Comparative combustion kinetics for in situ combustion process

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Abstract

In this research, thermal characteristics and combustion kinetics of three crude oils (13–27°API) were investigated using DuPont 9900 thermal analysis system (TG/DTG). A sample size of 10 mg, heating rate of 10°C min^{-1} were used in the temperature range of 20–700°C under air atmosphere. Theoretically, combustion of fuel can be initiated whenever oxygen comes in contact with fuel. However, the temperature, composition of fuel and oxygen supply dictates the nature of this reaction. In combustion with air, three distinct reaction regions were identified in all crude oils studied known as low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO). A computer program was developed for automatically processing the data to estimate the reaction parameters using different models and the results are discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In situ combustion is a thermal oil recovery in which the energy is generated in the reservoir, creating a combustion front that is propagated through the reservoir by continuous air injection. Success of this process depends mainly on the crude oil and rock properties as well as operational conditions. While much work has been carried out to study the thermal and fluid dynamics aspects of the in situ combustion process, the chemical reaction kinetics remain the least investigated aspects of underground combustion. Limited kinetic data are available in the petroleum literature on the rates and nature of the partial oxidation reactions and the high temperature combustion reactions of crude oils. Thermal analysis is defined as

the measurement of change in chemical and physical properties of a sample as a function of temperature or time. In recent years the application of thermogravimetry (TG/DTG) and differential scanning calorimeter (DSC) for the study of pyrolysis and combustion behaviour of fossil fuels has gained wide acceptance among research workers, and is of exceptional significance for economy.

Bae [1] investigated the thermo-oxidative behaviour and fuel forming properties of crude oils and concluded that crude oils can be classified according to their oxidation characteristics. Verkocy and Jha [2] performed TG/DTG experiments on heavy oils and cores. They have estimated kinetic and thermochemical data for low temperature oxidation (LTO), cracking, coking and combustion reaction in cores and oils. Yoshiki and Philips [3] used DTA and TG/DTG at high temperatures and pressures and concluded that both LTO and high temperature oxidation (HTO) rates increased with pressure as

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Nomenclature

A	pre-exponential factor (1 min^{-1})
E	activation energy (kJ mol^{-1})
k	specific rate constant
n	reaction order
R	universal gas constant (kJ mol^{-1} K)
T	temperature at selected weight loss (°C or K)
w	mass of sample remaining (mg)

Greek letters

α	reacted fraction at the time t
β	heating rate (°C min^{-1})

did the exothermicity of each. Burger and Sahuquet [4] used DTA to illustrate catalytic effect of some metallic derivatives and to investigate how the properties of both oil and porous media influence crude oil combustion. Drici and Vossoughi [5] applied DSC and TG/DTG to crude oil combustion in the presence and absence of metal oxides. They observed that in the presence of a large surface area such as silica, the surface reactions are predominant and unaffected by the small amount of metal oxide present. Kok [6] characterised the combustion properties of two heavy crude oils by DSC and TG/DTG. On combustion with air, three different reaction regions were identified, known as LTO, fuel deposition (FD) and HTO. Heat values and reaction parameters are also obtained from DSC and TG/DTG experiments. Verkocy and Kamal [7] performed TG/DTG and DSC on heavy oils collected from wells under primary, steam-flood and fire-flood production and on cores. They have estimated kinetic and thermo-chemical data for thermolysis, LTO and combustion reaction rates which were non-linearly dependent on the heating rate.

2. Experimental

Experiments were performed using the DuPont 9900 thermal analysis system with thermogravimetry (TG/DTG) module. TG/DTG has the capability of measuring the weight loss either as a function of temperature or time in a varied but controlled atmo-

Table 1
Properties of crude oils

Crude oil	Specific gravity	°API gravity	Viscosity at 20°C (cP)
Crude oil 1	0.894	26.7	37
Crude oil 2	0.942	18.7	2260
Crude oil 3	0.979	12.9	51935

sphere. Prior to the experiments, TG/DTG system was calibrated with calcium oxalate monohydrate for temperature readings and silver was used in order to correct for buoyancy effects. Experiments (TG/DTG) were performed with a sample size of ~10 mg, at heating rate of 10°C min^{-1}. Air flow rate through the sample pan was kept constant at 50 ml min^{-1} in the temperature range of 20–700°C. For repeatability, experiments were performed twice. The crude oils used during the experiments were from Turkish oil fields. Properties of crude oils are shown in Table 1.

3. Kinetic theory

The calculation of kinetic data is based on the formal kinetic equation.

$$\frac{d\alpha}{dt} = k\alpha^n \tag{1}$$

The temperature dependence of k is expressed by the Arrhenius equation.

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{2}$$

3.1. Unity model

In this model [6], since the measured rate of mass loss accounts for gross changes in the system, the Arrhenius-type reaction model assumes that the rate of mass loss of the total sample dependent only on the rate constant, the mass of sample remaining and the temperature. The final form of the equation is as follows.

$$\log\frac{dw/dt}{w} = \log A - \frac{E}{2.303RT} \tag{3}$$

3.2. Coats and Redfern model

Coats and Redfern [8] developed an integral method, which can be applied to TG/DTG data, assuming the order of reactions. The correct order is presumed to lead to the best linear plot, from which the activation energy is determined. The form of the equation, which is used for analysis, is as follows.

$$\log \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \log \left(\frac{AR}{\beta E} \frac{1-2RT}{E} - \frac{E}{2.303RT} \right) \tag{4}$$

3.3. Ratio model

Michelson and Einhorn [9] developed a model based on the Arrhenius kinetic model. The form of the equation, which is used for analysis, is as follow.

$$\log \frac{-(\mathrm{d}w/\mathrm{d}t)_j}{-(\mathrm{d}w/\mathrm{d}t)_i} = \frac{E}{2.303R} \frac{T_j - T_i}{T_i T_j} \log \left(\frac{w_i}{w_j} \right)^n \tag{5}$$

3.4. Ingraham and Marrier model

Ingraham and Marrier [10] developed a simplified method for the determination of a heterogeneous reaction exhibiting linear kinetics. The form of the equation, which is used for analysis, is as follows.

$$\log \frac{\mathrm{d}w}{\mathrm{d}T} = \log T - \log \beta + \log A - \frac{E}{2.303RT} \tag{6}$$

3.5. Freeman and Carroll model

The Freeman and Carroll [10] model is one of the most widely used in the literature for performing the kinetic analysis of reactions. The form of the equation, which is used for analysis, is as follows.

$$\frac{\Delta \ln(\mathrm{d}\alpha/\mathrm{d}t)}{\Delta \ln(1-\alpha)} = \left(-\frac{E}{R} \right) \frac{\Delta(1/T)}{\Delta \ln(1-\alpha)} \tag{7}$$

3.6. Flynn–Wall model

The Flynn–Wall [10] method uses the thermogravimetric curve to calculate the activation energy of the Arrhenius constant. The form of the equation, which is used for analysis, is as follows.

$$E = \left(-\frac{R}{b} \right) \frac{\mathrm{d} \ln \beta}{\mathrm{d}(1/T)} \tag{8}$$

4. Results and discussion

Theoretically, combustion of fuel can be initiated whenever oxygen comes in contact with fuel. However, the temperature and composition of the fuel and oxygen supply dictate the nature of this reaction. In combustion with air, three distinct reaction regions were identified in all crude oils studied (Fig. 1). A reaction up to 390°C was the first region identified and called as LTO. A second transition region takes place between 390 and 490°C and called as FD. The final reaction of crude oil inferred from the TG/DTG curves takes place between 490 and 600°C and called as HTO. Burnout temperatures that represent the temperature where sample oxidation is complete were also identified for the crude oils and found that the heavier oils exhibit lower burnout temperatures comparing with light oil (Table 2). For a given temperature interval, the extent of decomposition is found greater at a slower rate of heating than for a similar sample heated at a faster rate (Fig. 2). From the experiments performed (5, 10, 15, 20 and 25°C min^{-1}), it should be noted that although the decomposition temperatures are changed with heating rate, the weight losses remained nearly same.

Six different models, all based on Arrhenius kinetic theory, was used for kinetic analysis of combustion data as obtained from TG/DTG curves (Fig. 2). Activation energy values for LTO region was low compared with FD and HTO regions. In LTO region, heavier oil exhibit somewhat lower activation energy, however at HTO region higher activation energies

Table 2
Reaction intervals and burnout temperatures of crude oils

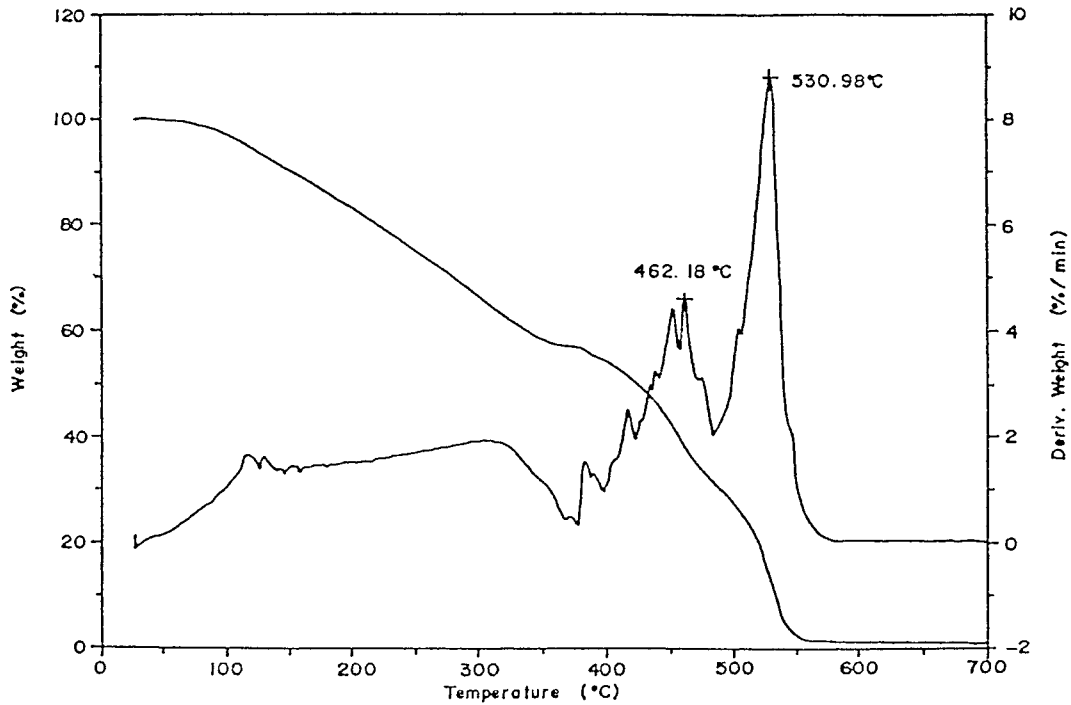| Crude oil	LTO (°C)	FD (°C)	HTO (°C)	Burnout (°C)
Crude oil 1	20–380	380–480	480–585	585
Crude oil 2	20–385	385–485	485–575	575
Crude oil 3	20–390	390–490	490–565	565

Fig. 1. TG/DTG curve of crude oil 3.

were found as the °API gravity of the crude oil decreased. In Coats and Redfern model reaction orders are assumed as 1/2, 2/3, 1, 3/2 and 2. In the model developed by Michelson and Einhorn ratio is selected as 1.1 to give enough points to determine reliable correlation covering the desired portions of the curve.

Similar results were obtained in activation energy and Arrhenius constant values when the models are compared with each other (Table 3). Linear least square correlation coefficients for the identified linear portions varied between 0.95 and 0.99 in all models studied.
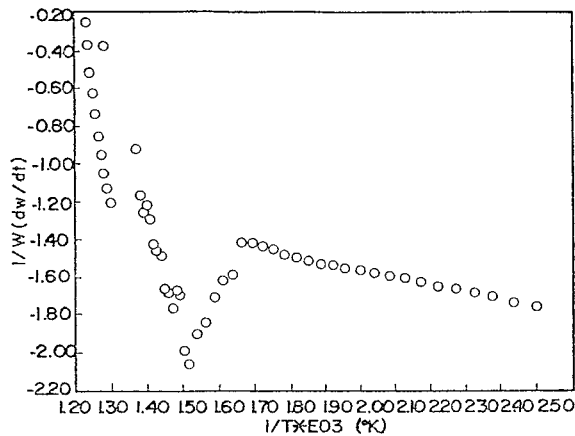
5. Conclusions

This research demonstrated that thermal characterisation of crude oils by thermal analysis is a novel technique. The following conclusions were derived from the research conducted.

Fig. 2. Arrhenius plot of crude oil 3 (unity method).

- In combustion of crude oils three distinct reaction regions were identified as LTO, FD and HTO.
- Kinetic parameters of the samples were obtained using six different models and it was observed that heavier oil exhibit lower activation energy, however higher activation energy values were obtained in HTO region as the °API gravity of crude oil decreased.

Table 3
Kinetic parameters of crude oils (E, kJ mol^{-1}; n, reaction order)

Crude oil	Kinetic parameter		Unity	Coats and Redfern	Ratio	Ingraham and Marrier	Freeman and Carroll	Flynn–Wall
Crude oil 1	n	LTO	1	1	1.04	1	1	1
		FD	1	1	0.96	1	1	1
		HTO	1	1	0.80	1	1	1
Crude oil 1	E	LTO	12.5	15.2	9.2	11.2	14.1	22.4
		FD	96	114	89	128	145	147
		HTO	228	242	232	274	289	332
Crude oil 2	n	LTO	1	1	1.18	1	1	1
		FD	1	2/3	1.10	1	1	1
		HTO	1	1	0.91	1	1	1
Crude oil 2	E	LTO	10.9	14.1	10.4	12.8	23.4	27.4
		FD	146	167	129	144	109	116
		HTO	263	269	260	274	300	231
Crude oil 3	n	LTO	1	1	1.14	1	1	1
		FD	1	2/3	0.61	1	1	1
		HTO	1	1	0.82	1	1	1
Crude oil 3	E	LTO	8.2	11.1	10.5	11.8	17.4	21.5
		FD	144	164	143	154	161	209
		HTO	288	292	275	267	312	324

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