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Coalescence of Water Droplets in Water-in-Crude Oil Emulsions*

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Abstract: Water separated from water-in-crude oil emulsions by chemical demulsification. Coalescence rates of water droplets have been studied in the presence of chemical demulsifier (Decylamine). Droplet size was measured. Fastest coalescence rate was observed during first minute. Binary coalescence time during this period was 10 sec when 50 mg L⁻¹ of Decylamine was added and 5 sec in the presence of 100 mg L⁻¹ of Decylamine emulsifier. Also polyhydric alcohol demulsifiers were investigated. Results show a strong connection (correlation) between good performance (fast coalescence) and the demulsifiers.

Key words: Coalescence, demulsification, w/o emulsion, polyhydric alcohol, efficiency

INTRODUCTION

Demulsification of crude oil forms an integral part of crude oil production and chemical demulsification is an important step in demulsification sequence. In chemical demulsification, chemical known as demulsifier is added to the water-in-crude oil emulsion. These demulsifiers are surface active agents (surfactants) and develop high surface pressure at crude oil-water interface (Graham *et al.*, 1980; Bhardwaj *et al.* 1994). It results in replacement of rigid film of natural crude oil surfactants by a film which is conducive to coalescence of water droplets. Only qualitative information is available about the rates of coalescence of water droplets in such emulsions, i.e. the rate is fast or slow. Chemical demulsification is the most widely applied method of treating water-in-oil and oil-in-water emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The formulation of an emulsion demulsifier for a specific petroleum emulsion is a complicated undertaking. In petroleum system, asphaltenes and resinous substances comprise a major portion of the interfacially active components of the oil (Sjoblom *et al.*, 1992; Johansen *et al.*, 1989; Urdahl *et al.*, 1992; Siffert *et al.*, 1984). Asphaltenes and resinous are large polyaromatic and polycyclic condensed ring compounds containing heteroatoms (Urdahl *et al.*, 1992; Moschopedis *et al.*, 1976). Chemically, asphaltenes and resins are represent the pentane or hexane insoluble portion of the oil (Anderson and Bird, 1990; Moschopedis *et al.*, 1976; Ferworm *et al.*, 1993). The objective of this research is to qualitatively study the coalescence and separation of water droplets in emulsions.

MATERIALS AND METHODS

Crude oil samples were obtained from Petronas Refinery at Melaka. A detailed procedure for the water-in-crude oil (w/o) emulsions preparation and their procedures including the formation of w/o emulsion, their characteristics and methods of preparation are thoroughly described in a previous study by Abdurahmman *at al.* (2006). Here the work merely describes the main experimental steps. Three crude oils were used: crude A from Iran oilfield, crude B from Kuwait oilfield and crude C from

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Table 1: Physico-chemical properties of crude oils A, B and C

Crude oil	Crude A	Crude B	Crude C
Density (g cm^{-3})	0.874	0.788	0.857
Viscosity (cp)	28.300	10.400	15.600
Surface tension (m Nm^{-1}) at rate 30°C	30.300	22.500	27.600
Interfacial tension (m Nm^{-1}) at rate 30°C	28.800	20.350	25.600

Table 2: Physical properties of crude oils used in the experiments

Crude oil	Density (g cm^{-3})	Asphaltene (% w/w)	Resin (% w/w)	R/A ratio	Pour point
A	0.874	1.5	9.0	6	15
B	0.788	0.3	3.6	12	-8
C	0.857	0.8	6.4	8	9

Table 3: Composition of w/o emulsion formulations and their corresponding stabilities

Emulsion	Stabilizer	Wt. (%) stabilizer in ext. phase (oil)	Emulsion type	% internal phase
1	LSWR	0.50	w/o	50
2		0.75	w/o	55
3		2.00	w/o	60
4		5.00	w/o	70
5	Triton X-100	0.75	w/o	50
6		0.90	w/o	55
7		1.50	w/o	60
8		3.00	w/o	70
9	SDDS	1.00	w/o	65
10		1.50	w/o	70
11		3.00	w/o	75
12		3.50	w/o	80
13	Span 83	4.50	w/o	50
14		6.00	w/o	55
15		1.50	w/o	60
16		6.80	w/o	70

Malaysia. Their respective compositions and fractions were shown in Table 1 and 2, respectively. For preparation of water-in-crude oil emulsions, the agent in oil method was implemented, that is; the Emulsifying agent dissolved in the continuous phase (oil) and water added gradually to the mixture (oil+emulsifying agent). emulsions were agitated vigorously using a standard three blade propeller at room temperature (25-30°C). The volume of water settled to the bottom was read from the scale on the beaker with different times. The prepared emulsions were used to check for w/o or o/w emulsions. All emulsions investigated were type of water-in-oil emulsions (oil continuous). Coalescence of water droplets was studied at two different demulsifier concentrations, 50 and 100 mg L^{-1} on the basis of emulsion volume. Surfactants used in this study are the commercially available Triton-X-100, Sodium Dedocyl-Sulphate (SDDS), sorbitan monooleate (Span 83) and Low Sulphur Wax Residue (LSWR).

The concentrations of water in samples were 10-90% by volume. The composition of w/o emulsion formulation and their corresponding stabilities are given in Table 3 which shows the surfactants used for the present study.

RESULTS AND DISCUSSION

The first part of this research deals with the formation, production and stabilization of w/o emulsions, while in the second part discusses the emulsion breaking (demulsification) of w/o. Table 3 shows emulsions made of LSWR and Triton-X-100 with 50, 55, 60 and 70% (v/v) internal phase. For the 50 and 55% emulsion, a higher solids concentration was found (6 mg mL^{-1} oil versus 2 mg mL^{-1}) allowed easier emulsification and slowed the settling process. The 60 and 70% emulsions were appeared fairly stable with little settling. The LSWR and Triton-X-100 stabilized emulsions

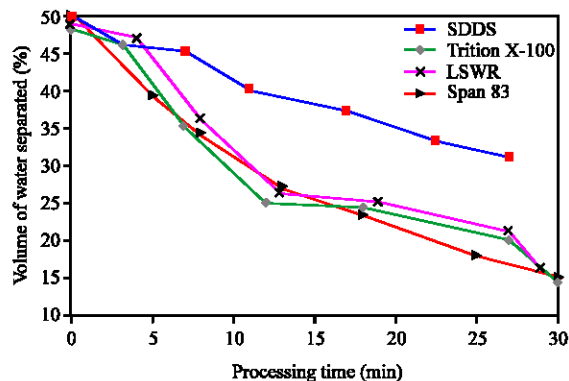


Fig. 1: Change of emulsion stability for crude oil A emulsions (50-50% w/o) as function of processing time and emulsifier applied

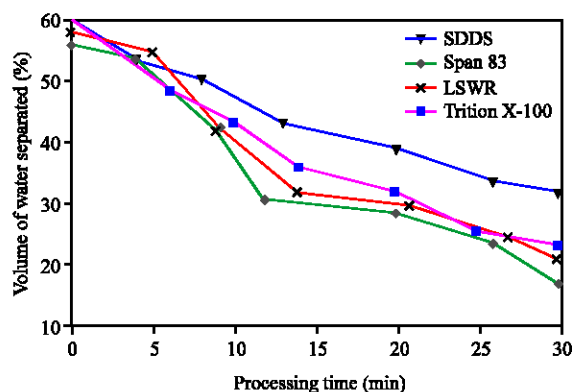


Fig. 2: Change of emulsion stability for crude oil C emulsions (50-50% w/o) as function of processing time and emulsifier applied

exhibited only slight coalescence over two days (Fig. 1). Some globule formation was observed and settling occurred. In contrast, the Span 83 emulsions were different from LSWR and Triton-X-100 emulsions, even at similar dispersed phase volume fractions. The difference between surfactant concentrations for the 50 and 55% (v/v) emulsions made by Span 83 appeared very significant on emulsions stability. High Span 83 concentrations increased emulsion stability; therefore, for high concentration of Span 83, the viscosity of w/o emulsion increased considerably and the emulsion droplets lost their shape. The emulsion stability for crude oil A and C were examined as function of processing time and emulsifier applied. Stability was evaluated via the ratio of the total water separated. As depicted in Fig. 1 and 2, in most cases, stability of emulsion increases with processing time. It is worth noticing that all surfactants permit a very long time for separation of the water phase (emulsion more stable). However, the maximum amount of water separated from Crude oil A was 50% and crude oil C was 60% (Fig. 1, 2), respectively. From these observations, the classification in terms of decreasing stability efficiency is therefore, the following; SDDS>Triton-X-100>LSWR>Span 83, respectively.

Effects of Resin/Asphaltene Ratios on Emulsion Stability

The presence of asphaltene and resin in crude oil can stabilize the emulsion. Asphaltene and resin act as an emulsifying agent, which reduce the interfacial tension and to induce repulsive forces between

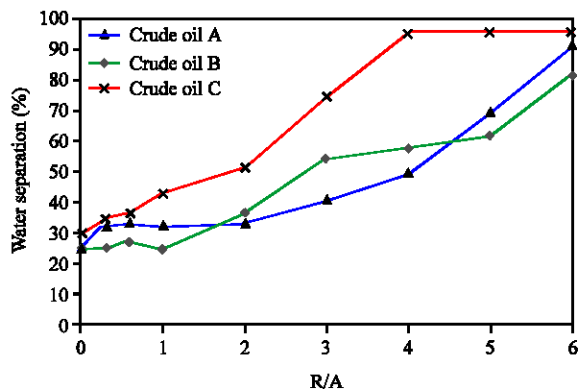


Fig. 3: Effect of adding resins (varying R/A) from different crude oils on emulsion stability

the droplets. Therefore, the resin/asphaltene ratio (R/A) is an important parameter to predict the emulsion stability. Resins increase the solubility of asphaltene in the crude and minimize the asphaltene interaction with water droplets. The resin/asphaltene ratio (R/A) may be expected to provide valuable information on tight emulsion formation. In this regards, the R/A ratio for oils A, B and C were found as 6, 12 and 8, respectively. Our experiment results showed that crude oil B fractions which has higher R/A ratio, 13 was separated easily than that of lower R/A ratio (crude A and C). It may concluded that, when R/A ratio decreased, the emulsions are become tighter and harder to break. High resin concentration keeps more of the asphaltene dissolved in the oil phase, based on this fact, crude oil A found more stable than crude B and C.

Effects of Added Resins and Resin Type

The next logical step in the investigation was to determine the effect of increasing the amount of added resins (i.e., increasing the R/A ratio) at constant asphaltene concentration and to investigate the effect of adding resins isolated from different crude types. Figure 3 shows the effect of adding resins from all three crude types on the stability of emulsions produced from model oil containing 0.3 w% crude A asphaltenes. The first order effect was that R/A ratios ≥ 3 did good diminish the emulsifying propensity of these model oils to a significant extent. The emulsion were completely resolved when R/A ratio = 4 with crude B. When R/A = 6, all emulsions were resolved. It should also be noted that the stability observed for emulsions at an R/A = 3 the amount of water separated from the three crude oils A, B and C as; 41, 75 and 55%, respectively. The maximum amount of water decanted when R/A ratio = 6, which 92, 83 and 96%, respectively.

Effects of Asphaltene Concentration

The concentration of asphaltenes in the oil should also have a substantial effect on the emulsion stability. The results in Fig. 4 where the concentration of asphaltenes was increased both at a constant resin concentration of 1.3 w% and at a constant R/A ratio of 1, do indeed prove this to be true. In comparing the two curves in Fig. 4, the constant resin concentration curve shows more water resolution (100%) than the constant R/A ratio (68%) curve at asphaltene concentration of 0.5%.

Demulsification is the breaking of a crude oil emulsion into oil and water phases. From point view, the oil producer is interested in two aspects of demulsification; the rate or speed at which this separation takes place and the amount of water left in the crude oil after separation. Coalescence of water droplets was studied at two different demulsifier concentrations, 50 and 100 mg L⁻¹ on the basis of emulsion volume. Emulsion was stirred at 750 rpm. Water droplet size was measured till 150 min

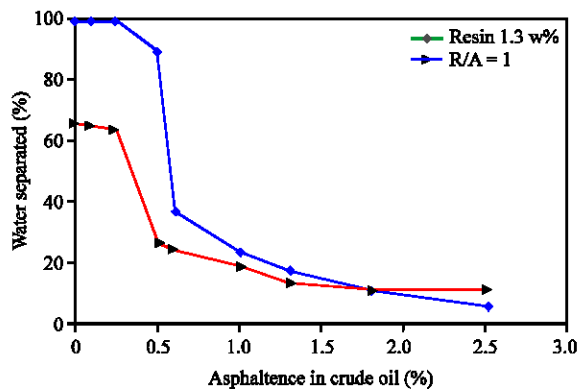


Fig. 4: Comparison of varying versus fixed R/A ratio on emulsion stability

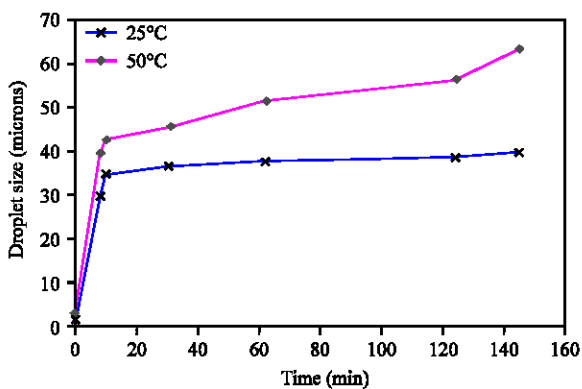


Fig. 5: Variation in droplet diameter with time for 50 mg L⁻¹ demulsifier

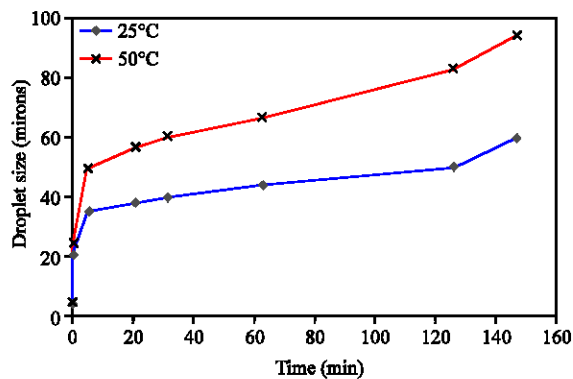


Fig. 6: Variation in droplet diameter with time for 100 mg L⁻¹ demulsifier

and the first measurement was taken after 5 min. These experiments were carried out at 25 and 50°C. The results of these experiments are shown in Fig. 5 and 6, respectively. It was observed that the droplet size grows very rapid during the early droplet time (first 7 min) and then followed by very slow increase in size. It observed also increase in demulsifier will accelerate the coalescence of droplet

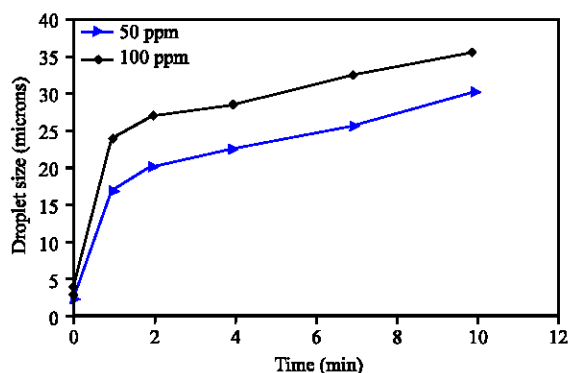


Fig. 7: Variation in droplet diameter with time for short duration

faster. Since the initial coalescence was very rapid, therefore, another set of experiments was conducted to observe growth in droplet size within shorter time frame. In this experiment changes in droplet size were observed from 1 to 10 min and temperature during the experiment was 25°C. It was observed that from these results, the first minute is most important in droplet coalescence, as shown in Fig. 7.

Due to limitations inherent in the experimental procedures, it was not possible to run experiments at shorter periods with good reliability of time scale. Coalescence of water droplets leads to decrease in surface area of dispersed phase.

CONCLUSIONS

Water-in-crude oil emulsions have great importance in the oil industry. Results from this study tend to support the proposed mechanism in which emulsion stability is governed primarily by the state of solubility of asphaltenes in the crude oil. Coalescence of water droplets in water-in-crude oil emulsions, in the presence of a demulsifier is characterized by very short initial coalescence time (few sec). High resin-asphaltene ratio R/A decreases emulsion stability.

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