



Study on the formation, determination, and removal of elemental sulfur in ultra-low sulfur gas oil



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ABSTRACT

The question as to the formation of elemental sulfur in petroleum has never been definitely settled, although there are many references in the literature to the presence of elemental sulfur in distillates. In connection with studies on sulfur compounds in petroleum distillates, the presence and behavior of elemental sulfur in gas oil, especially in ultra-low sulfur gas oil are important. A rapid and accurate method for the analysis of elemental sulfur by GC–PFPD was developed and a series of experiments was carried out to clarify the formation mechanism of elemental sulfur. The results showed that $(\text{NH}_4)_2\text{S}_n$ was found to be easily oxidized to free sulfur when contacted with air and the oxidation of ammonium polysulfide was the main formation mechanism of elemental sulfur in the hydrotreating of gas oil. It was revealed that nitrogen-containing molecules in the oil feed and NH_4^+ contained in the HDS catalyst can result in the formation of $(\text{NH}_4)_2\text{S}_n$. A method with high efficiency and selectivity to remove elemental sulfur from hydrotreated gas oil by Na_2S washing was developed for analysis purpose.

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1. Introduction

Deep desulfurization of gas oil has become one of the most important approaches to meet the increasingly stringent environmental requirement and quality standard of gas oil [1]. In order to develop more active hydrotreating catalysts that can achieve deep hydrodesulfurization of gas oil, investigations on sulfur content and sulfur distribution are very important, especially for gas oil with sulfur content lower than 50 ppm or 10 ppm in the near future [1–5].

Not only some refractory substituted dibenzothiophenes (DBT) but also elemental sulfur has been detected in hydrotreated oil [6,7], which indicated that elemental sulfur was produced during the HDS process of gasoline or gas oil. The mechanism of the formation of elemental sulfur in the HDS process has not been clarified yet. Several possibilities were considered [6]: (1) Cracking or recombination of H_2S during HDS reaction; (2) Oxidation of H_2S after HDS reaction; and (3) Oxidation of ammonium polysulfide $((\text{NH}_4)_2\text{S}_n)$.

Once stable elemental sulfur is formed, it is difficult to remove by conventional methods, such as alkaline washing or nitrogen stripping. Therefore, the total sulfur analysis results of the hydrotreated oil cannot reflect the activity of hydrotreating catalyst, and the choice for the best catalyst may be misled by the result.

To eliminate the elemental sulfur from petroleum products, several conventional methods were developed for the removal of elemental

sulfur from hydrocarbon fractions, such as adsorption by heavy metals like silver, copper, or mercury.

Elemental sulfur is a primrose yellow solid with several structures, such as S_2 , S_6 , S_7 , and S_8 , and the structure and state change with temperature [8,9]. Microanalysis methods for the determination of elemental sulfur include chemical methods [10–12] and instrumental methods such as electrochemical analysis, chromatography, and XPS, among which the chromatographic method is quick, simple, and accurate [13,14].

In the present work, the elemental sulfur in hydrotreated gas oil was determined by a GC–PFPD method. The formation mechanism of elemental sulfur was investigated by a series of laboratory experiments and a simple and feasible method of removing elemental sulfur was developed.

2. Experimental

2.1. Analysis method of elemental sulfur

Sulfur solutions with different sulfur contents were prepared with chemically pure sublimed sulfur as solute and analytically pure toluene as solvent. The weight percentage content of the sulfur solutions was 300, 196, 104, 52, 20, and 10 ppm.

A gas chromatograph equipped with a pulsed flame photometric detector (GC–PFPD), and a fused silica capillary column, was used to analyze the elemental sulfur and organic sulfur compounds in gas oil. The conditions of the GC–PFPD were appropriate for the analysis of the sulfur distribution in hydrotreated gas oil. Initially the oven temperature

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was set at 80 °C and maintained for 2 min, then the temperature was raised to 280 °C at a rate of 6 °C/min. The inlet and detector temperatures were both 300 °C.

2.2. Experimental methods on possible formation mechanism of elemental sulfur

Because the composition of gas oil is very complex, several simple solutions instead of real gas oil were used to imitate the formation of elemental sulfur, avoiding the influences of other components in gas oil. Several experiments were designed, according to the possible formation mechanisms proposed in the literature.

2.2.1. Experiment 1: oxidation of H₂S to produce elemental sulfur

A solution of H₂S in cyclohexane was prepared (sample A) and 1 μl of the solution mixed with 1 μl air was injected into the GC inlet set at 200–300 °C. The elemental sulfur produced from H₂S was then detected by the PFPD detector. In contrast, another 1 μl sample without air was injected, and analyzed by GC–PFPD.

2.2.2. Experiment 2: oxidation of (NH₄)₂S_n to produce elemental sulfur

Several drops of ammonia were added to Sample A, and the resulting solution was called sample B (solution of (NH₄)₂S_n). Several drops of NaOH aqueous solution were added to sample B, and the mixed solution was labeled sample C. Samples B and C were analyzed by GC–PFPD.

2.2.3. Experiment 3: investigation of the origin of (NH₄)₂S_n

A solution of dibenzothiophene (DBT) in toluene was used as feed-stock of the HDS reaction to study the formation of (NH₄)₂S_n. Another solution with DBT and quinoline was used to measure the influence of nitrogen-containing molecules on the (NH₄)₂S_n formation. Two different catalysts were used for the HDS reactions, one was a bulk Ni–Mo catalyst (named catalyst A) derived from porous ammonium nickel molybdate ((NH₄)H₂Ni₂(OH)₂(MoO₄)₂) [15], the other was a commercial NiMoP/Al₂O₃ catalyst (named catalyst B). The HDS reactions were carried out in a continuous flow pressure microreactor, at 280 °C, a H₂ pressure of 4.0 MPa, a liquid hourly space velocity (LHSV) of 2.0 h⁻¹, and an H₂/oil ratio of 500. The sulfur in the products after HDS was determined by GC–PFPD.

2.3. Removal of elemental sulfur from hydrotreated gas oil

Washing gas oil with a Na₂S solution was applied for analysis purpose. The Na₂S washing was carried out as follows: A 10 wt.% Na₂S aqueous solution and a hydrotreated gas oil were mixed with a volume ratio of 10:1. The mixture was stirred for 2 h at the desired temperature and separated by a tap funnel. The separated gas oil was washed more than 3 times with water.

3. Results and discussion

3.1. Analysis method of elemental sulfur by GC–PFPD

The analysis conditions are one of the most important factors that influence the sulfur structures detected by GC–PFPD, because the structure of elemental sulfur depends on temperature [13]. In order to study whether S₈ can be decomposed during the chromatographic analysis, the influence of injection temperature was investigated between 120 and 320 °C. The results (Fig. 1) show that only one peak is present in the GC spectrogram when the injection temperature was lower than 180 °C and the peak intensity increased with temperature, while three peaks were detected when the injection temperature was higher than 180 °C. The three peaks at higher temperature represent S₆, S₇, and S₈. Based on the phase changes of elemental sulfur with temperature and the GC–MS analysis by Zhao et al., [9] the peak at lower temperature is attributed to S₈. We conclude that it was difficult to evaporate

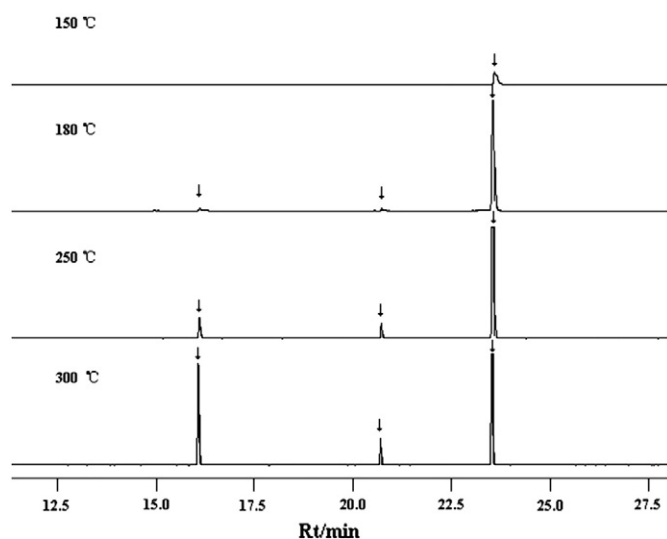


Fig. 1. Influence of injection temperature on the analysis of elemental sulfur.

elemental sulfur at lower temperature and that as a consequence the quantitative result of the determination of elemental sulfur might be too low. When the injection temperature was higher than 180 °C, elemental sulfur mainly pyrolyzed to S₆, S₇, and S₈. A too high injection temperature might lead to the pyrolytic decomposition of compounds in gas oil and accelerate the damage of the capillary column. Therefore the appropriate injection temperature for sulfur determination was chosen as 300 °C.

Solutions of elemental sulfur with different sulfur contents were analyzed by GC–PFPD and the peak areas of elemental sulfur are shown in Table 1. The results show that three S peaks were present for all solutions with sulfur content varying from 52 to 300 ppm. The peak area ratios of S₆/S₇ and S₇/S₈ were almost constant, which indicates that the structure characteristics of elemental sulfur presented some regularities and that the concentration did not affect the structure transformation. However, only one or two peaks of elemental sulfur were present in the spectrograms when the sulfur content was very low.

A quantitative curve was drawn of the sum of the square roots of the peak areas against the sulfur content (Fig. 2), according to the sulfur species analyzed by the GC–PFPD. Fig. 2 shows that there is a linear relation between the square root of the peak area and the sulfur content. Therefore, elemental sulfur could be determined quantitatively by GC–PFPD when the sulfur content was lower than 300 ppm.

3.2. Study of the formation mechanism of elemental sulfur

3.2.1. Oxidation of H₂S to elemental sulfur

Large amounts of H₂S are generated during the HDS process, and some H₂S dissolves in the hydrotreated oil, which might become oxidized after contact with air. It is well known that H₂S could not be oxidized to elemental sulfur at room temperature, but at elevated temperature H₂S might be oxidized. In order to study at how much

Table 1
Peak areas of elemental sulfur with different sulfur contents.

Sulfur content/ppm	Peak area				
	S ₆	S ₇	S ₈	S ₆ /S ₇	S ₇ /S ₈
300	139,668	30,577	407,695	0.343	0.075
196	74,548	14,646	204,130	0.365	0.072
104	24,823	4706	66,848	0.371	0.070
52	6998	1329	18,454	0.379	0.072
20	702	–	2113	0.332	–
10	–	–	332	–	–

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