Effect of Coolant Temperature and Stirring Rate in the Separation of Oil from Bilge Water using a Stirred Freeze Crystallizer

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Abstract. Each year, marine activities has contributed to nearly half of the discharged oil into the oceans, where 10% of it were dumped bilge oil. The tankers release oily and chemical residue, causing pollution to the marine environment due to excessive contamination of bilge water. Therefore, all marine ships over 400 tons are required to install an oil-water separator (OWS) system on board to limit the discharge of oil into the oceans. However, the current OWS technologies such as gravity and centrifugation method have difficulties to comply with the oil/grease discharge standard of 15 mg/L set by Malaysia’s Department of Environment (DOE). This paper aims to introduce progressive freezing (PF) process as a new OWS method where it separates two liquid compounds based on their freezing point difference. One with higher freezing point will solidify first while another one will remain as liquid. In this study, the effect of coolant temperature and stirring rate towards oil/grease values were investigated. It was found that the highest efficiency of the PF process was obtained at stirring rate of 200 rpm and coolant temperature of -6°C. In addition, the best oil/grease value obtained was found to be lower than the discharge standard permitted by the Department of Environment (DOE), Malaysia.

Keywords: Bilge water; Oil/Grease; Oil-Water Separation; Progressive Freezing

1. Introduction

Shipping has an important role in developing human society over the years, where widely separated parts of the world has been linked by the shipping activities through commercial relationships. In fact, shipping industry is still developing from time to time with rapid industrial and digital economy growth. In Canada, shipping industry has been established since 1840 and is now undergone significant technological advances, where the size of ships that carry containers for international use continues to increase [1]. Even in Malaysia, the government has launched an initiative namely Malaysia Shipping Master Plan that ensure the shipping industry is focused on developing itself and has a guidance for future development. This initiative is taken place from 2017 until 2022 with a “Revitalizing Shipping for a Stronger Economy” theme [2].

However, aside from on-the-ground activities such as lubricants, refineries and petrochemical industries, it is undeniable that shipping activities has contributed to marine pollution, especially in this 20th century where carriage of the cargos by the ships is increasing. Every year, millions of tons of oily wastes and waste oils are generated as the by-products of the ships [3]. One of the contributors to the water pollution by the operating marine vessels is the discharging of oily bilge water. Typically, for marine vessels, the oily wastes and waste oil that contain mixture of oily fluids, water, grease and lubricants as well as other wastes coming from various sources accumulate in the bilge space, which is the lowest part of the vessel [4].

Routine, the accumulated oily bilge water must be discharged out of the bilge spaces to maintain the stability of the vessel, hence eliminating the possibility of the ship to be in the conditions that can cause hazard to it [5]. The wastes discharged can eventually cause water pollution, which lead to many
negative impacts to the human, environment and marine populations. Oily bilge water may poison marine organisms because it might cover plants and tiny animals when it floats on the surface of the water and carried into the shoreline. It can cause disturbance to the life cycles of the plant and the respiration of the animals [6].

Hence, many governments and international industry bodies are working on the marine pollution issue, especially originated from shipping industry, such as Marine Environmental Protection Committee (MEPC), the International Convention for the Prevention of Marine Pollution from Ships (MARPOL) and Department of Environment (DOE), Malaysia. In order to solve the problem, oily wastewater treatment is critical and need to be installed and operated effectively to prevent the pollution as well as to ensure that the water discharged overboard is within the legal limits.

Conventionally, there were vast ways to treat bilge water, specifically to remove oil which includes centrifugation, coagulation and filtration [7]. However, these technologies have difficulties to comply the 15 mg/L discharge standard. Therefore, in this study, progressive freezing (PF) has been introduced as an alternative method for oil-water separation, utilizing a stirred freeze crystallizer. PF is a separation process that works based on the difference in freezing point of the components of the liquid. In this process, one liquid component is separated through crystallization that occurs at its freezing point and subsequently leave behind a highly concentrated unfrozen solution [8]. Thus, the objective of this study is to introduce progressive freezing (PF) process as a new OWS method where it separates two liquid compounds based on their freezing point difference. The performance of the separation is evaluated through the percentage of oil and grease removal at different coolant temperature and stirring rate of the crystallizer.

2. Materials and methodology

2.1 Materials
Oily bilge water with initial oil and grease values of 63 mg/L was collected from PETRONAS ULG95 Arwen tanker located at Lumut Maritime Terminal, Perak, Malaysia. A mixture of ethylene glycol and water at a volume ratio of 50:50 was prepared as the coolant in a refrigerated water bath (Protech, Malaysia). Hydrochloric acid and sodium sulfate are used to prepare the treated samples to determine the total oil and grease measured by using total oil and grease (TOG) analyzer.

2.2 Experimental Setup
The apparatus and device involved are cylindrical freeze crystallizer (RnR Tool & Machining, Malaysia), a digital stirrer (IKA, Malaysia), two retort stands (Benua Sains Sdn. Bhd., Malaysia) and a refrigerated water bath (Protech, Malaysia) and TOG analyzer. Basically, the sample, which is the oily bilge water, was placed in the crystallizer, meanwhile, the coolant was stored in the water bath where the temperature is being controlled at the desired values. The retort stand was used to hold the crystallizer while it was immersed into the refrigerated water bath. Digital stirrer was used to stir the sample so that the separation can take place more efficiently. TOG analyzer was later used to measure the oil and grease content in the sample, both before and after the separation take place. Figure 1 shows the experimental setup of the PF process.
2.3 Experimental Procedure
The temperature of the coolant was then set to the desired value (-2 to -10°C). After the temperature was reached, 500 mL of oily bilge water sample was poured into the crystallizer. The speed of the digital stirrer was then set at desired stirring rate (50 to 250 rpm). The crystallizer was immersed in the coolant and the sample was stirred for 50 minutes to let the crystallization to take place. The crystallizer was taken out from the refrigerated water bath and the sample in liquid form was transferred into a sample bottle to measure the oil and grease content by using TOG analyzer. From the final readings of oil and grease obtained, the values were then compared with the limit that has been set by Malaysian DOE, which is 15 mg/L, and percentage of oil and grease removal was finally calculated by using equation (1) below:

\[
\text{Percentage removal (\%)} = \frac{C_0 - C}{C_0} \times 100
\]

Where:
\(C_0\) = concentration of oil and grease before testing, mg/L
\(C\) = concentration of oil and grease after testing, mg/L

2.3.1 Manipulation of Coolant Temperature. The coolant temperature was varied from -2 to -10 °C, at interval of 2, whereas the stirring rate and cooling time is kept constant at 200 rpm and 50 minutes, respectively.

2.3.2 Manipulation of Stirring Rate. The stirring rate was varied from 50 to 250 rpm, at interval of 50, while the coolant temperature and cooling time are fixed at -10°C and 50 minutes, respectively.

3. Results and discussion

3.1 Effect of Coolant Temperature
In this study, the effect of coolant temperature on oil and grease removal has been conducted by manipulating the temperature from -2 to -10 °C. The results obtained is shown is Table 1 and Figure 2 below.

| Table 1: Effects of coolant temperature on oil and grease removal |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Sample | Stirring rate (rpm) | Cooling time (min) | Coolant temperature (°C) | Initial oil and grease value (mg/l) | Final oil and grease value (mg/l) | Percentage removal (%) |
| 1     | 200              | 50              | -2              | 63              | 45.7           | 27.5            |
| 2     | 200              | 50              | -4              | 63              | 32.5           | 48.4            |
Table 1 shows the samples that comply with the limit set by the DOE are sample 3 and 5, which are 13.2 and 14 mg/L, respectively. The separation of oil and water for sample 3 is conducted at coolant temperature -6℃, while sample 5 is run at -10℃.

As can be seen from the graph in Figure 2 above, the oil and grease concentration after testing decreased sharply from coolant temperature -2 to -6 ℃. However, the reading started to increase and decrease back at -8 and -10℃, respectively. The highest percentage removal is 79%, where the coolant temperature is adjusted at -6℃.

Theoretically, the solid crystal and front growth rate in crystallization process is controlled by coolant temperature [9]. Coolant temperature is a vital parameter in the experiment, where lower coolant temperature could result in lower value of effective partition constant (K), indicating the high purity of solid crystal formed [10]. However, if the temperature is too low, the solid crystal will freeze faster, and the impurity may trap in the ice layer formed. In an analysis that has been done by [11], they concluded that even slightly change in coolant temperature affects the ratio of organic contamination in ice.

3.2 Effect of Stirring Rate
In this experiment, the stirring rate is varied from 50 to 250 rpm. Table 2 and Figure 3 below show the results of the experiment.

| Sample | Stirring rate (rpm) | Cooling time (min) | Coolant temperature (℃) | Initial oil and grease value (mg/L) | Final oil and grease value (mg/L) | Percentage removal (%) |
|--------|---------------------|--------------------|--------------------------|------------------------------------|----------------------------------|------------------------|
| 1      | 50                  | 50                 | -10                      | 63                                 | 35.1                             | 44.3                   |
| 2      | 100                 | 50                 | -10                      | 63                                 | 31.9                             | 49.4                   |
| 3      | 150                 | 50                 | -10                      | 63                                 | 25.5                             | 59.5                   |
| 4      | 200                 | 50                 | -10                      | 63                                 | 14                               | 77.8                   |
250 50 -10 63 27.8 55.9

| Stirring rate (rpm) | Oil and Grease (O/G) value (mg/L) |
|---------------------|----------------------------------|
| 0                   | 40                               |
| 50                  | 35                               |
| 100                 | 30                               |
| 150                 | 25                               |
| 200                 | 20                               |
| 250                 | 15                               |
| 300                 | 10                               |

Table 2 shows that the oil and grease concentration after the testing for sample 4 managed to achieve the limit discharge set by the DOE since the value is lower than 15 mg/L.

The oil and grease reduction changed as the stirring rate changed. The oil and grease content should be decreasing as the stirring rate increased [8,10,12]. However, in this experiment, the oil and grease decreased as the stirring rate decreased from 50 to 200 rpm. As the stirring rate is further increased to 250 rpm, the oil and grease value suddenly increased. This might be due to the interruption of crystal growth that happened at vigorous stirring at 250 rpm. Somehow, the significant decrement of oil and grease content when the stirring rate is from 150 to 200 rpm indicate that 200 rpm is the most efficient stirring rate for the effective separation. It resulted in the lowest concentration of oil and grease, where the percentage oil and grease removal was the highest, which is 77.8%.

Basically, stirring rate, which is the flow rate of the solution, is introduced to reduce the accumulation of solute near the ice-liquid interface due to the constant flow distribution provided by the stirrer. Higher flowrate will reduce the advance rate of the ice front, resulting in higher purity of crystal formed [9]. This statement has been agreed by Okawa et. al in their paper in 2009, where they mentioned that solidification rate will become slower when the flow rate is higher, hence, less solute will be entrapped in the ice [12]. It has also been concluded that higher purity of crystal will be produced at higher flow rate [10].

4. Conclusion

Oily wastewater treatment has now become vital to prevent pollution from occurring so that other negative consequences to the Earth, including human being, animals and plants, can be avoided. Many researches have been done to treat the wastewater that contains oil since then until now. Different methods have been proposed.

In this study, PF method is introduced as one of the methods for oily bilge water treatment. From the study that has been conducted, it can be concluded that the oil and water can be separated via PF method. The stirred freeze crystallizer is able to concentrate the bilge water, hence reducing the content of oil and grease so that it can comply with the discharge limit that has been set by DOE. Other than that, coolant temperature and stirring rate are the two parameters that have been proven to affect the
efficiency of the separation since they can influence the purity of the crystals formed. The stirring rate obtained was 200 rpm meanwhile coolant temperature is -6°C.

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