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Evaluation of different demulsifiers for Marpol oil waste recovery

Yiu-hung Yau[a,*], Victor Rudolph[b], Kin-chung Ho[a], Cat Chui-man Lo[a], Kam-chau Wu[a]

[a] School of Science and Technology, The Open University of Hong Kong, Hong Kong, China
[b] School of Chemical Engineering, The University of Queensland, Australia

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ABSTRACT

Marpol oil waste composed of wasted oil with seawater which is challenging for waste treatment. Therefore, emulsified seawater has to be broken down for recovering the oil content involving chemical destabilizer to disperse water droplets or destroy emulsifiers.

This study aims to evaluate 37 products of demulsifiers (cationic, non-ionic and anionic) based on ability of water removal from Marpol oil waste. The results show that anionic and nonionic surfactants were found to be effective demulsifiers exhibiting good property for oil and water separation. The efficiency of the nonionic demulsifiers increases with the dosage up to a certain extent after which the efficiency falls. However, anionic demulsifiers do not show any decrease in efficiency at higher doses. Among all the tested anionic demulsifiers, sodium dioctyl sulfosuccinate (ALCOPOL O70 PG), sodium dioctyl sulfosuccinate (ALCOPOL O CONC 60%) and Oligoguluronate (DP9-6661) were with most outstanding performance. Additionally there is a general improvement in the performance of screened demulsifiers with increased temperature (70 °C). Sodium dioctyl sulfosuccinate (ALCOPOL O70 PG), sodium dioctyl sulfosuccinate (ALCOPOL O CONC 60%) and sodium dodecyl benzene sulphonate (DP9-6661) reached water removal performance percentage as 75%, 66.3% and 56.7% respectively after 30 h. When the water content of recovered oil was reduced to a certain level (below 10%), the heat valve was about 40 MJ/kg. The recovered Marpol oil waste was suggested to apply for low-quality fuel usage such as cement kilns and waste incinerators with its property of high energy value, low sulphur content and Polychlorinated Biphenyls (PCBs).

1. Introduction

Several million tonnes of oil are released annually into the world's oceans from shipping operations, presenting a major contribution to environmental degradation and a significant economic loss. These Marpol waste is an abbreviation for marine pollutant, which is typically composed of bunker C oil and bilge waste [1–3]. In Hong Kong, these Marpol waste is usually collected from the vessels in Victoria Harbour. Predominantly, emulsification occurred between seawater and bunker C oil fuel, together with minor quantities of bilge and wastewater, and this process is then believed to occur mostly in the storage tanks of vessels when there are sufficient mixing conditions due to movement of the vessel on the sea [1,4–6].

Marpol oil waste generated was directly discharged into the sea or being treated by waste oil collectors normally. However, it does not only waste non-renewable natural resources but it also causes serious environmental pollution such as serious damage to marine lives [1–3,5,7]. Therefore, these Marpol oil waste should be collected and treated properly.

Separation of the oil and water content from Marpol waste is significant for discharge and oil recovery. There is large amount of water in both the free state and emulsified state when it is pumped out from the vessels. Free water can be separated from the Marpol waste by simple settling but separating the emulsified water is much complicated. Seawater is a natural emulsifier which increases the viscosity of the waste oil, which make it difficult and enhance energy consumption to transfer from the barges to shore tanks for processing [5]. Water and salts in seawater further bring serious problems to the refinery processes such as corrosion and scaling. Moreover, salinity within Marpol waste decreases the medium hydrophilicity. This make emulsifier is more soluble in oil (external phase), and emulsion stability was then increased in high salinity [8,9].

Beside the potential environmental problems of Marpol discharge, petroleum resources are expected to become scare in many parts of the world [10,11]. The basic objective in Marpol oil recovery is to develop methods that create an energy recycling practice.

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[*] Corresponding author.
E-mail address: yhyau@ouhk.edu.hk (Y.-h. Yau).

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Removal of water from the emulsions is a key practice to convert oil waste into reusable energy [5,12,13]. These water contents were believed to affect the physical properties of recovered Marpol oil waste. For example, the water content often contain small amount of water soluble metals e.g. Na, K and Ca that cause corrosion of turbo engine at high temperature and lowering the quality of the fuel oil [5]. Moreover, Marpol oil waste includes emulsified seawater with high salinity, which reduces feasibility of direct recovery.

Currently, there are several available methods for enhancing the separation of water-in-oil emulsion, such as chemical demulsification [14–17], gravity or centrifugal settling [18], pH adjustment, filtration [19], membrane separation [20] and electrostatic demulsification [21]. However, most of the methods may need high cost and energy consumption such as centrifugal settling, heating treatment, electrostatic demulsification, and etc. On the other hand, some methods may not be effective to remove emulsified water from the Marpol oil waste. For example, Marpol oil wastes are too viscous to flow through the membrane and further block the pores during membrane filtration [5].

Applying demulsifying agents may then be one of the appropriate methods for water removal in Marpol oil recovery. It uses demulsifier to displace the emulsifiers from the interface and destabilize the emulsion when suitable demulsifier is provided. In a stable emulsion, the minute droplets of dispersed phase are stabilised by an interfacial film or stabilizing agent such that the droplets do not coalesce and do not respond to gravity settling. To break down the emulsion, the breaking of interfacial film is the key step [19–24]. The efficiency of using demulsifier for demulsification then depends on the factors including type of the demulsifier, water content in the emulsion and emulsion age [8,14,16,17,21,25,26]. A great number of demulsifiers have been formulated and used. The chemical structures for those demulsifiers are suitable as the lyophobic and lyophilic portions within the molecule can be custom-designed with the nature of the solvent and the conditions of use. Many more of chemical structures are still being formulated because the performance of demulsifiers is known to be crude oil specific and as field conditions change, the demulsifier requirements also changes [22–24]. Much research work has been carried out on emulsion breaking and separation of liquid phases in the petroleum industry [8,13,17,27–29]. No relevant research, however, has been done on recovery of oil from Marpol oil wastes [5]. Therefore, theoretical background is useful but extensive testing is absolutely necessary to select the most effective and efficient demulsifier [8,12,14,17]

In this study, characteristics in terms of types of the emulsion, water content and the settleability of the water content in Marpol oil waste was investigated. Each of different ionic and nonionic demulsifier specific for Marpol oil wastes was screened. Heating was applied to improve the performance for selected demulsifier. Recovered oil was then evaluated in terms of physical properties for fuel application.

2. Materials and methods

2.1. Marpol oil waste collection

Marpol oil wastes were obtained from the vessels in Hong Kong. A total 82 oil waste samples were collected from different barges in Hong Kong. A clean coliwasa was used to obtain the oil sample from the storage tank (Fig. 1). Coliwasa is used for obtaining a representative and full-depth sample from stratified liquids. It is used to obtain a vertical column of liquid representing an accurate vertical-section of the sampled material.

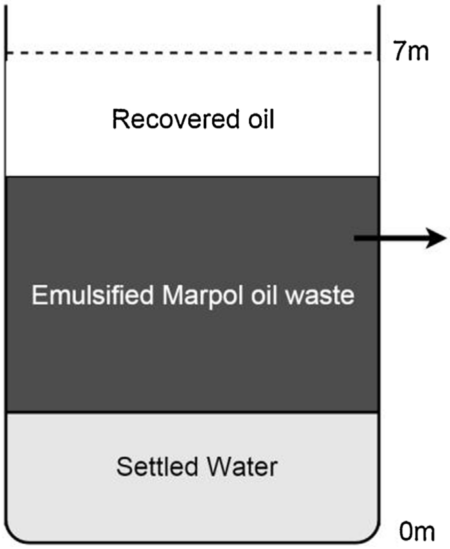

Fig. 1. Marpol oil waste samples from storage tank.

2 L of Marpol oil waste was then collected into containers. The oil waste sample is allowed to settle for 24 h at room temperature (21 °C). After the sample is settled, any free water separated at the bottom of sampling bottle will be drained off and removed. After draining, the sample was agitated using a magnetic stirrer for 10 min. This will facilitate uniform distribution of the emulsion and unsettled water throughout the mass of the Marpol oil waste in the container. Then, a few drop of the waste oil are poured into two beakers filled with toluene and water respectively to determine the types of the emulsion.

2.2. Settling test

250 mL of oil sample was transferred into each of dry measuring cylinders, and was stoppered. The volume of water layer formed at the bottom of the cylinder was recorded over 3 years for gravity separation under quiescent conditions and visual observations made. The water content was calculated directly from the ratio between initial volume and amount of water remained in the bottom of cylinder. Karl Fischer Titration method (ASTM E203) was also used to confirm the water content remaining in the emulsion samples.

2.3. Demulsifiers

The demulsifiers applied to the oil emulsions are obtained from the global manufacture of surfactants. These surfactants are of the anionic (numbered in A1–A12), cationic (numbered in C1-C15) and nonionic (number in N1-N10) types, which have been developed for oil/water separation. A1 to A3 have negative sulphonated head groups, A4 to A7 have negative sulphate groups and A8 to A12 have negative phosphate head groups. N1 to N10 are ethylene and propylene oxide copolymers, with hydroxyl end groups. C1 to C6 are quaternary ammonium chloride, C7 to C12 are ethoxylated amines and C13 to C15 are ethoxylated diamines.

2.4. Screening test of demulsifiers

2 L of waste oil sample was collected into glass bottles. Bottle tests were conducted at room temperature (21 °C) and 70 °C respectively. Water-in-Marpol oil emulsions (24%) were prepared in a glass bottle, which was mixed with a magnetic stirrer at 100 rpm for 10 min to ensure that the contents were uniformly distributed before filling up the 250 mL cylinders. At the same time, 0.05% to 2% by volume concentration of demulsifier was delivered using a micro