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Enhanced biodesulfurization of bunker oil by ultrasound pre-treatment with native microbial seeds

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ABSTRACT

This work investigated the effect of ultrasound on the biodesulfurization of bunker oil by the native microbial cells in oil/water biphasic system. The operational parameters for the desulfurization procedure such as ultrasonic irradiation time, ultrasonic wave amplitude, biocatalyst initial concentration and ratio of oil phases to aqueous phases were studied. An obviously positive effect was observed after introduction of ultrasound into the BDS system. The sulfur content of bunker oil did not decrease in absence of ultrasound pre-treatment. After ultrasonic pre-treatment, about 10–20% of sulfur was removed for the samples without any additive and was dependent on ultrasonic irradiation time, ultrasonic wave amplitude, biocatalyst initial concentration and ratio of oil phases to aqueous phases. During the desulfurization, even though an easily available carbon source, glycerol, was supplied, some low molecular weight hydrocarbons can be consumed by cells as carbon source, resulting in a loss in the fuel value or energy loss.

1. Introduction

Bunker oil, which is derived from crude oil and a bottom product of petroleum refining, is one of the most commonly used forms of marine fuel for shipping. The supply of bunker oil to marine vessels is a multi-billion dollar industry in Singapore [1]. The composition of bunker oil is complex and encompasses a rich mixture of alkanes, alkenes, aliphatic and aromatic hydrocarbons which contributes much to its high viscosity nature [2]. Especially with the presence of asphaltenes, which have an extremely complex structure and a relatively high molecular weight, it increases the difficulty for the refinery of bunker oil [3]. Furthermore, bunker oil contains elevated levels of sulfur (1.5–4 wt%) which generate serious air pollution during combustion due to SO_x emission [4]. As land-based sources of SO_2 emission are gradually coming down, those from shipping show a continuous increase [5,6]. It has also been suggested that merchant fleets are significant contributors to global anthropogenic emissions [7]. Annual SO_2 emissions from ships were estimated at 16.2 million tonnes in 2006, rising to 22.7 million tonnes in 2020 under the "business-as-usual" scenario [5]. Therefore, there is an urgent need for removing the main contaminants such as sulfur from Bunker oil.

Currently, oil sulfur content is treated and removed by hydrodesulfurization (HDS) process for industrial purpose, in which hydrogen gas is used in presence of metallic catalysts (metal oxides) to reduce sulfur to H_2S. However, to reach a satisfactory level of sulfur removal, this process requires high temperature (200–450 °C) and high pressure (up to 100 atm). Moreover, it is difficult to remove some hetercyclic sulfur compounds such as dibenzothiophene (DBT) and substituted DBTs which are major sulfur content in bunker oil [8].

Recently, biodesulfurization (BDS) process using microorganisms is known to be an alternative technology to remove sulfur from crude oil with mild processing conditions and reasonably low treatment cost [9]. Moreover, BDS processes have been expected to remove the recalcitrant organic sulfur compounds found after the conventional hydrodesulfurization (HDS) treatment, mainly polycyclic aromatic hydrocarbons (PAH) as dibenzothiophene (DBT) [10–12]. For the BDS process to be effective, however, the solubilization of insoluble or slightly soluble organ sulfur compounds into aqueous solution is a prerequisite. Especially for bunker oil, which has the higher viscosity than gasoline and diesel, the low solubility in aqueous phase might be one of major limitations to BDS. Reducing the viscosity of bunker oil and increasing the contact of bunker oil with biocatalyst is the critical step in BDS. In previous studies [13–16], the BDS process was improved substantially through accelerating the transfer of DBT from oil phase to cell surface by adding surfactants to form emulsion and adding

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Table 1
Elemental and chemical composition of bunker oils.

Elemental composition (%w/w)	MFO 380
Carbon	81.2 ± 0.5
Hydrogen	15.2 ± 0.7
Nitrogen	0.52 ± 0.2
Sulfur	3.17 ± 0.1
Asphaltene	9.4 ± NA
Vanadium (mg/kg)	116.3 ± 5.2
Nickel (mg/kg)	42.1 ± 2.4
Water content	NA
Dynamic viscosity (Pa s @ 40 °C)	0.79

organic solvent to increase solubility. However, organic solvents and surfactants have been known to cause secondary pollution problems after treatment. Also there may be a difficulty associated with separation that requires adding demulsifier to demulsification or conventional energy-intensive processes such as distillation. In addition, solvents have been known to rupture the microbial cell during the BDS process [14].

It is well known that the use of ultrasound can significantly improve the liquid–liquid interfacial area through emulsification [17]. Very fine ultrasonic emulsions, which are much smaller in size and more stable than those obtained conventionally, greatly improve the interfacial area available for reaction, increase the effective local concentration of reactive species, and enhance the mass transfer in the interfacial region. Therefore it leads to a remarkable increase in solubility [18,19]. Furthermore, the cavitational energy produced by the ultrasound induced the formation of highly reactive radicals and cleavage of covalent bonds, causing the cracking of heavy oil to a lighter fraction, viscosity decrease and N and S conversion [20]. Several reports showed that ultrasound can significantly improve oxidative desulfurization in petroleum industry [21–25].

Based on these reports, we theorized that the application of an ultrasound to pre-treat the bunker oil before the BDS process would enhance BDS efficiency of bunker oil through enhancing the mass transfer of organosulfur compounds from oil to aqueous solution. This work investigated the desulfurization of bunker oil by growing cells of the native microbial seed in oil-to-water media after the ultrasonication pre-treatment oil samples. The effectiveness of this process on commercial bunker oil was evaluated. The operational parameters for the BDS procedure such as ultrasonic irradiation time, ultrasonic wave amplitude, biocatalyst initial concentration and ratio of oil phases to aqueous phases were investigated.

2. Materials and methods

2.1. Bunker oil

Bunker oil MFO 380 used in this study, which was a kind of very heavy oil with maximum viscosity of 380 centistokes, was kindly provided by the Maritime and Port Authority (MPA) of Singapore. Elemental and chemical composition of bunker oil is shown in Table 1.

2.2. Chemicals

Dibenzothiophene (DBT) (>98% purity) and dichloromethane (DCM) were purchased from Sigma–Aldrich, Singapore and all other chemicals used were analytical grade without further purification. Ultra pure water produced of a Millipore Milli-Q system was used to prepare all solutions in this study.

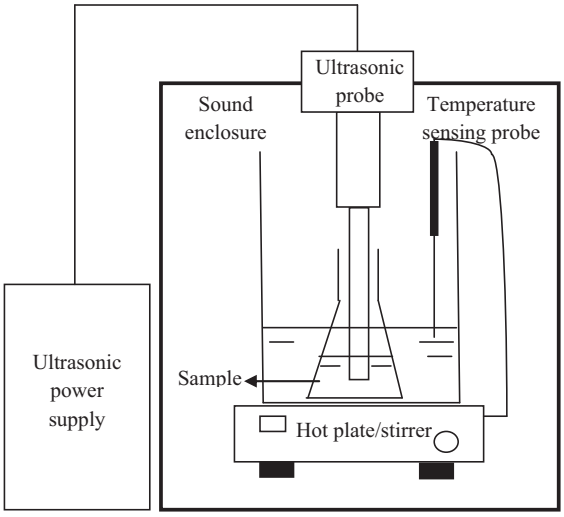

Fig. 1. Schematic diagram of ultrasound experimental setup.

2.3. Preparation of media

The basal salt medium (BSM) used for enrichment of microorganisms and BDS reaction steps was prepared as suggested by Li et al. [26] with some modifications and it was composed by KH_2PO_4 2.44 g L^{-1}, Na_2HPO_4 4.76 g L^{-1}, $MgCl_2{\cdot}6H_2O$ 0.4 g L^{-1}, NH_4Cl 2.0 g L^{-1}, $CaCl_2{\cdot}2H_2O$ 1.0 mg L^{-1}, $FeCl_3{\cdot}6H_2O$ 1.0 mg L^{-1}, $MnCl_2{\cdot}4H_2O$ 4.0 mg L^{-1} and 10 g L^{-1} glycerol.

2.4. Microbial seeds and incubation

Microbial seeds were enriched from an oil contaminated soil collected from the surface of an oil-contaminated parking lot, Singapore. Ten gram of soil was suspended in 100 ml of BSM, supplemented with 0.2 mmol L^{-1} DBT (added from a stock containing 100 mmol L^{-1} DBT in anhydrous ethanol) as sole sulfur source. The suspension was incubated on a rotary shaker (200 rpm) at room temperature for 5 days. After incubation, the soil mixture was briefly centrifuged at 3300 rpm for 30 min, and 5 mL of the supernatant was transferred to a 250 mL flask containing 100 mL of fresh BSM supplemented with DBT, and the mixture was reciprocally shaken for 5 days. The above procedure of enrichment was repeated four times before the enriched culture was used as the seed in the biodesulfurization test.

2.5. Ultrasonic pre-treatment

Fig. 1 shows the experimental setup used to conduct ultrasonic pre-treatment bunker oil sample. The reactor was a 250 mL Erlenmeyer flask that contained a biphasic system of 1 g bunker oil MFO 380 and 45 mL BSA aqueous solution. Ultrasound was generated by an XL2020 Sonicator® ultrasonic processor (Misonix Incorporated, New York, USA) equipped with a 20 kHz frequency probe (5 "L × 1.5" diameter, 12.7 cm × 3.8 cm), which was vertically dipped into the oil–BSM mixture. The position of the probe could be altered. The cycle time and the amplitude ratio could be varied. The temperature of the reactor was controlled using a constant-temperature hot plate with a temperature sensing probe. The accuracy of the temperature control was ±1 °C.

2.6. Biodesulfurization of bunker oil

After ultrasonic pre-treatment, 5 mL enriched culture (late exponential phase, about 6.5 g L^{-1}) were added into Erlenmeyer