

Investigation of Auto Ignition Condition under Different Parameters

Razzaghi, Samaneh

Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, I.R. IRAN

Kharrat, Riyaz^{*+}

Petroleum University of Technology, Petroleum Research Center, Tehran, I.R. IRAN

Rashtchian, Davood

Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, I.R. IRAN

Vossoughi, Shapour

Lawrence, KS 66045-7609, Kansas University

Saraji, Soheil

Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, I.R. IRAN

ABSTRACT: *In this work, the potential of auto-ignition of heavy oil during in-situ combustion (ISC) process was studied. Kinetic studies were carried out using Thermo Gravimetric Analyzer (TGA), Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetric (ARC) techniques. Effects of oxygen partial pressure, reservoir pressure and clay on auto ignition condition were investigated on a number of different heavy oil samples from south west Iran mixed with silica sand or crushed carbonate rock and clay. Based on the experimental results obtained by TGA runs, the kinetic equation was derived for different oil samples in the presence of different sands. Effect of partial pressure of oxygen in the injected air was studied. Results showed that at atmospheric pressure, the peak of low temperature combustion (LTC) by producing CO was initiated at 300 °C when air was injected. Also, enriching the injected air by oxygen lowers the LTC by up to 50 °C. When the experiments were extended to reservoir pressure of 1300 psi, it was found that activation energy in the LTC region was lowered. As a result, initiation of LTC was started at 115 °C when air was injected. The DSC experiments, under non-isothermal condition showed that increasing the oxygen partial pressure resulted in more heat being evolved during the high temperature combustion reactions. Also, the effect of clay as a catalyst was studied and it was found that the activation energy decreases considerably when clay is present in the system. The decrease in activation energy was from 359 to 149 kJ/gmole for one sample.*

KEY WORDS: *In situ combustion, Kinetic, Heavy oil, Auto-ignition.*

^{*} To whom correspondence should be addressed.

⁺ E-mail: Kharrat@put.ac.ir

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INTRODUCTION

In planning oil recovery by In Situ Combustion (ISC), one problem is how to ignite the oil formation in the injection well. A satisfactory ignition is of prime importance in initiating a successful in-situ combustion process. Many different devices have been developed and employed to achieve ignition safely and efficiently. Ignition devices are divided into two categories:

1- External heat injection which includes electric or gas heating and hot fluid injection to supply heat mainly through the well bore to the ignition zone.

2- Internal heat generation which includes spontaneous ignition and chemical ignition, and which generates heat completely within the ignition zone itself.

This can be achieved by injecting an easily reacting chemical compound prior to injecting air or by initiating auto ignition in the oil formation by changing the oxygen content of the air. For auto ignition to be favoured in a well the behaviour of the oil-containing strata surrounding the air injection point should be approximate to adiabatic; that is heat generated by chemical reaction should be greater than heat lost to the surroundings. Fig. 1 shows a schematic interpretation of the potential for auto ignition to occur at an enriched air injection point in an oil well. Oil will be oxidized at the enriched oxygen concentrations used the oxidation reactions being weakly exothermic.

Under the adiabatic conditions, the heat generated by this oxidation (H_R) is greater than the heat lost (H_L) due to contact with the reservoir surroundings. As a consequence the temperature in the region of the injection point will slowly increase. Eventually the temperature will reach the 300 °C region and the low temperature combustion (LTC) reactions will be initiated. These will result in a much more rapid and increased rate of heat release. The temperature will rise and eventually the conditions for the high temperature (HTC) reactions will occur initiating the 'in-situ combustion' process. The overall process is termed 'auto ignition' [1].

Several theoretical and experimental studies have been reported in the literature concerning the kinetics and auto ignition of the in-situ combustion process. *Shoeppel* [2] proposed a mathematical approximation of the field conditions by using a radial model and determined temperature and oxygen concentrations as a function of radius and time.

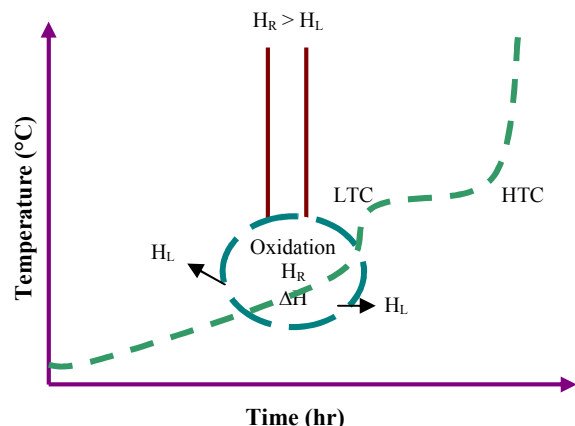


Fig. 1: Schematic interpretation of auto-ignition process at enriched air injection point.

Tadema and Weijdem [3] calculated the ignition time of oil sand on the basis of measured oxidation rates of the crude oil. *Burger* [4] constructed a numerical model for computing the ignition conditions (ignition delay and position of the ignition zone) as a function of reservoir, oil and gas flow characteristics. *Fassihi et al.* [5] identified three groups of reactions, namely low temperature oxidation (LTO), medium (MTO) and high temperature (HTO) reactions. *Hughies et al.* [6] observed activation energy of the high temperature oxidation reaction decreased with increasing surface area of the solid. Their observations showed that as the partial pressure of oxygen was reduced to below 0.1 bar, it resulted in a sharp increase in the overall activation energy. Decreasing the oxygen partial pressure caused the peak burning temperature to increase. They also performed a number of thermogravimetric experiments and found values of the activation energy to vary from 100 to 350 kJ/gmol while the order of reaction with respect to fuel concentration varied from 0.7 to 1.7. *Vossoughi and El-Shoubary* [7] identified three major reactions from TGA thermograms. A kinetic model derived for the HTO reaction regime by using the power law. Linear regression of the data points produced values of 123.5 MJ/kmol and 5.18×10^{-7} (kPa.hr)⁻¹ for the activation energy and frequency factor, respectively. *Kok and Keskin* [8] investigated the thermal characteristics and combustion kinetics of three crude oils using the TGA/DTG techniques. They observed that the heavier the oil the lower the activation energy in the LTO region. However, higher activation energy values were obtained for the HTO region as the °API gravity of crude oil decreased.

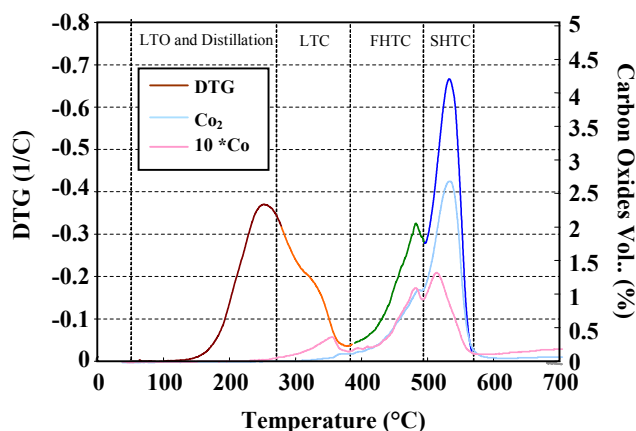


Fig. 2: Typical DTG plot for heavy oil sample a-2.

Classification of Reaction Regions

Combustion of crude oil in porous media is not a simple reaction but follows several consecutive and competing reactions occurring through different temperature ranges [5]. Generally, in order to simplify the studies, investigators have traditionally grouped these competing reactions into three classes:

- (1) low temperature oxidation (LTO),
- (2) intermediate temperature, fuel formation reactions,
- (3) high temperature oxidation (HTO) or combustion of the solid carbonaceous residue (coke).

In this paper, the temperature ranges are classified in a new order (Figs. 2 and 3) as:

- 1- Distillation and low temperature oxidation (LTO), temperatures below 250°C.
- 2- Low temperature Combustion (LTC), temperatures between 250-300 °C.
- 3- High temperature Combustion (HTC), temperatures between 400-600 °C.

In most papers there is confusion between the LTO and LTC regions. Previously, the low temperature oxidation was said to occur at temperatures below 400 °F (200 °C) and yield water and partially oxygenated hydrocarbons such as carboxylic acids, aldehydes, ketones, alcohols, and hydroperoxides [9] and could not be distinguished in TGA/DTG thermograms.

Nonetheless, LTO can be identified from the appropriate endothermic section of the corresponding DSC trace. However, as can be seen in Figs. 2 and 3, LTC occurs above 250 °C and is a combustion process since the combustion products CO and CO₂ are evolved.

High temperature combustion includes fuel deposition and coke combustion reactions. It sometimes can be

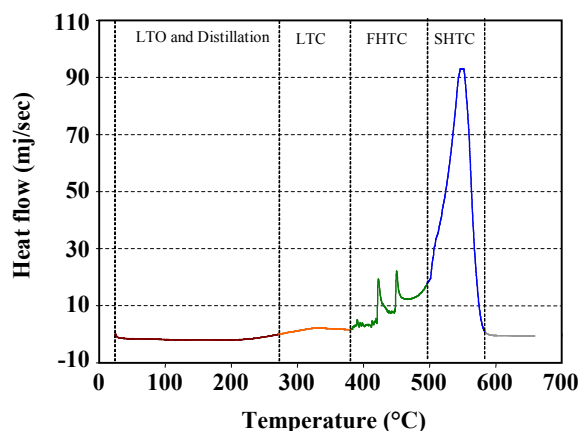


Fig. 3: Typical DSC plot for heavy oil sample a-2.

distinguished as two peaks: first high temperature combustion (FHTC) and second high temperature combustion (SHTC). Fig. 2 shows a typical DTG thermogram and identifies the four reaction zones.

Kinetic Model

Thermogravimetry analyzer and differential scanning calorimetry methods are used to study the kinetic of a chemical reaction and determine basic kinetic constants such as the reaction rate constant, activation energy, order of the reaction, and frequency factor.

The reaction rate constant, K, was calculated at each part by reaction kinetic model below:

$$\text{Reaction rate} = -\frac{d\alpha}{dt} = K \cdot \alpha^n \cdot P_{O_2}^m \quad (1)$$

Where:

$$\alpha = \frac{(w - w_f)}{(w_i - w_f)} \quad (2)$$

$$P_{O_2} = y_{O_2} \cdot P_{inj}, \text{ kPa} \quad (3)$$

$$d\alpha/dt = DTG, \text{ s}^{-1} \quad (4)$$

As the activation energy for a reaction is essentially independent of temperature, a plot of Log (K) versus 1/T is a straight line with slope of -E/R, hence the value of E can be determined. The Arrhenius equation gives:

$$K = F \cdot \exp\left(\frac{-E}{RT}\right) \quad (5)$$

Since the frequency factor F is temperature dependent, the value of F at a particular temperature, T, can be calculated via:

$$\text{Log}(F) = \text{lig}(K_T) + E/RT \quad (6)$$

This current kinetic study of in-situ combustion was undertaken in order to:

- Obtain modeling parameters including the Arrhenius activation energy (E) and the frequency factor (F) for the crude oils investigated.
- Identify the reaction regimes of a particular crude oil as discussed in the previous section.
- Determine the possibility of spontaneous ignition, if the crude oil is kept in contact with air or enriched air at the reservoir temperature.

EXPERIMENTAL

Experimental Set-Up

A Thermal Analysis© model SDT2960 thermogravimetric analyzer (TGA) and a Polymeric Laboratories Thermal Science Divisions©, Model Single differential scanning calorimeter (DSC) equipped with a temperature programmer and a X-Y recorder were used to investigate the thermal characteristics of the crude oil under study as shown in Fig. 4. The TGA unit produced a derivative thermogram simultaneously with the weight loss thermogram. Analysis of the TGA effluent gas as well as the effluent gas in-situ combustion runs was carried out using a non-dispersive Infra Red analyzer (IR).

An Accelerating Rate Calorimeter (ARC) consists of the calorimeter unit with the sample-holder, a power, thermal control, and main processor units. The main processor is used to enter parameter values and control the experiment. It also processes the results to obtain kinetic and thermal values. Further analysis of results is performed on a Pentium-PC using a special software package. The two ARC systems at the university of Calgary have been extensively and specially modified for reliable operation up to 6,000 psi, while tracking highly exothermic combustion reactions. They use specially developed sample holders, made of Hastelloy-C weighing approximately 24.3 gm. To investigate the effect of pressure on auto ignition, ARC studies were carried out on two heavy oil samples.

Experimental Procedure

To investigate Auto-Ignition Temperature in heavy oil reservoirs, two sets of experiments were carried out by Thermogravimetric Analyzer (TGA), Differential Calorimeter (DSC) equipment and Accelerating

Table 1: Properties of the oils, sand and carbonat.

Sample NO.	Sample type	Oil API gravity	Grain size (mesh)
a-1	Pure Oil	8	-
a-2	Oil+Carbonate	8	50-150
b-1	Oil+Sand+Clay	19	50-150
b-2	Oil+ Carbonate+Clay	19	50-150
c-1	Pure oil	22	-
c-2	Oil+Sand+Clay	22	50-150
c-3	Oil+Carbonate+Clay	22	50-150

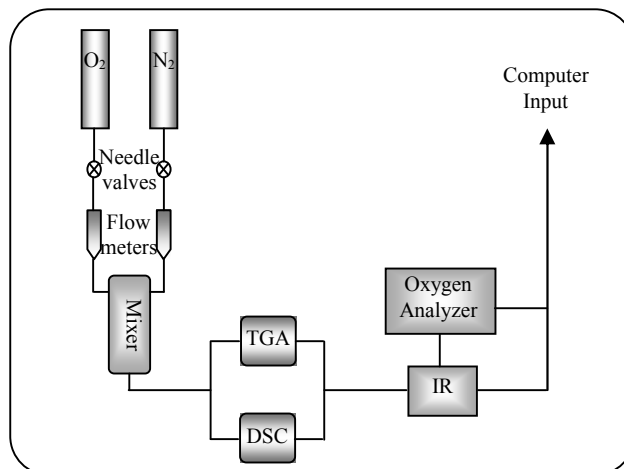


Fig. 4: TGA/DSC experimental set-up.

Calorimeter (ARC) for different oil samples from South-West of Iran.

Isothermal and non-isothermal thermogravimetric experiments were conducted on three different crude oils from Iranian oil fields. Each oil was investigated in its original form and also mixed with either sand or crushed carbonate with Montmorillonite. The properties of the oils, sand and carbonate are given in table 1.

The TGA/DSC instruments were equipped for evolved gas analysis via an infrared analyzer. The Infrared detect CO₂, CO, Hexane and Propane. As shown in Fig. 5, detected exhaust gas help to recognize reaction mechanism of oil sample. Experiments were conducted in atmospheres containing different percentages of oxygen (21 % - 80 %) in nitrogen at atmospheric pressure. The crude oil samples were heated to 700 °C at a linear heating

rate of 10 °C/min. When the reaction temperature had reached 700 °C, almost no carbon monoxide or dioxide gas was detected in the effluent line, indicating that the oxidation/combustion reactions were completed. When oil sample was mixed with crushed carbonate rock, because of decomposition of carbonate around 800 °C, CO₂ was detected at this temperature (Fig. 6). The TG/DTG data obtained were used to evaluate the kinetic parameters E and F for each experimental condition via the Arrhenius model discussed above.

In order to produce an accurate data the TGA/DSC equipments were calibrated by obtaining the activation energy and the frequency factor for calcium carbonate and Al₂O₃. In addition, duplication of the runs was also reproduced.

The objective of the ARC work was to identify the auto ignition temperature at which the oil reacts with air and to determine the Arrhenius oxidation kinetic parameters of the oil, with and without reservoir carbonate rock under reservoir pressure. All ARC tests were performed with the crude oil in contact with air at reservoir pressure or higher, in the temperature range of Tres to 500 °C.

Combustion tube tests were performed to investigate the ability of the oil sample to realize fire front maintenance after auto ignition at reservoir conditions. This part of study will be investigate in our next paper.

RESULTS AND DISCUSSION

Effect of Oxygen Partial Pressure on Auto ignition Condition

This study investigated the effect of oxygen partial pressure on auto ignition conditions by evaluating the kinetic parameters including activation energy and frequency factor under different oxygen partial pressures. According to TGA/IR (Figs. 2 and 3) curve, different reaction zone was selected. The Arrhenius plot (K vs 1/T) for each reaction zone (LTC, HTC) at different oxygen content was obtained. According to literature⁷, and the result obtained in this work (Fig. 7) activation energy is not affected by oxygen partial pressure, consequently results of sample a-1 was plotted at different P_{O2} in a single graph. This enabled us to reduce error by passing only one line among these data. This plot provided unique activation energy for one sample at different exposed oxygen partial pressure.

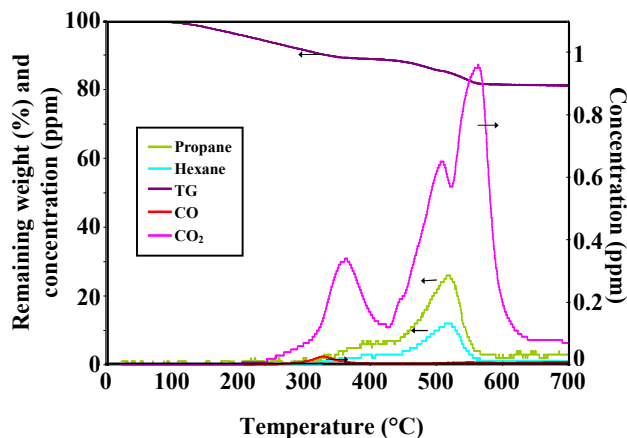


Fig. 5: Typical TGA run with detected exhaust gases.

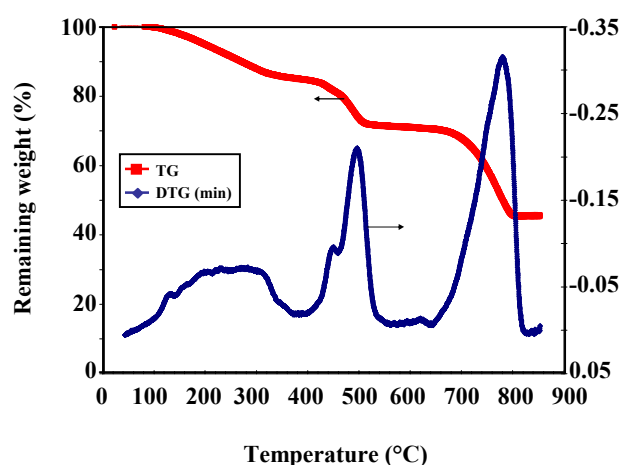


Fig. 6: Typical TGA curve of mixture of oil with crushed carbonate.

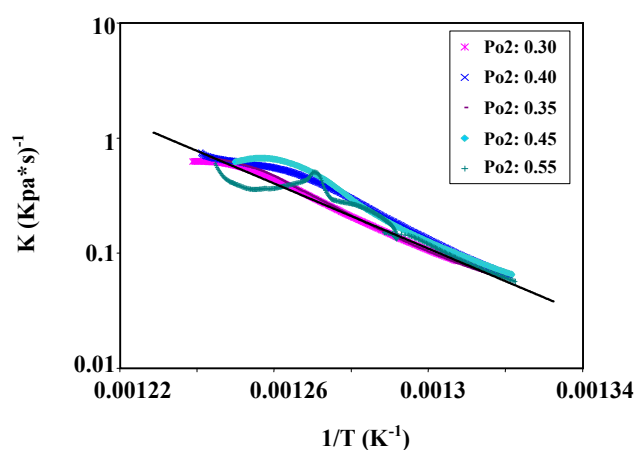


Fig. 7: Arrhenius plot for HTC reaction zone of sample a-1 at different oxygen content.

Table 2: Values of the E and F of the fHTC and sHTC reaction zones for sample a-1.

Oxygen partial pressure	fHTC		sHTC	
	E (kJ/gmole)	F (kPa*min) ⁻¹	E (kJ/gmole)	F (kPa*min) ⁻¹
21 %	212.90	2.90E+13	373.69	1.34E+23
30 %	212.90	3.54E+13	373.69	4.68E+23
35 %	212.90	3.66E+13	373.69	4.91E+23
40 %	212.90	3.33E+13	373.69	6.21E+23
45 %	212.90	4.09E+13	373.69	6.84E+23
50 %	212.90	2.06E+13	373.69	4.62E+23
55 %	212.90	2.62E+13	373.69	4.88E+23

Table 3: Values of the E and F of the HTC reaction zones for sample b-1.

Oxygen partial pressure	HTC	
	E (kJ/gmole)	F (kPa*min) ⁻¹
21 %	78.38	3.81E+05
50 %	78.38	5.82E+05
80 %	78.38	5.28E+05

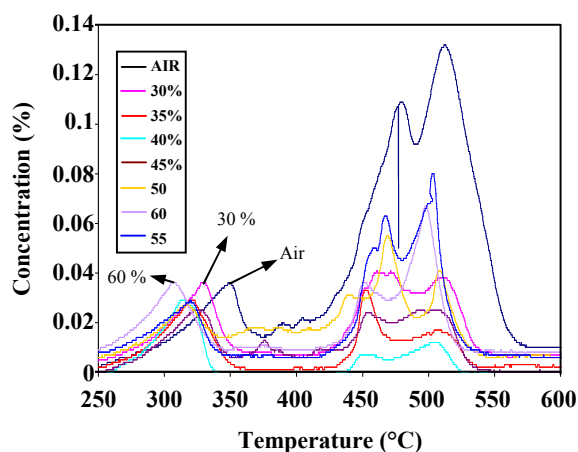


Fig. 8: CO concentration curve of TGA test for different oxygen content in sample a-1.

For example in sample b-1 (table 3) at HTC zone, calculated activation energy value was 76, 89 and 77 for air, 50 % and 80 % oxygen content respectively. According to this data activation energy dose not change sharply. In this regard average activation energy was

calculated for sample b-1. This procedure was applied for other samples (a-1, c-1 and c-2). This has also been observed by *Hughies* [10] and *Elshubary* [7]. However, as demonstrated in Fig. 8, LTC reaction starts at a lower temperature as the oxygen concentration is increased. The maximum carbon monoxide evolution for the low temperature combustion reaction occurred at 300 °C for 60 % oxygen content whilst the same is around 353 °C for air.

The activation energy and frequency factor values calculated for sample a-1 are summarized in table 2. Whilst the activation energies are consistent for the fHTC and sHTC reaction zones, the frequency factor increases to maximum values of 4.09×10^{13} and 6.84×10^{23} at 45 % oxygen concentration for fHTC and sHTC respectively.

The kinetic parameters obtained for the HTC reaction zone of sample b-1 are tabulated in table 3 for different oxygen contents. The frequency factor shows the same trend as was observed for sample a-1. So with using TGA the kinetic parameter and kinetic model of every sample were calculated to use in simulation of process as a next step of study.

Differential Scanning Calorimetry (DSC) experiments were also performed to study the effect of oxygen partial pressure on auto ignition. The DSC module had two copper trays, one acting as the sample tray and the other as a reference tray. The reference sample was crushed carbonate rock or sand depending on the contents of the sample tray. DSC traces, under non-isothermal conditions, consisted essentially of two exothermic peaks (Fig. 9). As can be seen in Fig. 9, the heat released during

Table 4: Values of the E and F of the HTC reaction zone for sample c-2 and c-3.

Oxygen partial pressure	Sample C-1		Sample C-2	
	E (kJ/gmole)	F (kPa*min) ⁻¹	E (kJ/gmole)	F (kPa*min) ⁻¹
21 %	205.56	5.87E+11	149.49	3.54E+8
50 %	205.56	2.1E+12	149.49	4.24E+8
80 %	205.56	3.19E+12	149.49	4.58E+8

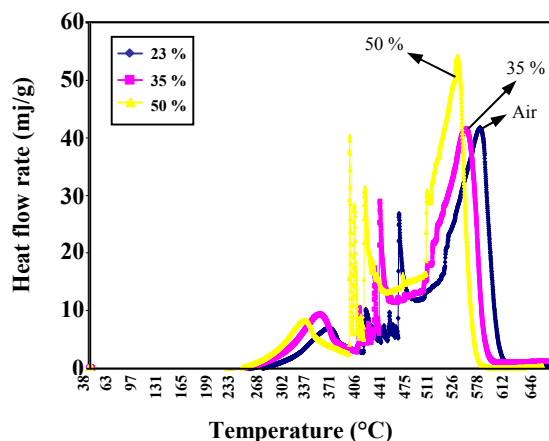


Fig. 9: DSC plots for sample b-2 at different oxygen contents.

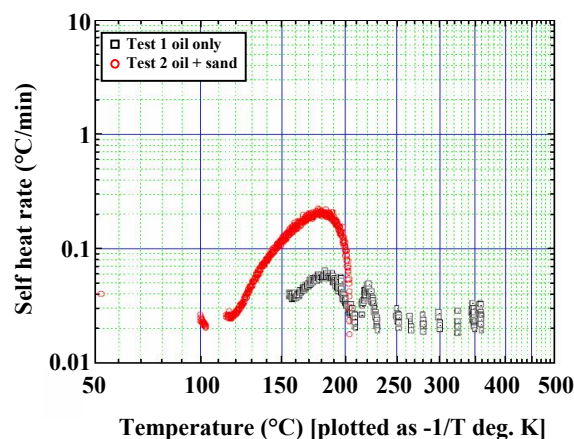


Fig. 10: Self heat rate vs. temperature plot for sample a-1 and Sample a-2.

each reaction increased while oxygen content was increased from 21 to 50 %.

The effect of increasing oxygen partial pressure is to decrease the starting temperature of the LTC reactions and to release more heat during each reaction region, since in heavy oil samples the composition of light hydrocarbon such as methane and ethane is low. However, increasing oxygen contents in LTC and HTC reaction has less effect than light oil samples. As a result, activation energies and Frequency Factor determined for each of the reaction zones remained essentially constant during a particular reaction with increasing oxygen content.

Effect of Clay on Auto ignition Condition

Experiments were undertaken to investigate the possible influence of clay in the presence of crushed carbonate rock on the kinetic parameters. Samples c-1 and c-2 were a mixture of crude oil (26 %) with crushed carbonate rock without clay and with 10 % montmorillonite, respectively. A small sample, 5 mg, was then transferred to the TGA pan and the TGA experiment then

carried out. As shown in table 4, activation energy for sample c-1 is 205 kJ/gmole and that of c-2 149 kJ/gmole respectively. Thus the presence of the clay more than halved the activation energy of the HTC process. Presumably the increase in surface area due to the presence of the clay provides many more site for the reaction to initiate lowering the activation energy requirement.

Effect of Pressure on Auto Ignition

The Accelerating Rate Calorimeter (ARC) is an instrument that is capable of operating up to high pressures (6,000 psi) and studying exothermic reactions in the range 30 to 500 °C. Other commercially available instruments (DTA, DSC, TGA and EGA) are limited to low and medium pressures.

The ARC technique was used to examine the auto ignition behaviour of the samples as well as the extent and continuity of the exotherm traces obtained in an experiment. Sample a-1 was tested in a closed ARC configuration at an initial pressure of 1300 psi, (8.96 MPa)

Table 5: Arc results for sample a-1 and a-2.

Arc results	Sample a-1	Sample a-2
Exotherms (°C)	156-210 215-230 230-385 (intermittent)	115-205
LTC Exotherms (°C)	155-210	115-205
Max. $\Delta T_{\text{adiabatic}}$ (°C) ²	54	90
$\Delta T/\Delta t_{\text{maximum}}$ (°C/min) ³	0.061	0.221
Kinetic parameters		
Activation energy (kJ/gmole)	72.618	80.556
Reaction Order, n	1	1
Frequency factor, A (n=1), (ln(1/sec))	107	126

at a typical reservoir temperature of 40 °C. The test produced an exotherm in the low temperature range that started at 156 °C with an endpoint of 210 °C (table 5). For the purposes of analysis, this was termed the major exotherm.

However, it was shortly followed by continuous low-level exothermic activity for the remainder of the test, prior to attaining the equipment's maximum temperature of 502 °C. The maximum attained self heat rate of 0.061 °C/minute indicates that the oxidation reactions occurred only in the low temperature (LTO) range.

Failure of the reactions to make the transition to the high temperature range (generally considered as rates greater than 10 °C/minute) may be a function of limited oxygen available at low pressure and/or the formation of an oxidized film or "skin" on the surface of the oil which limit oxygen contact with the bulk of the oil sample. The major exotherm corresponding to the low temperature range was matched with the Arrhenius model using an activation energy of 72.66 kJ/gmole and a reaction order of 1.0.

As shown in Fig. 10 for the a-2 sample containing crushed carbonate rock shows that, initially, a-2 exhibited a continuously increasing exothermic response at a lower ignition temperature than did a-1 (115 °C for a-2 as compared with 156 °C for a-1). The upper limit of the low temperature range, however, was similar compared to the exotherm of the a-1 test. Unlike a-1, no exothermic activity was observed in the high temperature range. It is possible that the absence of reactivity in the high temperature range was a consequence of all the available

oxygen having been consumed in the low temperature range and thus no oxygen was available to react in the high temperature range. The maximum self-heat rate observed for a-2 was 0.221 °C/minute which is more than triple that of a-1, but still well below the threshold assigned to high heating rate reactions. The increased reaction rate is likely a result of the increased surface area available for reaction, imparted by the addition of the crushed carbonate.

The activation energy was calculated to be 83.16 kJ/gmole with a reaction order of 1.0.

CONCLUSIONS

Based on the results obtained the following conclusions can be made:

- 1- Activation energy was independent of the oxygen partial pressure.
- 2- The presence of clay resulted in a lower activation energy and this could be due to the surface area of clay which results in more coke deposition.
- 3- DSC runs indicated that an increase in oxygen partial pressure would increase the heat release.
- 4- The LTC initiation was decreased with increasing oxygen partial pressure. It means that the light component of heavy oil sample react faster in the presence of more oxygen.
- 5- The initiation temperature of the LTC reaction was reduced with addition of clay to oil sample under reservoir pressure from 256 °C to 156 °C.
- 6- Auto ignition occurred at 115 °C according to ARC Test at reservoir pressure. This indicates the importance of pressure in the auto ignition study.

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Nomenclatures

- w Weight of oil at any point during the reaction (mg)
w_i Weight of oil at the beginning of the reaction (mg)

w_f	Weight of oil at the end of the reaction (mg)
y_{O_2}	Percent of oxygen in injected gas stream
P_{inj}	Pressure of injected stream (kPa)
n, m	Reaction orders
K	Reaction rate constant ($\text{kPa}^{-1} \text{s}^{-1}$)
F	Frequency factor ($\text{kPa}^{-1} \text{s}^{-1}$)
E	Activation energy (J/mole)
R	8.314, Universal gas constant (J/(mole K))

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