. Thermal analysis curves have also been used to determine the heat values and reaction parameters of crude oil. Higher activation energy values were found as the API gravity of the crude oil decreased. Kok et al. [5] used pressurized differential scanning calorimeter (PDSC) to obtain information on the combustion characteristics of crude oils and their mixtures in two chemically different matrix materials, sand and limestone. Crude oil and sand/limestone mixtures were prepared to give a composition of 10–wt% crude oil in matrix. The PDSC curve clearly demonstrates two distinct transitional stages, namely combustion of liquid hydrocarbons and combustion of coke. The kinetic part of this research is concerned with only one peak namely the coke combustion. Two different kinetic models analysed kinetic data and the results are discussed. Kok and Karacan [6] presented the results of an experimental study on the determination of pyrolysis behaviour and kinetics of six crude oils by differential scanning calorimeter and thermogravimetry. Crude oil pyrolysis indicated two main temperature ranges where loss of mass was observed. The

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first region between ambient and to 400 °C was distillation. The second region between 400 °C and 600 °C was visbreaking and thermal breaking. It was observed that as crude oil gets heavier cracking activation energy increases. Activation energy of cracking also shows a general trend with asphaltenes content. Goncalves et al. [7] investigated the thermal behaviour 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, characterisation 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. Kok 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 all crude oil samples studied, known as low temperature oxidation, fuel deposition and high temperature oxidation.

Experimental

In this research, thermo-oxidative properties of three crude oils of different origin in limestone matrix (92% calcite and 6.6% dolomite) were determined with simultaneous thermogravimetry and differential thermal analysis (TG–DTA) systems. The experiments were carried out with ~10 mg, crude oil-limestone sample (15 wt% crude oil in the mixture) at 10 °C/min heating rate. Air flow rate through the sample pan was kept constant at 50 mL min^{-1}, in the temperature range of 20–900 °C. Prior to the experiments TGA–DTA system was calibrated for temperature readings with calcium oxalate monohydrate. Duplicate experiments were performed to ensure reproducibility. Properties of crude oil samples are given in Table 1.

Table 1 Properties of crude oil sample

Property	Crude oil-1	Crude oil-2	Crude oil-3
°API gravity/°API	12.9	18.8	26.1
Viscosity/cP	51900	2260	37.5
$<C_{15+}$/%	16.9	n.a	21.8
Saturates/%	18	n.a	45
Aromatics/%	31	n.a	29
Resin/%	22	n.a	14
Asphaltene/%	29	n.a	12
Calorific value/cal g^{-1}	9670	11150	11300

n.a. Not available

Results and discussion

In thermo-oxidative reactions of crude oils in limestone matrix two distinct reaction regions were identified (Figs. 1, 2, 3). A reaction in the temperature range of 100–220 °C was actually the first reaction region and called as low temperature oxidation (LTO). A second reaction region is observed between 390 and 560 °C, which is called as high temperature oxidation (HTO) which contributes most of the exothermic heat of reaction. In all the crude oil samples studied, LTO is observed below 300 °C with the minimum mass loss because of the fact that asphaltenes molecules are so heavy and resistant that oxygen does not affect this fraction until very high temperatures are reached. Reaction intervals and corresponding peak temperature (from DTG curves) of the crude oil samples are given in Table 2. The reaction peaks which is observed in the temperature range of 600–790 °C is related to the decomposition of limestone.

In LTO region the average mass loss was around 8.5%, whereas it was around 10.0–10.5% in high temperature oxidation (HTO) region. It was also observed that the burnout temperatures (temperature at which the oxidation completed) was lower (~570 °C) in heavier crude oil compared to medium and light crude oils (~590 °C).

Kinetic analysis

In the kinetic analysis part of this research, four different models were used to identify the thermo-oxidative kinetics in low temperature and high temperature reactions, respectively. In Arrhenius model [9–11], it is assumed that the rate of mass loss of the total sample is dependent only on the rate constant, the mass of the sample remaining and the temperature. The final form of the equation assuming first-order kinetics is as follows:

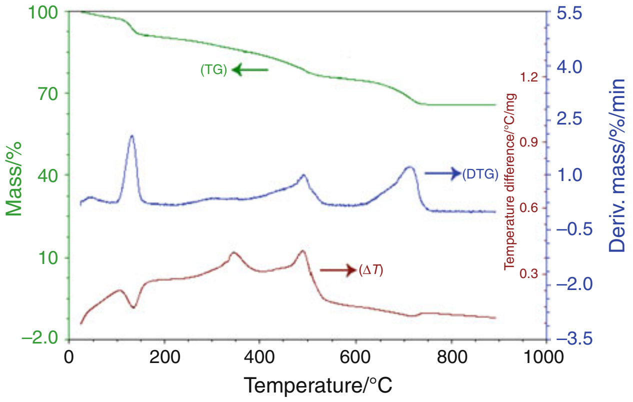

Fig. 1 TG–DTA figure of crude oil-1

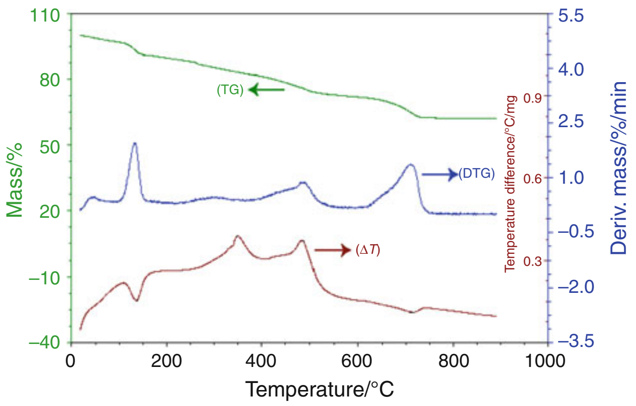

Fig. 2 TG–DTA figure of crude oil-2

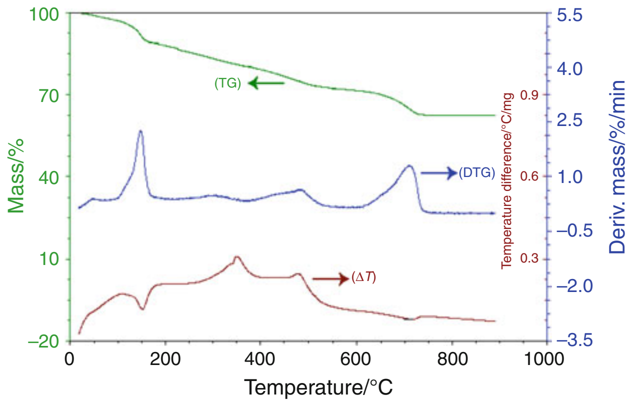

Fig. 3 TG–DTA figure of crude oil-3

Table 2 Reaction intervals and peak temperatures of crude oil sample

Property	Crude oil-1	Crude oil-2	Crude oil-3
LTO reaction region/°C	100–190	100–185	100–180
LTO peak temp./°C	140	145	150
HTO reaction region/°C	380–590	370–575	360–570
HTO peak temp./°C	495	498	500

$$\log[(\mathrm{d}W/\mathrm{d}t)/W] = \log A_r - E/2.303RT \tag{1}$$

Coats and Redfern [12] developed a kinetic model which describes the rate of disappearance of sample in the following form:

$$\log[-\log(1-\alpha)/T2] = \log[(A_r/\beta E)(1-2RT/E)] - [E/(2.303RT)] \tag{2}$$

Ingraham and Marrier [13] developed a simplified method for the determination of a reaction exhibiting linear kinetics. The final form of the equation, which is used for analysis, is as follows:

Table 3 Activation energy/kJ mol^{-1} values of crude oil samples

	Arrhenius	Coats and Redfern	Ingraham and Marrier	Differential
Crude oil-1				
LTO	23.8	13.3	26.9	59.3
HTO	33.8	26.3	36.7	101.1
Crude oil-2				
LTO	23.4	9.6	25.1	55.4
HTO	31.7	25.3	34.4	96.9
Crude oil-3				
LTO	19.6	8.2	12.4	30.2
HTO	22.8	22.9	25.7	77.1

$$\log(\mathrm{d}W/\mathrm{d}T) = \log T - \log\beta + \log A - (E/2.303RT) \tag{3}$$

In differential method [14–17], first the linear regression is calculated and then the kinetic parameters of the samples are determined using the following equation:

$$\ln[(\mathrm{d}\alpha/\mathrm{d}t)/f(\alpha)] = \ln A_r - E/RT \tag{4}$$

where dW/dt is the rate of mass change, E is the activation energy, T is the temperature, R is the gas constant, β is the heating rate and A_r is Arrhenius constant.

Throughout the study, it was observed that the activation energy values of the crude oil samples in limestone matrix is varied between 8.2 and 59.3 kJ mol^{-1} in low temperature oxidation and 22.8–101.1 kJ mol^{-1} in high temperature oxidation region (Table 3). It was observed that the activation energy values of the light crude oil sample (high °API) were lower in each kinetic model studied. On the other hand, activation energy values of the crude oil samples in high temperature oxidation region were higher than low temperature oxidation region which is similar to most investigations previously reported in the literature.

Conclusions

In this research, a comparative study has been conducted to investigate the thermal behaviour of crude oils oil from three different fields. In the combustion of crude oils, two distinct reaction regions were identified known as LTO and HTO, respectively. It was found that the heavy oil exhibits lower burn-out temperatures compared to the medium and light crude oils. It was also observed that the activation energy of crude oils is increased as the °API gravity of the crude oil decreased.

References

1. Bae JH. Characterization of crude oil for fire-flooding using thermal analysis methods. Soc Pet Eng AIME. 1977;17–3:211–8.
2. Ranjbar M, Pusch G. Pyrolysis and combustion kinetics of crude oils, asphaltenes and resins in relation to thermal recovery processes. J Anal Appl Pyrolysis. 1991;20:185–91.
3. Ranjbar M. Influence of reservoir rock composition in crude oil pyrolysis sand combustion. J Anal Appl Pyrolysis. 1993;27–1: 87–95.
4. Kok MV. Use of thermal equipment to evaluate crude oils. Thermochim Acta. 1993;214:315–24.
5. Kok MV, Sztatisz J, Pokol G. High pressure DSC applications on crude oil combustion. Energy Fuels. 1997;11:1137–42.
6. Kok MV, Karacan O. Pyrolysis analysis and kinetics of crude oils. J Therm Anal Calorim. 1998;52:781–8.
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;64–2:06–697.
8. Kok MV, Keskin C. Comparative combustion kinetics for in situ combustion process. Thermochim Acta. 2001;369–2:143–7.
9. Kok MV. An investigation into the combustion curves of lignites. J Therm Anal Calorim. 2001;64–3:1319–23.
10. Kok MV. Thermal investigation of Seyitömer oil shale. Thermochim Acta. 2001;369–371:149–55.
11. Kok MV, Pamir R. Non-isothermal pyrolysis and kinetics of oil shales. J Therm Anal Calorim. 1999;56:953–8.
12. Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. Nature. 1964;201–491:68–9.
13. Ingraham TR, Marrier P. Activation energy calculation from a linearly increasing temperature experiments. Can J Chem Eng. 1965;43–6:354–6.
14. Kok MV, Acar C. Kinetics of crude oil combustion. J Therm Anal Calorim. 2006;83–2:445–9.
15. Kok MV. Influence of reservoir rock composition on the combustion kinetics of crude oils. J Therm Anal Calorim. 2009;97–2: 397–402.
16. 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.
17. Kok MV, Gundogar AS. Effect of different clay concentrations on crude oil combustion kinetics bythermogravimetry. J Therm Anal Calorim. 2010;99–3:779–83.