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THE POTENTIAL OF ENVIRONMENTAL FRIENDLY CHEMICALS IN SEPARATING WATER-IN-OIL (W/O) EMULSIONS

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ABSTRACT

A heavy crude oil has been increasingly important sources of hydrocarbons in many parts of the world, in which transportation of this heavy crude oil to refinery can be a problem. During the lifting, transportation and processing of oil, frequently emulsions either water-in-oil (w/o) or oil-in-water (o/w) are created. Formation of these emulsions during oil production is a costly problem, both in terms of chemicals used and due to production losses. The traditional methods of eliminating these emulsions, utilize high heat and chemicals which forces the emulsion to separate into water, hydrocarbons and solids are disadvantageous from both economic and environmental perspectives. In this study, the potentials of an environmental friendly chemicals in demulsification of crude oil emulsions was investigated. The study begun with some characterization studies to provide understandings of fundamental issues. Results obtained from this study, will expose the capability and potentials of environmental friendly chemicals in demulsification of water-in-crude oil emulsions.

KEYWORDS: demulsification, w/o emulsion, surfactant, heavy crude, hydrocarbons.

INTRODUCTION

Emulsions can always be encountered in all levels of oil recovery and refinery stages in the industries including the drilling process of crude oil, production, processing plant and emulsions in the pipeline transportation system (Mushrush, G. W. et al., 1995; Schramm, L. L., 1992). Upon rigorous stirring, crude petroleum and water form emulsions even though the produced emulsion immediately breaks down if the stirring is stopped. Emulsions are always grouped either as oil droplets in water (O/W) or water in oil droplets (W/O) relying upon the nature of dispersed and continuous phases (Gafanova, O. V. et al., 2001). However, studies are constantly being conducted on water dispersed in droplets of O/W emulsions itself (W/O/W) and O/W/O emulsion (Langevin, D. et al., 2004). Emulsifiers or stabilizing agents are generally amphiphilic in nature because of their hydrophobic and hydrophilic parts. Therefore, they permit such compounds to be soluble in both phases of the emulsion thus, acting at the interface between oil and water (Sheng, J. J., 2011). Coalescences are normally prevented by the compounds when either a rigid film is created surrounding the dispersed phase or dispersed droplets are repelled electrically. Crude oil always has its composition as a variety of mixture of organic and inorganic compounds. This can be explained by the fact that the origin of the reservoirs, depth and age are not the same to one another (Speight, J. G., 1991). Generally, crude oil is made up of some parts of hydrogen and carbon with some traces of nitrogen, oxygen and sulphur plus, integrated metallic molecules like iron, copper, nickel and vanadium (Speight, J. G., 1980).

MATERIAL AND METHODS

Material

The chemicals used were Span 80, Span 83, Triton X-100 as the emulsifiers. To accomplish the objective of this study, heavy and light crude oil samples were obtained from PETRONAS Refinery, Melaka. These two types of crude oil were mixed in a 50-50% proportion to obtain a well-mixed crude oil sample for the emulsion experiments. Here the work merely describes the main experimental steps. Water in crude oil emulsions were prepared by dispersing distilled water in crude oil at room temperature with standard three blade propeller at speed of 2000 rpm. The emulsifying agent was used as received without any further

Emulsifying method

Generally, emulsion is prepared by adding water to crude oil in a specific ratio. The aim is to prepare 50ml of crude oil emulsion sample for the purpose of this study. Firstly, 0.5% concentration of emulsifying surfactant is added to sample crude oil. The water-in-oil ratios used are 50-50% and 30-70% by total volume and the emulsifiers' concentration is varied from 0.5-2.5%. Emulsion sample prepared is subjected to a mixing speed of 2000 RPM. Mixing is done by vigorous agitation by using a standard three blade propeller at an operating temperature of 28-30ºC. Emulsifier is added to oil and stirred for 4 minutes and then, water is added and the mixture is stirred for another 6 minutes, which total up to be 10 minutes.

Emulsion testing

Upon mixing, the type of emulsion whether W/O or O/W is studied by conventional filter paper test. The emulsion sample is dropped on a piece of filter paper. It is then allowed to spread on the filter paper. The type of emulsion is determined by observing the speed of the emulsion sample spreading on the filter paper. W/O emulsion spreads slower than O/W emulsion on the filter paper. Since W/O emulsion is of the main interest of the study, phase inversion is done by diluting the O/W emulsion with more water. The flow chart for research activities is shown in Figure 2.1 below.

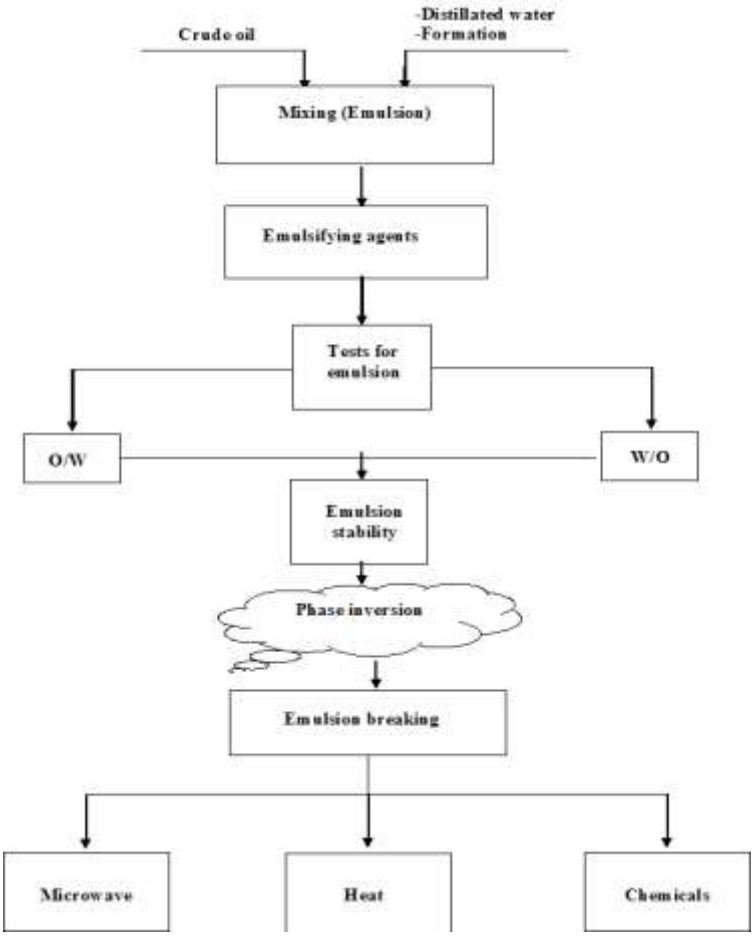

Fig. 2.1: Research Sample preparation and separation procedures

Viscosity, Shear Rate and Shear Stress

The viscosity, shear rate and shear stress of the W/O emulsion sample is determined by using the Brookfield Rotational Digital Viscometer Model LV/DV-III with UL adaptor. The Brookfield Viscometer apparatus was equipped with a water bath thermostat, a spindle set, and software of Brookfield Rheocalc Version 1.2. For measuring the viscosity of emulsion, a small sized diameter spindle is used with a cell containing about 9ml of the test crude oil emulsion sample. The fluid parameters like shear stress and viscosity and specified shear rates can be determined. The Brookfield

Viscometer apparatus works by the principle of driving a spindle immersed in the crude oil sample. The rotating speed determines the measuring range. The rheometer is cleaned thoroughly after measuring each emulsion sample.

Interfacial Tension and Surface Tension

Interfacial Tension and Surface Tension is analyzed by using the Surface and interfacial tension measurement standard test method (ASTM) in Surface Tension Analyzer model DST 60 A. This unit is readily equipped with a glass sample container and a ring. The crude oil sample is inserted into the container and the ring is adjusted and calibrated at the surface of the crude oil sample. The ring used in this experiment is kept in a very clean and dust free condition. After every measurement taken, the ASTM is cleaned with 70% ethanol and burnt with a blue flame from a Bunsen burner.

Droplet size

The droplet size distribution of emulsion can be analyzed an determined by using the Carl Zeiss research microscope equipped with the digital camera and AxioVission AC image analysis software. The measurement of the droplet size of the crude oil emulsion sample is done without any further dilution.

Gravitational Stability Test

The emulsion stability was measured based on the amount of separated water from the prepared emulsions after 24 h. O/W emulsions prepared at different conditions were tested for their stability by transferring the emulsions into test tube, the latter were left at room temperature to rest for a while. The volume of separated water was recorded after 24 hour since the time homogenization was performed. By dividing the amount of water separated from the emulsion to the initial amount of water in the emulsion, the percentage of separated water from the prepared emulsions was achieved. The amount of water separated was noted at every 2 hour, 5 hour, 12 hour and 24 hour. The water separation in percentage was calculated as separation efficiency (e) from volume of water observed in the cylinder as in Equation 1

$$water\ separation = \frac{volume\ of\ water\ separated,ml}{original\ volume\ of\ water\ in\ emulsion,ml}\ x\ 100\% \qquad \text{(Equation1)}$$

RESULTS AND DISCUSSION

Water content analysis

The water separation for each emulsifier respect to each w/o ratio is tabulated in Table 1 and its respective trend is illustrated in Figure 1 and Figure 2 for 50-50% w/o and 30-70% w/o.

Table 1: Amount of water separated for every type of emulsifier with respect to percentage of w/o emulsion.

	50-50% (w/o)				30-70% (w/o)			
emulsifiers	concentration (%)	water separated (ml)		time(days)	emulsifiers	concentration (%)	water separated (ml)	time(days)
span 80	0.5	0		3 days	span 80	0.5	0	3 days
	1.5	0		3 days		1.5	0	3 days
	2.5	0		3 days		2.5	0	3 days
span 83	0.5	0		3 days	span 83	0.5	0	3 days
	1.5	0		3 days		1.5	0	3 days
	2.5	0		3 days		2.5	0	3 days
triton-x-100	0.5	3.5		1	triton-x-100	0.5	0	3 days
		7.75		1.5		1.5	0	3 days
		12		2		2.5	0	3 days
		21.5		2.5				
		31		3				
	1.5	5		1				
		10.5		1.5				
		16		2				
		24		2.5				
		32		3				
	2.5	8		1				
		13.5		1.5				
		19		2				
		26		2.5				
		33		3				

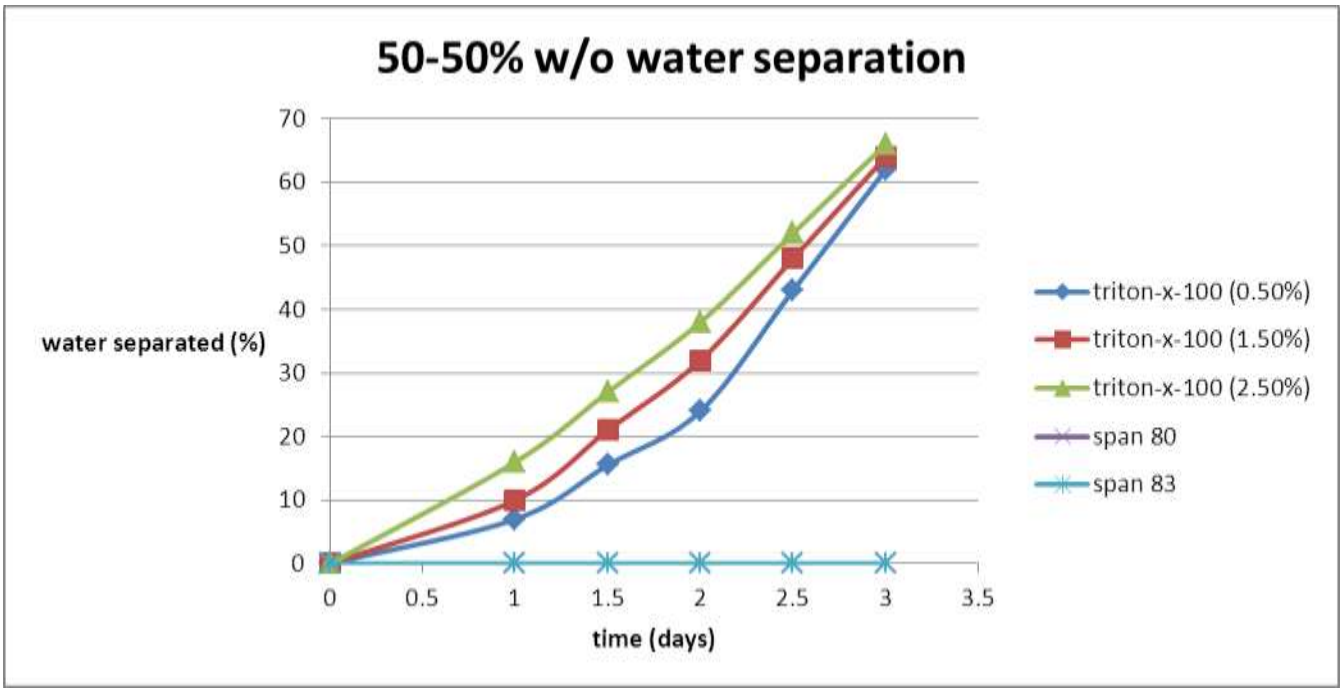

Figure 1: The water separation trend lines for 50-50% w/o emulsion.

From the result collected in Table 1, the graph of water separation versus time is illustrated as shown in Figure 1. Based on the figure above, triton x-100 has highest percentage of water separation at 2.5 % emulsifier concentration at 50-50% of ratio. Hence, the Triton-X-100 emulsion prepared is concluded as the most unstable emulsion compared to other emulsifiers. Span 80 and Span 83 emulsions, visibly, have no water separation. These data can be explained by the fact that the coalescence rate decreases with increasing dispersed phase volume fractions as a result of an increase in the entropy for an effective collisions between the continuous phase and its dispersed droplets (N.H. Abdurahman et al., 2013). However, the viscosity increases significantly beyond this limit due to phase inversion (N.H. Abdurahman et al., 2013).

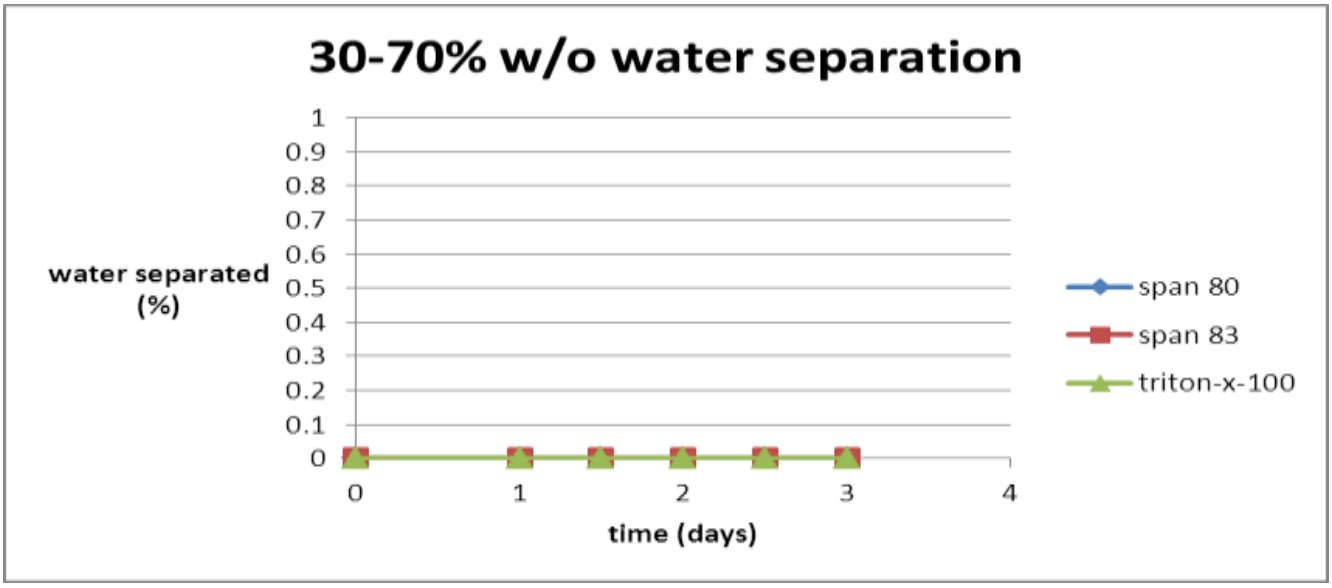

Figure 2: The water separation trend lines for 50-50% w/o emulsion.

These trend lines in Figure 2 show that with the increase in the continuous phase (oil) at 30-70%, the emulsions were stable without any water separation. As a rule of thumb, a considerably high amount of oil in w/o emulsions is significantly important in designing an emulsion transport system. To ensure, less space in the pipelines is occupied by water as it can reduce crude oil transportation efficiency and corrode the pipelines, water content in emulsion will be brought down to a least possible amount during the preparation of emulsion itself. Even so, oil content in the emulsions beyond a certain limit would only result in the increase of viscosity due to the occurrence of the phase inversion (S. N. Ashrafizadeh et al., 2010). The homogenous emulsions were prepared at a high speed mixer (2000 RPM) at a longer mixing time at about 15 minutes to ensure good mixing of water and oil. There was no water separation noticed even after 7 days of observation. This can be explained by the fact that water separation strongly depends on emulsion droplet size and its distribution.

Temperature and Viscosity

The relationship between temperature and viscosity is plotted as in Figure 3.

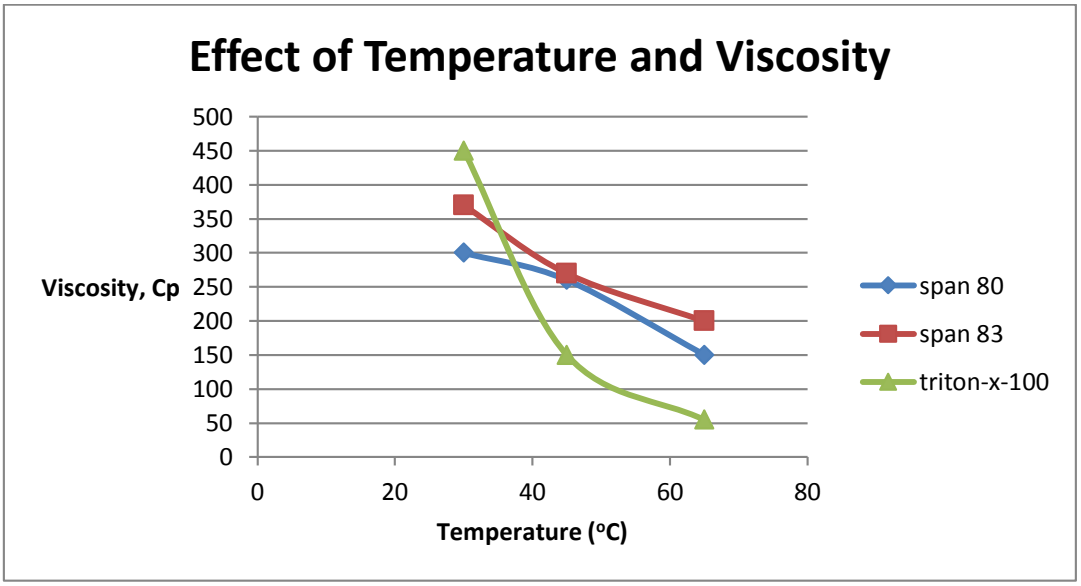

Figure 3: Relationship between temperature and viscosity.

Different temperatures such as 30, 45 and 65ºC were used to heat the crude oil emulsion to study their effect on the emulsion viscosity. The graph shows that with an increase in temperature, Span 83 shows highest viscosity. These emulsions were prepared at 30-70% water in oil ratio in 2.5% emulsifiers. They were mixed at 2000 rpm for about 10 minutes. Temperature has always been an important factor in affecting crude oil emulsion viscosity and its behavior. Apart from that, temperature also affects the viscosity- shear rate relationships. Figure 3.3 clearly illustrates the viscosity on temperature ranging from 50 to 500. Viscosity decreases as temperature increases. As the emulsifier concentration increases, the droplet size gets smaller as there is very low interfacial tension between the molecules. Therefore as the droplets get smaller and smaller, the total amount of droplets inn touch with the surface increases, leading to increase in viscosity (Masood et al., 2013).

Tensiometer readings

The surface tension for pure components water and oil and the interfacial tension for oil and water mixture were tested to determine their respective characteristics. A tensiometer was used in obtaining the results at room condition. The temperature was set to 28ºC. The surface tension between water and air was 66.988 mN/m while the surface tension between oil and air was 28.602 mN/m. Besides, the interfacial tension between oil and water is 0.661 mN/m.

CONCLUSIONS

The oil-in-water emulsions were successfully prepared using crude oil samples with water in the presence of span 80, span 83 and triton x-100 as surfactants. It can be concluded the coalescence rate decreases for increasing dispersed phase volume fractions due to the increased entropy for the effective collisions between the dispersed droplets. One of the main purposes of making water in oil emulsions in crude oil transportation pipelines is to reduce energy

consumption in pumping them throughout the pipelines besides reducing surface contacts between the crude oil and the pipelines which would, in turn reduce the corrosion and precipitation inside the walls of pipelines.
Viscosity can be controlled over a temperature range of 50-70 °C. It can also be concluded that the stability of w/o emulsion can be improved by controlling the amount of water. The stability of emulsion increases as water content decreases but only up to the phase inversion point. The gravity tests clearly show that 30-70% w/o which has less water content compared to 50-50% w/o emulsion has a better stability as there are no water separation even when they are left for 7 consequent days to observe water separation.

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