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KINETIC ANALYSIS OF CRUDE OILS BY A WEIGHTED MEAN ACTIVATION ENERGY APPROACH

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Abstract

A weighted mean activation energy method was applied to describe the reactivity and combustibility of crude oils via simultaneous TG/DTG. Thermal experiments were conducted with a non-isothermal method at a heating rate of 10°C min^{-1} with excess air. Reaction rates increased progressively with increasing temperature. The rate data were fitted to an Arrhenius equation; the plots showed three distinct reaction regions. Weighted mean activation energies (E_{wm}), of the crude oils were calculated and a correlation was established between E_{wm}, API gravity and peak temperatures during high-temperature oxidation.

Keywords: activation energy, combustion, crude oil, differential scanning calorimetry, kinetics, thermogravimetric analysis

Introduction

Determination of the composition and kinetics of crude oils is of great importance for the petroleum industry. In the past few years, new methods for the evaluation of fuel samples have emerged which employ two thermal analysis techniques: thermogravimetric analysis (TG/DTG) and differential scanning calorimetry (DSC). Numerous researchers have used TG/DTG and DSC to investigate the effects of reservoir minerals on in-situ combustion [1–3]. Their results showed that crude oil combustion is catalysed by clays because of the increased surface area.

DSC and TG/DTG techniques have also been used as screening tools for in-situ combustion processes by several researchers [3, 4]. They have developed procedures to obtain the necessary kinetic and combustion parameters. The coal combustion experiments carried out by Smith *et al.* [5] indicated that the rate of coal combustion increased progressively with increasing temperature. The rate data were fitted to an Arrhenius equation; the plots showed four distinct regions of combustion. apparent activation energies were calculated for each region. Cumming [6], using

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the work of Smith *et al.* as the basis of his research, developed a method to describe the reactivity of combustibility of fuel samples, which he called 'a weighted mean activation energy'. He proposed that his method could supplant the method of Smith *et al.* which involves the used of several temperatures on the TG/DTG curve. It has been shown that the techniques of DSC and TG/DTG can usually be applied for the study of coals and crude oils. These applications range from routine characterization to pyrolysis, combustion and kinetic studies.

Experimental

A DuPont 9900 Thermal Analyzer with TG/DTG module was used. TG/DTG measures the amount and rate of change in mass of a sample, either as a function of increasing temperature or isothermally, as a function of time, in a varied but controlled atmosphere. A dynamic (non-isothermal) method was utilized with a heating rate of 10°C min^{-1} on a 10 mg sample in a flowing air atmosphere up to 800°C. Duplicate runs were made to ensure reproducibility. TG/DTG was calibrated for temperature readings with calcium oxalate monohydrate. It was also essential to calibrate the balance for bouyancy effects for the quantitative estimation of mass changes. The material chosen for the investigation of such effects was silver, which has a melting point of 960.8°C. The six crude oils analysed in this research were from Turkish oil fields, in the °API range 11–26. The properties of these crude oils are given in Table 1.

Results and discussion

The combustion kinetics of crude oils is extremely complex, but if certain broad generalizations are made, certain useful information can be deduced. Since the sample size is small and there is an excess air supply, the progress of the reaction is independent of the oxygen concentration. It is therefore reasonable to assume that the oxidation can be described by first-order kinetics. Thus, the following relationship holds;

$$\mathrm{d}W/\mathrm{d}t = A_\mathrm{r}\exp(-E/RT)\,W \tag{1}$$

Equation (1) can be put in the following form:

$$\log(1/W\,\mathrm{d}W/\mathrm{d}t) = \log A_\mathrm{r} - E/2.303RT \tag{2}$$

or

$$\log k = \log A_\mathrm{r} - E/2.303RT \tag{3}$$

where $\mathrm{d}W/\mathrm{d}t$=instantaneous rate of mass loss (mg/min.); W=mass of unburned material (mg); A_r Arrhenius constant (min^{-1}); E=activation energy (kJ mol^{-1}); R=universal gas constant (J g^{-1} mol K); and T=temperature (K).

In the plot of log*k* *vs.* $1/T$, there appear to be regions of marked linearity. The slopes of these linear portions are proportional to the activation energy, and the intercepts to the Arrhenius constant.

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 fuel. Therefore, the concept of weighted mean activation energy, E_{wm}, was applied to determine the overall reactivity of crude oils [6]:

$$E_{\mathrm{wm}} = F_1E_1 + F_2E_2 + F_3E_3 + \ldots\ldots + F_nE_n \tag{4}$$

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

Figure 1 shows the combined TG/DTG plot of B. Raman crude oil. Three distinct reaction regions were identified, as observed for most of the crude oils [7–9]. A reaction that occurred up to 660 K was the first reaction region; it was designated low-temperature oxidation (LTO). A second reaction region was observed between 660 and 750 K and was designated fuel deposition (FD). The final reaction of crude oils took place between 750 and 870 K, and was designated high-temperature oxidation (HTO). Figure 2 shows the log*k* *vs.* $1/T$ plot for B. Raman crude oil. For each crude oil, three reaction regions of marked linearity were identified. The linear least squares correlation coefficients for the identified linear portions varied from 0.89 to 0.98.

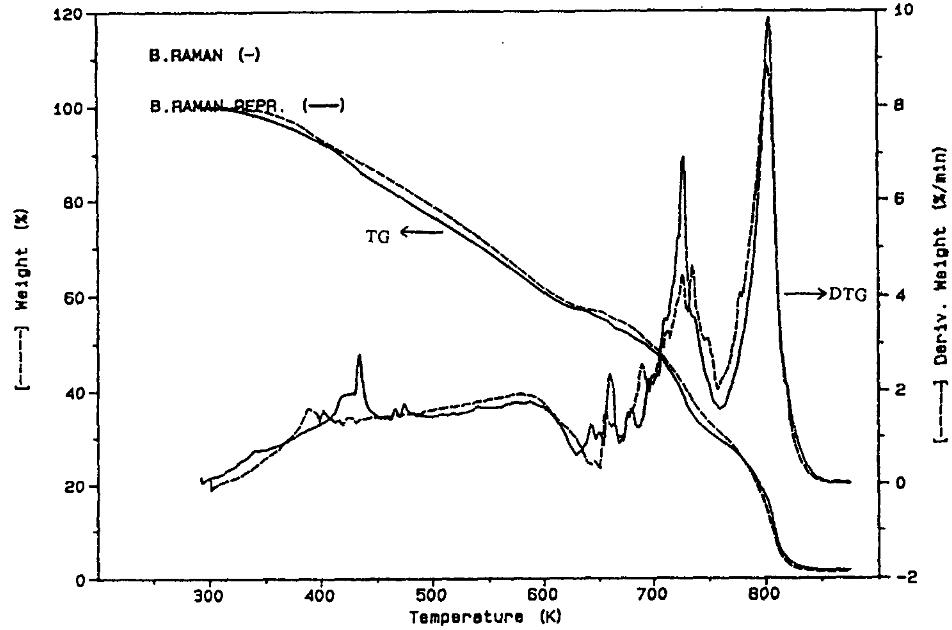

Fig. 1 TG/DTG of B. Raman crude oil (Orig. & Repr.)

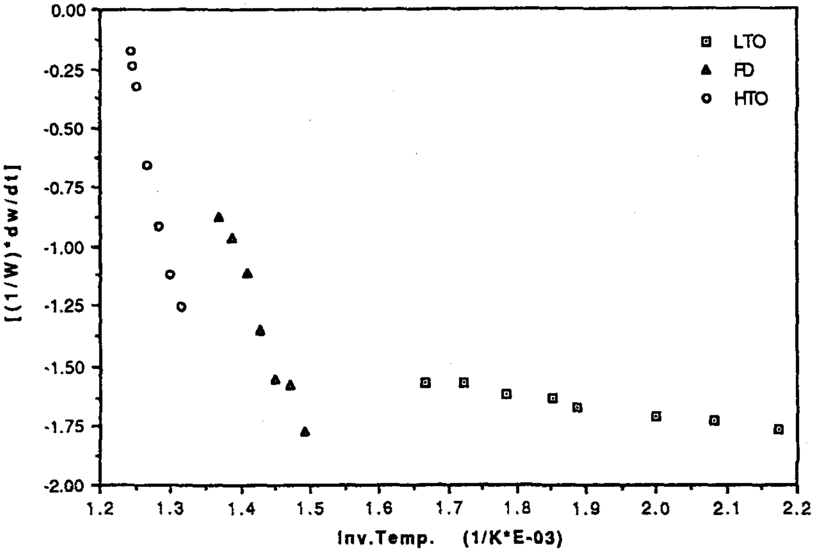

Fig. 2 Arrhenius plot of B. Raman crude oil

Apparent activation energies were determined from the slopes of the straight lines for each reaction region; the results are given in Table 2. Although these values define the apparent activation energies of the reaction regions, they do not identify the overall reactivities of the crude oils. To meet this requirement, weighted mean activation energies of the crude oils were calculated. The procedure for B. Raman crude oil is given below:

Mass loss over first region of Arrhenius linearity:
(Btw 390–590 K); 28.5% so $F_1=0.285$.
Therefore, $E_1F_1=8.2\times0.285=2.34$ kJ mol^{-1}.

Mass loss over second region of Arrhenius linearity:
(Btw 650–735 K); 17.2% so $F_2=0.172$.
Therefore, $E_2F_2=144\times0.172=24.76$ kJ mol^{-1}.

Mass loss over third region of Arrhenius linearity:
(Btw 750–845 K); 31.5% so $F_3=0.315$.
Therefore, $E_3F_3=288\times0.315=90.72$ kJ mol^{-1}.

The weighted mean activation energy of B. Raman crude oil is therefore $E_{\mathrm{wm}}=2.34+24.76+90.72=117.8$ kJ mol^{-1}.

The above treatment was applied to all the crude oils studied and the resulting E_{mw} values are given in Table 2. Peak temperatures (temperatures at which the rates of mass loss are maximum), asphaltene contents obtained by solvent extraction and amounts of material available for HTO from TG data are given in Table 1.

It can be seen from Figs 3 and 4 that definite correlations were obtained between the mean activation energies of crude oils and the °API gravities or peak temperatures. The mean activation energies of the crude oils increased as the °API gravities of the crude oils decreased.

Table 1 Properties of crude oils

Crude oil	API Gravity	Visc./cp	% Asphal.	Mater.(TG)	T_{peak}/K
Garzan	26.1	37	12	20	827
Raman	18.7	2260	28	28	814
B. Kozluca	15.9	7200	37	36	755
Camurlu	15.2	63880	26	–	792
B. Raman	12.9	51935	29	30	805
Ikiztepe	11.3	225250	28	–	775

Table 2 Apparent and mean activation energies of crude oils (kJ mol^{-1})

Crude oil	$T_{low\ oxid}$	Fuel deposition	$T_{high\ oxid}$	E_{mw}
Garzan	12.5	96.0	228.5	67.4
Raman	10.9	146.1	263.0	94.5
B. Kozluca	7.3	101.7	268.7	100.5
Camurlu	7.8	125.1	271.1	112.3
B. Raman	8.2	144.0	288.0	117.8
Ikiztepe	8.0	111.6	290.1	131.9

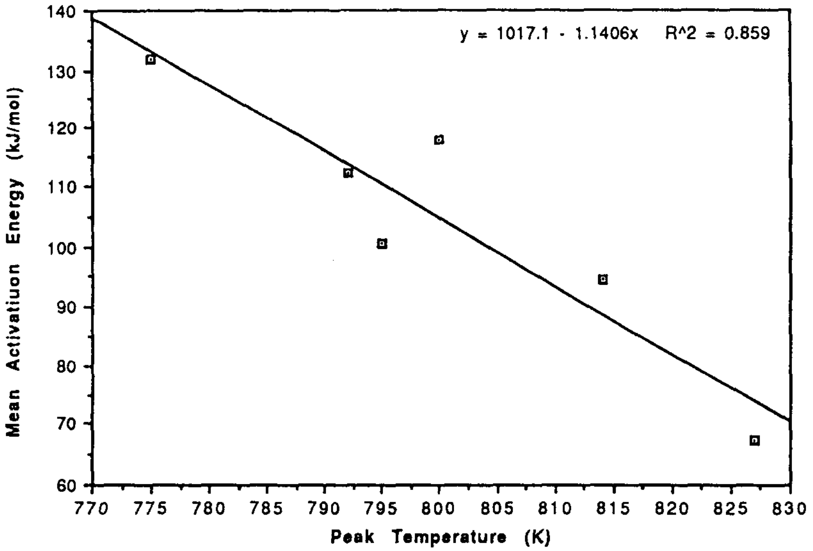

Fig. 3 Peak temp. *vs.* mean activation energy curve of crude oils

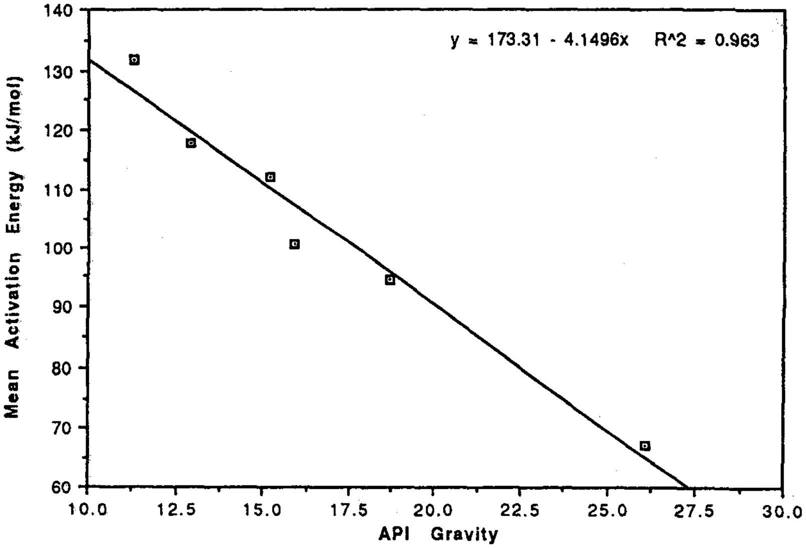

Fig. 4 API Gravity *vs.* mean activation energy curve of crude oils

Conclusions

Three distinct reaction regions were obtained for all of the crude oils analysed, designated the low-temperature oxidation, fuel deposition and high-temperature oxidation respectively. The overall reactivities of the crude oils were determined by using a weighted mean activation energy method. On the basis of this research, it was found that this is a reliable method for analysis of the overall kinetic data. The analysis of six crude oils with different °API gravities led to definite correlations between the mean activation energies of the crude oils and their °API gravities or peak temperatures.

References

1 S. Vossughi and O. Drici, Soc. Petroleum Eng., 8 (1982) 493.
2 S. Vossughi and O. Drici, Soc. Petroleum Eng., 10 (1985) 117.
3 S. Vossughi and O. Drici, J. Thermal Anal., 27 (1983) 17.
4 S. Vossughi and O. Drici, SPE Paper 11073.
5 B. Smith, Fuel, 60 (1981) 458.
6 J. W. Cumming, Fuel 63 (1984) 1436.
7 M. V. Kök and E. Okandan, Fuel, 71 (1992) 1499.
8 M. V. Kök and E. Okandan, Fuel, 73 (1994) 500.
9 M. V. Kök, Thermochim. Acta, 214 (1993) 315.