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Review

Determination of Dispersion Predictability on Oil Spill Dispersant Using the Warren Spring Laboratory LR 448 Test and Swirling Flask Test

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ABSTRACT

One of a method used to clean the oil spill is using oil spill dispersant. Availability of dispersant on sea surface reduces the tension and lead to separation of oil and seawater. Early studies showed dispersed oil has a higher rate of degradation than oil in a surface slick, which poses a lesser threat to the environment. However, in recent times with abundant brands of dispersants present, the need to test the effectiveness of oil spill dispersant is increasing. The objective of this study is to determine the relative effectiveness of approved and local dispersants on crude oil and to compare the effectiveness result of two different laboratory tests, which is Warren Spring Laboratory (WSL) LR 448 protocol and Swirling Flask Test (SFT). Five dispersants (A, B, C, D, and E) were tested with Malaysia's benchmark crude oil, Tapis Blend (API Gravity 44°). Experiments were conducted using a UV-VIS spectrophotometer at a Dispersant to Oil Ratio (DOR) of 1:20 for both protocols. Seawater temperature and salinity were set at 29°C and 30 ppt respectively. Results of the WSL protocol showed that dispersants A, C, D, and E marked a relatively lower range of effectiveness between 2.46% to 41.56% index of effectiveness. Only dispersant B (84.31%) did pass the minimum effective range of ≥50%. Contrarily, SFT presents an increasing range of effectiveness with three dispersants (B, D, and E) passed the minimum range of efficiency with 92%, 61.85% and 52.95% respectively. Overall, SFT produces a higher percentage of efficiency compared to WSL. This study could contribute as a baseline to produce a significant test method and a robust data of dispersants supported to be used during oil spill incidents.

***Keywords**: Dispersant, Index of effectiveness, Oil spill, Swirling Flask Test, Warren Spring Laboratory.*

INTRODUCTION

Demand for petroleum has been increasing over the years. Oil spills on the sea are one of a serious threat to the environment and probably happened globally in different levels of the environment such as on land, at sea and even freshwater.[1] Major oil spill incidents have been occurring since 1967 with the Atlantic Empress incident, which happened due to the collision of Atlantic Empress and the Aegan Captain causing a massive oil spill proportions touching almost 3,000,000 tons. Following the major oil spill was the Exxon Valdez occurred in the Reef of Bligh in the Alaskan waters in the late 1980s. The spill demolished the marine flora and fauna caused enormous impacts on marine life. One of the most memorable oil spill incident to date was the BP oil spill in 2010. About 5 million barrels of oil had spilled into the Gulf of Mexico, and it was considered the worst oil spill in US history leaving an impactful effect on the nation on years to come.[2-4]

Several methodologies have been adapted for oil spill cleanup considering the ecosystem of marine life and to human as well. One of a well-known method used for oil spill cleanup is applying dispersant.[5] Oil can disperse naturally, depending on the types of oil and weather condition. Generally, dispersants are a mixture of three components: surfactant, solvents, and additives. The most important component of a dispersant is the portion of surfactant. Surfactant usually consists of a water-loving (hydrophilic) on one end and oil-seeking (oleophilic) on the other end. When the molecular structure of a dispersant is introduced into a mixture of oil-water, the molecules align themselves so that the hydrophilic portion is dissolved in the water, and the oleophilic segment is solvable in oil. Applying dispersant on oil slick help breaking of oil into smaller particles by increasing oil surface area and facilitates dispersion of oil. Chemical dispersants are combinations of surfactants and solvents usually applied on oil slick through spraying aimed to eradicate oil from the surface and let it disperse into water column.[6]

Knowing the demand of oil spill dispersant have been elevating, numerous companies have been claiming their dispersant is the most efficient in cleaning up. Malaysia is one of the countries chose to use chemical dispersants to treat oil spill during an incident happened when a tanker laden equipped with marine diesel sank down at the southern state of Johor, near Singapore. Chemical dispersants were sprayed from two marine department boats more than two miles from the incident place.[7]

Conducting a study on the effectiveness of oil spill dispersant is considered one of a significant test to avoid misuse of dispersant application. In Southeast Asia countries, research on dispersant effectiveness had been taken place such as in Singapore[8] and in Indonesia.[9] In Malaysia, even though there have been many dispersant products introduced in the market, the study of oil spill dispersant effectiveness is still scarce. There is no update of such information found in the literature. Different countries conducted different types of effectiveness test. The most common procedures used are the Labofina, also known as the rolling flask or Warren Springs Apparatus, the Mackay apparatus also known as Mackay-Nadeau-Steelman (MNS) procedure, Swirling Flask Test (SFT) and the most recent the Baffled Flask Test.[10]

The main objective of this study was to observe the differences in effectiveness results from two different protocols, Warren Spring Laboratory (WSL-LR448), and Swirling Flask Test, (SFT) on light crude oils using five dispersants, where two of them have been approved for usage in Malaysia, two originated from Southeast Asia countries and one is a local dispersant. Both protocols have different types of beakers used, shaking and settling time, application of dispersant and mixing energy set for each test.

MATERIALS AND METHODS

Dispersant Products

The five selected dispersants were supplied by Malaysia Marine Department with 1 dispersant ranked high (>80% effectiveness), 3 intermediate products (≥40 – 80 ≤ effectiveness), and 1 low ranked (<40% effectiveness) (Table 1).

.**Table 1.** Type of dispersants use in this study

Type	Venue of Usage	Category	Effectiveness (%)
A	Malaysia	Local	<40
B	Worldwide	Imported	>80
C	Southeast Asia	Imported	≥40 – 80 ≤
D	Worldwide	Imported	≥40 – 80 ≤
E	Southeast Asia	Imported	≥40 – 80 ≤

Crude Oils and Seawater

The oil chosen for this experiment is Tapis Blend Crude Oil, API Gravity 44.9 ESD 97, light oil. Properties of oil is given in the database published by the environment Canada website.[11,12] Filtered seawater drawn from the treated reservoir tank was used and its temperature and salinity were maintained at 29±2 °C and 30-±2 ppt.

WSL Oil Extraction and Analysis

The determination of the efficiency index of oil spill dispersants was performed according to WSL Report LR 448 (OP) revised February 2007 using Dichloromethane (DCM) as a solvent instead of chloroform.

SFT Oil Extraction and Analysis

The protocol of SFT analysis is derived from Sorial et al.[13] with a minor modification. A 250ml Erlenmeyer flask, SCHOTT, Duran Germany with a bottom side spout was used as a replacement of modified Erlenmeyer flask.

Calibration of the UV- Vis Spectrophotometer

The calibration solutions for both tests were prepared according to protocols on the day tests were performed. For SFT, each of the standard stock solutions was prepared differently following the dispersants. The absorbance of each dispersed oils was measured using the UV-Vis spectrophotometer (Shimadzu UV-1280).

RESULTS AND DISCUSSION

An obvious increasing trend of dispersant percentage value can be seen in Figure 1 for SFT while WSL recorded a relatively lower value for all dispersants. Figure 2 and 3 shows dispersant effectiveness values tested using SFT and WSL respectively. For WSL, the benchmark is set at 50%, and only one (1) dispersant passed the benchmark that is Dispersant B. For SFT, Sorial et al.[13] stated the dispersant is to be at least 45% effective and three (3) dispersants; Dispersant B, D, and E past the minimum effectiveness value. The difference between the percentage of effectiveness when this study uses five same dispersants and crude oil for both tests lies in the technique introduced by each method, as shown in Table 2.

Figure I. Results of dispersant effectiveness for both SFT and WSL tests

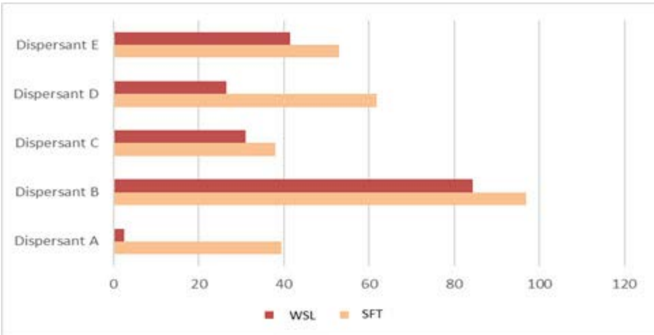

Figure 2. Effectiveness values of each dispersants tested using WSL

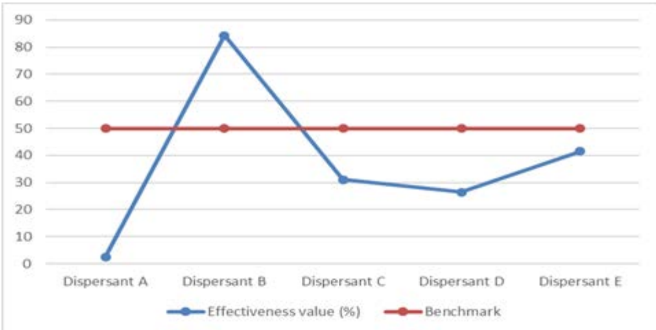

Figure 3. Effectiveness value of each dispersants tested using SFT

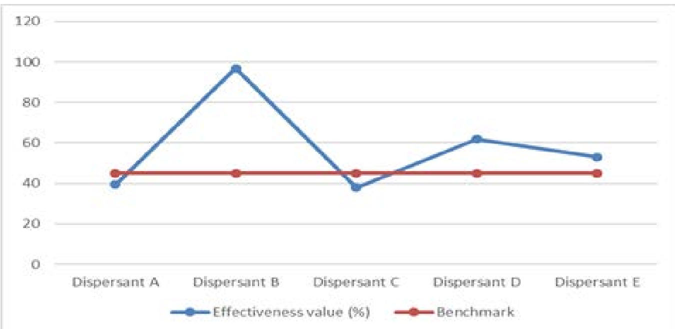

Table 2. Differences of methods of dispersant effectiveness test

Test	Types of test flask	Mixing energy	Mixing time (min)	Settling time (min)	Application of dispersant
WSL	Standard conical separating funnel	Axis of rotation between 15mm and 20mm	2	1	One- drop
SFT	Conical flask with a side spout	150rpm	20	10	Premix

Different countries have their own threshold of dispersant effectiveness pass minimum value. Following the protocols, WSL has been introducing the minimum dispersant effectiveness level at 50% (Figure 2), however, few countries adapted to WSL such as France, United Kingdom, and Greece set the minimum effective level to be at 60%. Meanwhile, for SFT, Spain that is following the EPA[14] SFT protocol set the effectiveness minimum level to be at ≥50% instead of 45% (Figure 3). Each country regulated the minimum effectiveness value according to their oceanic conditions and it can be inferred that only high-quality dispersants are allowed to be used in the marine waters.

Mixing Energy

Energy dissipation rate or mixing energy is a vital parameter in dispersant effectiveness test. Both WSL and SFT have a different variation of mixing energy experimental system. WSL uses low mixing energy, whereas SFT set the mixing energy at 150 rpm. Mixing energy is needed to reduce the interfacial tension between oil and water. Huge penetration of oil layer into seawater is observed in SFT test as all dispersant displayed a higher percentage of effectiveness compared to WSL. Even though no laboratory test reproduced the accurate mixing and turbulence to real oceanic conditions, the energy set at 150 rpm is prominent enough for oil-dispersant-water interaction to let dispersed oil entering the water column. Since WSL use low mixing energy, little dispersion is seen in most dispersants tested aside from Dispersant B. In dispersant E, very little dispersion can be seen. With sufficient energy, the formation of smaller droplets will be high and produce a stable dispersion since smaller droplets have a lesser tendency to resurface. Even though it is important, Kaku et al.[15] and Fingas[16] mentioned the energy dissipation rate is not evaluated in most dispersant effectiveness tests, and the correlation study between mixing energy and efficiency is still scarce. It is found that dispersion effectiveness is directly proportional to mixing energy, however; the proportionality varies among oil dispersant-combinations.[17-19]

Mixing Time

The dispersant is never stable and usually settles at rest hence makes time important in influencing dispersion. However, for certain dispersant products stabilization of dispersion can be achieved by agitating them very slowly. 20 minutes of mixing time are used in SFT, meanwhile, WSL only mixes for 2 minutes. A significant increase of mixing time in SFT signifies an improved effectiveness value than WSL, but Fingas et al.[17] concluded only a slight upward trend is observed when mixing time increases in his study but does not contribute to an outstanding dispersion value. A recent study by Pan et al.[20] have been correlating dispersant effectiveness value by comparing dispersant with different mixing time set at 5, 10, 60, and 120 minutes concluded a steady increase was noticeable with an increase in mixing time, however, the difference in each effectiveness value was not that notable.

Settling Time

One of the requirements for a chemical dispersant to form oil droplets is the need to let dispersant settled so it will penetrate and mix into the oil. After mixing, both tests let the solution to settle which lead dispersant drop started breaking down and herding the oil. SFT let the mixture settled at rest longer than WSL and shows a higher effectiveness trend when compared to WSL. Inclusion of settling time into an experimental protocol may influence the measured concentration of oil in the water column over time. Some literatures[21-25] proposed that a 10 minutes standard settling times be applied in the laboratory test and is supported by Lentinen and Vesala[23] that found dispersion value in MNS test declined in the beginning after agitation discontinued but achieved stabilization with settling-time greater than 10 minutes.

Application of Dispersant

The procedure in which oil and dispersant are combined (premixed or one-drop) might be affecting dispersant performance tests greatly. In the SFT method, pre-mixing has been predicted to increase the effectiveness value due to oil and dispersant contact earlier as opposed to the one-drop version in WSL. The one and two drop addition versions in the test is the addition of dispersant to an oil slick to estimate the effect of dispersant-herding of oil on test results.[26,27] Herding eventuates when dispersant interacts with the water surface. Presence of surfactant molecules in dispersant allows them to direct themselves according to their hydrophilic-lipophilic components. Clayton et al.[26] mentioned the outcome are surfactant molecules can push or herd the oil aside which may lessen the dispersion performance when dispersant does not acquire access to the oil.

Oil Type

Types of oil play a huge role in determining value of effectiveness. This study uses Tapis Blend Crude Oil, which is a light oil, and widely used in our country for transportation. Medium to very light oil may generate a high value of efficiency. Holder et al.[28] conducted a study by expressing dispersant efficiency as LCL95, which was found to be inversely proportional to viscosity of oil, for both dynamic and kinetic. In other words, low viscosity, lighter oils dispersed easier than high viscosity, heavy oils. Nevertheless, he did not expect WSL would produce a unique dispersant effectiveness value that is in poor correlation with the oil physical properties. Oils with higher viscosity would produce lower dispersion effectiveness since it would withstand the breakup of oil droplets.[29] Thus, a follow up study on dispersant interaction with different range of crude oils needs to be conducted so that a robust data on dispersant effectiveness tested on different types of oil can be referred when there is occurrence of oil spill. The results shown WSL have a lower value of effectiveness than SFT, but Environmental Research Ottawa[30] found WSL produces a higher effectiveness value for the mid to high viscosity oils, unlike SFT that signifies quantifiable dispersion for light to very light test oils only.

Temperature and Salinity

Even though the differences in temperature and salinity of seawater were not studied in this paper, both factors are considered crucial in determining dispersant effectiveness. According to US Environmental Protection Agency, both protocols were required to be conducted at 22°C, and 34 ppt. However, in this study we used the readily available seawater at 29±2 °C and 30±2 ppt respectively. The primary intention of dispersant formulation for use in sea water is to provide maximal efficiency at normal seawater salinity. When salinity is high, the effectiveness value of dispersant also increases by preventing the movement of surfactant molecule into the water phase.[31] Chandrasekar et al.[32] conducted study at three different salinities;10 ppt, 20 ppt, 34 ppt with a temperature rise from 5±1°C to 22± 1 °C. The results discerned an increment in percentage effectiveness, but decreased at 35± 1°C. Yudiana et al.[9] concluded the largest area of total absorbance was found at 26°C with 133.49abs and suggested dispersant works effectively on the temperature range of 26°C to 36°C. A higher water temperature increases the solubility of dispersants in water thus affecting the temperature of spilled oil. When temperature rises reduction of oil viscosity occurs and leads to improvement of dispersion. Generally, for most-oil dispersant combination, dispersion efficiency increases when salinity and temperature increases.

CONCLUSION

The few differences in both the Warren Spring test and Swirling Flask test methods generate a different value of dispersion in effectiveness tests. Combining all factors, SFT produces a higher percentage of efficiency compared to WSL. Conducting dispersant effectiveness test based on bench- scale test is needed to predict the dispersion value for oil spill dispersant during oil spill response. Even though WSL records a lower effectiveness value than SFT, WSL is more realistic to the real occurrence of the oil spill. Each of these factors can be studied in detail to produce a significant test method and maximum effectiveness value at local seawater temperature and salinity while providing a robust data of dispersants supported to be used during the oil spill in Malaysian waters.

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CONFLICTS OF INTEREST

We have no conflicts of interest with nobody and have nothing to declare.

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