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High pressure TGA analysis of crude oils

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Abstract

A high pressure thermogravimetric analyser (HPTGA) has been used to explore the effect of total pressure (100, 200 and 300 psig) on the combustion behaviour and kinetics of crude oils. In combustion with air, three different reaction regions were identified, known as low-temperature oxidation, fuel deposition and high temperature oxidation. The Coats and Redfern procedure was applied to determine the kinetic parameters of the crude oils studied.

1. Introduction

Thermal analysis is defined as the measurement of the change in chemical or physical properties of a sample as a function of time or temperature. Although thermal analysis techniques (DSC, TGA and DTA) have been widely used during the last decade for the characterisation of minerals, clays, polymers, food and coal, their application in research related to the petroleum industry has been limited.

Attempts to use differential thermal analysis (DTA) to study crude oil combustion go back to 1959 when Tadema [1] showed that DTA curves obtained from the combustion of crude oil in the presence of sand showed two distinct regions of reaction. These two regions were called low and high temperature oxidation and started at around 220 and 350°C, respectively. Bae [2] investigated the thermo-oxidative behaviour of the fuel-forming properties of various crude oils. The results indicated that oils can be classified according to their oxidation characteristics. No complete correlation could

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be established between the viscosity, composition or density of the crude oil and the thermo-oxidative characteristics of the oil. Nickle et al. [3] observed the effect of oxygen partial pressure on crude oil combustion using pressurised differential scanning calorimetry (PDSC) on a crude oil of 9.3 API in oxygen partial pressures ranging from 0.02 to 2.8 MPa. They observed that increasing oxygen partial pressure sharpens the low temperature oxidation (LTO) and high temperature oxidation (HTO) peaks and shifts them to lower temperatures. Yoshiki and Philips [4] using DTA and TG at high temperatures and pressures from 0.1 to 6.9 MPa, concluded that both LTO and HTO rates increased with pressure as did the exothermicity of each. Belkharchouche et al. [5] used PDSC to obtain information on the magnitude and rate of the heat changes accompanying combustion of oil and oil core samples. They concluded from the experiments that the overall exothermicity of combustion increases with increasing total pressure and with oxygen partial pressure up to 34% of oxygen and observed that increasing the matrix surface area causes the LTO to become predominant. Philips et al. [6] used PDSC for an investigation of the pyrolysis and oxidation of Athabasca oil sands at pressures up to 6.9 MPa. No results were quoted on the effect of sand grain size. Indrijarso et al. [7] used PDSC to study the effect of sand particle size, pressure, oxygen partial pressure and carbon dioxide addition on the heat evolution during combustion of heavy oil/sand mixtures. They concluded that decreasing particle size and increasing pressure tended to increase the extent of LTO, thus favouring fuel lay-down. Drici and Vossoughi [8] applied DSC and TGA to crude oil combustion in the presence and absence of metal oxides. Vanadium, nickel and ferric oxides behaved similarly in enhancing the endothermic reactions. In the presence of a large surface area such as with silica, the surface reactions were predominant and unaffected by the small amounts of metal oxide present. Vossoughi and Drici [9] developed a kinetic model of the insitu combustion process from the TG and DSC data. They used a kinetic model to predict the fuel deposition and combustion rate in two combustion tube runs. Kok [10] applied DSC and TGA to characterise the pyrolysis and combustion properties of two heavy crude oils. In pyrolysis experiments, temperature ranges where distillation and visbreaking occur were identified. In combustion experiments, three different reaction regions were identified known as LTO, fuel deposition (FD) and HTO. Kinetic parameters were also determined using TGA and DSC curves. Indrijarso [11] studied the thermo-oxidative behaviour of crude oil oxidation under non-isothermal conditions using a modified pressurised micro-balance. Three major reaction regions were identified as distillation/LTO, cracking/first combustion and HTO/second combustion. The effects of heating rate, gas flow rate, total pressure, oxygen-enriched air and surface area of the sand have also been investigated.

2. Experimental

2.1. Equipment

Experiments were carried out using a Sartorius 4406 high pressure micro-balance which was constructed by modification of the commercial equipment. The Sartorius micro-balance was modified to permit operation up to 600 psi and 750°C at constant heating rates and under various gas flow conditions.

2.2. Samples

Crude oils used in this present study were from different origins (Venezuelan, Huntington Beach and Garzan) with ° API gravities of 12, 18.5 and 26.7 respectively. Detailed properties of the crude oils are listed in Table 1.

2.3. Procedure

The experimental procedure involves placing 15 mg of sample in the sample holder, setting the heating rate and flow rate of the purge gas (air), then commencing the experiment. All experiments were performed at a linear heating rate of 10°C min^{-1} over the temperature range of 25–600°C with a gas flow rate of 100 ml min^{-1} within the total pressure range of 100–300 psig. Prior to experiments, the HPTGA was calibrated for temperature readings and buoyancy effects. In order to assess the reproducibility, experiments were performed twice. Fig. 1 shows a schematic diagram of the thermobalance; details of the design and operating conditions are given elsewhere [11].

3. Results and discussion

In this research, a sequence of pressurised thermogravimetric analysis (HPTGA) experiments was carried out to explore the effect of total pressure (100, 200 and 300 psig) on the combustion behaviour and kinetics of crude oils.

3.1. Combustion experiments

Although crude oils are complex mixtures with widely varying physical properties, they undergo similar reactions when heated. In an oxidative environment, three distinct reaction regions were identified in all the crude oils studied (Fig. 2). A reaction

Table 1
Properties of the crude oils studied

Properties	Venezuela	H. Beach	Garzan
° API gravity	12.2	18.5	26.7
Viscosity/cp	3700	1740	37
C/%	n.a.	84.33	85.55
H/%	n.a.	11.31	11.7
N/%	n.a.	0.82	n.a.
S/%	n.a.	1.9	n.a.

n.a., not available.

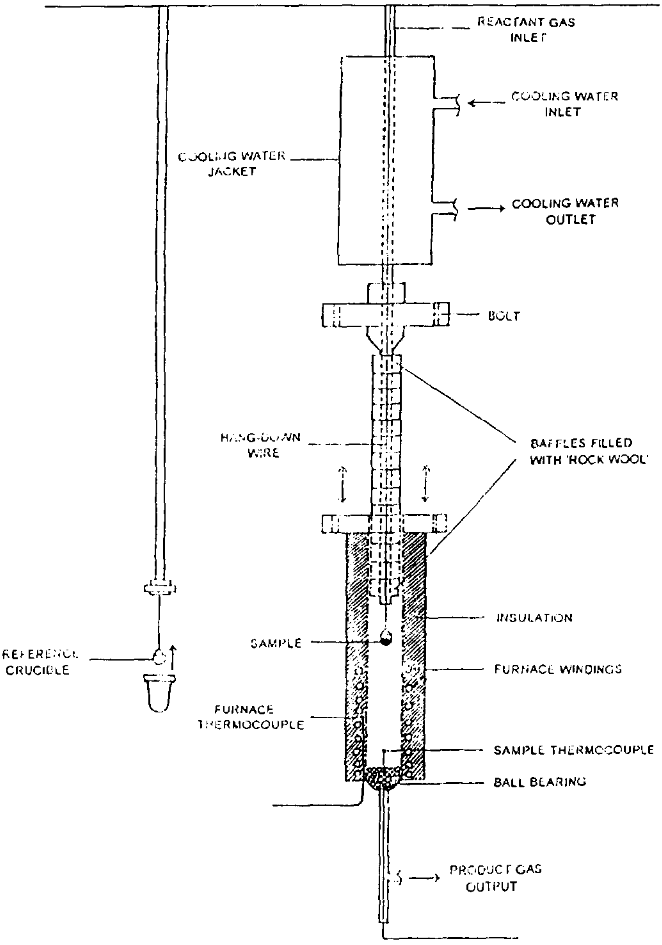

Fig. 1. Schematic of the thermobalance special attachment.

up to 320°C was actually the first reaction, called the low temperature oxidation, LTO. A second transition zone takes place between 320 and 410°C and is called fuel deposition, FD. The final reaction of the crude oil inferred from the thermograms takes place between 410 and 555°C and is called the high temperature oxidation, HTO. The effect of total pressure on the reaction regimes was observed qualitatively within the range of 100–300 psig. All the reaction regimes shifted from low to higher temperature regions as the total pressure was increased in all the crude oils studied. Reaction intervals of the crude oils at various total pressures are given in Table 2.

The main characterisation points in the TGA thermograms are the peak and burn-out temperatures. Peak temperatures represent the maximum rates of weight loss; burn-out temperatures indicate where sample oxidation is complete. Peak and burn-

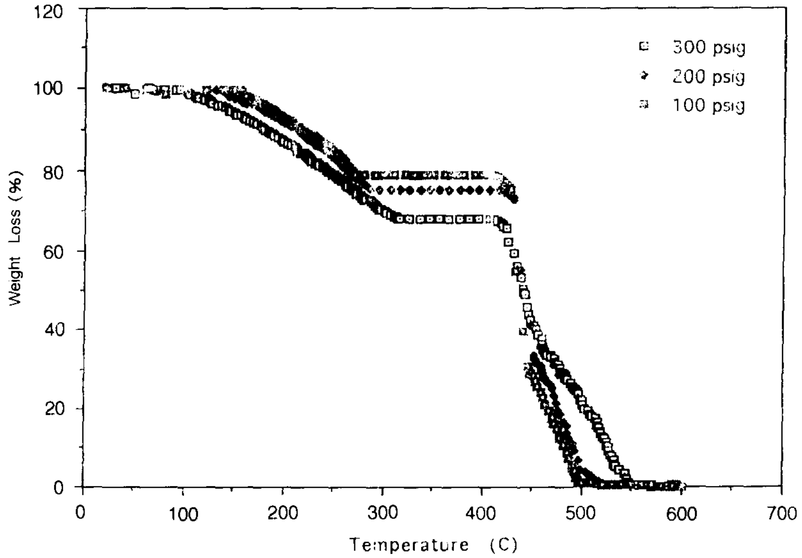

Fig. 2. Weight loss vs. temp. thermogram of Huntington Beach crude oil.

Table 2
Reaction intervals of the crude oils in °C

Crude oil	Pressure/psig	LTO	FD	HTO
Venezuela	100	25–300	300–360	360–495
	200	25–310	310–375	375–520
	300	25–315	315–405	405–530
H. Beach	100	25–290	290–410	410–500
	200	25–295	295–420	420–520
	300	25–315	315–425	425–545
Garzan	100	25–295	295–405	405–500
	200	25–305	305–410	410–515
	300	25–320	320–415	415–555

out temperatures of the crude oils at various total pressures are given in Table 3. It can be concluded that as the total pressure increased, peak and burn-out temperatures were increased and, as expected, heavier oils exhibited lower burn-out temperatures at each pressure.

It was observed that as pressure increased the weight loss percentage in the low temperature oxidation region increased, causing less reactant to be available for cracking at higher temperature. The percentage weight losses in reaction regions within each pressure range are listed in Table 4.

Table 3
Peak and burn-out temperatures of the crude oils in °C

Crude oil	Pressure/psig	Peak temp.	Burn-out temp.
Venezuela	100	430	495
	200	432	520
	300	434	530
H. Beach	100	431	500
	200	433	520
	300	438	515
Garzan	100	434	505
	200	449	515
	300	470	555

Table 4
Weight loss data of the crude oils in %

Crude oil	Pressure/psig	LTO	FD	HTO
Venezuela	100	17.06	0.14	82.80
	200	18.92	0.12	80.96
	300	20.06	0.10	79.84
H. Beach	100	21.00	0.16	78.84
	200	24.88	0.14	74.98
	300	31.77	0.10	68.13
Garzan	100	22.09	0.09	77.82
	200	28.68	0.07	71.25
	300	36.18	0.08	63.74

3.2. Kinetic analysis

Weight loss kinetics during combustion is a complex phenomenon since numerous components and species are simultaneously oxidised. As expected, combustion reactions for crude oils are highly complex, therefore the kinetic data calculated should be regarded as apparent data representing complex and consecutive reactions. In this research solid phase thermal decomposition is described by the following rate expression [12]

$$dx/dt = k(1-x)^n$$

$$x = (W_0 - W_t)/(W_0 - W_f)$$

$$k = Ae^{-E/RT}$$

where k is the rate constant, n the order of reaction, W_0 the initial sample weight, W_t the sample weight at time t, W_f the final weight, A the Arrhenius constant, E the activation

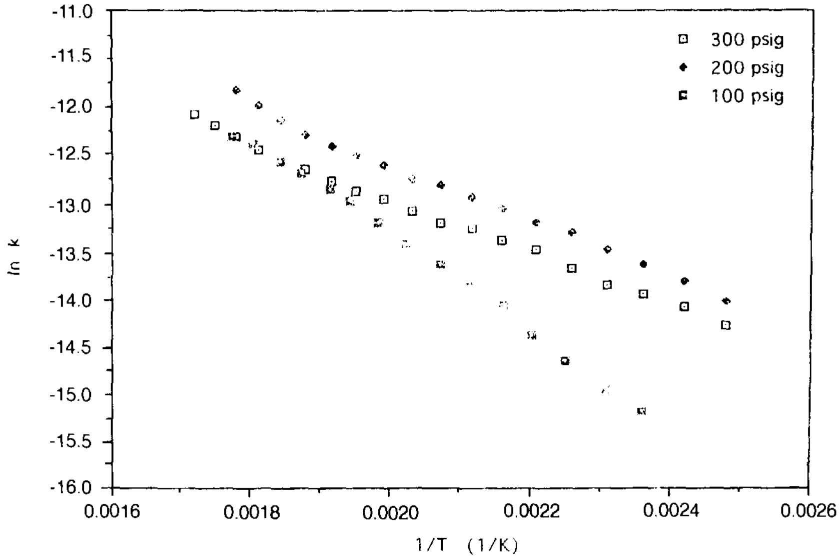

Fig. 3. Arrhenius plot of Huntington Beach crude oil at various pressures, LTO region.

energy, R the gas constant, and T absolute temperature for a linear heating rate, $b = \mathrm{d}T/\mathrm{d}t$. By combining the above equations, rearranging, integrating and taking the natural logarithm and assuming $n = 1$, we obtain

$$\ln[-\ln(1-x)/T^2] = \ln(AR/bE)[1-(2RT/E)] - (E/R)\,1/T$$

A plot of $\ln[-\ln(1-x)/T^2]$ vs. $1/T$ should result in a straight line of slope $= E/R$. The value of E obtained graphically is substituted in the above equation to calculate the Arrhenius constant, A. Typical plots to obtain apparent activation energies are shown in Figs. 3 and 4. Activation energy values obtained for low temperature and high temperature oxidation regions at 100 psig are given in Table 5. No effect of pressure was observed on the kinetic parameters.

Table 5
Kinetic parameters of the crude oils ($E = \mathrm{kJ\ mol^{-1}}$)

Crude oil	E(LTO)	c.c.	E(HTO)	c.c.
Garzan	22.6	0.995	99.6	0.981
H. Beach	23.9	0.992	77.9	0.963
Venezuela	41.1	0.995	97.1	0.988

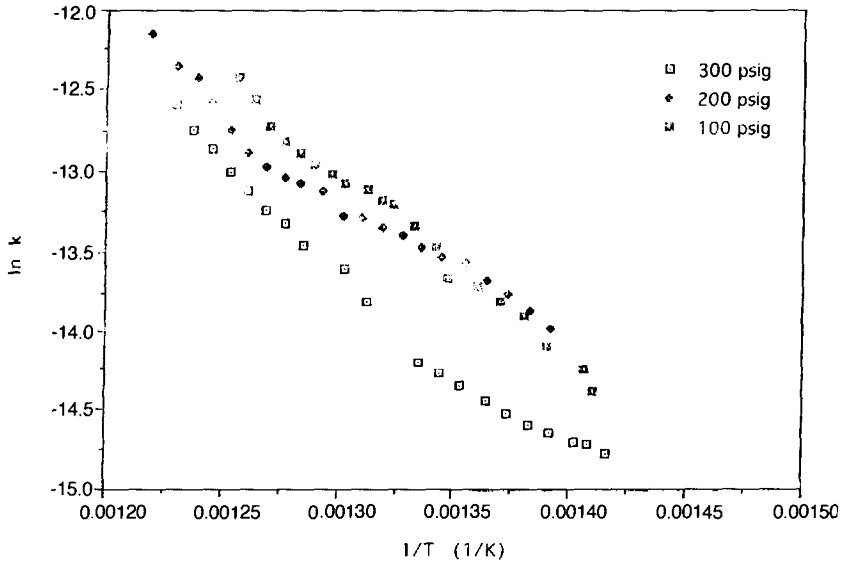

Fig. 4. Arrhenius plot of Huntington Beach crude oil at various pressures, HTO region.

4. Conclusions

A high pressure thermogravimetric analyser was used to study crude oil oxidation under pressurised conditions. Three different reaction regions were observed from the thermograms in an oxidising environment subjected to a constant heating rate. These were low temperature oxidation, fuel deposition and high temperature oxidation reaction regions. The Coats and Redfern method was used to obtain the kinetic parameters. Activation energies of the low and high temperature oxidation reactions were calculated to be in the range of 22.6–41.1 kJ mol^{-1} and 77.9–99.6 kJ mol^{-1} respectively.

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