Sulfur Analysis and Sulfur Transfer Rule During Simulated Thermal Processing of Heavy Oil

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Abstract. The distribution and transfer of sulfide in the thermal reaction process are studied. It has found that different types of sulfur have different distribution patterns in the refining process. Thiophene derivatives with better thermal stability are mainly distributed in the heavy components, while mercaptans and small molecular thioethers with poor thermal stability are mainly distributed in the light components. During the thermal reaction, part of the sulfide will decompose or react to produce sulfide with a smaller molecular weight, which will be transferred to light components or gases. The thermal reaction temperature has a certain effect on the product yield and sulfur content. As the reaction temperature increases, the liquid yield increases and the sulfur content decreases, but the thermal reaction temperature has little effect on the sulfide type distribution.

Keywords: Sulfur transfer, thermal processing, sulfur distribution, heavy oil.

1. Introduction

With the increase in the extraction of global petroleum resources, the recoverable volume of high-quality crude oil has decreased. Crude oil has gradually developed in the direction of deterioration of high sulfur content, high acid value, and heavy quality [1]. The increase in sulfur content in crude oil has led to an increase in the cost of refining companies, and put forward more stringent requirements on the refining process. Changes in the sulfur content of crude oil will have corresponding changes in the sulfur content of each stream and distillate in the device and the distribution of sulfur types. This change in sulfur content will affect the quality of the produced product, causing the product to fail to meet the requirements, and further processing is required to meet the product quality requirements [2]. Therefore, it is very important to grasp the distribution of sulfur in each process of refining and its distribution characteristics, which is of great significance to the elimination of potential safety hazards in the refinery and the evaluation of equipment transformation space [3].

Sulfur is an important element in petroleum. Sulfur in petroleum products mainly exists in the form of mercaptans, sulfides, disulfides, thiophenes, benzothiophenes and their derivatives [4]. Fuel oil products basically contain sulfur substances. The presence of sulfur substances will cause the oil to generate SO₅ substances when burning, which will promote the emission of NOₓ substances and particulate matter [5]. The presence of sulfur in crude oil is the main reason for the presence of
sulfides in fuel oil. As the sulfur content of crude oil increases, the sulfur content of fuel oil will also change accordingly [6]. At present, hydrodesulfurization technology is widely used in industry to achieve the purpose of desulfurization of fuel oil. However, the cost of this technology is relatively high and the reaction conditions are relatively harsh, which requires us to develop a lower cost process. The goal of hydrodesulfurization is to achieve the purpose of desulfurization [7]. No matter what method is used, the determination of the distribution of sulfide in the device is essential.

Therefore, the research on the analysis and transfer of various types of sulfides in petroleum and its products is of great significance in the development of the refining process, the innovation of equipment and the elimination of potential safety hazards. To this end, this paper conducts a simulated thermal conversion reaction on heavy oil in the refinery, studies the sulfur content of the product and analyzes the sulfur composition, and initially explores the law of sulfur transfer in the refining process, so as to provide guiding recommendations for production.

2. Experimental reagents and methods
All reagents were of analytical grade and were used as received without further purification. Isopropanol, silver nitrate, ammonia, sodium hydroxide, petroleum ether (60-90 °C), isopentane were provided by Xiya Reagent Co., Ltd or Aladdin Reagent Company.

2.1. Heavy oil thermal reaction experiment
Remove a certain amount of crude oil into the reactor, install the reactor, and use nitrogen to remove the air in the reactor. Adjust the electric heating mantle to reach the specified temperature, quickly put the reactor into the heating mantle, connect the condenser tube, collect the liquid at the end of the condenser tube, and collect the gas at the end of the liquid collection. After 40 minutes of reaction, the gas was taken out with nitrogen, and the total reaction time was 1 hour. The collected liquid, gas and coke products are distributed and weighed and the yields of formic acid gas, liquid and coke are combined.

2.2. Determination of total sulfur content
The ANTEK9000 total sulfur analyzer is used to measure the sulfur content in gas, liquid and solid materials. Put the sample into a furnace above 1000 °C to completely burn. The sulfur element was converted into SO₂. The sulfur dioxide absorbs ultraviolet light and converts it into excited sulfur dioxide. When the excited state returns to the steady state, fluorescence is emitted, and the detector detects a signal. According to the called standard curve, the sulfur concentration can be obtained by integrating the curve.

2.3. Determination method of mercaptan sulfur content in oil
Using silver nitrate alcohol standard solution as a titrant, potentiometric titration was performed in a sodium acetate-isopropanol solvent system with a sample dissolved. According to the potential jump point, determine the end point of the titration. From the amount of silver nitrate alcohol standard solution consumed during a potential jump, the thiol sulfur content is calculated according to the stoichiometric relationship between silver nitrate alcohol and mercaptans.

2.4. Determination of sulfide sulfur content
Using lead tetraacetate-glacial acetic acid solution as the titrant, the system was subjected to oxidation-reduction titration. Among them, lead tetraacetate is the oxidant, and a small amount of KBr aqueous solution is the catalyst. Potentiometric titration is performed in an environment of glacial acetic acid and toluene. The end point of the titration is determined according to the potential jump point. According to the volume of lead tetraacetate used for titration, calculate the sulfide sulfur content of the sample.
3. Experimental results and discussion

3.1. Product distribution after thermal reaction

After the crude oil undergoes thermal reaction, the quality of the liquid and coke obtained is shown in Table 1. The gas quality is obtained by the method of subtraction.

| Temperature reflux / °C | Sampling quality / g | Coke quality / g | Liquid quality / g | Gas quality / g |
|-------------------------|----------------------|------------------|-------------------|-----------------|
| 480                     | 24.1754              | 1.0653           | 20.0248           | 3.0853          |
| 520                     | 20.7451              | 0.8093           | 18.4631           | 1.4727          |

From the data in Table 1, the calculated liquid gas, yield and green coke rate are shown in Figure 1.

Through the research on the product yield distribution, it is found that the liquid yield of the crude oil is higher than 80%, while the yield of coke and gas is lower. It shows that the crude oil composition is lighter and the quality is better. As the temperature increases, the liquid yield increases, while the coke yield decreases. It shows that in the process of processing the heavy oil, increasing the temperature can increase the yield of gasoline and diesel, reduce coke products, and increase the added value of products.

3.2. Total sulfur content and distribution of thermal reaction products

The total sulfur content of the gas, liquid and coke products after the thermal reaction were measured respectively, and the experimental results are shown in Figure 1.

In order to compare the transfer law of sulfide in the thermal reaction process, the yield and sulfur distribution were compared. The experimental results are shown in Figure 2.
Figure 2. The yield, sulfur content, and sulfur distribution in gas-liquid-solid products after thermal reaction (left picture after reaction at 480°C, right picture after reaction at 520°C).

It can be seen from the data in Table 6 that there is little difference between the two. As the temperature increases, the migration of sulfur to the heavy components intensifies, and the sulfur content in the liquid decreases. As the temperature rises, the amount of hydrogen sulfide generated by the thermal reaction of sulfur in the raw material increases, and the sulfur content of the gas increases with the rise of temperature [8]. It can be seen from the influence of the reaction temperature on the sulfur distribution that during the thermal reaction, increasing the temperature can promote the transfer of sulfur to the gas phase, which is beneficial to reduce the sulfur distribution in coke and liquid products.

From the thermal reaction sulfide analysis results, it can be seen that as the reaction temperature increases, the total sulfur content of the coke decreases, and the sulfur content of the liquid decreases. This is because as the reaction temperature rises, the hard-to-decompose thiophene sulfides further undergo polycondensation reaction and enter the coke. For mercaptans, as the reaction temperature increases, the mercaptan sulfur content increases slightly, indicating that the temperature rises, causing a part of the sulfide to be further cracked into small molecules of mercaptans, resulting in an increase in the mercaptan content [9].

3.3. Influence of thermal reaction on the distribution of sulfur types of products
Two types of sulfur, mercaptan and sulfide, in the liquid product obtained after the thermal reaction were analyzed, and the results are shown in Table 2.

Table 2: Analysis of mercaptan sulfide sulfur in liquid products

| Temperature reflex / °C | Thiol sulfur content / μg. g⁻¹ | Sulfide sulfur content / μg. g⁻¹ |
|-------------------------|-------------------------------|-------------------------------|
| 480                     | 84.28                         | 413.01                        |
| 520                     | 85.25                         | 399.98                        |

It can be seen from Table 2 that at the two reaction temperatures, there is little difference in the content of thiol and thioether sulfur. The content of thiol sulfur increases with the increase of temperature, while the change law of thioether sulfur content is opposite [10]. Compared with crude oil, after thermal reaction, the content and proportion of sulfide sulfur are reduced, indicating that sulfide sulfides are unstable under high temperature conditions and are prone to decomposition.

According to the potentiometric titration method, thiols and thioethers in the liquid products are measured. The sulfur distribution of the liquid products is shown in Figure 3.
It can be seen from the distribution of sulfur types in the liquid product in Figure 4 that mercaptans are the least, sulfides are also less, and the other types are mainly thiophene-type sulfides. It shows that after thermal reaction, mercaptans and thioethers are easily converted, mainly through the formation of hydrogen sulfide or dehydrogenation to thiophene sulfides. From the perspective of reaction temperature, different temperatures have little effect on the distribution of sulfur types in the liquid product [11]. It shows that under the condition of 500 °C in thermal reaction, carbon-sulfur bonds are very active, and mercaptans and thioethers are easily converted. Since carbon-sulfur bonds are very active, the effect of temperature is not obvious.

3.4. Sulfur transfer law of heavy oil during thermal reaction

Based on the analysis of sulfur composition, a schematic diagram of the transfer of various types of sulfides during the thermal reaction process is summarized. See Figure 4.

![Sulfur transfer in thermal reaction](image)

**Figure 4.** Thermal reaction sulfur transfer diagram
4. Conclusions
During the thermal reaction of heavy oil, the mercaptan and sulfide are easy to crack at high temperature, and accumulate to light components and intermediate components in the refining process. The thiophene is not easy to decompose, and it mainly accumulates in heavy components during oil refining. The thermal reaction temperature has a certain effect on the product yield and sulfur content. As the reaction temperature increases, the liquid yield increases and the sulfur content decreases. The thermal reaction temperature has little effect on the distribution of sulfide types.

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