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NON-ISOTHERMAL KINETIC ANALYSIS AND FEASIBILTY STUDY OF MEDIUM GRADE CRUDE OIL FIELD

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In this research, non-isothermal kinetics and feasibility study of medium grade crude oil is studied in the presence of a limestone matrix. Experiments were performed at a heating rate of 10°C min^{-1}, whereas the air flow rate was kept constant at 50 mL min^{-1} in the temperature range of 20 to 600°C (DSC) and 20 to 900°C (TG). In combustion with air, three distinct reaction regions were identified in all crude oil/limestone mixtures, known as low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO). The activation energy values were in the order of 5–9 kJ mol^{-1} in LTO region and 189–229 kJ mol^{-1} in HTO region. It was concluded that the medium grade crude oil field was not feasible for a self-sustained combustion process.

Keywords: *activation energy, crude oil, feasibility study, limestone, non-isothermal kinetics, thermal analysis*

Introduction

In recent years, thermal analysis techniques to study the combustion-pyrolysis behavior and kinetics of fossil fuels have gained a wide acceptance among researchers. 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. These investigations were made in an attempt to determine the feasibility of air injection into deep light oil reservoirs, and the extent of any interactions between the fractions in a whole oil sample by comparing the behavior of pure fractions with the behavior of mixtures of these fractions in the crude oil. Goncalves *et al.* [2] reported the application of thermal analysis techniques to study the thermal behavior of asphaltenes from Brazilian oil. The approach involves kinetic studies of the thermal decomposition of asphaltenes under controlled conditions by thermogravimetry (TG), characterization of volatile fractions by thermogravimetry and differential thermal analysis coupled with gas chromatography/mass spectrometry (TG-DTA/GC/MS) and by gas chromatography/mass spectrometry (GC/MS) in the volatile recovered. The coke formed was also studied after being decomposed into smaller molecules using selective oxidation. Sonibare *et al.* [3] studied the thermal behavior of the Nigerian oil sand bitumen in an oxidizing environment using non-isothermal thermogravimetric analysis (TG) and differential thermal analysis (DTA). Three regions of mass loss corresponding to low-temperature oxidation, fuel deposition and high temperature oxidation were identified. Increasing the heating rate caused a shift in the reaction regions and peak temperatures to higher temperatures. No effect of gas flow rate was observed on the reactions. Dong *et al.* [4] 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. The results show that the peak activation energy for pyrolysis of the asphaltenes is 245 kJ mol^{-1}. Freitag and Verkoczy [5] studied the low-temperature oxidation (LTO) reactions of the SARA fractions separated from two crude oils in the presence of their reservoir sands at temperatures between 130 and 230°C. The results indicated that the usual approach to modeling LTO - the use of a very few single-step Arrhenius-rate equations - could not be made to reflect the observed reaction kinetics. Ambalae *et al.* [6] used TG to obtain information on the pyrolysis and combustion behavior of both crude oil and its asphaltenes, each mixed with reservoir sand. Of all the saturate, aromatic, resin and asphaltene fractions, asphaltenes contribute the most to the formation of coke (fuel). Temperature-ramped as well as the isothermal pyrolysis experiments on whole oil and asphaltenes were analyzed to determine the temperature at which coke formation was maximized. Furthermore, isothermal combustion curves

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for coke derived from whole oil and asphaltenes were obtained to provide reliable data for calculating the kinetics of the reactions. Shiskin [7] used high-resolution differential scanning calorimetry to accurately establish the temperature intervals of oxidation/distillation of the major components of crude oils. The experimental TG-DSC curves show that the temperature scan of the run can be divided into six regions, of which the first belongs to simple distillation of the sample's liquid constituent (the distillate) and the others to oxidative cracking distillation of the solid (heavy) residue. The latter occur in the order paraffins+ light oils, middle base oils, heavy base oils, condensed aromatics (resins) and asphaltenes. Kök [8] reviewed instances where thermal analysis techniques have been applied for fossil fuel characterization and kinetics. The scientific results clearly showed that thermal analysis is a well established technique used in crude oil characterization. Li *et al.* [9] examined the oxidation, behavior of three crude oils (light oil, medium oil and Athabasca bitumen) by using the pressurized differential scanning calorimeter (PDSC) at pressures from 110 to 6.894 kPa. Pure hydrocarbon aromatics and paraffin samples were also selected for the current study. The study shows an increase of pressure results in an increase in the rate of oxidation reactions and heat released from the oxidation reactions. Kök *et al.* [10–21] applied DSC and TG/DTG to crude oil, oil shale and asphaltite combustion and the SARA fractions of crude oils. Three distinct reaction regions were identified in all crude oil samples studied, known as low temperature oxidation, fuel deposition and high temperature oxidation. On the other hand, two distinct exothermic peaks were identified known as low and high temperature oxidation in oil shale and asphaltite samples. Effect of heating rate, metallic additives, crude oil and matrix type,°API gravity, clay type and different kinetic models were studied and discussed.

Experimental

In the first part of the experiments (crude oil+limestone mixtures) were performed using a thermal analysis system with TG/DTG and DSC modules. Experiments were performed with a sample size of ~10 mg, at a heating rate of 10°C min^{-1}. The air flow rate over the sample pan was kept constant at 50 mL min^{-1}, in the temperature range of 20 to 600°C (DSC) and 900°C (TG). Prior to the experiments, the instruments were calibrated for temperature readings, using indium as reference material. The balance was calibrated for the buoyancy effect allowing the quantitative estimation of mass changes and all the experiments were performed twice for repeatability. Properties of the crude oil sample and lithology are given in Table 1 respectively.

Table 1a Properties of crude oil sample

Property	Crude Oil
°API Gravity	26.12
Viscosity/cP	37
$<C_{15}+$/%	21.8
Saturates/%	45
Aromatics/%	29
Resin/%	14
Asphaltenes/%	12
Sulfur/%	2.2
Calorific value/cal g^{-1}	11300

Table 1b Properties of lithology (limestone)

Property	Limestone
Calcite/%	92.0
Dolomite/%	6.6
Quartz/%	1.2
Kaolinite/%	0.2
Porosity/%	20
Permeability/darcy	10
Oil saturation/%	15
Mesh size/%	–60

Results and discussion

In TG/DTG experiments, a series of reactions were observed during the oxidation of crude oil in porous media by air injection known as LTO, FD and HTO reactions. In thermogravimetry experiments, a reaction up to 400°C was actually the first region and called LTO. This reaction rate is proportional to the specific surface area of the matrix. A second reaction region takes place between 400–650°C and is called FD. During this reaction, the crude oil is coked and deposited on the solid matrix as fuel. The initial oil saturation, specific surface area of the rock, perme-

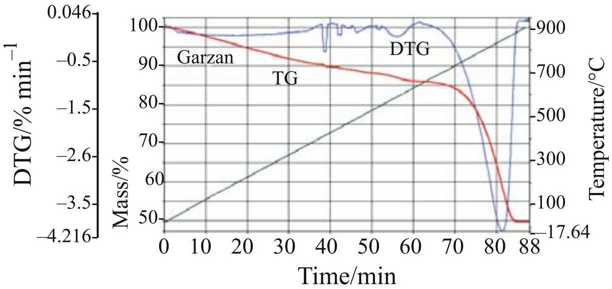

Fig. 1 TG/DTG curve of medium grade crude oil

Table 2 Reaction regions, peak and burn-out temperatures of crude oil sample

Reaction regions	Peak temp. and reaction interval/°C
LTO region	100–400
Peak temp. (LTO)	220
FD region	400–650
Peak temp. (FD)	620
HTO region	650–880
Peak temp. (HTO)	840
Burn-out temp.	870

ability and porosity are the main properties affecting fuel deposition. The final reaction, known as HTO, takes place between 650–870°C (Fig. 1). This reaction forms the greatest combustion to the exothermic heat of reaction when crude oil/limestone is heated in an oxidizing environment. Reaction intervals and the peak-burn-out temperatures of the crude oil sample are given in Table 2 respectively.

Kinetic analysis

Mass loss kinetics during crude oil combustion is a complex phenomenon since numerous reactions proceed simultaneously, therefore the kinetic data calculated should be regarded as apparent data representing complex and consecutive reactions. Since the sample size is small and there is an excess air supply outside the sample pan, the progress of the reaction may be independent of the oxygen concentration. It is therefore reasonable to assume that the oxidation can be described by first-order kinetics. In this study, three different kinetic methods (Arrhenius, Coats and Redfern, Ingraham and Marrier) were applied in order to determine the kinetic parameters of the medium crude oil sample in limestone matrix.

In the first approach (Arrhenius method), the method assumes 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 with reaction order of unity. Application of this model to the TG/DTG curves is easy and fast. So the final form of the equation of Arrhenius-type kinetic method takes the following form [10].

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

Coats and Redfern developed an integral method which can be applied to TG/DTG data assuming different order of reactions. The correct order is presumed to lead to best linear plot from which the activation energy is determined. The final form of the equation is as follows [22]

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

Ingraham and Marrier [21] developed a simplified method for the determination of a heterogeneous reaction exhibiting linear kinetics. In this model reaction order is assumed as 1. The final form of the equation, which is used for analysis, is as follows [23].

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

where α=fraction of sample decomposed (%); T=temperature (K); A=pre-exponential factor ($s^{–1}$); R=gas constant (8.314 J $mol^{–1}$ $K^{–1}$); E=activation energy (kJ $mol^{–1}$); β=heating rate (°C $min^{–1}$); T=temperature (K); dw/dt=the loss in mass from unit area in the period of time; n=reaction order.

Using the above mentioned methods, activation energy and pre-exponential factor for the low and high temperature oxidation regions were determined with the assumption of unity reaction order (Table 3). The average activation energy values for low and high temperature oxidation regions were 6 and 189 kJ $mol^{–1}$ for Arrhenius model, 9 and 229 kJ $mol^{–1}$ for Coats and Redfern model, 5 and 216 kJ $mol^{–1}$ for Ingraham and Marrier model respectively. In general, similar activation energy values were obtained for different kinetic methods. Differences between the activation energies of the samples can be explained with the different equation parameters and assumptions that those models based on.

Feasibility study

The first step in feasibility study is to identify the oxidation behaviour of crude oil. By analyzing the TG/DTG curves, the reaction regions were obtained as mentioned above. Also the required front temperature (the temperature at which total crude oil sample was consumed) was observed from TG/DTG curves.

Table 3 Activation energy (kJ $mol^{–1}$) and pre-exponential factor ($s^{–1}$) values of the crude oil sample

Kinetic methods	LTO		HTO	
	Activation energy	Pre-exp. factor	Activation energy	Pre-exp. factor
Arrhenius	6	$1.70\cdot10^{2}$	189	$6.90\cdot100^{7}$
Coats–Redfern	9	$1.35\cdot10^{12}$	229	$1.20\cdot10^{15}$
Ingraham–Marrier	5	$5.10\cdot10^{1}$	216	$1.40\cdot10^{13}$

The heat of reaction of the crude oil sample was determined from DSC curve using the area of reaction that includes the energy required for cracking and vaporization. In order to determine the minimum crude oil content required for self-sustained combustion (W_{min}) and oil content of reservoir (W_r), the following equations was utilized [24]

$$W_{min}=(\rho_{bulk}C_{bulk}\Delta T_{min})/(\Delta H) \quad (4)$$

$$W_r=S_o\rho_o\theta \quad (5)$$

where: W_{min}=mass/unit volume (lbm cuft^{-1}); ΔT_{min}=required minimum front temperature (°F); ΔH=heat value of crude oil (Btu lbm^{-1}); θ=porosity (%); ρ=density (lbm cuft^{-1}); C=specific heat constant (Btu lbm^{-1} F^{-1}).

The measured and calculated data used in the calculation of minimum crude oil content (W_{min}) and oil content of reservoir (W_r) are given in Table 4. In order to evaluate the feasibility of the process, W_{min} and W_r are compared. When reservoir crude oil content is lower than minimum crude oil content, the process was considered as non-feasible as in this medium gravity crude oil field.

Table 4 DSC, TG/DTG, W_{min} and W_r values

Property	Crude oil value
T_{min}/°F	1110
ΔT_{min}/°F	1090
ρC/Btu cuft^{-1} F^{-1}	9.94
ΔH/Btu lbm^{-1}	28
W_{min}/lbm cuft^{-1}	37
W_r/lbm cuft^{-1}	5.7

Conclusions

In this research, non-isothermal kinetic analysis and feasibility study of medium grade crude oil is determined using thermal analysis techniques. In TG/DTG experiments, a series of reactions were observed during the oxidation of crude oil in porous media by air injection known as, LTO, FD and HTO reactions. Different kinetic methods were applied and the kinetic parameters are determined for LTO and HTO regions. It was observed that the fuel amount was not sufficient to sustain the combustion front for the oil field studied, so the method is considered as non-feasible.

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