INFLUENCE OF RESERVOIR ROCK COMPOSITION ON THE COMBUSTION KINETICS OF CRUDE OIL

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In this research, the effect of different lithology (limestone and sandstone) on the combustion of light crude oils was investigated using thermal analysis techniques. Three distinct reaction regions were identified in all of the crude oil+limestone and sandstone mixtures, known as low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO), respectively. Kinetic analysis of the crude oil+limestone and sandstone mixtures was performed using Coats and Redfern method and the results are discussed.

Keywords: activation energy, crude oil, kinetics, limestone, sandstone, thermal analysis

Introduction

Thermal analysis characterizes the physical and chemical properties of substances, depending on the temperature at a defined heating rate (dynamic measurement) or on the time at a constant temperature (static measurement). Techniques developed to continuously monitor physical or chemical changes of a sample which occur as the temperature of a sample is increased or decreased. Thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) are the principal thermoanalytical methods. Much of the work on thermal analysis of crude oils was directed towards the combustion and/or pyrolysis behavior of the samples and kinetic studies. Effect of different metallic additives on the combustion properties of crude oils is also studied.

Al-Saffar *et al.* [1] studied the oxidation behavior of a North Sea light crude oil and its individual SARA fractions (saturates, aromatics, resins and asphaltenes) in the presence of consolidated cores. Such an investigation allows a quantitative study of the temperature intervals at which evaporation, oxidation and combustion effects operate for each fraction. Kök [2] applied simultaneous TG-DTA to characterize the light crude oil combustion in the presence and absence of metal oxide. In crude oil-limestone mixture, three main transitional stages are detected. These are distillation, low-temperature oxidation (LTO) and high temperature oxidation (HTO) regions respectively. In the case of experiments with Fe-chloride at different amounts, the shape of TG-DTA curve is changed considerably. Kök [3] investigated the reac-

tion rates related to an in-situ combustion process and the effect of heating rate and crude oil type on the reaction rates. It was observed that oxidation of crude oil porous media follows a series of reactions. These reactions can be divided into three regions: low temperature oxidation, fuel deposition, and high temperature oxidation. Produced gas analysis was used to determine the activation energy of the samples. Li *et al.* [4] used TG and DTA techniques to investigate oxidation behavior using thermal fingerprinting effects on pure paraffin samples and mixtures of pure components with crude oil. The results demonstrated that each paraffin sample shows different oxidation behaviors at low temperatures and high temperatures. Kök and Bagci [5] studied the light crude oil combustion and kinetics in the presence of copper chloride and magnesium chloride by TG-DTA. It was also observed that, as the mol% of magnesium chloride increased, the high-temperature oxidation peak shifted to the lower-temperature region reflecting more homogeneous composition of the solid residue. Goncalves *et al.* [6] applied TG to evaluate the thermal behavior of five refinery atmospheric distillation residues (ATR) obtained from different Brazilian crude oils. The asphaltenes were extracted of each sample and their influence on coke formation was studied. It was observed that they have a great contribution on carbonaceous residues formation during pyrolysis and that the heavier the ATR sample, the higher is the contribution of other heavy components present in ATR samples. Kök *et al.* [7] determined the combustion characteristics of crude oils in the presence of a limestone matrix using the thermogravimetry (TG/DTG). It was observed that the indi-

vidual activation energies for each reaction region may be attributed to different reaction mechanisms, but they do not give any indication of the contribution of each region to the overall reactivity of the crude oils. Dong *et al.* [8] used thermogravimetry to determine the pyrolysis kinetics of the asphaltenes of Chinese crude oil. The distributed activation energy model (DAEM) was used to analyze these complex systems. A linear relationship can be found from the plots of logarithm of the pre-exponential factor against the activation energy at selected conversion values. This phenomenon known as the compensation effect was explained and it was in agreement with the estimated chemical structure determined by NMR. Kök [9] investigated the role of clay on the combustion and kinetic behavior of crude oils in limestone matrix. A uniform trend of decreasing activation energies was observed with the addition of clay. It was concluded that clays surface area affects the values of Arrhenius constant, while it is the catalytic properties of clay, which lower the activation energies of all the reactions, involved in the combustion process. Kök and Acar [10] investigated the thermal characterization and kinetics of light crude oil in the presence of limestone matrix. TG/DTG is used to characterize the crude oil in the temperature range of 20–900°C, at 10°C min⁻¹ heating rate using air flow rate of 20 mL min⁻¹. Five different kinetic methods used to analyze the TG/DTG data to identify reaction parameters as activation energy and Arrhenius constant. On the other hand different $f(\alpha)$ models from literature were also applied to make comparison.

Experimental

Four high °API crude oil samples used during the experiments were from different Turkish oil fields. Crude oil samples of different properties were mixed with crushed limestone and sandstone samples (+40–50 mesh). In the crude oil limestone and sandstone mixtures, the final oil saturation was considered as 15%. Properties of crude oils, limestone and sandstone samples are given in Table 1.

TG/DTG experiments were performed with DuPont 2000 thermal analysis system. TG/DTG has the capability of measuring the mass loss and derivative, either as a function of temperature or time in a varied but controlled atmosphere. Prior to the experiments, thermal analysis systems were calibrated with calcium oxalate monohydrate for temperature readings and silver for buoyancy effects. TG/DTG experimental procedure involves placing sample (10 mg) setting the heating (10°C min⁻¹) and air flow rate (50 mL min⁻¹), then commencing the experiment in

Table 1a Properties of crude oils

Crude oil	Viscosity (cp, at 20°C)	°API gravity
Crude oil-1	3.6	30.1
Crude oil-2	11.7	31.5
Crude oil-3	7.0	37.1
Crude oil-4	1.8	47.4

Table 1b Properties of limestone and sandstone lithology

| Properties	Limestone	Properties	Sandstone
Calcite/%	92.0	Silica/%	97.0
Dolomite/%	6.6	Iron-alum/%	2.1
Quartz/%	1.2	Calcium/%	0.7
Kaolinite/%	0.2	Salts/%	0.2

the temperature range of 20–900°C. All the experiments were performed twice for repeatability.

Results and discussion

Thermal analysis

Theoretically combustion of oil can be initiated whenever oxygen comes in contact with fuel. However, the temperature, composition of the fuel and the oxygen supply dictate the nature of this reaction.

In combustion with air, three distinct reaction regions were identified in crude oil+limestone mixtures studied (Table 2). A reaction up to ~380°C was actually the first reaction region and called low temperature oxidation (LTO). Low levels of carbon oxides in the effluent gas stream and low peak temperatures characterize this reaction. A second reaction takes place between ~380–440°C and it is called fuel deposition (FD). During this reaction, the crude oil is coked and deposited on the solid matrix as fuel. The final reaction known as high temperature oxidation (HTO), that takes place in between ~440–580°C
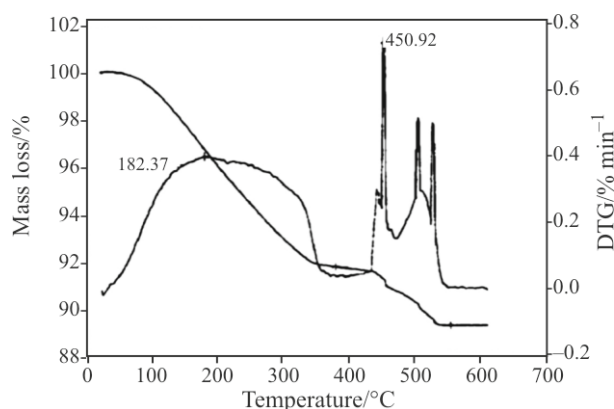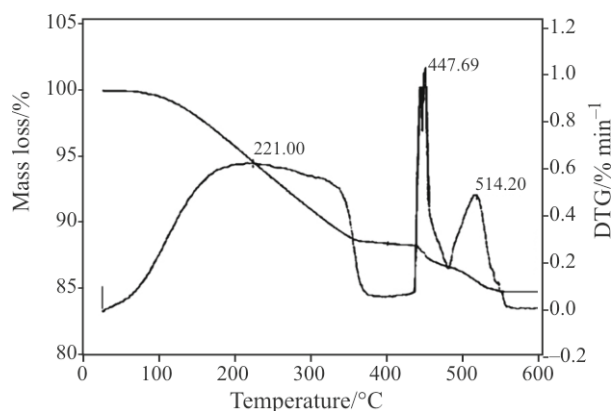

Fig. 1 TG/DTG curve of crude oil-2+limestone

Fig. 2 Arrhenius curve of crude oil-2+sandstone

and contributes most of the exothermic heat of reaction when crude oil+limestone is heated in an oxidizing environment (Fig. 1). In crude oil+sandstone mixtures three distinct reaction regions were also identified (Fig. 2). The only difference is in the temperature intervals and the peak temperatures of the reaction regions (Table 3).

The main characterization point on TG/DTG curve is the peak temperature, where rate of mass loss is maximum. Beyond the peak temperature of high temperature oxidation region, the derivative curve falls rapidly where the prevailing temperature is called burn-out temperature. This temperature represents the temperature where sample oxidation is complete (Tables 4 and 5). It was observed that there is no

clear effect of °API gravity and viscosity of crude oil samples on peak and burn-out temperatures [10–17].

Kinetic analysis

In combustion process, kinetic analysis for crude oils and crude oil+limestone and sandstone mixtures is a complex study, because of the presence of the numerous complex components and their parallel and consecutive reactions.

Coats and Redfern [16] developed the model which found a wide application in analyzing the TG/DTG data. In this model, the rate of disappearance of sample may be expressed by:

$$d\alpha/dt = k(1-\alpha)^n \tag{1}$$

where : $\alpha = (W_{initial} - W_T)/(W_{initial} - W_{final})$.

$$k = A\exp(-E/RT) \tag{2}$$

For a linear heating rate, say, β, °C min^{-1}

$$\beta = dT/dt \tag{3}$$

Combining Eqs (1)–(3), rearranging and integrating,

$$d\alpha/(1-\alpha)^n = A/\beta e^{-E/RT} dT \tag{4}$$

The right hand side of the Eq. (4) has no exact integral, but by making the substitution and integration, the equation takes the following form.

Table 2 Reaction intervals of crude oil+limestone mixtures

Crude oil	Low temp. oxidation, LTO/°C	Fuel deposition, FD/°C	High temp. oxidation, HTO/°C
Crude oil-1+limestone	25–360	360–400	400–550
Crude oil-2+limestone	25–350	350–410	410–540
Crude oil-3+limestone	25–340	340–420	420–530
Crude oil-4+limestone	25–380	380–440	440–580

Table 3 Reaction intervals of crude oil+sandstone mixtures

Crude oil	Low temp. oxidation, LTO/°C	Fuel deposition, FD/°C	High temp. oxidation, HTO/°C
Crude oil-1+sandstone	25–380	350–480	480–560
Crude oil-2+sandstone	25–360	360–485	485–545
Crude oil-3+sandstone	25–350	340–490	490–560
Crude oil-4+sandstone	25–360	360–495	495–555

Table 4 Peak and burn-out temperatures of crude oil+limestone mixtures

Crude oil	Peak temperature/°C, LTO	Peak temperature/°C, HTO	Burn-out temperature/°C
Crude oil-1+limestone	195	500	575
Crude oil-2+limestone	180	510–535	570
Crude oil-3+limestone	150	490	580
Crude oil-4+limestone	200	470–510	575

Table 5 Peak and burn-out temperatures of crude oil+sandstone mixtures

Crude oil	Peak temperature/°C, LTO	Peak temperature/°C, HTO	Burn-out temperature/°C
Crude oil-1+sandstone	280	520	565
Crude oil-2+sandstone	220	515	560
Crude oil-3+sandstone	240	510	555
Crude oil-4+sandstone	220	515	550

Table 6 Kinetic parameters of crude oil+limestone mixtures

Crude oil	Reaction order, LTO	Activation energy/ kJ mol^{-1}, LTO	Reaction order, HTO	Activation energy/ kJ mol^{-1}, HTO
Crude oil-1+limestone	~2/3	13.8	~2/3	116.1
Crude oil-2+limestone	1	25.6	1	106.6
Crude oil-3+limestone	1	11.7	1	93.7
Crude oil-4+limestone	1	12.6	1	110.5

Table 7 Kinetic parameters of crude oil+sandstone mixtures

Crude oil	Reaction order, LTO	Activation energy/ kJ mol^{-1}, LTO	Reaction order, HTO	Activation energy/ kJ mol^{-1}, HTO
Crude oil-1+sandstone	~1/2	16.7	1	49.8
Crude oil-2+sandstone	~1/2	16.0	1	66.0
Crude oil-3+sandstone	1	14.2	1	45.9
Crude oil-4+sandstone	1	18.6	1	71.8

$$1-(1-\alpha)^{1-n}/(1-n)=ART^2/\beta E(1-2RT/E)e^{-E/RT} \quad (5)$$

taking logarithms of each side,

$$\log[(1-(1-\alpha)^{1-n})/(T^2(1-n))]=$$
$$\log[(AR/\beta E)(1-2RT/E)]-[E/(2.303RT)] \quad (6)$$

for all values of n except $n\#1$, in which case Eq. (6) after taking the logaritm, it becomes:

$$\log(-\log(1-\alpha)^{1-n}/T^2)=$$
$$\log[(AR/\beta E)(1-2RT/E)]-[E/(2.303RT)] \quad (7)$$

Thus a plot of either $\log((1-(1-\alpha)^{1-n})/(T^2(1-n)))$ *vs.* $1/T$ or, $\log(-\log(1-\alpha)^{1-n}/T^2)$ *vs.* $1/T$ where $n=1$, should result in a straight line of slope$=-E/2.303R$ for the correct value of n.

In analyzing the TG/DTG data, reaction orders were assumed as 1/2, 2/3, 1 and 3/2, respectively. It is clearly identified that activation energies for LTO are low compared to HTO region. It was observed that the reaction orders were varied between 2/3 and 1 for crude oil+limestone samples and 1/2 and 1 for crude oil+sandstone samples. In both LTO and HTO region higher activation energies were found with some exceptions that as the °API gravity of the crude oil decreased and as the viscosity is increased (Tables 6 and 7). In both crude oil+limestone and sandstone samples it was difficult to determine the kinetic parameters in fuel deposition region, so it is not considered in the analysis.

Acknowledgements

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