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Simultaneous recovery and desulfurization of bitumen from oil sand using ultrasound irradiation

超音波を利用したオイルサンドからのビチューメン回収過程における脱硫の検討

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1. Introduction

Deposits of oil sand exist throughout the world, and major deposits have presently been found in Alberta (Canada) and Orinoco (Venezuela).[1] Oil sands are a mixture of bitumen (heavy oil), siliceous material such as sand and sandstone, and water. Open-pit mining and SAGD (Steam Assisted Gravity Drainage) are used as the main quarrying methods. Open-pit mining is employed for oil sand located on or near to the surface. The bitumen content of oil sand is 10–15 wt%. Therefore, in order to use bitumen as a fuel source, it must be extracted from oil sand. The main industrial processes used to extract bitumen from oil sand are treatment with hot water (~ 100°C) and steam (> 100°C) in rotating drums.[1] These high temperatures relate to concern of high energy consumption. To overcome this problem, researchers have been studying on recovery of bitumen from oil sand at lower temperature. Previous study has been reported that bitumen was successfully recovered from oil sand and then collected using ultrasound irradiation and hydrogen peroxide solution (H_2O_2) after the addition of sodium hydroxide (NaOH).[2, 3]

Alberta bitumen includes 4.6±0.5 wt% of sulfur. Based on the analysis of X-ray absorption near-edge structure spectroscopy (XANES), 62% is aromatic and 38% is aliphatic sulfur.[4, 5] Many studies has been carried out about desulfurization of crude oil. Oxidative desulfurization (ODS) is the current method for the desulfurization technology because it can be carried out under mild conditions such as low temperature and pressure. Hydrogen peroxide has been used widely as an oxidizing reagent because it is strong oxidant and environment-friendly. The ODS process has the oxidation process of sulfur using H_2O_2 followed by its removal process using alkali solution. ODS is used for removing thiophene in most crude oils and coals. In our previous study, ODS was carried out to produce bitumen with a low sulfur content using ultrasound irradiation.[6] And the removal ratio of sulfur in bitumen reached 52% using H_2O_2 (30 wt %) and NaOH (saturated) under ultrasound irradiation. However, to improve the ratio of desulfurization, it is necessary to disperse bitumen in water. Bitumen recovery process and ODS process are very similar procedure. Therefore, it seems to carry out simultaneously.

In this study, we focused on dispersion (emulsification) of bitumen in the solution to increase surface area of oxidation reaction and to improve recovery rate of bitumen from oil sands. Acetic acid (CH_3COOH) was used as a surfactant in this study. In this manuscript, we mention about the effect of CH_3COOH on bitumen emulsification and desulfurization.

2. Experimental

1 g of bitumen was treated in H_2O_2 solution (30 wt %, 20 ml) with the addition of CH_3COOH (5 ml) at 85°C followed by NaOH (saturated) treatment under ultrasound irradiation for 10 min each treatment (**Fig.1**). All the reagents were analytical grade and purchased from Wako Corp. (Japan).The sulfur intensity of treated bitumen was analyzed using an X-ray fluorescence spectrometer (XRF; Shimadzu EDX-7000) with vacuum measurement unit and a 5mm of collimator.

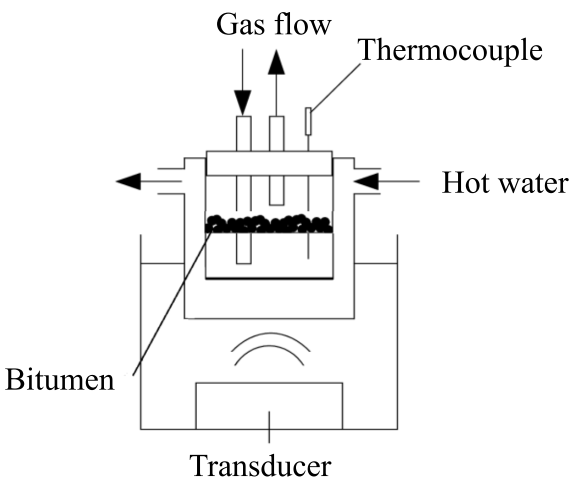

Fig.1 Schematic design of experimental apparatus of desulfurization at 85°C without surfactant.

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3. Results and Discussion

Fig. 2 shows the appearance of bitumen in the H_2O_2 solution without (a) and with (b) addition of CH_3COOH. After irradiated (28kHz, 200W) for 10 min in H_2O_2 and CH_3COOH, the bitumen was successfully dispersed into the solution to form oil/water emulsion. Next, we performed to remove sulfone which was generated by oxidation of sulfur using alkali solution. **Fig. 3** showed the sulfur intensity of raw and treated bitumen for each condition. After this result, oxidation of sulfur using H_2O_2 is effective to reduce sulfur intensity in bitumen. Comparison of sulfur intensity with and without addition of CH_3COOH, the addition of CH_3COOH is higher than the sulfur intensity without the addition of CH_3COOH (H_2O_2 and NaOH only). We considered that CH_3COOH reacted with NaOH solution, thus, the concentration of NaOH solution for sulfur removal was reduced. We confirmed that the addition of CH_3COOH improves bitumen emulsification. However, the reaction of CH_3COOH with NaOH solution suppressed further sulfur removal in bitumen. From this study, we confirmed that the treatment of bitumen with H_2O_2 and NaOH is the best condition for sulfur removal as it can remove 52% of sulfur in bitumen.

The emulsification of bitumen was successfully achieved with the addition of CH_3COOH into the H_2O_2 solution. Hence, we treated oil sand using H_2O_2, CH_3COOH and NaOH solutions to perform the simultaneous process of bitumen recovery and bitumen oxidative desulfurization. 3 g of oil sand was placed into a solution containing of H_2O_2 (30 wt %, 20 ml) and CH_3COOH (5 ml) at 85°C. The solution was treated under ultrasound (28 kHz, 200W) irradiation for 10 min. Then, a saturated NaOH (20 ml) solution was added into the solution. The solution was irradiated for 10 min. As the results, the emulsification of bitumen in the solution was not achieved. Besides that, oil sand was also floated on the solution without the separation of bitumen from sand. This appearance is also similar with the condition of treated oil sand in high conc. H_2O_2 solution.[3)] The surface electrical charge of bitumen and sand plays a significant role for bitumen liberation from sand. Silica (sand) zeta potential becomes positive at low pH (pH<2) solution and it makes difficult to recover bitumen from oil sand. Therefore, our future plan is recovery of the bitumen from oil sand using surfactants, such as tetrahydrofuran, which don't effect on pH of the solution.

References

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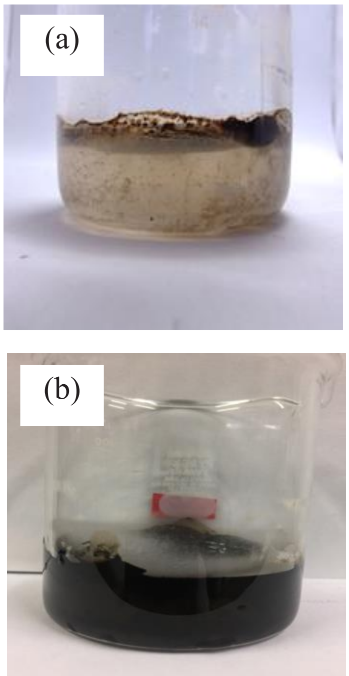

Fig.2 Appearance of without addition (a) and addition of CH_3COOH (b) into the H_2O_2 solution including bitumen followed by irradiation for 10 min at 85°C

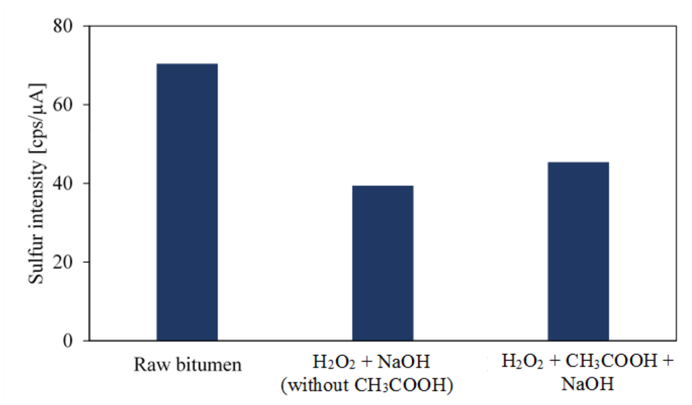

Fig.3 Sulfur intensity of raw and treated bitumen