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Ultrasound-assisted oxidative desulfurization of bitumen and analysis of sulfur forms in the treated bitumen

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1. Introduction

Bitumen is the heavy oil including in oil sand. Oil sand, which is a natural resource, is composited by heavy oil (9–13%) , silica sand (80–85%) and water (3–7%) [1]. Synthetic crude oil is produced by separation of bitumen from sand followed by refining it. However, since bitumen contains about 5 wt% sulfur [2], using the bitumen without desulfurization treatment produces harmful air pollutants (e.g. SO_x). Hence, desulfurization treatment for bitumen has been developed. Currently, the hydrodesulfurization method is used as a desulfurization technology for bitumen. This method removes sulfur from bitumen as hydrogen sulfide by reacting with hydrogen gas at high pressure (8.8 MPa) and high temperature (200–450 °C) using catalyst such as CoMo or NiMo supported Al_2O_3 [3]. However, such the high temperature and high pressure condition relates to high energy consumption. Therefore, oxidative desulfurization has been studied as a desulfurization method that can be performed at low temperature and atmospheric pressure. The oxidative desulfurization method oxidizes sulfur in bitumen to sulfoxide (S=O) and sulfone (O=S=O) groups using H_2O_2, and the sulfur, which increased the polarity, is removed from bitumen as sulfate by reacting with NaOH. The oxidative reaction and the oxidized sulfur removal reaction proceed at the interface between heavy oil and the aqueous solution. Thus, sufficient mixing of the two solutions is required. Therefore, we have been focused on stirring effect of ultrasound to apply for the oxidative desulfurization method. Bitumen shows a very high viscosity at room temperature (2.5×10^5 cP) and the high viscosity means that it does not have fluidity. Increasing the fluidity is necessary to improve the reactions of oxidative desulfurization processes. Increase of the temperature and addition of organic solvents are the way to reduce the bitumen viscosity. Hence, we focused on condensate, which is used as a diluent to transport bitumen to the refinery plant. In the previous study, 66.1% of sulfur was removed from bitumen using n-pentane, which is the main component of condensate, H_2O_2 (15 wt%) and NaOH (5 mol/l) under ultrasound (28 kHz) irradiation [4].

Sulfur in bitumen makes two main sulfur forms, sulfide (aliphatic) and thiophene (aromatic). It is necessary to treat each chemical form of sulfur appropriately for more efficient desulfurization. The purpose of this study is to investigate the chemical form of sulfur remained in bitumen after oxidative desulfurization with ultrasound.

2. Experiment

Bitumen (1 g) and n-pentane (15 ml) were added into a jacket-type beaker which can keep constant temperature at 20 °C. Then, ultrasound (28 kHz, 200 W) was irradiated to the solution in beaker for 10 min. Next, H_2O_2 solution (15wt%, 15 ml) was added to the beaker followed by ultrasound irradiation for 30 min. Finally, NaOH solution (10 mol/l, 15 ml) was added to the beaker followed by ultrasound irradiation for 30 min. To confirm the effect of ultrasound in the oxidative desulfurization process, stirring (500 rpm) condition was also performed (**Table I**).

The sulfur contents in the bitumen treated under various conditions were analyzed using combustion ion chromatography and the desulfurization ratios were calculated using the following equation (1).

$$\text{Desulfurization ratio (\%)} = \frac{\mathrm{Sb}}{\mathrm{Sa}} \times 100 \quad (1)$$

S_a (wt%): Weight percentage of sulfur in raw bitumen
S_b (wt%): Weight percentage of sulfur bitumen treated

The sulfur form in bitumen after oxidation and desulfurization process was confirmed by XANES (X-ray Absorption Near Edge Structure) analysis using BL-11B (High Energy Accelerator Research Organization).

3. Results and discussion

Table I shows the condition of oxidation and desulfurization treatment using ultrasound (US) and stirring (STR). The sulfur content (S_a) of the bitumen (raw bitumen) used in this experiment was 5.01 wt%. **Fig. 1** shows the desulfurization ratio of bitumen treated by each condition. This result indicated that the condition A, ultrasound is utilized for both H_2O_2 and NaOH treatment, showed the highest desulfurization ratio (68.1%). Okawa et al. desulfurized 82% of bitumen using tetrahydrofuran (THF) and 28 kHz ultrasound [5]. On the other hands,

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nonpolar n-pentane used in this study is less dispersibility of bitumen and less hydrophilic than THF. Therefore, the desulfurization ratio in this study is lower than the ratio of previous research. Condition B, H_2O_2 treatment using ultrasound followed by NaOH treatment using stirring, showed only 8.4%. Condition D showed the lowest ratio, 1.2%. This result indicated that almost sulfur was not removed with only stirring. However, the desulfurization ratio of condition C showed 64.1%, which was the next best result after condition A. Therefore, it is estimated that the NaOH treatment with ultrasound contributed to high desulfurization ratio. The organic layer (n-pentane + bitumen) and the aqueous layer (H_2O_2 solution) were added with equal volume into the beaker, and H_2O_2 treatment using ultrasound (condition A) made partially miscible of bitumen and aqueous solution (**Fig. 2a**). Following the H_2O_2 treatment, NaOH solution was added into the solution. The miscibility of n-pentane in the organic layer with aqueous solution and the high density of the 10 mol/l NaOH solution probably led to the separation of the two layers. Therefore, it is necessary to transfer the oxidized sulfur from bitumen to the aqueous layer, and it is thought that ultrasound was more effective than stirring in the mixing action (**Fig. 2b**). **Fig. 3** shows the results of XANES analysis of bitumen after H_2O_2 and NaOH treatment in condition A. After H_2O_2 treatment, it was confirmed that the thiophene-derived peak at 2473.3 eV was smaller and the sulfoxide (around 2475 eV) and sulfone (around 2479 eV) peaks became larger than the peaks of raw bitumen. Thus, it was clarified that the sulfur in bitumen was oxidized. The thiophene peak after NaOH treatment was larger than that after H_2O_2 treatment, and the two oxidized sulfur peaks became smaller. It can be considered that the proportion of unoxidized thiophene remaining in bitumen increased because the oxidized sulfur was removed by NaOH. Therefore, it is suggested that sufficient oxidation of thiophene lead to increasing the desulfurization ratio. These results indicated that ultrasound is necessary to use at NaOH treatment to proceed desulfurization of bitumen efficiently and it is important to investigate a sufficient sulfur oxidation method.

Acknowledgment

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Reference

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Table I Experimental condition of oxidative desulfurization process.

Condition	H_2O_2 treatment	NaOH treatment
A	US	US
B	US	STR
C	STR	US
D	STR	STR

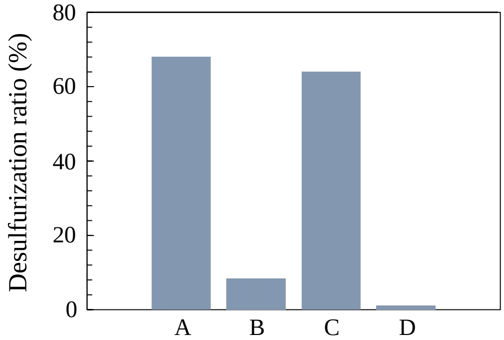

Fig. 1 Desulfurization ratio of bitumen treated by each experimental condition.

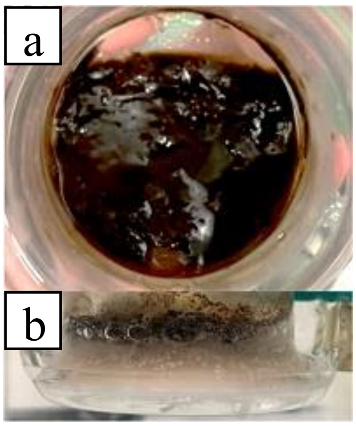

Fig. 2 Appearance of the bitumen in solutions after H_2O_2 treatment (a) and during NaOH treatment (b).

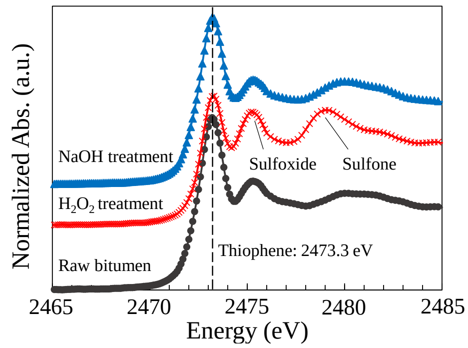

Fig. 3 XANES spectrum of bitumen after each treatment at experimental condition A.