

Compositional Characteristics and Geochemical Significance of *N*-alkanes in Process of Crude Oil Cracking

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Abstract: The simulation experiments with crude oil samples have been performed in laboratory by using high temperature simulative techniques, and the characteristics of change of compositions have also been analyzed by geochemical methods in the cracking process. The results indicate that before a large number of gaseous hydrocarbons being generated by cracking of crude oil, the *n*-alkanes of high molecular weight from crude oil has already begun to be pyrolyzed, and C₁₅⁺ hydrocarbon mainly cracked into C₆–C₁₄. With increasing maturity, C₆–C₁₄ is further transformed into C₁–C₅, accompanied by the output of benzene, ultimately forming methane and cracking bitumen. In the pyrolysis of *n*-alkanes process, abundance of benzene and its homologue show significantly increasing, which can be used as potential distinguishing marks of crude oil cracking. Besides, comparative simulation experiments on *n*-hexadecane have been performed in laboratory by the same experimental condition, and it shows that the characteristics of change of compositions are basically the same as that of *n*-alkanes in crude oil.

Key Words: oil cracking; simulation experiment; *n*-alkanes; *n*-hexadecane; benzene series

1 Introduction

Because of the development in the natural gas exploration and expansion of the research areas, genesis study on gases generated due to crude oil cracking is gaining increased attention. Crude oil Cracking is the process that alkane molecules are broken down into lower hydrocarbons by breaking the carbon–carbon and carbon–hydrogen bonds using high temperature. In the past decade, several scholars carried out a large number of experimental studies based on different needs^[1–7]. They focused on the changes in the rate of gas production, the composition characteristics of gaseous products, and the difference between the crude oil cracking gas and the kerogen cracking gas in chemical composition.

The *n*-alkanes are often the dominant components in crude oil. During the cracking process, changes in the characteristics of oil and component characteristics of products can represent the characteristics of the crude oil cracking to a larger extent. The main purpose of this study is to analyze the characteristics of *n*-alkanes distribution and the components characteristics of

experimental products in the oil cracking process by simulation experiment and to provide the basis for the study of oil.

2 Samples and experiments

The samples of crude oil cracking stems from Yangwu 2 wells of Manjiaer Depression in Tarim Basin. The main geochemical characteristics of samples are shown in Table 1. The process of crude oil cracking is compared with the process of cetane cracking for accuracy.

All the samples were studied using the open system (PY-GC) pyrolysis experiment. Each 300 ug sample was first placed in an annealed stainless steel reactor that was sealed. Then, the reactor containing the sample was placed into the SGE pyrolysis furnace, and air in the reactor was displaced by helium. The reactor was heated to 350 °C quickly and for durations of 40 min. When the temperature of the reactor was decreased from 350 °C to room temperature, the stable carbon isotopes, gas compositions were analyzed using GC and

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Table 1 Physical properties of crude oil samples in pyrolysis experiments

Physical properties	Yangwu 2 wells
Depth (m)	6453.0–6499.35
Layer	O
Density ($\text{g}\cdot\text{cm}^{-3}$)	0.8544
Viscosity ($\text{mm}^2\cdot\text{s}^{-1}$)	4.9
Pour point ($^{\circ}\text{C}$)	<–40
Sulfur (%)	0.01
Wax (%)	0.02
Resin + Asphaltene (%)	16.6

GC-IR-MS. After the residual gas in the stainless steel reactor was expelled using helium, the residual samples after simulation on 350 °C were continually simulated in the same manner at various temperatures of 400, 450, 500, 550, 600, 650, 700, 750, 800 and 850 °C, respectively. Figure 1 shows the chromatographic characteristics of products at different temperatures of simulation experiment.

3 Results and discussion

3.1 Changes in characteristics of composition of high-carbon *n*-alkane in crude oil cracking process

As shown in Fig. 1, at the low-level temperature of 350 °C phase, the composition and distribution of *n*-alkanes are substantially the same as that of the sample after the crude oil cracking. In other words, an effective cracking reaction of the crude oil has not occurred at this stage, where the amount of the C_{25}^{+} *n*-alkanes is low.

Based on the group compositions and the changes in the characteristics of C_{15}^{+} , $\text{C}_{66}\text{--}\text{C}_{14}$, $\text{C}_{26}\text{--}\text{C}_5$, methane etc yield in the process of crude oil cracking, Hill et al. presented the changes of the characteristics in the different oil cracking maturity of crude oil^[7]. The main characteristic is that the high-carbon hydrocarbon compounds gradually change to the low-carbon hydrocarbon compounds in the process of crude oil cracking (Fig. 2).

It is very important to note that between 350 and 600 °C, the amount of cracking gas generated in the crude oil is less; however, in the presence of large amount of $n\text{C}_{25}\text{--}n\text{C}_{32}$ of *n*-alkanes, generation of cracking gas significantly increases (Figs. 1 and 2). We have the following questions. What are the factors that are related to the distribution of *n*-alkanes? What is the meaning for genesis?

A large number of studies have shown that the crude oils with different genetic types contain macrocrystalline wax (< $n\text{C}_{40}$) and microcrystalline wax (> $n\text{C}_{40}$) in different degrees. High-molecular-weight hydrocarbons (HMWHCs) concentration technology and high-temperature gas chromatography (HTGC) analysis techniques can be adopted to systematically detect the microcrystalline wax, and $n\text{C}_{90}$ of *n*-alkanes can be detected using the existing experimental conditions.

It is significant to note that $n\text{C}_{25}\text{--}n\text{C}_{35}$ macrocrystalline wax with the advantage of the crude oil parity does not exist in the Red Wash field of the United States; however, microcrystalline wax $n\text{C}_{43}\text{--}n\text{C}_{60}$ odd carbon has obvious advantages. Many experts believe that the high-carbon microcrystalline wax can easily crack and form medium chain length *n*-alkanes and then the odd-carbon number that is predominant of macrocrystal wax with medium chain becomes weak. Based on the scientific research on macrocrystalline wax and microcrystalline wax of Zhang 9 wells, Wei 135 wells ect. of Nanyang Depression in China, the results show that the distribution and causes of this phenomenon also exists^[8]. In other words, the type of microcrystalline wax alkane can not be detected by conventional chromatography, but certain amount of such compounds exists in the crude oil. However, as the maturity increases, a crack can occur in the middle of the hydrocarbon chain length of these compounds (Figs. 1 and 3). It is obvious that this is consistent with the rules stated by Pepper and Dodd^[4] and Hill et al.^[7] described the changes of the composition of compounds in the process of the crude oil cracking. The crude oil cracking begins by breaking the HMWHCs into lower-medium chain length of hydrocarbons and then the generation of cracking of gaseous hydrocarbons occurs.

In other words, in the simulation experiment, at 400–600 °C, the amount of generated $\text{C}_1\text{--}\text{C}_5$ short chain of gaseous hydrocarbons is thimbleful, but this does not mean that the cracking of *n*-alkanes is ineffective. This is basically consistent with that proposed by Hill et al.^[7], that is, in the early stage of crude oil cracking, the conversion of C_{15}^{+} hydrocarbons to $\text{C}_6\text{--}\text{C}_{14}$ hydrocarbons occurs.

3.2 Characteristics of composition and distribution of low-carbon number of *n*-alkanes

The content of gaseous *n*-alkanes in crude oil is often low, and to certain extent, it will increase along with the decrease in density of crude oil. As the temperature of the simulation experiment increases, the process of crude oil cracking occurs from which the low-carbon number of *n*-alkanes are generated.

3.2.1 Characteristics of $\text{C}_1\text{--}\text{C}_5$ gaseous hydrocarbon

As shown in Fig. 1, in the simulation experiment, at 350–550 °C, the amount of gaseous hydrocarbons was still low and did not increase, which reflects that the generation of gas by pyrolysis is low. In other words, when the simulation temperature is below 550 °C, the cracking of the crude oil is not effective. Figure 4 clearly illustrates the characteristics.

Compared with Fig. 3, it is clear that the pyrolysis process of *n*-alkanes is a step-by-step process. In the temperature range of 350–550 °C, the amount of gaseous hydrocarbons is less; at this stage, the number of high-carbon *n*-alkanes is

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