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Separation and Desulfurization of Bitumen from Oil sand Using n-Pentane and Ultrasound

n-ペンタンと超音波を用いたオイルサンドからのビチューメンの分離及び酸化脱硫

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1. Introduction

Oil sand is deposited mainly in Canada and Venezuela, and is a mixture of heavy oil called bitumen(3-20 wt%), sand(80-87 wt%), and water (3-6 wt%) [1]. Bitumen is a heavy oil whose light components are decomposed underground by bacteria, etc., and is used for a fuel as synthetic crude oil. Since bitumen has a very high viscosity at room temperature (250,000 cP), it is difficult to separate it from sand, but since the viscosity decreases with heating. The viscosity is reduced to about 1000 cP at 80 °C [2] and bitumen can be separated from sand [3,4]. Then, condensate (a type of crude oil collected during natural gas production) [5] is added as a diluent in order to transport the recovered bitumen to the refining plant through a pipeline. Since the bitumen contains about 5 wt% sulfur [2], desulfurization treatment is necessary. Currently, hydrodeslfurization method is adopted for bitumen and desulfurization is occured with high pressure hydrogen gas(8.8 MPa) at high temparature(200-450 °C) using a catalyst such as $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ [6]. However, the aspect of energy consumption is an issue. Oxidative desulfurization method is an attractive desulfurization method which can be performed with low temperature and atmospheric pressure. The mechanizm of desulfurization is following. Organic sulfur in bitumen is oxidized by H_2O_2 and then the oxidized sulfur is removed by NaOH solution from the bitumen to the aqueous solution. Ultrasound has been studied to recover bitumen from oilsand and to desulfurize from bitumen more effectively. It is reported that the desulfurization ratio was improved by ultrasound irradiation because the bitumen was dispersed in the solvent and the reaction with the solution was promoted [7].

It has been reported that 90% of bitumen could be recovered from oil sand at room temperature by utilizing ultrasound and tetrahydrofuran (THF) as a diluent of bitumen [8]. However THF is not used in the field. Hence, it is necessary to adopt other organic solvents to reduce the viscocity of bitumen. Condensate is actually used in Canada as a diluent to reduce the viscocity of bitumen. However, there is no report about both treatment of separation and desulfurization of bitumen from oil sand by using condensate. Therefore, the purpose of this study is to reduce the viscosity of bitumen in oil sand using n-pentane, which is the main component of condensate, to separate bitumen from sand using ultrasound, and to desulfurize bitumen by oxidative desulfurization method.

2. Experimental

2.1. Separation of bitumen from oil sand

1 g of oil sand(Alberta, Canada) was added to a jacket-type beaker that can keep the constant temparature at 20 °C, and 15 or 30 ml n-pentane was added. Then, ultrasound(28 kHz) was irradiated for 20 or 60 min. After that, in order to investigate the proportion of bitumen separated from sand, the beaker was transferred to a water bath and 15 ml ion-exchanged water was added into the beaker. The n-pentane(boiling point : 38 °C) was evaporated by heating at 45 °C for 2 hours, and bitumen and warm water formed two layers. Bitumen was collected from upper layer.

2.2 Oxidative desulfurization of bitumen

1 g of bitumen(Alberta, Canada) and 40 ml of n-pentane were added to a jacket-type beaker, and ultrasound was irradiated. Then, 1 ml of H_2O_2(concentration of 5 or 30 wt%) was added, and ultrasound was irradiated under air flow at 50 or 100 ml/min. 1 ml of NaOH(10 mol/l) was added and ultrasound was irradiated. Finally, 30 ml of ion-exchaned water was added and ultrasound was irradiated to separete water-soluble sodium sulfate from bitumen to the aqueous solution. Ultrasound irradiation time is 30 min and the reaction temperature is 20 °C.

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3. Results and discussion

3.1. Separation of bitumen from oil sand

The bitumen was separated from oil sand using n-pentane and ultrasound. And we changed the additional amount of n-pentane and irradiation time of ultraosund to decide the apropriate condition. Then, the recovered bitumen (including sand and water) was analyzed by thermogravimetry-differential thermal analysis, and the purity of bitumen was calculated from Eq. (1).

$$\text{Purity of bitumen (\%)} = \frac{\mathrm{Wb}}{\mathrm{Wb+s}} \times 100 \quad (1)$$

W_{b+s} (g): Weight of bitumen and sand in recovered sample

W_b (g): Weight of bitumen in recovered sample

The bitumen separated from the oil sand contains sand. Therefore, if the separation is not sufficient, the purity shows a low percentage. **Fig. 1** shows the purity of bitumen under each condition. Bitumen content in raw oil sand was 19.0%. It was found that increasing the amount of n-pentane does not lead to an improvement of purity. On the other hand, longer sonication time made higher purity of bitumen. Therefore, it was cleared that extending the ultrasonic irradiation time rather than increasing the amount of n-pentane promotes the separation of bitumen from sand.

3.2. Oxidative desulfurization of bitumen

We investigated the effects of air injection rate and H_2O_2 concentration on sulfur oxidation of bitumen under ultrasound assisted oxidative desulfurization. The oxidized bitunmen was analyzed using Fourier transform infrared spctrometer (**Fig. 2**). In this manuscript, we introduce the results using three treatment conditions, and each combination of H_2O_2 concentration and air injection rate is following; (1) 5 wt%, 50 ml / min, (2) 5 wt%, 100 ml / min, (3) 30 wt%, 100 ml/min. From **Fig. 2**, a peak of 1024 cm^{-1} derived from S = O bond was confirmed in all samples. The desulfurization ratio under each condition was 40.2% by (1), 49.4% by (2), and 46.7% by (3), respectivery. Condition (2) showed the good result. H_2O_2 reacted with NaOH and O_2 bubbles were generated. Especially high concentration of H_2O_2 generated a large number of bubbles. These bubbles brought bitumen to the surface of solution before oxidated sulfur moving to the solution. Thus, we think 5 wt% concentration is suitable for sulfur oxidation.

4. Conclusion

In this study we approached separation of bitumen from sand and oxidative desulfurization for bitumen using n-pentane and ultrasound. We found that longer sonication time is more effective than increasing amount of n-pentane to facilitate separation of bitumen from sand. Besides, high concentration of H_2O_2 did not increase desulfurization ratio of sulfur.

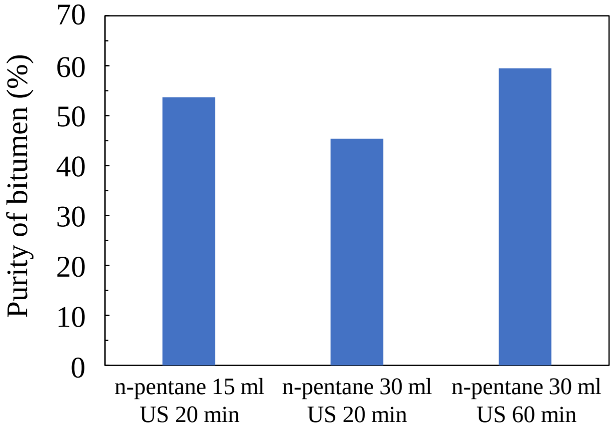

Fig. 1 Purity of recovered bitumen treated by each experimental condition.

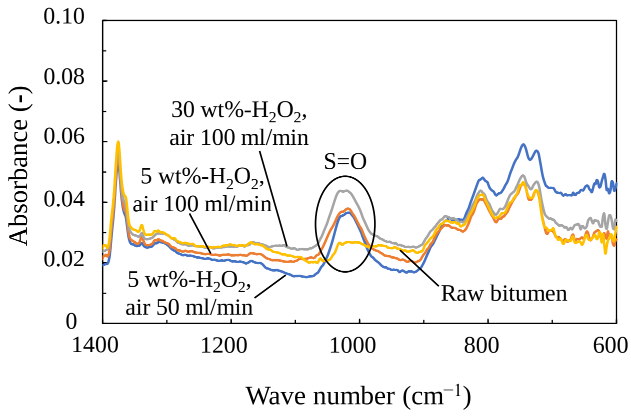

Fig. 2 FT-IR spectra of bitumen samples oxidized at two different H_2O_2 concentrations and two different air flow rate.

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