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Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60^{th} birthday

THERMOKINETIC INVESTIGATION OF OXIDATION OF HEAVY OIL AND ITS MODEL COMPOUNDS

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This paper presents and discusses the thermokinetic parameters of oxidation of heavy oil (Nanyang deposit) and selected model compounds (*n*-dotriacontane, stearic acid and octadecanol). The method introduced in this work defines the key parameters which affect the quality of the numerical simulation of the energy balance equation of the in situ combustion process simulation experiment and the actual process in the field.

A microcalorimetric technique is combined with a thermokinetic approach developed at the Institute of Chemistry to calculate the thermal energy of reactions such as oxidation of heavy oil or other compounds in in-situ combustion occurring in a porous medium as a function of time at different temperatures and pressures. The kinetic parameters were determined from calorimetric and chemical experiments.

The oxidation of hydrocarbons proceeds by way of a complex chain of radical reactions involving a large number of intermediate products. At enough high temperatures these reactions proceed to completion and yield carbon dioxide and water. At lower temperatures oxidation is incomplete and yields a very large number of oxygenated hydrocarbons [1, 2].

Steam injection results in many physical changes occurring in the reservoir. During in-situ combustion processes both physical changes and chemical reactions occur simultaneously or sequentially in the vicinity of the

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combustion front. It is generally believed that the process is controlled by these reactions. The in-situ oxidation during combustion of crude oil is an exothermic reaction, cracking reactions could be endothermic while various catalytic and non-catalytic reactions take place in the reservoir. It would be wrong to assume that there are only a few pseudocomponents involved in the reactions and that CO_2 and CO are the only products [3, 4]. Also the kinetics of the reactions are far from simple. Therefore the heat generated in the process cannot be represented by the following simple equations:

$$Q = R_c \cdot \Delta H_c \quad [3] \tag{1a}$$

or

$$Q = R_r \cdot \Delta H_{rxn} \tag{1b}$$

It is difficult to obtain a correction expression for R_c or R_r and ΔH_c or ΔH_{rxn} for different kinds of crude oils from different fields by assuming the kinetic parameters of the oxidation reaction of a pure alkyl compound. Although the term ΔH_c denotes the heat of combustion of a crude oil it should be emphasized that the process of burning taking place in the combustion zone in the field or in a combustion tube in the laboratory involves more than simple combustion. Rather, there are various oxidation processes taking place simultaneously. The term ΔH_{rxn} is correct as long as the data is obtained from the appropriate experiments. Therefore, the chemical simulation of the in-situ combustion process has to be developed in order to model the process. The oxidation of hydrocarbons under different conditions; temperature, pressure etc. provides the necessary information to be incorporated in a model relevant for industrial application.

The objectives of the present study were:

1) to investigate the thermokinetics of oxidation of heavy oil from the Nanyang oil field and of model compounds *n*-dotriacontane, stearic acid and octadecanol.

2) to calculate the kinetic parameters of the reactions. The results obtained were used in direct support of a feasibility study of the heavy oil project of the Nanyang deposit.

An internal generation term was introduced to the energy balance equation of the numerical model in order to simulate different combustion processes based on the results of this study. Furthermore, the results of this study should improve the control of the in-situ combustion process and improve the yield of useful products from the various natural hydrocarbons.

Experimental

Materials

The crude oil studied was obtained from the Nanyang oil field. It has a gravity of between 0.938 and 0.996 g/cm^{3}at 25°. The viscosity of the degassed crude is from 111 to 7515 cP at 50°. The crude oil has a paraffin content of 4.6–20.1% (dry weight) and a bitumen content of 11.1–37.0%. The asphaltene contained in the bitumen was precipitated by *n*-heptane was found to be of negligible quantity. The acid number of the crude oil was 3.0 mg KOH/g.

The *n*-dotriacontane, stearic acid and octadecanol used in the experiments were of commercial grade and were used without further purification.

Commercial quartz pre-heated to 1200° was used to simulate a reservoir rock.

Apparatus

Carbon, hydrogen and nitrogen were determined using an elemental analyser (Carlo Erba model 1102)

The oxidation process was investigated using a home made apparatus modified from previous work [5]. The process is depicted in a flow diagram in Fig. 1a. Gaseous products were detected and identified using a gas chromatograph (SP2306 Beijing Analysis Instrument Factory). The heat generation during the oxidation process was measured using a Calvet Microcalorimeter (BT 2.15 from Seteram France) equipped with a gas flow system designed and built by ourselves. The oxidation of crude oil was monitored using a differential thermal balance (LCT–1, Beijing Optic Instrument Factory) in the range 50 to 550°.

Procedure

The experimental samples consisting of quartz covered with the various materials to be analysed were packed in the calorimetric vessel and the vessel was placed in the experimental cell of the calorimeter. Pure quartz was packed in the control calorimetric cell which was placed into the reference cell of the calorimeter [9, 10] see Fig. 1a. The calorimeter was brought to the desired temperature while nitrogen was flowing through the calorimetric system at the rate of 15 ml/min. After about three hours the temperature was stable and the calorimetric recording showed a straight line. Then, air or pure oxygen was admitted into the calorimetric system. This was con-

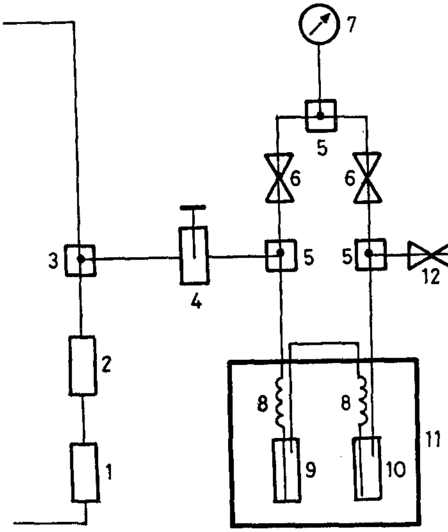

Fig. 1a Calorimetric system of thermokinetic investigation for chemical simulation
1. Absorbing tube of CO_2, 2. Absorbing tube of H_2O, 3. Three-way valve, 4. Pressure stabilizer, 5. Three-way connection, 6. Cut-off valve, 7. Pressure meter, 8. Pre-heating pipe, 9. Sample cell, 10. Reference cell, 11. Calorimeter, 12. Regulating valve, 13. Flow rate stabilizer, 14. Flow meter

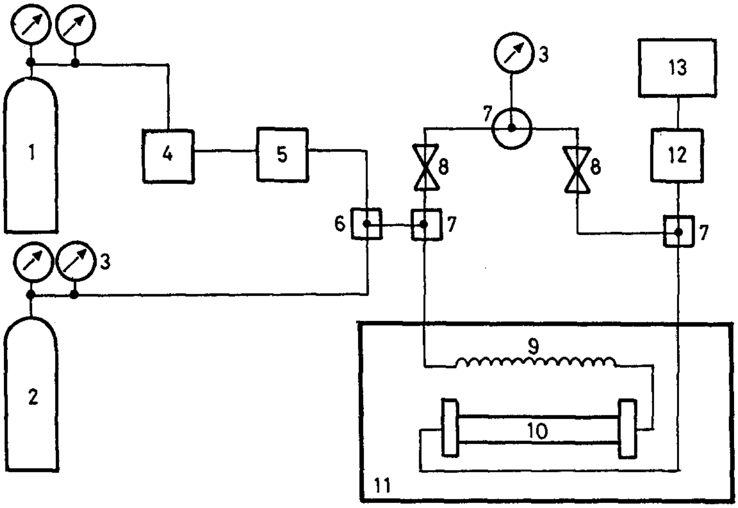

Fig. 1b Investigation system for chemical kinetics
1. Oxygen, 2. Nitrogen, 3. Pressure meter, 4. Oxygen purifier, 5. Pressure stabilizer, 6. Three-way valve, 7. Three-way connection, 8. Cut-off valve, 9. Pre-heating pipe, 10. Reaction tube, 11. Thermostat, 12. Cooling pipe, 13. Flowing rate controlling and measuring system and absorbing tube of acid gas product

tinued until no change in the recording of the calorimeter could be observed. The calorimeter was calibrated by electric heating in order to obtain the constants necessary for correction.

Chemical kinetic experiments, shown in Fig. 1b, were carried out under approximately the same gas flow and operation conditions except that an oxidation reactor was used instead of a calorimetric cell.

Results and discussion

The results of the elemental analysis are given in Table 1. The results of thermal analyses are presented in Figs 2 and 3. These show the TG and DTA curves recorded under dynamic air and Ar purge, respectively. Thermogravimetric and differential thermal analysis were used as a combined technique in this study. This combination proved more sensitive than the separate techniques as it was easy to identify the oxidation behaviour of the crude oil and to distinguish each step in the process. Figure 2 presents typical TG and DTA curves for crude oil under dynamic air purge. A distillation process took place around 100° resulting in an endothermic peak on the DTA curve combined with a small weight loss recorded on the TG curve in this temperature range. Low temperature oxidation (LTO) of the crude oil took place in the temperature range 280–395° as indicated by an exothermic thermogram on the DTA curve and a distinct weight loss. This could be the product of light oil distillate. The following step was recorded at 410–520° as a major exothermic reaction and a large mass loss. This could be due to combustion and possibly simultaneous crude oil cracking. The marked differences between the curves shown in Figs 2 and 3 are due to the difference in purging gas, being air and argon, respectively. Cracking reactions dominate over oxidation under argon while under air some residual air may remain in the system.

Typical calorimetric curves for the oxidation of crude oil, *n*-dotriacontane, stearic acid and octadecanol are shown in Figs 4 to 7. After calculating the results obtained for the lower temperature range, of around 150°, the actual heat generation at the beginning of the oxidation process of oil can be expressed as

$$W(t) = 74.5 \cdot P_{(O_2)} \tag{2}$$

where $P_{(O_2)}$ is the partial pressure of oxygen in air. For a purge gas of constant oxygen content of 48.94% at 1.50 atm and experimental conditions as described, the reaction constant was found to follow the relationship:

$$\mathrm{dln}K_r = 22.59 - 7679 \cdot (1/T) \tag{3}$$

with a good correlation coefficient of $r = 0.985$ where K_r is the reaction constant in the oxidation of crude oil. T is the temperature in K. The calculated activation energy was 63.8 kJ/mol and the Arrhenius constant of $6.47 \cdot 10^3$. These results are in good agreement with those from several studies reported in [5, 6].

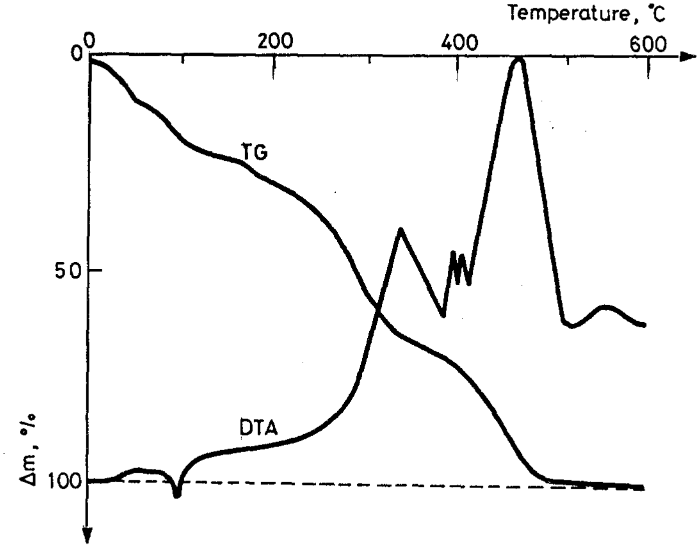

Fig. 2 TG and DTA curves of crude oil in dynamic air purge

An increase in the reaction rate as a function of increase in oxygen content was observed and is shown in Fig. 5 and as a function of temperature in Fig. 6. The curve in Fig. 7 shows that oxidation of the model compounds *n*-dotriacontane, stearic acid and octadecanol took place. There is a considerable difference between the three model compounds and the crude oil.

Potentiometric titration of acidic products of the oxidation experiment were carried out to improve their characterization. The titration curves for crude oil and *n*-dotriacontane are shown in Figs 8 and 9. The titration curve of crude oil and pure $C_{32}H_{66}$ are shown. These have clear inflection points marking the end points of the titration. The titration curves show distinct shapes for the oxidation products of the various model compounds which also differ in total acidity. It can be concluded that the chemical characteristics of crude oils could have a strong effect on the oxidation products and thus on the heat generation characteristics.

Table 1 Elemental determination of reagents used

Reagent used	C, wt %	H, wt %	N, wt %	S, wt %	O, wt %
$CH_3(-CH_2-)_{30}CH_3$	85.27	14.71	0.00	0.00	0.00
$CH_3(-CH_2-)_{16}COOH$	75.77	12.60	0.00	0.00	11.63
$CH_3(-CH_2-)_{16}CH_2OH$	79.90	14.14	0.00	0.00	5.90
crude oil used	78.52	11.89	0.85	<0.3	8.44

The results of the analysis of the gaseous products are given in Table 2. The yield and composition of the different gaseous products changed during the progress of the oxidation process. These results provide further indication that the process is very complex.

The preceding results and conclusions show that the in-situ combustion process is not only associated with physical changes but also with complex chemical reactions. The reactions take place in a porous medium which adds

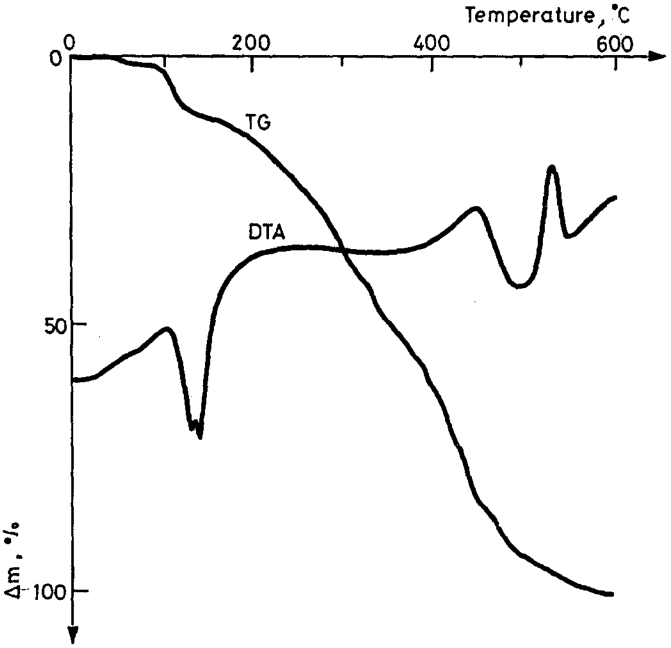

Fig. 3 TG and DTA curves of crude oil in dynamic Ar purge

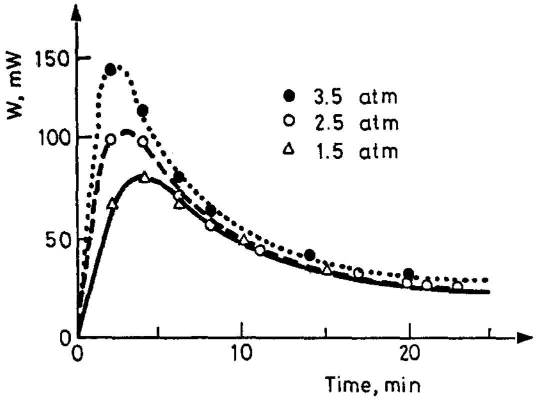

Fig. 4 Thermokinetic curves of oxidation of crude oil at different pressures

to the complexity. The complexity is further amplified in real in-situ combustion processes where natural substances in the reservoir rock may act as catalysts. Consequently the consideration of simple chemical reaction mechanism or elemental processes are clearly inappropriate in describing this type of system. This was previously recognized in several studies such as by A. L. Benham [7]. In general, the chemical reaction may be represented by the stoichiometric equation:

$$CH_n + [(2m+1)/(2m+2)+n/4]\,O_2$$

$$\rightarrow m/(1+m)\,CO_2 + 1/(1+m)\,CO + (m/2)\,H_2O \qquad (4)$$

where n is the atomic hydrogen to carbon ratio of the fuel and m is the molar CO_2/CO ratio in the oxidation products.

The rate can be described following [10, 11] as

$$R_r = k \cdot (P_{O_2}) \cdot C^8 \qquad (5)$$

Table 2 Gas products analyses

Time, h	CO_2, %	CO, %	O_2, %	N_2, %	CH_4, %	H_2O, %
9.72	2.88	6.26	2.31	52.79	0.73	35.01
18.70	12.02	1.06	2.38	79.10	0.61	4.83
24.23	1.71	1.52	13.92	70.81	0.00	12.75
38.18	15.12	0.82	2.85	60.87	0.67	19.51

where P_{O_2} is the partial pressure of oxygen and p, 8 are the reaction orders. The heat generation, as previously defined, should be described as:

$$Q = \Delta H_r xn \cdot R_r \tag{6}$$

where $\Delta H_r xn$ is the heat of the respective reaction, its value differs for different types of reactions. Therefore there is a need for intensive investigation of the theory and the experimental parameters of reaction kinetics of in-situ combustion. Results of the type reported here obtained directly from simulation experiments are better than those reported previously [1, 9–11]. In this study several key parameters and their relationship such as the heat

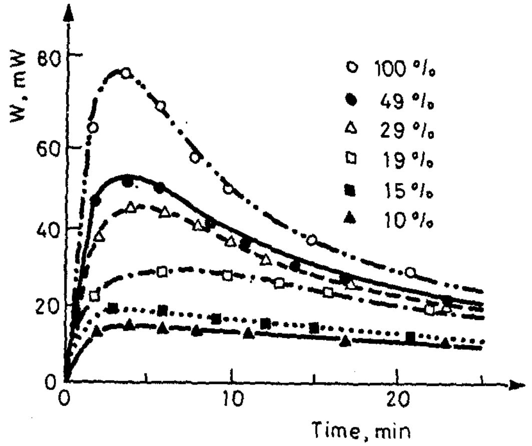

Fig. 5 Thermokinetic curves of oxidation of crude oil with different contents of oxygen

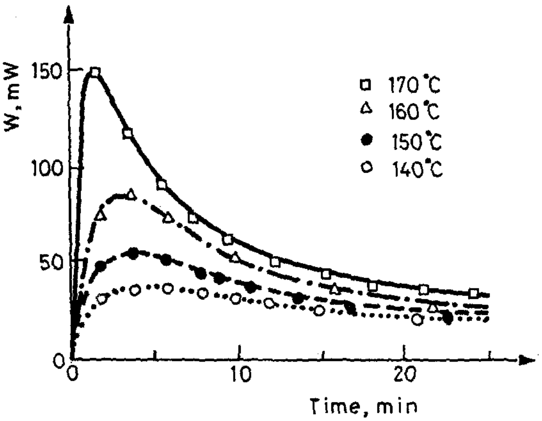

Fig. 6 Thermokinetic curves of oxidation of crude oil at different temperatures

generation $q(t)$ (in thermal power $W(t)$) were obtained directly from calorimetric determinations and may be expressed as function of other parameters as:

$$q = f(T, P_{O_2}, C_i \ldots, t) \tag{7}$$

The chemical simulation experiments are needed in this area of in-situ combustion research in order to support the numerical simulation of the process as well. The combined information will improve the operation and control of the in-situ combustion processes in the field.

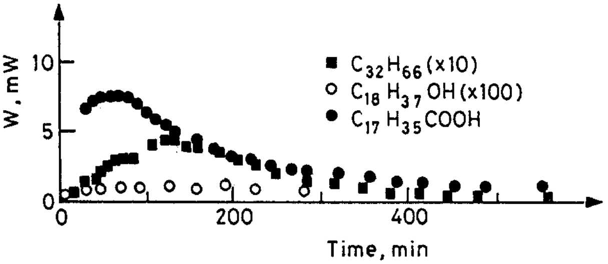

Fig. 7 Thermokinetic curves of oxidation of $C_{32}H_{66}$, $C_{18}H_{37}OH$ and $C_{17}H_{35}COOH$ in dynamic air (19.74% O_2) purge at 150°

Even the oxidation of *n*-dotriacontane proved to be a complex process as shown in Fig. 7, while the oxidation of stearic acid and octadecanol are less so. It seems that the actual mechanism differ under different experimental conditions.

Conclusions

1) A chemical simulation method for in-situ combustion of heavy oil in calorimetric vessels complemented by TG and DTA analysis was carried out in order to derive physical and chemical parameters of the process. Encouraging preliminary results were obtained.

2) The process of in-situ combustion is strongly affected by the operation temperature, the pressure and oxygen content of the purge gas and the chemical composition of the crude.

3) At low temperature the thermokinetic data obtained are suitable for the study of oxidation of hydrocarbons through accurate kinetic parameters of the reaction.

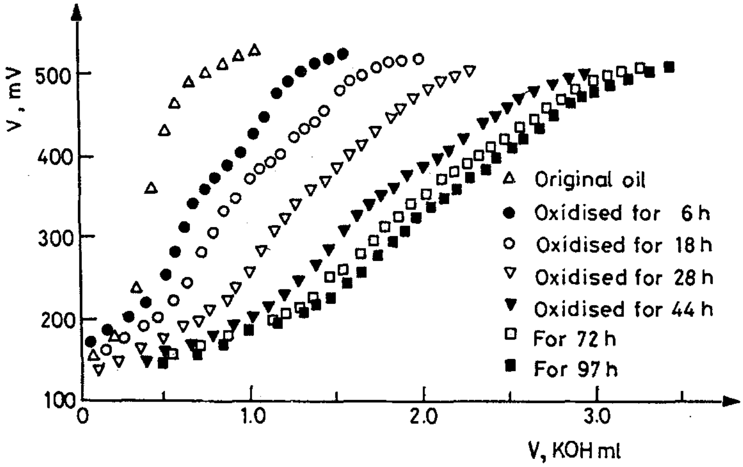

Fig. 8 Potentiometer titration curves of oxidation of products of crude oil

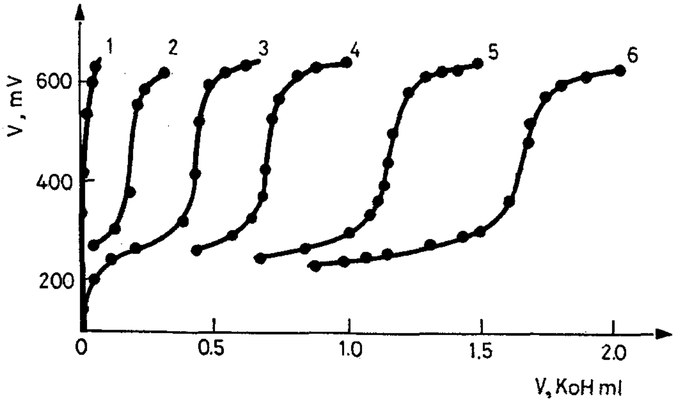

Fig. 9 Potentiometer titration curves of oxidation products of $C_{32}H_{66}$

4) The chemical simulation method has the potential of providing accurate parameters and expressions which can be used for the numerical simulation of in-situ combustion processes thus improving the process control in the field in terms of control of the reaction and its products.

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Zusammenfassung — Vorliegende Arbeit beschreibt und diskutiert die thermokinetischen Parameter der Oxidation von Schwerölen (Lagerstätten Nanyang) und ausgesuchter Modellverbindungen (n-Dotiacontan, Stearinsäure und Oktadekanol). Das hier vorgestellte Verfahren definiert die Schlüsselparameter, die die Güte der numerischen Simulation der Energiebilanzgleichung bei den Experimenten zur Simulation von in situ Verbrennungsprozessen und des jeweiligen Prozesses beeinflussen.

In Verbindung mit einer thermokinetischen Näherung wurde an der Academia Sinica ein mikrokalorimetrisches Verfahren entwickelt, mit deren Hilfe man die thermischen Reaktionsenergien wie z.B. für die Oxidation von Schwerölen oder anderen Verbindungen während der in situ Verbrennung in porösen Materialien als eine Funktion der Zeit bei verschiedenen Temperaturen und Drücken berechnen kann. Die kinetischen Parameter werden aus kalorimetrischen und chemischen Experimenten ermittelt.