Affect of Viscosity and Droplet Diameter on water-in-oil (w/o) Emulsions: An Experimental Study

A.N. Ilia Anisa, and Abdurahman H.Nour

Abstract—The influence of viscosity on droplet diameter for water-in-crude oil (w/o) emulsion with two different ratios; 20-80 % and 50-50 % w/o emulsion was examined in the Brookfield Rotational Digital Rheometer. The emulsion was prepared with sorbitan sesquiolate (Span 83) act as emulsifier at varied temperature and stirring speed in rotation per minute (rpm). Results showed that the viscosity of w/o emulsion was strongly augmented by increasing volume of water and decreased the temperature. The changing of viscosity also altered the droplet size distribution. Changing of droplet diameter was depends on the viscosity and the behavior of emulsion either Newtonian or non-Newtonian.

Keywords—Diameter, phase ratio, viscosity, water-in-crude oil (w/o).

I. INTRODUCTION

In the petroleum industry, the viscosity of crude oil is the crucial part to investigated. The viscosity of crude oil in industry is about flow properties of emulsion which involve two-phase flows between water and crude oil. Emulsion is a system which dispersion of a liquid phase to another and exhibit unstable thermodynamically. Water is normally present in crude oil reservoirs or is injected as steam to simulate oil production [1, 6]. Water and crude oil mixed while rising through well and passing through valves and pumps to form water-in-crude oil (w/o) stable emulsion particularly. Stable emulsion contain of 60 to 85 % water [7].

The stable emulsion arises in heavy oil which, generally have greater viscosity [1]. Essentially w/o emulsion form spontaneous due to the presence of natural surfactant such as asphaltenes and resins in the crude oil and these natural surfactants are strongly have correlation with viscosity of the crude oil. Viscosity of crude oil (continuous phase) increases as number of suspended particle increases and reveal the emulsion more stable [1, 4 and 9].

A vast amount of research has been done on the rheological characterization of emulsions in droplet size distribution [3, 5]. However, most of studied were based on viscosity effects

onto droplet size distribution and refractive index of oil-inwater (o/w) emulsion. Through this paper, the rheological properties which, affect the stability of emulsion, temperature, phase ratio and stirring process will be further investigated and their relative with droplet size distribution for w/o emulsion also scrutinized.

II. EXPERIMENTAL SET UP

A. Material

Three types of crude oil were examined in this study whereas donated by Petronas Refinery Melaka. The properties of crude oil as shown below:-

TABLE I Crude Oil Characteristics						
	Crude Oil A	Crude Oil B	Crude Oil C			
viscosity (cP)	183.6	24.6	207.8			
density (g/mL)	0.8459	0.8345	0.8394			
API gravity	29.27	33.82	26.48			
pour point (°C)	-19.5	-12	-20.4			

Oil viscosity was measured using viscometer (Brookfield Rotational Digital Rheometer Model LV/DV-III) with a heating/cooling water bath. This viscometer was equipped with UL adaptor and spindles 31. The crude oil used in this study was considered as a Newtonian fluid because the viscosity of the crude oil remains almost constant while being measured with a viscometer at different speed rotation.

The emulsifier used in the experiments was sorbitan sesquiolate (Span 83) acquired from Sigma-Aldrich, USA. Span 83 is non-ionic and oil soluble group. The emulsifier was added into crude oil without further dilution.

B. Procedures

The emulsion was prepared by adding 0.1 wt% Span 83 of continuous phase into the crude oil. This solution (Span 83 + crude oil) was mixed until 1 minute to ensure the mixing solution become homogenous. Water-in-crude oil emulsion was prepared by adding water (dispersed phase) slowly to the solution with varied volume of water and crude oil. All the measurements were made under the following conditions unless otherwise specified: the ratio of oil to water was 2:8

A.N. Ilia Anisa, master students from Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Malaysia (phone: +6013-2073589; e-mail: nia_ilianisa@yahoo.com).

Abdurahman H. Nour, associated professor also as lecturer from Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Malaysia (phone: +6 012-9134403; e-mail: nour2000_99@yahoo.com).

and 5:5 by volume; the stirring intensity, 1500 rpm; the mixing time, 5 min and prepared at room temperature $(27^{\circ}C)$. The prepared emulsions were checked for o/w or w/o emulsions using tube test and filter paper. Only w/o types was chosen for further study. The emulsion was measured the refractive index using refractometer to identified type of prepared emulsion.

The rheological measurements for all the samples was carried out with Brookfield Rotational Digital Rheometer Model LV/DV-III with UL adaptor and spindles 31 in measuring viscosity, shear rate and shear stress.

The droplet diameter of each emulsion (20-80 % and 50-50% w/o) was observed through Carl Zeiss research microscope before connected with digital camera and determined by AxioVission AC software. The effect of refractive index (R.I) in emulsion was examined using refractometer from Mattler Toledo.

III. RESULTS AND DISCUSSION

A. Effects of Phase Ratios

It has been reported that the phase ratio persuaded the droplet size distribution [2]. As change the ratios, the viscosity also altered and affected the stability, thus effects the droplet size distribution. The droplet size distribution for 50-50 % and 20-80 % w/o were measured and illustrated.



Fig. 1 Droplet size distribution at (a) 50-50 w/o emulsion and (b) 20-80 w/o emulsion

The effect of size distribution at varied phase ratio (20-80 % and 50-50 % w/o) is shown in Fig. 1 for crude oil B. As examined the droplet size distribution, higher water cut (50-50 % w/o emulsion) obtained tighter emulsion than lower phase ratio (20-80 % w/o emulsion). The tighter emulsion is exhibit fine emulsion than coarse. It was clearly showed that 20-80 % w/o which lower water cut have smaller droplets size diameters. The average droplet size for 20-80 % w/o and 50-50 % w/o are 20.76 μ m and 26.60 μ m. An increase in water cut for 20-80 % and 50-50 % w/o, the ability the droplets tend to aggregate also higher, thus coalesce by formed single and larger unit of droplet through eliminated rigid film surround the droplets.

Fig. 2 and 3 show the effects of phase ratio for both ratio (20-80 % and 50-50 % w/o) emulsion against viscosity using different types of crude oil. The viscosity increased linearly with increasing of water cut due to the increase of hydrogen bonds, leading to decrease in the molecular distances of the emulsion system as well as an increase of resistance to flow.

From Fig. 2, both crude oil A and C, the viscosity was function to the shear rate compared to crude oil B. This clearly shows that crude oil A and C follow the Newtonian behavior

but not for crude oil B. For 20-80 % w/o emulsion, crude oil B displays the viscosity is not correlated with shear rate. The type of crude oil can be a good reason for behavior of crude oil. Crude oil B has lower viscosity and light crude oil compared with crude oil A and C.

As the dispersed phase function (water) of dispersion is increased, the dispersion rheology changes significantly due to the frequency of droplet interaction increases. Therefore, as the results coalescence faster in high cut, the number of the droplets in an aggregates change with time. Since any change in the dependence of the viscosity on rate of shear could not be observed, the decreased in viscosity would be brought about the broadening of the droplet size distribution.



Fig. 2 The behavior of emulsion for 50-50 % w/o emulsion at different type of crude oil



Fig. 3 The behavior of emulsion for 20-80 % w/o emulsion by plot viscosity versus shear rate (T=25°C)

B. Effects of Temperature

The effects of temperature for the emulsion also had been studied. Temperature changes usually cause changes in the emulsion stability whether invert the emulsion or may break the emulsion. Surfactant is usually most effective when near the point of minimum solubility in the solvent when it was dissolved. Since the solubility of the surfactant normally changes when temperature changes, the stability of emulsion also change [7]. When temperature was increased, the flow molecules through the interfaces also increased resulting in a decrease in emulsion stability. The flow molecules correlated with viscosity. The increasing temperature results in decreasing the viscosity. From Stoke's and energy balance equation,

$$\mathcal{V}_m = \frac{g D^2 (\rho_w - \rho_o)}{18\mu} \tag{1}$$

Where D is droplet diameter; $(\rho_w - \rho_o)$ is density different of water and crude oil respectively and μ is the viscosity of emulsion. From Eq. (1), the settling velocity, v_m was inversely proportional with viscosity. v_m was increased as decreasing viscosity. The viscosity is very sensitive to temperature hence; the increment temperature caused reduction of emulsion viscosity.

Fig. 4 and 6 demonstrated the effect of emulsion viscosity obtained from Eq. (1). Both phase ratios show the decreasing of viscosity as increasing temperature. However at 90°C (in 50-50 % w/o), crude oil B acquired the increasing temperature and this is expected due to phase inversion point is reached.



Fig. 4 Effects of viscosity at varied temperature in 50-50 % w/o

Fig. 5 illustrated the droplet size distribution at 90°C due to phase inversion is expected ensue. At this point the separation occurs and emulsion is converted from water-in-oil (w/o) to oil-in-water (o/w). The type of emulsion also can be measured through refractive index (RI) where at ambient temperature for 50-50 % w/o emulsion the RI is 1.5029 and the value is decreased as increasing temperature and at 90°C, the RI increased; 1.5045 respectively.



Fig. 5 Photograph of droplet size distribution under microscope (50-50 % w/o emulsion) at 90°C

TABLE II EFFECTS OF TEMPERATURE IN VISCOSITY AND AVERAGE OF DROPLET DIAMETER AT VARIED PHASE RATIO

	50-50 % w/o		20-80 % w/o	
temperature (°C	viscosity (cP)	average droplet diameter (µm)	viscosity (cP)	average droplet diameter (µm)
25	340.76	20.76	51.00	26.60
50	149.83	26.73	57.00	20.45
70	83.00	35.73	75.00	15.55
90	97.69	44.19	87.00	13.64

However, for 20-80 % w/o emulsion (in Fig. 5), crude oil B displays the viscosity increased with temperature. This result can be explained by compared the behavior of emulsion. Which at 50-50 % w/o emulsion, the emulsion is expected from non-Newtonian because of the content of water cut and near to the phase inversion point. In case for 20-80 % w/o emulsion, they were followed Newtonian behavior because the viscosity of emulsion is no longer a unique function of the phase ratio because droplet size distribution plays as dominant factor.

The value of RI as following temperature from ambient (25°C), 50, 70 and 90°C were 1.4495, 1.50, 1.5038 and 1.5046, correspondingly. The RI obtained increasing as decreasing the droplet size distribution.



Fig. 6 Effects of viscosity at varied temperature in 20-80 % w/o

C. Effects of Stirring Speed

The effects of stirring speed were examined through plot graph of viscosity versus varied stirring process from 500 to 2000 rpm. For each stirring speed condition, the droplet size distribution is determined by microscope associated to an image analysis. From Table III, it is obviously shows that increasing the stirring speed results an increasing the viscosity of emulsion for both phase ratios; 50-50 w/o % and 20-80 w/o % emulsion.

TABLE III EFFECTS OF STIRRING SPEED TO VISCOSITY AND AVERAGE OF DROPLET DIAMETER AT VARIED PHASE RATIO

	50-50 % w/o		20-80 % w/o	
Stirring speed (rpm)	viscosity (cP)	average droplet diameter (µm)	viscosity (cP)	average droplet diameter (µm)
500	152.69	60.34	19.81	35.60
1000	251.58	33.34	24.91	30.14
1500	340.76	20.76	49.00	26.60
2000	493.16	15.82	56.45	14.92

The effects of viscosity at varied stirring speed displays on Fig. 7. 50-50 % w/o emulsion obtained the higher viscosity compared to 20-80 % w/o emulsion, thus decreased the droplet size distribution (Fig. 8). This is expected since the increasing water cut into emulsion, also increased the droplet size distribution because of elimination of protective rigid film and enhances the droplets to coalesce.



Fig. 7 Effects of viscosity at varied phase ratio on stirring speed (rpm)



Fig. 8 Effects of mean droplet diameter at varied phase ratio

IV. CONCLUSION

This paper shown the viscosity is affected on droplet size distribution for Newtonian and non-Newtonian behavior; the

viscosity is consequence for refractive index as factor controller. Light crude oil (B) exhibit non-Newtonian behavior in both ratio (50-50 and 20-80 % w/o) and crude oil C obtained non-Newtonian at higher water cut.

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REFERENCES

- [1] A. Hannisdal, " Particle-stabilized emulsions and heavy oils". Ph.D Thesis. Norwegian University of Science and Technology. Trondhein, Norway, 2005. Retrieved on 17 March 2009 from www.chemeng.ntnu.no/research/polymer.
- [2] A., Mohamed, M., Dong, D., Yang and I., Raphel. "Determination of water-in-oil emulsion in porous media". Ind. Eng. Chem. Res. 48, pp. 7092-7102, 2009.
- [3] D., Dan and G., Jing "Apparent viscosity prediction of non-Newtonian water-in-crude oil emulsions". Journal of Petroleum Science and Engineering 53, pp. 113-122, 2006.[4] L., L. Schramm, "Emulsions, foams and suspensions; Fundamental and
- application", 2005. Weinheim: Wiley-VCH Verlag GmBH & Co.
- [5] M., A. Farah, R., C. Oliveira, J., N. Caldas and K., Rajagopal, "Viscosity of water-in-oil emulsions: Vaiation with temperature and water volume fraction". Journal of Petroleum Science and Engineering 48, pp 169-184, 2005.
- [6] M., Fingas and H., Fieldhouse, "Formation of water-in-oil emulsions and application to oil spill modeling". Journal of Hazardous Materials 107, pp. 37-50, 2004
- M., J. Rosen. Surfactant and Interfacial Phenomena, 2004. John Wiley & [7] Sons. Inc, Hoboken, New Jersey,
- N., Othman, M., A. Azali, M., T. Fahme, "Demulsification of liquid [8] membrane emulsion by using continuous high voltage coalesce". Jurnal Teknologi, 49(F) Dis. 2008: 467-474, 2008.