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Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60th 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

$$Q = R_r \cdot \Delta H_{r \times n} \tag{1b}$$

It is difficult to obtain a correction expression for R_c or R_r and ΔH_c or $\Delta H_{r \times n}$ 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 $\Delta H_{r \times n}$ 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.