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# COMBUSTION CHARACTERISTICS OF CRUDE OIL-LIMESTONE MIXTURES

## High pressure thermogravimetric analysis and their relevance to in-situ combustion

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## Abstract

High pressure thermogravimetric analysis (HPTG) was used in order to study the oxidation of crude oil in a porous medium under pressurised conditions for simulation of in-situ combustion during oil recovery. Three distinct reaction regions were observed from the HPTG curves in an oxidising environment subjected to a constant heating rate. These were low temperature oxidation, fuel deposition and high temperature oxidation. The method of Coats and Redfern was used to obtain kinetic parameters and the results are discussed.

**Keywords:** combustion, crude oil, kinetics, thermogravimetric analysis

## Introduction

The application of thermal energy to petroleum reservoirs as a means of increasing crude oil recovery has been given a great deal of attention and improved thermal methods are continuously to be developed. The thermal energy may be introduced from the surface in the form of either hot water, oil, gases or steam. It may also be generated in-situ by burning a part of the oil in the underground reservoirs, a process known as in-situ combustion. In-situ combustion is a complex process which involves simultaneous heat and mass transfer in a multiphase environment coupled with chemical reactions belonging to crude oil combustion. While much work has been carried out to study the thermal and fluid dynamics aspects of the in-situ combustion process, the combustion characteristics in limestone's containing crude oil remain the least investigated aspect. Thermal analysis techniques, such as differential scanning calorimetry (DSC), thermogravimetry (TG) and differential thermal analysis (DTA) have been used in the petroleum industry to identify the combustion and pyrolysis characteristics of crude oils. Although various authors have pointed out the potential of different techniques of thermal analysis, studies on the quantitative and qualitative description of the combustion characteristics and kinetics involved in burning crude oil using thermal analysis techniques have been limited.

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Nevertheless, attempts have been made to use thermal analysis methods in connection with crude oil combustion. Tadema [1] described the existence of two main reactions resulting from combustion of mixtures of various oils and sands. Bausaid [2] measured the reaction rate between carbon and oxygen in porous media. His results indicated first order dependency of the carbon combustion rate with respect to both carbon concentration and oxygen partial pressure. Burger and Sahuquet [3] studied the kinetics of oxidation reactions involved in in-situ combustion but did not present a kinetic model in the form that would enable the prediction of the in-situ combustion parameters. Dabbous and Fulton [4] investigated the kinetics of low temperature oxidation (LTO) of crude oils in porous media and indicated that the reaction order with respect to oxygen was between 0.5 and 1. However the order of reaction was dependent on the crude oil and not on the porous media. Verkocy and Jha [5] performed experiments on heavy oils and on cores. They have estimated kinetic and thermochemical data for analysis, low temperature oxidation, cracking, coking and combustion reaction in cores and oils. Bae [6] studied the thermo oxidative behaviour of crude oils. He indicated that the amount of heat generated by the low temperature oxidation depends on the specific crude oil. No attempt was carried out to determine reaction order or heat value in his study. Drici and Vossoughi [7] used DSC to investigate the effects of the surface area on crude oil combustion. The experiments were conducted on crude oil alone and in the presence of clays, silica and alumina with variable surface areas and they concluded that the surface area has an effect on the shape the curve. Nickle *et al.* [8] observed the effect of the oxygen partial pressure on crude oil combustion using pressurised differential scanning calorimetry (PDSC). They concluded that increasing oxygen partial pressure sharpens the low temperature and high temperature oxidation peaks and shifts them to lower temperatures. Kök and Okandan [9] determined the kinetic parameters of in-situ combustion by tubular reactor and thermogravimetric experiments. Three reaction regions for combustion of crude oil in porous media were observed in these experiments and are defined as low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO). Belkharchouche *et al.* [10] used PDSC to obtain information on the magnitude and rate of the heat changes accompanying combustion of oil and oil core samples and concluded from the experiments that the overall exothermicity of combustion increases with increasing total pressure and with increase of the oxygen partial pressure up to 34% of oxygen. They also observed that increasing the matrix surface area causes the LTO to become predominant. Indrijarso *et al.* [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/low temperature oxidation, cracking/first combustion and high temperature oxidation/second combustion. The effect of heating rate, gas flow rate, total pressure, oxygen-enriched air and surface area of the sand has also been investigated.

## Experimental

Experiments were carried out using a Sartorius 4406 high pressure microbalance which was constructed by modification of the commercial equipment. The

**Table 1** Properties of crude oils

| Properties | Venezuela | H. Beach | Garzan |
|---|---|---|---|
| API Gravity | 12.2 | 18.5 | 26.7 |
| Viscosity (cp) | 3700 | 1740 | 37 |
| C (wt%) | n.a | 84.33 | 85.55 |
| H (wt%) | n.a | 11.31 | 11.7 |
| N (wt%) | n.a | 0.82 | n.a |
| S (wt%) | n.a | 1.9 | n.a |

n.a: not available.

**Table 2** Properties of limestone and sandstone

| Limestone | | Sandstone | |
|---|---|---|---|
| Calcite (wt%) | 92.0 | silica (wt%) | 97.0 |
| Dolomite (wt%) | 6.6 | iron-alum. (wt%) | 2.1 |
| Quartz (wt%) | 1.2 | calcium (wt%) | 0.7 |
| Kaolinite (wt%) | 0.2 | salts (wt%) | 0.01 |
| Mesh size | –60 | mesh size | –60 |
| Porosity (vol%) | 20 | porosity (vol%) | n.a |

n.a: not available.

Sartorius microbalance was modified in order to permit operation up to 600 psi and 750°C at constant heating rates and under various gas flow conditions. Crude oils used in this present study were from different origins (Venezuela, Huntington Beach and Garzan) with °API gravities of 12.0, 18.5 and 26.7 respectively. Detailed properties of the crude oils and the limestone/sandstone matrix are given in Tables 1 and 2 respectively. The experimental procedure involves placing 15 mg of sample into the sample holder, setting the heating rate and flow rate of purge gas (air), then commencing the experiment. All experiments were performed at a linear heating rate of 10°C $\text{min}^{-1}$ over the temperature range of 25–600°C with a gas flow rate of 100 ml $\text{min}^{-1}$ within the total pressure range of 100–300 psi. Prior to the experiments the HPTG instrument was calibrated for temperature readings and buoyancy effects. In order to assess the reproducibility, experiments were performed twice. Figure 1 shows a schematic diagram of the thermobalance where the details of the design and operating conditions are given elsewhere [11].

## Results and discussion

In this research, high pressure thermogravimetric analysis (HPTG) experiments were carried out to determine the combustion and kinetic properties of crude oil-limestone mixtures in order to simulate the in-situ combustion process.

Theoretically, combustion of oil can be initiated whenever oxygen comes in contact with fuel. However, the temperature, composition of the fuel and the oxygen

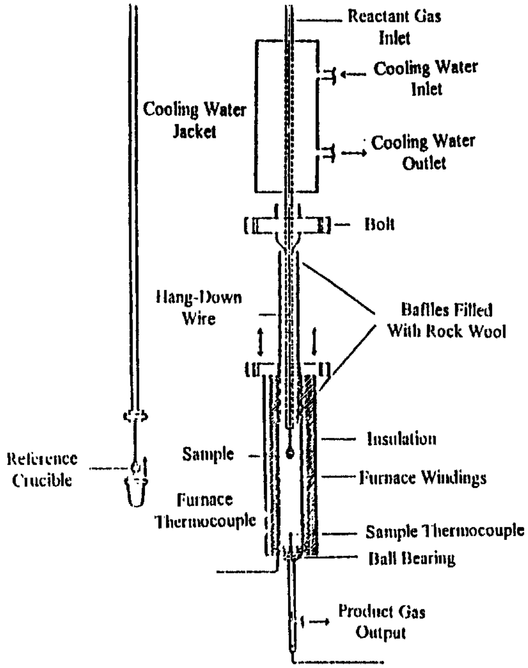

Fig. 1 Schematic diagram of high pressure TG equipment

supply dictate the nature of this reaction. In combustion with air, three distinct reaction regions were identified in all crude oil-limestone mixtures studied (Fig. 2). A reaction up to 350°C was actually the first region and called as LTO. Low temperature oxidation reactions are characterised by low levels of carbon oxides in the effluent gas stream, and low peak temperatures. This reaction rate is proportional to the specific surface area of the matrix. A second reaction region takes place be-

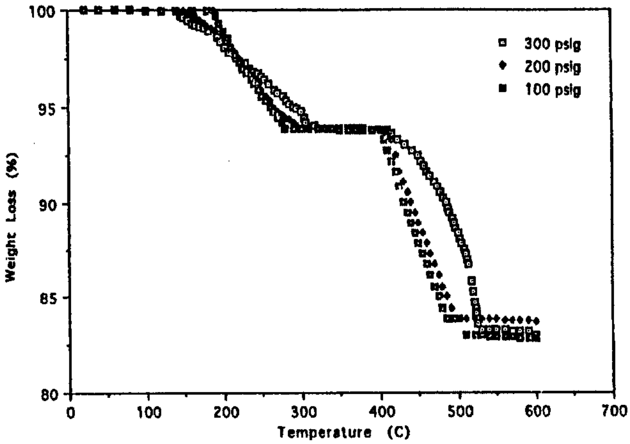

Fig. 2 Mass loss *vs*. *T* curve of H. Beach crude oil+limestone

**Table 3** Reaction interval (°C) of crude oil+matrix in air at different pressures (psi)

| Crude oil | Pressure (psi) | 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 |
| H. Beach (Sst) | 100 | 25–320 | 320–405 | 405–515 |
| | 200 | 25–325 | 325–410 | 410–520 |
| | 300 | 25–330 | 330–415 | 415–530 |

tween 350–435 °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 HTO, which takes place between 435–540 °C contributes most of the exothermic heat of reaction when crude oil/matrix is heated in an oxidising environment. Reaction intervals of the crude oil/limestone mixtures at various total pressures are presented in Table 3. The effect of the total pressure on the reaction regimes was observed qualitatively within the range of 100–300 psi. All the reaction regions shifted to higher temperatures as the total pressure increased. Low temperature and high temperature oxidation inter-

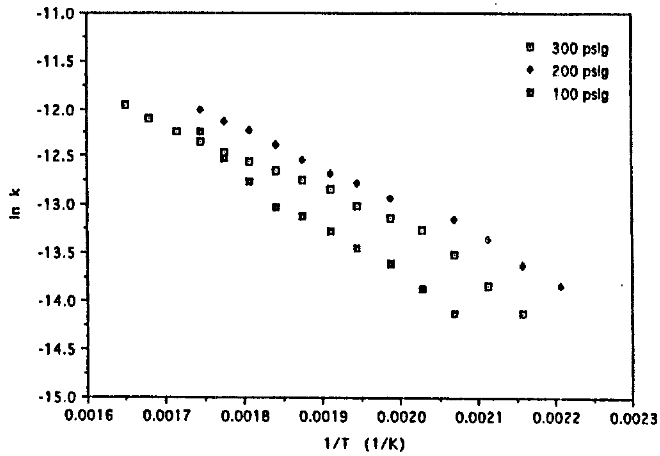

**Fig. 3** Arrhenius plots of H. Beach crude oil+limestone at various pressures-LTO region

vals occurred at higher temperatures when the total pressure increased from 100 to 300 psi. As the crude oil gravity increased reaction zones occurred at higher temperatures at 300 psi. In order to see the effect of the matrix on the combustion properties of crude oils at different pressures, experiments with Huntington Beach also were performed in a sand mixture under the same experimental conditions. Compared to crude oil/limestone experiments the low temperature oxidation reaction seems to correspond with a higher temperature region, and the high temperature oxidation reaction to a somewhat lower temperature region which may be due to the different porosities of the matrices.

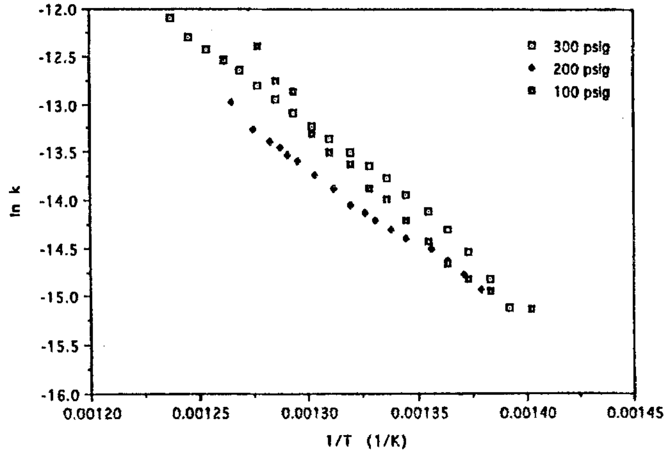

Fig. 4 Arrhenius plots of H. Beach crude oil+limestone at various pressures-LTO region

Mass loss kinetics during combustion is a complex phenomenon since numerous reactions proceed simultaneously. 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 the oxidation reactions are described by the following rate expression:

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

$$x = (W_0-W_t)/(W_0-W_f) \quad (2)$$

$$k = Ae^{-E/RT} \quad (3)$$

where: $k$ – rate constant, $n$ – order of reaction, $W^0$ – initial sample weight, $W_t$ – sample weight at at time $t$, $W_f$ – final weight, $A$ – pre-exponential factor, $E$ – activation energy, $R$ – gas constant, $T$ – absolute temperature.

For a linear heating rate: $b=dT/dt$.

By combining above equations, rearranging, integrating and taking the natural logarithm and by assuming $n=1$, we obtain the Coats and Redfern equation [12].

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

A plot of $\ln[\ln(1-x)T^2]$ *vs.* $1/T$ should result in a straight line of slope$=-E/R$. Typical plots to obtain the apparent activation energies are shown in Figs 3–4, whereas the activation energy values obtained for the low temperature and high temperature oxidation regions are given in Table 4 for the different total pressures.

**Table 4** Kinetic parameters of crude oil+matrix ($E$=kJ mol$^{-1}$)

| Crude oil+mat. | $E$ (LTO) | c.c | $E$ (HTO) | c.c |
|---|---|---|---|---|
| Garzan+limest. | 32.2 | 0.979 | 151.5 | 0.987 |
| H. Beach+limest. | 31.8 | 0.994 | 133.8 | 0.993 |
| Venez+limest. | 31.3 | 0.996 | 122.4 | 0.988 |
| H. Beach+sandst. | 44.4 | 0.985 | 192.1 | 0.989 |

## Conclusions

High pressure thermogravimetric analysis (HPTG) was successfully employed to study of crude oil oxidation under pressurised conditions and at high temperatures in a porous medium corresponding to in-situ combustion oil recovery. Three distinct regions were observed in the HPTG curves in an oxidising environment. These were low temperature oxidation (LTO), fuel deposition (FD), and high temperature oxidation (HTO) regions. The method of Coats and Redfern was used to obtain kinetic parameters. Activation energies of the low temperature and high temperature oxidation reactions were calculated to be in the range of 31.3–44.4 kJ mol$^{-1}$ and 122.4–192.1 kJ mol$^{-1}$ respectively.

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