

Chemical Destabilization on Water in Crude Oil Emulsions

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Abstract—Experimental data are presented to show the influence of different types of chemical demulsifier on the stability and demulsification of emulsions. Three groups of demulsifier with different functional groups were used in this work namely amines, alcohol and polyhydric alcohol. The results obtained in this study have exposed the capability of chemical breaking agents in destabilization of water in crude oil emulsions. From the present study, found that molecular weight of the demulsifier were influent the capability of the emulsion to separate.

Keywords—Demulsification, emulsions, stability, breaking agent, destabilization.

I. INTRODUCTION

WATER is produced with crude oil in most cases. As been noted by Borges [3] emulsified water is generally present in crude oil as a result of the mixing occurring during production operations. Abdurahman *et al.*, [1] also mentioned that water is normally present in crude oil reservoirs or is injected as steam to stimulate oil production. The more common emulsions in the petroleum industry are of the water in oil type. Lixin *et al.* [9] has pointed out that these emulsions need to separate for economic and operational reasons. Besides, Abdurahman *et al.* [1] have state that it is necessary to separate the water completely from the crude oils before transporting or refining them. Minimizing the water level in the oils can be reducing pipeline corrosion and minimizing pipeline usage.

A. Emulsification

James [8] has defined emulsification as a process in the formation water in oil. There is a large variety of emulsification methods; simple shaking, mixing with rotor stator systems, liquid injection through porous membranes, or high pressure devices (homogenizers, liquid jets), etc as been mention in Langevin *et al.* [5] studies. Referring to Ariyani [2], an emulsion can be defined as a system containing two immiscible liquid phases that one of them dispersed as globules/ droplets on the other. The dispersed phased sometimes known as internal phase and the continuous phase as external phase. G. Chen and D. Tao [6] had reported that there are two basic form of emulsion. The first is oil in water (o/w) emulsion in which oil droplets are dispersed and encapsulated within the water column. The seconds is water in oil (w/o) emulsion which droplets of water are dispersed and encapsulated within the oil.

Souleyman [11] has stated that when oil and water are mixed in the presence of an emulsifying agent, the emulsifier is adsorbed on the surface of the oil or water particle, depending on the type of the surface- active agent used. This phenomenon reduces the interfacial tension, promotes the stabilization of finely dispersed particle, and controls the type of emulsion (i.e., oil-in-water or water-in-oil) that is produced. The adsorbed emulsifier also forms a physical and electrostatic barrier delaying the coalescence of the dispersed particles.

B. Demulsification

Demulsification has been defined by Fan *et al.* [12] as a process of breaking emulsions in order to separate water from oil, which is also one of the first steps in processing the crude oil. Byoung *et al.* [4] have pointed out that demulsification is an essential industrial process, mainly used for removing water and salt from crude oil. An effective demulsifier is a surface-active compound that can absorb onto the water/oil interface and change its properties such that water droplets aggregate and coalesce as been mentioned by Wu *et al.* [7] in their studies. They also have claimed that the efficiency of a demulsifier is determined by the nature of the emulsion and the characteristics of the demulsifying agent. Besides, demulsification can be achieved by three means: mechanical, electrical, and chemical. The addition of chemical demulsifiers is the most widely used method. Fan *et al.* [12] have cited that chemical demulsification consist of the addition of small amount of breaking agent (usually 1-1000ppm) to enhance phase separation, usually using surfactant, polymers, pure solvent or their mixture.

According to Ilyani [10] the colloidal species can come together in very different ways. In the definition of emulsion stability, it is considered against three different processes; creaming (sedimentation), aggregation and coalescence. Firstly, the flocculation (aggregation) is the process where interparticular distance between the droplets is strongly diminished due to a net attraction between the droplets. The individual droplets maintain their identity during this process occurred. The creaming or sedimentation is the formation of a droplet concentration gradient within the emulsion. Then, coalescence means the formation of large droplets with a concomitant phase separation. This process involves the elimination of the thin liquid films separating the dispersed droplets in a close-packed array. Finally, the Ostwald ripening is a phenomenon in polydispersed emulsion where large droplets will form at the expense of small one.

The objective of this research is to study the effect of chemical additives on demulsification of water in oil emulsions. There were three group of demulsifier used in the present study which consisted of amine, alcohol and polyhydric alcohol demulsifier.

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II. MATERIAL

In order to complete this research, three groups of demulsifier with different functional groups were used in this work namely amines, alcohol and polyhydric alcohol. All are acquired from Sigma-Aldrich, and Merck, Malaysia. In order to prepare emulsion, only one type of emulsifier has been used which is Span 83. The crude oil sample was obtained from PETRONAS Refinery which is from United Arab Emirates, UAE.

III. METHODOLOGY

The samples of water in oil emulsions were prepared by agitated the crude oil vigorously at 1800 rpm by using standard three blade propeller. The preparation was under ambient temperature. There was (0.1 w/w %) of Span 83 as an emulsifying agent was used as received without further dilution. In order to prepare water in oil emulsions, the agent in oil methods were followed, which the emulsifying agent first dissolved in the continuous phase (oil), then the water added gradually into the mixture (oil+ emulsifying agent). Bottle test was used in order to check the type of emulsions prepared is water in oil by dropped the emulsion into water the test tube. All the samples were water in oil emulsion type.

For chemical demulsification performance study, three group of demulsifying agents with different functional group were utilized in this paper namely amines, alcohol and polyhydric alcohol, respectively. Demulsifiers used were listed in Table 1. Concentration for all demulsifiers was constant (2 w/w %) relatively to ratio of oil weight. The water separation was calculated as separation efficiency, e from volume of water observed in the clear measurement cylinder as follow:

$$\% \text{ water separation, } e = \frac{V}{V_0} \times 100\% \quad (1)$$

Where, V is the volume of water separated V_0 is the original volume of water content.

TABLE 1
LIST OF DEMULSIFIERS USED IN EMULSIONS
DEMULSIFICATION TEST

Group	Demulsifier	Solubility
Amine	Pentylamine	Oil soluble
	Hexylamine	Oil soluble
	Octylamine	Oil soluble
	Diocetylamine	Oil soluble
Alcohol	Methanol	Water soluble
	Ethanol	Water soluble
	Propanol	Water soluble
	Butanol	Water soluble
Polyhydric Alcohol	PEG 300	Water soluble
	PEG 400	Water soluble

IV. RESULTS AND DISCUSSION

Figure 1 and 2 shows some typical results of demulsification experiments conducted to test the influence and performance of the amine group on the crude oil emulsion stability. The figures illustrate the separation of water and oil from water in oil emulsion as function of time, respectively.

From Figure 1, found that the octylamine has started to separate after seven hours and followed by hexylamine, pentylamine, and dioctylamine. The octylamine has separated up to 80% after 98 hours. Then it followed by hexylamine (44%) and pentylamine (4%). For dioctylamine case, observed that there was no separation occurred during the experiment. It only went through the flocculation and coalescence stage until end of the experiment. Figure 2 has illustrated the oil separation results for water in oil emulsion by using amines group as demulsifier. The octylamine has separated high amount of oil from emulsion compared to others. The hexylamine has become the second highest then followed by pentylamine.

According to the previous study done by Abdurahman *et al* [1], the descending sequence of amine demulsifier efficiency was due to high molecular weight factor which acts as flocculants in adsorption and interaction activities. Referring to Souleyman [11], an efficient oil soluble demulsifier usually decrease the interfacial tension gradient and the interfacial viscosity which causes an increase in the rate of film thinning and a decrease in the time it takes the film to reach a certain thickness as shows by octylamine, hexylamine, and dioctylamine, respectively. Ilyani [10] has mentioned in her thesis that for water in oil emulsion cases, the most effective demulsifiers are oil soluble or hydrophobic. This is because; oil is the continuous phase while water is the dispersed phase. Thus, the surfactants will absorb directly into the continuous phase without any resistance in optimum temperature. Regarding to this study, the solubility of amine group falls off as the hydrocarbon chains get longer which noticeably so after about six carbons. The small amines of all types are very soluble in water. The hydrocarbon chains have to force their way between water molecules, breaking hydrogen bonds between water molecules.

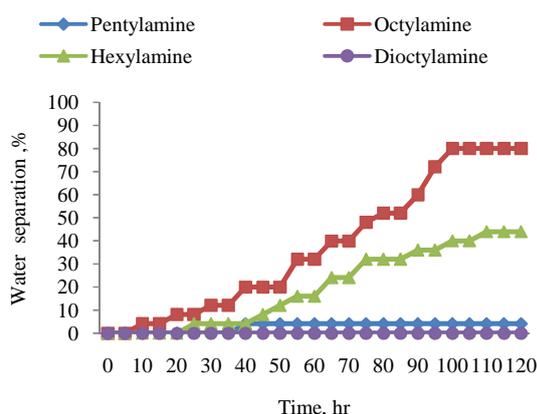


Fig. 1 The influenced of amine group demulsifier on water in crude oil emulsion stability (percentage of water separation)

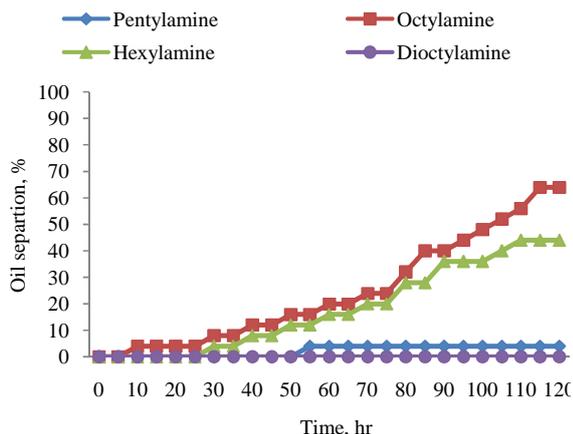


Fig. 2 The influenced of amine group demulsifier on water in crude oil emulsion stability (percentage of oil separation)

Demulsification of water in oil emulsion using alcohol emulsifier also experimented. From the results depicted in Figure 3, the effect of alcohol group demulsifier on water separation for water in crude oil emulsion can be arranged as butanol, propanol, ethanol, and methanol, respectively. Butanol has highest separation capacity (44%), followed by propanol (40%), ethanol (28%), and methanol (16%). Referring to Abdurahman, *et. al* [1], the water solubility of alcohol can be explained as low molecular weight alcohol are water soluble such as methanol and ethanol. However, four carbon and above have much lower water solubility. The water solubility influenced the effectiveness of demulsifier.

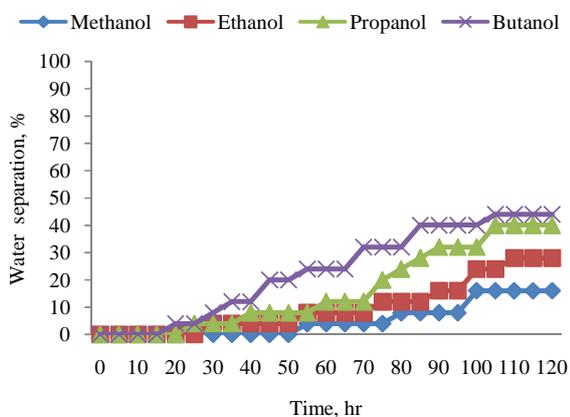


Fig. 3 The influenced of alcohol group demulsifier on water in crude oil emulsion stability (percentage of water separation)

The influence of polyhydric alcohol demulsifier towards water in oil emulsion also studied. Figure 5 and 6 depict the separation percentage of water and oil from emulsion as function of time, respectively. There were two type of demulsifier from polyhydric alcohol group which consisted of Polyethylene glycol (PEG) 300 and 400. Based on the experimental result in Figure below, the water separation occurred after five hours for PEG 400 (4%) and after 10 hours for PEG 300. From the Figure 5 and 6, observed that PEG 400 has high water and oil separation capacity

compared to PEG 300. This can be described based on water solubility of alcohol as been mentioned previously. From the previous study done by Abdurahman, *et. al* [1], the polar molecules are attracted to the hydroxyl group by hydrogen bonding that occurred between hydrogen of water molecule and the oxygen in the alcohol molecule.

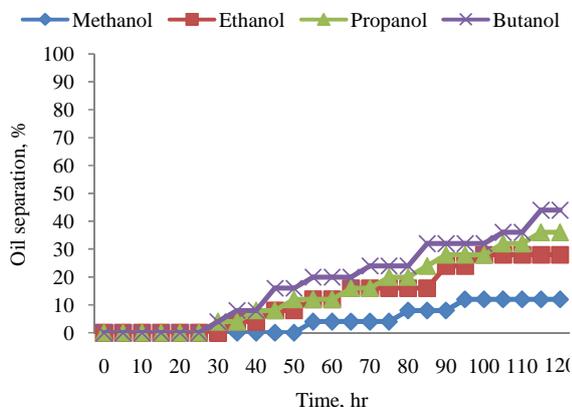


Fig. 4 The influenced of amine group demulsifier on water in crude oil emulsion stability (percentage of oil separation)

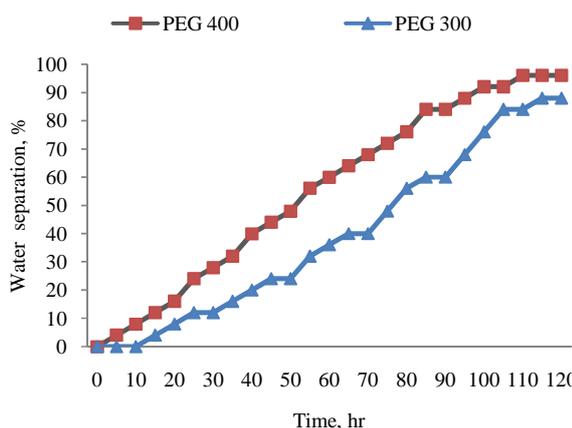


Fig. 5 The influenced of polyhydric alcohol group demulsifier on water in crude oil emulsion stability (percentage of water separation)

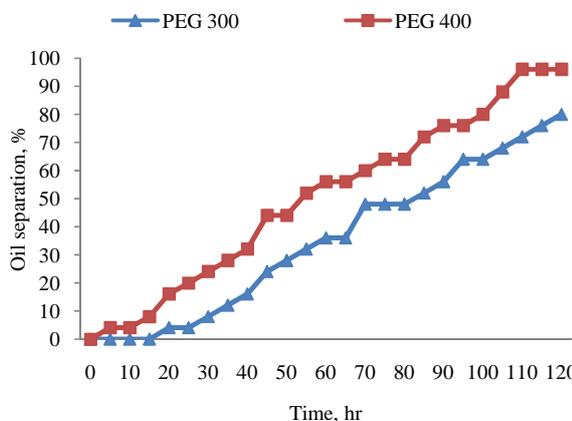


Fig. 6 The influenced of polyhydric alcohol group demulsifier on water in crude oil emulsion stability (percentage of oil separation)

V. CONCLUSION

Water in oil emulsion have great important in petroleum industry. So, there were various methods to treat the emulsion. The most widely used method in this treatment process is by using chemical demulsification. This process involves the use of chemical additives in order to accelerate the emulsion breaking process. The demulsifier adsorbs at the interfacial film, weaker the interfacial barrier and separate the water droplets.

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