

LIGHT CRUDE OIL COMBUSTION IN THE PRESENCE OF LIMESTONE MATRIX

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Abstract

In this study the combustion characteristics of crude oils (Karakuş and Beykan) in the presence of a limestone matrix were determined using the thermogravimetry (TG/DTG). Experiments were performed at a heating rate of $10^{\circ}\text{C min}^{-1}$, whereas the air flow rate was kept constant at 10 L h^{-1} in the temperature range of $20\text{--}900^{\circ}\text{C}$. In combustion with air, three distinct reaction regions were identified in all crude oil/limestone mixtures studied known as low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO). The individual 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. Depending on the characteristics, the mean activation energy of samples varied between 50.3 and 55.8 kJ mol^{-1} .

Keywords: crude oil, kinetics and activation energy, thermal analysis

Introduction

In recent years the application of thermogravimetry (TG/DTG), differential scanning calorimetry (DSC) and differential thermal analysis (DTA) to study the combustion and pyrolysis behavior of fossil fuels has gained a wide acceptance among researchers. Ranjar and Pusch [1] studied the effect of the oil composition, characterized on the basis of light hydrocarbon, resin and asphaltene contents, on the pyrolysis kinetics of the oil and the combustion kinetics of the fuel. The results of their investigations showed that the colloidal composition of oil and the heat transfer characteristics of the pyrolysis medium had a pronounced influence on fuel formation and composition. Ali and Saleem [2] investigated the asphaltenes precipitated from crude oils by thermogravimetric pyrolysis-GC analysis. The evolution of methane and other normal alkanes from all the asphaltenes under mild pyrolysis conditions indicates that these asphaltenes contain thermally labile alkyl groups on the periphery of these asphaltenes. Ranjbar [3] investigated the influence

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of composition of the reservoir rock on the pyrolysis and combustion behavior of crude oils in porous media. From the experimental results, he concluded that clay minerals present in the matrix enhance fuel deposition during the pyrolysis process and also catalyze the oxidation of fuel. Bae [4] investigated the thermo-oxidative behavior and fuel-forming properties of various crude oils. The results indicated that oils could 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. Vossoughi [5] used TG/DTG and DSC techniques to study the effect of clay and surface area on the combustion of selected oil samples. The results indicate that there was a significant reduction in the activation energy of the combustion reaction depending on the chemical composition of additives. Verkocy and Kamal [6] performed thermogravimetric analysis (TG/DTG) and pressurized differential scanning calorimetry (PDSC) investigations on heavy oils collected from wells under primary, steam flood and fire-flood production, and on cores. They estimated kinetic and thermochemical data for thermal decomposition, low-temperature oxidation and combustion reaction rates, which were non-linearly dependent on the heating rate. Kök [7] characterized 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. DSC-TG/DTG curves have also been used to determine the heat values and reaction parameters of crude oil. Higher activation energy values were found as the gravity of the crude oil decreased. Goncalves *et al.* [8] investigated the thermal behaviour of asphaltenes from crude oil using thermal analysis techniques (TG-DTA/GC/MS). The approach involved kinetic studies of the thermal decomposition of asphaltenes under controlled conditions by thermogravimetry (TG/DTG), characterisation of volatile fractions by TG and DTA coupled with gas chromatography/mass spectrometry and by gas chromatography/mass spectrometry of the volatiles recovered. The coke formed was also studied after having been decomposed into smaller molecules using selective oxidation. Kök and Iscan [9] applied DSC to crude oil combustion in the presence and absence of metal chlorides. It was observed that, in the presence of lower ratios of metallic additives, the surface reactions were predominant and the catalyst did not affect the reactions much. Three different reaction regions were identified as low temperature oxidation, fuel deposition and high temperature oxidation in all the samples studied. Barkia *et al.* [10] examined organic matter evolution and kinetics of combustion of fossil fuels was examined by TG and by DTA. An agreement was observed between both techniques where it was found that combustion of organic matter occurred in two steps.

Experimental

Experiments (crude oil+limestone mixtures) were performed using a DuPont 2000 thermal analysis system with a thermogravimetry (TG/DTG) module. Experiments were performed with a sample size of ~50 mg, at a heating rate of $10^{\circ}\text{C min}^{-1}$. The air flow rate over the sample pan was kept constant at 10 L h^{-1} in the temperature range of $20\text{--}900^{\circ}\text{C}$. Prior to the experiments, the instrument was 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 samples and lithology are given in Table 1.

Table 1a Properties of crude oil samples

Crude oil	API gravity	Viscosity/cP, at 20°C
Beykan	31.5	11.7
Karakuş	30.1	3.6

Table 1b Properties of lithology (limestone)

Calcite/%	Dolomite/%	Quartz/%	Kaolinite/%	Porosity/%	Mesh size/%
92.0	6.6	1.2	0.2	20	-60

Results and discussion

In combustion with air, three distinct reaction regions were identified in all crude oil/limestone mixtures studied. A reaction up to 350°C was actually the first region and called low temperature oxidation (LTO). Low levels of carbon oxides in the effluent gas stream and low peak temperatures characterize low temperature oxidation reactions. This reaction rate is proportional to the specific surface area of the matrix. A second reaction region takes place between 350 and 550°C and is called fuel deposition (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, permeability and porosity are the main properties affecting fuel deposition. The final reaction, known as high temperature oxidation (HTO), takes place between 600 and 800°C and forms the greatest combustion to the exothermic heat of reaction when crude oil/limestone is heated in an oxidizing environment (Fig. 1). Peak and burnout temperatures of the samples are given in Table 2.

Table 2 Results of DTA and TG/DTG curve analysis of crude oil samples

Sample	Peak temperature/°C			Burnout temperature/°C
	I	II	III	
Karakuş+Lst	210	455	782	840
Beykan+Lst	140	500	789	850

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.

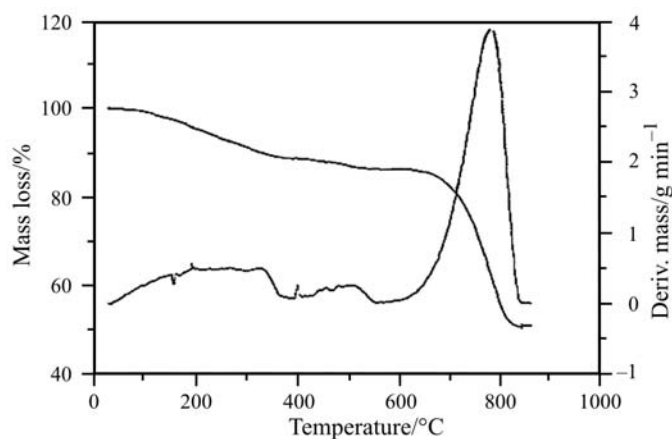


Fig. 1 TG/DTG curve of Karakuş oil+limestone

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 (Arrhenius method). In this method [13–15], the model 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 equation of Arrhenius-type kinetic model takes the following form.

$$dW/dt = kW^n; \quad (1)$$

$$k = A_r \exp(-E/RT) \quad (2)$$

Assuming first-order kinetics,

$$dW/dt = A_r \exp(-E/RT)W; \quad (3)$$

$$[(dW/dt)1/W] = A_r \exp(-E/RT) \quad (4)$$

Taking the logarithm of both sides,

$$\lg[(dW/dt)1/W] = \lg A_r - E/2.303RT \quad (5)$$

where dW/dt is the rate of mass change, E is the activation energy, T is the temperature, A_r is the Arrhenius constant and n is the reaction order. When $\lg[(dW/dt)1/W]$ is plotted vs. $1/T$, a straight line is obtained which will have a slope equal to $E/2.303R$ and from the intercept the Arrhenius constant can be estimated (Fig. 2). The individual activation energies for each reaction region can be notionally 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. Therefore, the concept of weighted mean activation energy, E_{wm} , as applied to determine the overall reactivity of the crude oil samples is proposed [16].

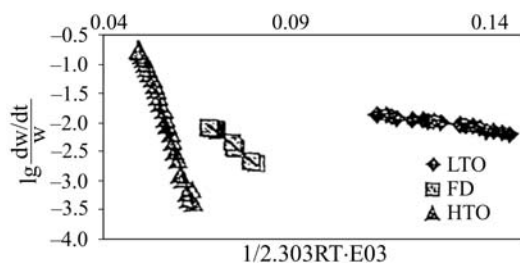


Fig. 2 Arrhenius curve of Karakuş oil+limestone

$$E_{wm} = F_1 E_1 + F_2 E_2 + F_3 E_3 + \dots + F_n E_n \quad (6)$$

where F_1, F_2, \dots are the mass fractions of the combustible content of the sample burned during each region of Arrhenius linearity, and E_1, E_2, \dots are the individual apparent activation energies obtained over each region.

Higher activation energy values are obtained in reaction regions at higher temperatures. Depending on the characteristics of crude oil samples, the mean activation energy values vary between 50.3 and 55.8 kJ mol⁻¹ (Table 3).

Table 3 Activation energy values of the crude oil samples (kJ mol⁻¹)

Sample	E			Mean E
	I. region	II. region	III. region	
Karakuş+Lst	9.9	51.9	200.1	55.8
Beykan+Lst	16.9	73.1	202.9	50.3

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