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Kinetic modeling of thermal cracking reactions

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ABSTRACT

This paper provides a kinetics model for thermal cracking of various oils over time frames which correspond to the long term storage at temperatures up to those experienced in an in situ combustion process. The model describes detailed kinetic mechanisms and concentration changes of individual species during the thermal cracking reactions. Also the modeling results are compared with the experimental data to verify their validity.

1. Introduction

Historically, the petroleum industry has tried to improve the recovery of heavy oils and oil sands that have reserves three times those of conventional oil reservoirs, but cannot be produced by conventional means. Current methods used to improve in situ bitumen production are cyclic steam stimulation and steam assisted gravity drainage. Steam injection increases the temperature in the reservoir, thereby reducing the bitumen viscosity and increasing its mobility. Sustained steam injection is facing barriers of water availability, high natural gas costs and air quality, hence air injection is again being considered as a method for in situ energy generation. In order to develop realistic designs for air injection or in situ combustion projects in bitumen reservoirs, it is necessary to understand the various reactions that are involved.

Three major reactions have been reported when in situ combustion (ISC) is utilized: (1) thermal cracking, (2) liquid phase low temperature oxidation (LTO), and (3) high temperature oxidation (HTO) of vapor, liquid and solid hydrocarbon fractions. Thermal cracking reactions are often referred to as the fuel deposition reactions for in situ combustion; the carbon–carbon bonds of the heavier hydrocarbon components are broken to form low carbon number hydrocarbon molecules plus an immobile fraction which is referred to as coke. Thermal cracking is used extensively in the upgrading of heavy oils and bitumen, however the time frames are generally much shorter than those associated with steam or air injection based oil recovery processes. The prime source of literature on thermal cracking of oils over long time frames is associated with steam injection or in situ combustion processes. A significant amount of data on the thermal cracking of Canadian heavy oils has been published by Hayashitani [1] and Millour et al. [2].

Compositional models have been developed to describe the change in the oil composition as a function of temperature and time. The thermal cracking models proposed by Hayashitani [1] and Millour et al. [2] provide a good understanding of the nature of the compositional changes which occur when Athabasca bitumen is cracked in the absence of oxygen. Millour et al. modified a semi-empirical model for low temperature oxidation to describe the Athabasca bitumen thermal cracking data of Hayashitani as well as that of a number of other Canadian heavy oils. Millour's model accounted for the coke initiation time and the conversion of maltenes and asphaltenes during thermal cracking. Millour reported that pre-oxidation of the oil reduced the coke initiation time and accelerated the thermal cracking rates at a given temperature. Wiehe [3] proposed a thermal cracking model in 1993 for reaction times associated with refinery cracking operations. This paper extends Wiehe's model to the time and temperature ranges typical of an in situ combustion process. Akin et al. [4] used a kinetic model that groups product into six pseudo-components (heavy oil, medium oil, light oil, two noncondensable gases and coke) to simulate dry forward combustion process. Their model includes the chemical reaction of cracking of heavy oil to light oil and coke.

For an explicitly correct kinetic representation of hydrocarbon cracking, a large number of chemical species would have to be considered. Such a system would be impractical, as it would increase the calculation burden. Therefore pseudo-components must be assigned to simplify the whole calculation procedure. The hydrocarbon phase is characterized in terms of maltenes, asphaltenes and coke. Maltenes are pentane and toluene (or benzene) soluble fraction and they may be further separated, for the purpose of modeling, into reactive maltenes and product maltenes. Asphaltenes are defined as the toluene (or benzene) soluble and pentane insoluble

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fraction of the original or the modified bitumen, and coke is defined as the toluene (or benzene) insoluble fraction of the bitumen.

The thermal cracking modeling presented in this article concentrates on the Hayashitani Athabasca bitumen data [1], as well as data for Pembina oil, Frisco Countess oil, North Bodo heavy oil, Athabasca bitumen from Drums 433 and 20. Hayashitani thermally cracked Athabasca bitumen in a closed system from 344 to 422 °C under an inert atmosphere in the absence of core and water for times ranging from 2 to 48 h. The latter data were generated under previous AOSTRA contracts. The AOSTRA data are reported in the reports by Bennion et al. [5–9]. Also included in this study are the thermal cracking data of Marguerite Lake bitumen which were generated under a contract with AOSTRA/BP [10]. As mentioned previously, this work evaluated the desirability of the Wiehe's model in describing the compositional changes of different oils when they are thermally cracked under temperature and time conditions associated with in situ processes. Table 1 summarizes the initial compositions of the oils. The terminology "Unoxidized" means that the initial oil was not pre-oxidized; while the terminology "Oxidized" means that the initial oil did undergo pre-oxidization prior to thermal cracking reactions.

2. Thermal cracking reaction model

Wiehe [3] developed a kinetic model which replicates the important features of thermal cracking reactions. His model describes the conversion of asphaltenes over the entire reaction range and of maltenes during the coke-induction period using first-order reactions. The model basis is that coke formation is triggered by a phase separation of undissolved asphaltenes. Product asphaltenes are initially soluble in the maltenes, but there exists a maximum solubility. When the solubility limit has been reached, the product asphaltenes will separate into a new liquid phase to form coke. The conversion of the undissolved asphaltenes into toluene-insoluble coke deviates from first-order behavior which is dominant in the coke-induction period. After the coke initiation period, an infinite reaction rate is used to reflect that this reaction rate is phase equilibrium controlled. The time prior to the start of coke formation is defined as the coke-induction period.

Parallel first-order reactions for the thermolysis of maltenes and asphaltenes are the two major reactions that happen during the coke-induction period. During this period the reactant asphaltenes are assumed to form only lower molecular weight products (product maltenes, product asphaltenes and gas). As long as the asphaltenes remain dissolved, maltenes will provide sufficient abstractable hydrogen to terminate asphaltenes-free radical recombination. As the conversion proceeds, the concentration of asphaltenes increases and the maltenes concentration decreases until the solubility limit, S_L, is reached. Beyond the solubility limit, the excess asphaltenes will separate to form a new phase. In this new phase asphaltenes radicals' recombination is frequent, causing a rapid reaction to form solid coke.

The coke-induction period, is modeled with two first-order reactions:

$$C_{malt,R} \xrightarrow{k_H} aC_{asp,P} + (1-a)C_{gas} \tag{1}$$

$$C_{asp,R} \xrightarrow{k_A} mC_{asp,P} + nC_{malt,P} + (1-m-n)C_{gas} \tag{2}$$

where $C_{malt,R}$ and $C_{asp,R}$ are reactive maltenes and asphaltenes concentrations (g/100 g original oil), respectively. C_{gas} is the generated gas concentration. The rate constants k_H and k_A are described by Arrhenius type relationships which are shown later in the paper.

Once the maximum solubility has been reached and new liquid phase appears, the system is described by the following equations:

$$C^{max}_{asp,P} = S_L(C_{malt,R} + C_{malt,P}) \tag{3}$$

$$C^{ex}_{asp,P} = C_{asp,P} - C^{max}_{asp,P} \tag{4}$$

$$C^{ex}_{asp,P} \xrightarrow{\infty} (1-y)C_{coke} + yC_{malt,P} \tag{5}$$

The terms $C_{malt,R}$, $C_{asp,R}$ and C_{gas} are unaffected by whether coke is forming or not and they are calculated as follows:

$$C_{malt,R} = C_{malt,ori} \cdot e^{(-k_H t)} \tag{6}$$

$$C_{asp,R} = C_{asp,ori} \cdot e^{(-k_A t)} \tag{7}$$

$$\begin{aligned} C_{gas} = {} & (1-a) \cdot C_{malt,ori} \cdot (1 - e^{-k_H t}) \\ & + (1-m-n) \cdot C_{asp,ori} \cdot (1 - e^{-k_A t}) \end{aligned} \tag{8}$$

In Eqs. (6)–(8), $C_{malt,ori}$ and $C_{asp,ori}$ are the original maltenes and asphaltenes concentrations respectively and t is the reaction time in seconds.

During the coke-induction period

$$C_{asp,P} = a \cdot C_{malt,ori} \cdot (1 - e^{-k_H t}) + m \cdot C_{asp,ori} \cdot (1 - e^{-k_A t}) \tag{9}$$

$$C_{asp} = C_{asp,R} + C_{asp,P} \tag{10}$$

$$C_{malt,P} = n \cdot C_{asp,ori} \cdot (1 - e^{-k_A t}) \tag{11}$$

$$C_{malt} = C_{malt,R} + C_{malt,P} \tag{12}$$

$$C_{coke} = 0 \tag{13}$$

where $C_{malt,P}$ and $C_{asp,P}$ are product maltenes and asphaltenes content, respectively.

The coke-induction period corresponds to the time when the maximum solubility of asphaltenes is reached. For times greater than the coke-induction period, $C_{asp,P}$ is given by the above Eq. (9) and the concentration of product maltenes and coke are given by

$$C_{malt,P} = \frac{yC_{coke}}{(1-y)} + n \cdot C_{asp,ori} \cdot (1 - e^{-k_A t}), \tag{14}$$

$$\begin{aligned} C_{coke} = (1-y)\{ & a \cdot C_{malt,ori} \cdot (1 - e^{-k_H t}) + m \cdot C_{asp,ori} \cdot (1 - e^{-k_A t}) \\ & - S_L[C_{malt,ori} \cdot e^{(-k_H t)} + n \cdot C_{asp,ori} \cdot (1 - e^{(-k_A t)})]\} \end{aligned} \tag{15}$$

Table 1
Original compositions of thermal cracked oils.

Oil	Oil initial composition and data set					
	Asphaltenes (g/100 g oil)	Maltenes (g/100 g oil)	Coke (g/100 g oil)	Gas (g/10 g oil)	Temperature range	Data sets
Pembina Oil (Unoxidized)	0.2	99.8	0	0	360–450 °C	4
Frisco Countess Oil (unoxidized)[a]	8.0	90.0	2	0	360–420 °C	3
Frisco Countess Oil (oxidized)	13.67	86.33	0	0	360–420 °C	3
North Bodo Oil (unoxidized)	11.8	88.2	0	0	360–420 °C	3
North Bodo Oil (oxidized)	15.2	82.4	2.4	0	360–420 °C	3
Marguerite Lake Bitumen	18.3	81.7	0	0	360–420 °C	3
AOSTRA Drum 433 (unoxidized)	20.7	79.3	0	0	360–420 °C	3
AOSTRA Drum 20 (unoxidized)	18.9	81.1	0	0	360–420 °C	3
Athabasca Bitumen (unoxidized)	19.96	80.04	0	0	303–452 °C	10

[a] Friso Countess Oil (unoxidized) shows the initial coke content is 2 g/100 g original oil, this was an unexpected initial composition. 2.4 g coke is initially present in the oxidized North Bodo oil because some maltenes of the original oil has been pre-oxidized to asphaltenes and then converted to coke.