


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

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Bitumen contains approximately 5 wt% sulfur so it must be removed before being used as fuel. Herein, we performed oxidative desulfurization of bitumen at room temperature using n-pentane and ultrasound to reduce bitumen viscosity and mix the bitumen-dissolved n-pentane and aqueous reaction solution physically. The oxidative states of sulfur in bitumen and desulfurization ratio were investigated to confirm the oxidative desulfurization process. Additionally, we developed a novel method for separating bitumen into maltene and asphaltene. Thus, 81.0% of sulfur in maltene was successfully removed by removing asphaltene, which is difficult to remove sulfur using n-pentane in oxidative desulfurization.

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Oil sand is a natural resource that is mainly produced in Canada and comprises a heavy oil bitumen (9–13 wt%), sand (80–85 wt%), and water (3–7 wt%).¹⁾ Bitumen is separated from oil sand mined by open-pit mining before upgrading to synthetic crude oil for use as fuel. The viscosity of bitumen is very high (2.5×10^5 mPa·s) at room temperature (20 °C),²⁾ making it difficult to separate bitumen from oil sand except by heating the oil sand or using organic solvents. Therefore, bitumen is separated from oil sand using hot water (≥ 80 °C) in Canada.³⁾ Because raw bitumen contains 4.6 ± 0.5 wt% sulfur,⁴⁾ it is necessary to remove the sulfur from bitumen to avoid the formation of sulfur oxides (SO_x), which causes environmental problems when used as fuel. Therefore, the desulfurization method of bitumen was investigated. Hydrodesulfurization is the conventional method for removing sulfur from bitumen. This technique removes sulfur as hydrogen sulfide (H₂S) by reacting sulfur in bitumen with H₂ gas in the presence of a catalyst including NiMo/Al₂O₃ or CoMo/Al₂O₃. The advantages of hydrodesulfurization include the reuse of H₂ and the efficient recovery of oil after treatment. However, the treatment process requires high temperature (200 °C–450 °C) and high H₂ pressure.⁵⁾ Thus, we focused on oxidative desulfurization at room temperature and atmospheric pressure.^{6–9)} In this method, thiophene is oxidized using hydrogen peroxide (H₂O₂), which is then removed to an aqueous solution using sodium hydroxide (NaOH).⁶⁾ Thiophene (aromatic) and sulfide (aliphatic) are the two sulfur forms found in bitumen. Without the need for oxidation treatment, sulfide is removed using NaOH solution to form sodium sulfide (Na₂S). However, because of steric hindrance, removing thiophene from bitumen with only NaOH is difficult.¹⁰⁾ Therefore, it is necessary to increase the polarity of sulfur by oxidizing it to form sulfoxide or sulfone. Duarte et al. reported that 98% of sulfur is removed from model oil containing thiophene using peracetic acid and methanol on oxidative desulfurization.⁹⁾ However, because bitumen is not fluid, mixing bitumen and aqueous solution at room temperature is difficult. Therefore, sufficient reaction area between bitumen and reaction solution is required for oxidation and sulfur removal. Hence, we focused on condensate as an organic solvent to reduce the viscosity of bitumen at room temperature. Condensate is a byproduct of natural gas production that is used in Canada as a diluent to reduce bitumen viscosity during the transportation of bitumen to a refining plant via a pipeline.¹¹⁾ However, mixing

condensate and aqueous reaction solutions is difficult because the main component of condensate is hydrophobic n-pentane. Therefore, we considered the use of ultrasound. When acoustic pressure becomes negative at the antinode of a standing wave, ultrasound irradiation generates bubbles from dissolved gases in the solution. The collapse of the bubbles eventually causes a strong jet flow.^{12,13)} Therefore, mixing bitumen and aqueous solution using ultrasound would expedite the oxidation and removal of sulfur in bitumen. We performed oxidative desulfurization of bitumen using ultrasound (28 kHz) and n-pentane at 20 °C.¹⁴⁾ Thus, 66.1% of the sulfur in the bitumen separated from oil sand was removed because bitumen-dissolved n-pentane was efficiently mixed with the reaction aqueous solution. However, it is unclear how the stirring effect of ultrasound contributes to the oxidation and desulfurization processes of bitumen. Clarifying this mechanism will improve the efficiency of oxidative desulfurization of bitumen. Therefore, here, we investigated the effect of ultrasound on the oxidative desulfurization of bitumen by analyzing the desulfurization ratio and the oxidative state of sulfur in bitumen before and after oxidation and desulfurization treatments. Furthermore, we developed a simple method for separating hydrocarbon forms from bitumen, and we performed oxidative desulfurization for each form to improve the efficiency of the desulfurization treatment.

The experimental equipment used was the same as in our previous study.⁷⁾ 1 g of bitumen (Alberta, Canada) containing 5.01 wt% sulfur (S_b) and 15 ml of n-pentane (Wako, 98%) were added to a beaker. An ultrasound generator (TA-4021; Kaijo) with a 28 kHz transducer was used to irradiate the solution for 10 min at 20 °C. The ultrasound irradiation output was set at 200 W, and the ultrasound power reached to the solution in the beaker was measured using the calorimetry method and the value was 12.5 W.¹⁵⁾ Subsequently, 15 ml of H₂O₂ aqueous solution (15 wt%) was added to the solution, followed by 30 min ultrasound irradiation. Finally, 15 ml of NaOH aqueous solution (10 mol l⁻¹) was poured into the solution, which was then irradiated with ultrasound for 30 min. The same experiment was conducted with mechanical stirring (500 rpm) instead of ultrasound to investigate the effect of ultrasound on the oxidative desulfurization of bitumen. After the desulfurization treatment, the bitumen was washed with ion-exchanged water until the pH is less than 7, followed by drying. The sulfur content of bitumen

after oxidative desulfurization was measured using combustion ion chromatography (AQF-100; Mitsubishi Chemical). During this analysis, sulfur in the sample was oxidized by combustion under ambient atmosphere at 900 °C and generated sulfur dioxide was dissolved in hydrogen peroxide solution and oxidized to sulfate ions. Subsequently, the solution was sent to the column with the eluent and the concentration of sulfur was determined via ion chromatography. The desulfurization ratio was calculated using the following equation:

$$\text{Desulfurization ratio}(\%) = \frac{S_b - S_a}{S_b} \times 100, \quad (1)$$

where S_b (wt%) is the weight percentage of sulfur in the bitumen before oxidative desulfurization treatment and S_a (wt%) is the weight percentage of sulfur in the bitumen after oxidative desulfurization. The desulfurization ratio of each condition of oxidative desulfurization treatment is shown in Table I. The desulfurization ratio of condition A, which was treated with ultrasound in both oxidation and desulfurization, was the highest value (68.1%) under these conditions. Furthermore, condition C, which is treated with stirring in the oxidation process and ultrasound in the desulfurization process, had the second highest desulfurization ratio (64.1%). The X-ray Absorption Near-Edge Structure (XANES) (BL-11B; High Energy Accelerator Research Organization) spectra of sulfur forms in bitumen after oxidation and desulfurization at condition A and after oxidation using a mechanical stirrer are shown in Fig. 1. The peak intensity of sulfoxide (2475.2 eV) and sulfone (2479.0 eV) increased after ultrasound oxidation based on the peak of thiophene (2473.3 eV),¹⁶⁾ indicating that the oxidation of sulfur in bitumen has proceeded. Additionally, the peak intensity derived from sulfur oxides decreased after desulfurization treatment based on the peak of thiophene, indicating that sulfur oxides are removed. However, when the bitumen is oxidized by stirring (dotted line), the peak intensity of sulfoxide increases but the peak of sulfone is not confirmed. Therefore, the oxidation of sulfur using ultrasound was more proceeded than using a stirrer because the jet flow generated by the collapse of bubbles efficiently mixed bitumen and aqueous solution. Under alkaline conditions, bitumen generates naphthenic acid, which is a surfactant, on its surface.¹⁷⁾ Bitumen and aqueous solutions are easily mixed, not only by ultrasound stirring but also by decreasing the interfacial tension of bitumen-dissolved n-pentane and aqueous reaction solution after the addition of NaOH. Therefore, sulfur oxidation occurs in the desulfurization process under ultrasound irradiation by reacting bitumen and H_2O_2 that remains after oxidation treatment at condition C. Thus, the desulfurization ratio showed the second highest value because of the

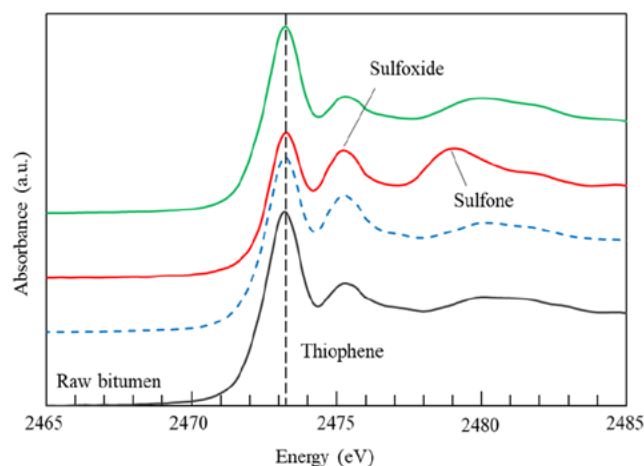


Fig. 1. (Color online) XANES spectra of bitumen after oxidation (red solid line) and desulfurization (green solid line) under condition A, and the spectra after oxidation using a stirrer (dotted line).

formation of sulfur oxides in bitumen even during the desulfurization process. The optimum desulfurization conditions were investigated in terms of the effect of the mixing method on oxidation and removal of sulfur in addition to our previous report.¹⁸⁾ However, the highest desulfurization ratio (68.1%) at 10 mol l⁻¹ NaOH solution was not significantly different from the previously reported desulfurization ratio (48.6%) at 5 mol l⁻¹ NaOH.¹⁴⁾ Thus, this oxidative desulfurization method is difficult to improve the desulfurization ratio. Next step, we investigated that desulfurization of hydrocarbon forms separated from bitumen. Bitumen is composed of light hydrocarbon maltene and heavy hydrocarbon asphaltene. Asphaltene is semisolid at room temperature because of its high molecular weight. Therefore, asphaltene is less useful for fuel because it precipitates as residue at the bottom of distillation columns during crude oil refining processes. Thus, we performed oxidative desulfurization on the maltene separated from bitumen to improve the desulfurization efficiency. Furthermore, we developed a simple method for separating bitumen into maltene and asphaltene using ultrasound. After adding 1 g of bitumen and 15 ml of n-pentane into the beaker, the slurry was obtained by ultrasound irradiation for 10 min [Fig. 2(a)]. Subsequently, ion-exchanged water was added to the beaker, followed by mechanical stirring (500 rpm) for 30 min, and two solution layers were appeared in the beaker. Part of the bitumen was dissolved in n-pentane, which has lower specific gravity than water, and the solids precipitated at the bottom of the beaker [Fig. 2(b)]. After the stirring treatment, asphaltene was recovered. The n-pentane layer was decanted to another beaker and n-pentane was evaporated by heating at 60 °C. The remaining liquid after evaporation of n-pentane, which was maltene, was recovered. Previous research reported that asphaltene can be dispersed stably in nonpolar n-pentane because resin, component of maltene, surrounds the asphaltene molecules.¹⁹⁾ Therefore, aggregation of asphaltene was inhibited and a slurry of bitumen and n-pentane was obtained after sonication. Because asphaltene has more polar functional groups than other hydrocarbon forms in bitumen, it has a higher affinity for water than n-pentane. Therefore, asphaltene transferred from n-pentane (upper layer) to water (lower layer), and precipitation of asphaltene occurred by

Table I. Desulfurization ratio of bitumen with each experimental condition [NaOH aq: 10 mol l⁻¹, treatment time: total 60 min (each 30 min)].

Condition	Treatment		Desulfurization ratio (%)
	Oxidation	Desulfurization	
A	Ultrasound	Ultrasound	68.1
B	Ultrasound	Stirring	8.4
C	Stirring	Ultrasound	64.1
D	Stirring	Stirring	1.2

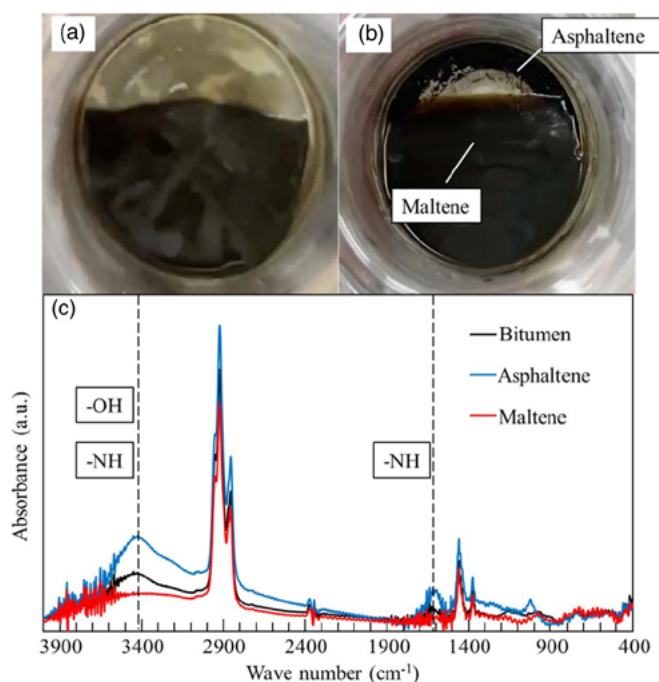


Fig. 2. (Color online) (a) Slurry of bitumen and n-pentane after sonication, (b) appearance of asphaltene from bitumen after stirring, and (c) FT-IR spectra of bitumen, maltene and asphaltene. Figures (a) and (b) are top view of samples in beaker.

stirring with water. Precipitation of asphaltene did not occur after ultrasound irradiation after the addition of water, instead of stirring mixed bitumen-dissolved n-pentane and water. The samples measured were prepared as pellet-type by mixing 1 mg of maltene or asphaltene with 100 mg of KBr followed by pressing using a hand-press device (MP-1; JASCO). The absorbance spectra of Fourier transform infrared spectroscopy (FT/IR-4600; JASCO) of separated maltene and asphaltene are shown in Fig. 2(c). The peaks derived from hydroxy and amide groups were confirmed around 3420 cm^{-1} in the spectrum of asphaltene. Additionally, the peak related to amide groups was confirmed at 1614 cm^{-1} .²⁰⁾ However, these peaks were not observed in the spectrum of maltene, indicating that bitumen is well separated into maltene and asphaltene. Furthermore, each sulfur content of maltene and asphaltene measured was 4.43 wt% and 6.88 wt%, respectively. Bitumen mined in the same region used in this experiment is composed of 82.2 wt% maltene and 17.8 wt% asphaltene.²¹⁾ Therefore, the weight percentage of sulfur in raw bitumen is calculated from this reported proportion and measured sulfur content of maltene and asphaltene, and the value is 4.87 wt%. The measured sulfur content of raw bitumen used in this experiment was 5.01 wt%. Therefore, the sulfur content confirmed the separation of maltene and asphaltene from bitumen. Then, the same procedure for bitumen was used to perform oxidative desulfurization on 0.5 g of maltene or asphaltene with the addition of 7.5 ml of n-pentane, hydrogen peroxide aqueous solution (15 wt%), and NaOH aqueous solution (10 mol l^{-1}). A similar experiment was also performed using a stirrer instead of ultrasound. The desulfurization ratio under each condition for oxidative desulfurization treatment is shown in Table II. Therefore, 81.0% of the sulfur in maltene could be removed using ultrasound, indicating that sulfur in maltene

Table II. Desulfurization ratio of maltene and asphaltene under each experimental condition.

Material	Treatment	Desulfurization ratio (%)
Maltene	Ultrasound	81.0
	Stirring	5.9
Asphaltene	Ultrasound	7.6
	Stirring	2.2

was removed more efficiently than in bitumen. The XANES spectra of maltene and asphaltene after oxidation and desulfurization using ultrasound are shown in Fig. 3. By using ultrasound, the peak intensity of sulfoxide can be increased based on the peak of thiophene after oxidation. Moreover, the peak intensity derived from sulfur oxides was decreased after desulfurization treatment based on the peak of thiophene, indicating that sulfur oxides are removed. However, the peak at 2480.4 eV was due to sulfate (SO_4^{2-}), forming sodium sulfate after desulfurization treatment. Therefore, the desulfurization ratio of maltene was higher than that of bitumen because sulfur in maltene is more easily oxidized by H_2O_2 than sulfur in asphaltene. Conversely, the chemical reaction of sulfur in asphaltene did not proceed because the spectra after oxidation and desulfurization of asphaltene remained unchanged. The dispersion of asphaltene in n-pentane does not occur because of the separation of the resin from asphaltene. Therefore, oxidative desulfurization of asphaltene was impossible because the reaction surface area of asphaltene and the aqueous solution was low. The presence of asphaltene reduces the efficiency of oxidative desulfurization of bitumen using n-pentane. Thus, the effective desulfurization of maltene is due to the asphaltene separation.

Compared with ultrasound, stirring did not proceed in sulfur oxidation in the bitumen. However, using ultrasound on desulfurization treatment effectively mixed bitumen and

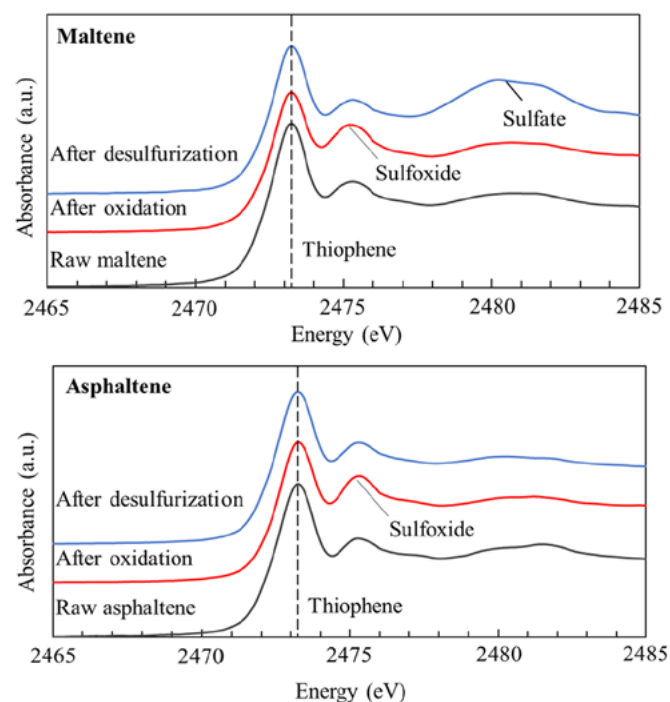


Fig. 3. (Color online) XANES spectra of maltene and asphaltene after oxidation and desulfurization using ultrasound.

H₂O₂ that remained after oxidation treatment, and sulfur was oxidized. Therefore, using ultrasound on the desulfurization process after oxidation using stirring could remove sulfur from bitumen as much as using ultrasound for oxidation and desulfurization treatments. We developed a simple method for separating bitumen into maltene and asphaltene at room temperature. Sulfur in maltene is removed more efficiently than sulfur in bitumen by oxidative desulfurization using ultrasound.

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