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## Catastrophic and Transitional Phase Inversion of Water-in-Oil Emulsion for Heavy and Light Crude Oil

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**Abstract:** The stability of emulsion plays an important role either for catastrophic or transitional phase inversion to break and inverse emulsion from w/o to o/w or vice versa. The stability of emulsion also depends on the rheology and characteristics of the crude oil. In this study, the characteristics of crude oil were investigated closely before emulsion was prepared to further study in catastrophic and transitional phase inversion. The prepared emulsion, volume fraction (10-90 to 60-40% w/o emulsion), stirring intensity (1500 rpm) for 5 min and heating temperature (22-90°C) were evaluated. Heavy crude oil pointed up the catastrophic phase inversion higher than light crude oil. While, transition phase inversion obtained for lighter crude oil as increasing temperature.

**Key words:** Catastrophic, transitional phase inversion, w/o emulsion, droplet size, stability, rheology

### INTRODUCTION

The concept of emulsion involves immiscible liquid to another liquid which also called as medium liquid. Term of emulsion typically use in some industries such as cosmetic, food, agricultural and oil industry. However in oil industry, the formation of emulsion is typically undesirable due to result in high pumping costs and reduced throughput (Nour and Yunus, 2006) and from Xia *et al.* (2004) about 80% of exploited crude oils exist in an emulsion state, all over the world.

The majority of literatures describing stability of emulsion depend on the rheology and crude oil characteristics (Hannisdal *et al.*, 2006; Schramm, 2005). The factors contributing to the rheological parameters and to the colloid structure of petroleum emulsions is a problem of great concern and economic importance to the oil companies in the production of oil from underground reservoirs (Evdokimov *et al.*, 2004).

Crude oil contains of a complex mixture of hydrocarbons<sup>s</sup> with indigenous surfactant and has no doubt enhanced the stability of emulsion by forming protective rigid film surround the droplets (Hannisdal *et al.*, 2006; Nour *et al.*, 2008). These compounds also called as natural surfactant can be precise to asphaltenes, resins, solid particles and wax. Asphaltenes is precipitates in the presence of aliphatic solvents while the resin fraction is defined as the fraction soluble in light alkanes, but insoluble in liquid propane.

Asphaltenes and resins are the most aromatic and most polar compounds of petroleum. Absorption of solid particles and wax may also contribute to the film strength thus make barrier surround the droplets.

Phase inversion is an important principle to improve viscosity correlation. The stability of emulsion can be scrutinized through the viscosity of emulsion. In industry, the extremely viscous fluid of crude oil used this type of method to break the water content in crude oil (Spiecker *et al.*, 2003). The inversion of emulsion engrosses changing the morphology of emulsion from w/o emulsion to o/w emulsion or vice versa. In generally, the phase inversion of emulsion can be segregated by two which catastrophic inversion and transitional inversion. Catastrophic inversion shows the variation of viscosity with increasing volume fraction of dispersed phase;  $\Phi$ . Transitional inversion is changing surfactant distribution over the phases. However, mostly of the phase inversion do not compare the types of crude oil and focus to oil-in-water especially for transitional inversion type (Gonzalez *et al.*, 2006).

This study examined the effect of three types of crude oil characteristics in rheology and phase inversion of catastrophic and transitional.

### MATERIALS AND METHODS

This research was conducted 2009 at University Malaysia Pahang's Laboratory.

**Table 1: Physical properties of crude oils**

	Crude oil A	Crude oil B	Crude oil C
Viscosity (cP) at 25°C	183.6	24.6	207.8
Density (g cm <sup>-3</sup> )	0.8459	0.8345	0.8494
°API density	29.226	33.819	26.481
pour point	-19.5	-12	-20.4
Water content (%)	7	0.65	2
Surface tension (m Nm <sup>-1</sup> )	13.276	13.046	13.659

**Table 2: Chemical properties of crude oils**

Crude oil	Asphaltenes	Resin	Wax	Solid particles	R/A
A	11.7	21.6	0.42	13.89	1.85
B	2.94	32.33	9.13	9.77	11
C	8	37.7	23.81	3.27	4.71

**Materials:** Three types of the crude oil namely crude oil A, B and C were used in this study. Prepared w/o emulsions formed with the original crude oil were found to be extremely stable and there was no separation observed (under gravity) even after a few days. Characterizations in physical and chemical of crude oil are reported in Table 1 and 2.

**Emulsion preparation:** Emulsions were prepared using Span 83 from nonionic surfactant as stabilizer of continuous phase was added into crude oil and agitated for 1 min to perform the homogeneous solution (Fig. 1). Water was added gradually into the solution as prevention step in executing foam. The emulsion was shaken vigorously at 1500 rpm in 5 min using three blade propellers. The prepared emulsion was checked whether water-in-oil (w/o) or oil-in-water (o/w) using test tube and only w/o was used for further steps.

**Methods**

**Density and API density of crude oil:** The density of crude oil is measured using pycnometer 20 mL (ASTM D70, NFT 66007). The samples is introduced to equilibrate to room temperature (27±0.2°C) in pycnometer and weighted. The pycnometer also filled with distillate water and weighted at same temperature. While for °API density, both density of crude oil and water, measured at 15.6°C as shown in equation below:

$$°AP\ Idensity = \frac{141.5}{d(at15.6^\circ C)} - 131.5 \tag{1}$$

$$d(at15.6^\circ C) = \frac{\rho_{sample}}{\rho_{water}} \tag{2}$$

**Pour point:** Pour point bath model K46100 from Koehler Instrument Company which conforms to ASTM D9 used to measure pour point for each crude oil. Crude oil was cooled at specified rate and examined the flow characteristics. The lowest temperature at which crude oil will flow is observed and stated as pour point.

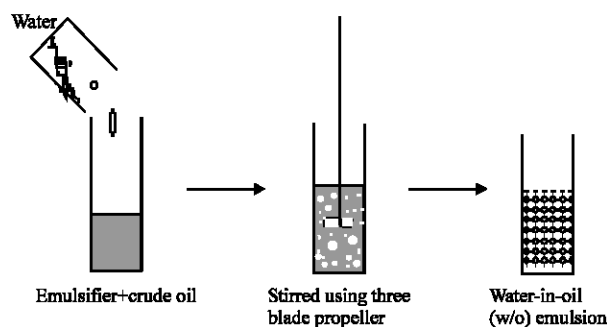


Fig. 1: Chematic diagram for preparing w/o emulsion system

**Water content:** The crude oil was injected using syringe 10 mL in Karl Fisher Analyzer model 787 KF Titrano brand Metrohm to analyse water content in crude oil.

**Surface tension:** Surface measurement standard test method (ASTM) is used and the equipment is Surface Tension Analyzer model DST 60 A. The experimental procedures follow standard procedure from DuNouy ring and the Wilhelmy plate.

**Viscosity measurement:** Brookfield Rotational Digital Rheometer Model LV/DV-III with UL adaptor and spindles 31 was used to measure viscosity, shear rate and shear stress. The Brookfield Rotational Digital Rheometer apparatus was equipped with a water bath thermostat, a spindle set and software of Brookfield Rheocalc Version 1.2. The rheometer was capable for providing the shear stress and dynamic viscosity from each determination. The rheometer was thoroughly cleaned between measurements of different samples.

**Droplet size measurement:** The instrument used is the Carl Zeiss microscope and a digital camera before connected with AxioVission AC software. All size measurements were done in duplicates and the average results were reported in this study. The effect of temperature on emulsion stability was investigated by measuring the droplet sizes (after emulsification) at various temperatures with an interval of 20°C.

**Separation of asphaltenes and solid particles:** Crude oil mixed with pentane and left for 24 h to settle down insoluble particles. After filtrate the mixing solution, precipitate and supernatant liquid are formed. Precipitate consists of precipitate asphaltenes and solid particles. Asphaltenes and solid particles are separated by added toluene into the solution.

**Separation of resin and wax particles:** Supernatant liquid is containing of resin, oil and wax particles. Silica gel is added into supernatant liquid to aid resins adsorb well on the silica before sedimentation and filtration process. Seven percent methanol in dichloromethane is added to desorb resin from silica. Resin is obtained through evaporated methanol and dichloromethane after filtrated absorbed fraction and solvent. Wax particles and oil is evaporated before proceeded with separation of wax crystal and oil.

**Fourier Transfer Infrared Spectrometer (FTIR) for asphaltenes and resin:** The FTIR asphaltene spectra were obtained by diffuse reflectance using a model Thermo Nicolet. The sample was prepared and inserted into pellet beside pure potassium bromide (KBr) powder. This KBr powder was utilised as die set before recorded into FTIR spectrophotometer. Each sample was scanning for 64 cycles, for the wavelength interval of 4000 to 400  $\text{cm}^{-1}$ , with a resolution of 4  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

**Crude oil characterization:** Three types of crude oils were selected for this study. The physic-chemical characterizations of these crude oils are presented in Table 1 and 2.

Result has shows that crude oil C is the heaviest and the lightest is crude oil B by comparing the viscosity of crude oil. Viscosity of crude oil increases proportional with density or inversely with API density (Ariany, 2004).

Surface tension involved the measurement of the force acting at a boundary between two phases. The measurement of surface tension important because indicate the relative formation and stability properties of crude oil (Denkissia *et al.*, 2004). The characteristics of crude oil also investigated closely in surface tension which crude oil C acquired the highest crude oil due to the higher viscosity thus increases force attraction between molecules.

From Auflem (2002) and Langevin *et al.* (2004), the asphaltenes content can be a good indicator in emulsion stability since asphaltenes plays an important part in emulsion stability. However from Table 2, the highest asphaltenes content in crude oil A followed by crude oil B and C. Herein crude oil C is the heaviest crude oil because the viscosity of crude oil is correlated to the wax content (Pedersen and Rnningsen, 2000).

The presence of resin also persuade in the emulsion stability. However, high content of resin reduced the emulsion stability due to the interaction of resins with asphaltenic aggregates render the aggregates less interfacially active. Therefore, the ratio resin to asphaltenes (R/A) can be an important factor to identify the emulsion stability. As increasing R/A ratio, the asphaltenes molecularly dissolved (Ali and Alqam, 2000; McLean and Kilpatrick, 1997; Miller *et al.*, 2001).

FTIR for Asphaltenes and Resin. Infrared analysis informs the functional groups exist in asphaltenes in crude oil A, B and C as shown in Fig. 2. Crude oil A, B and C indicate the presence of hydrocarbon bonded such as

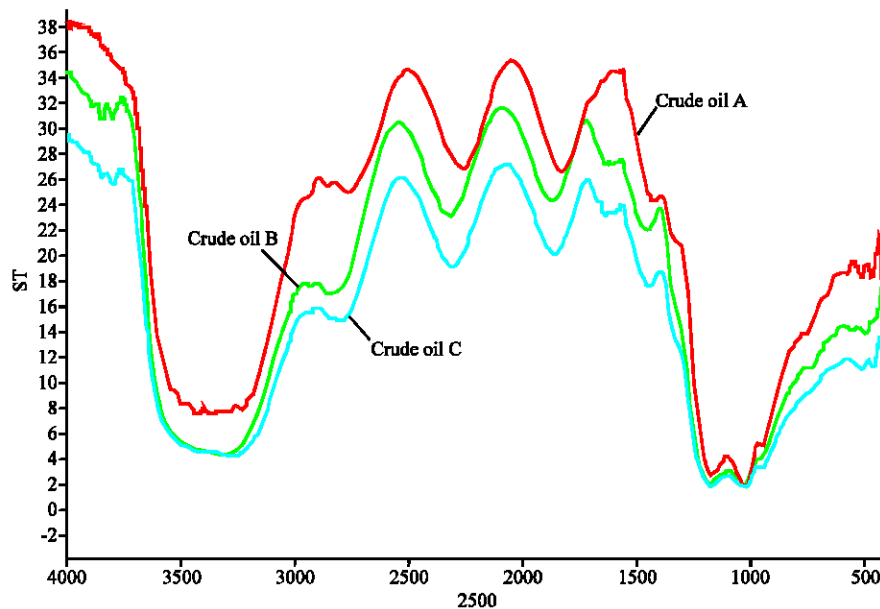


Fig. 2: FTIR spectra for asphaltenes crude oil A, B and C

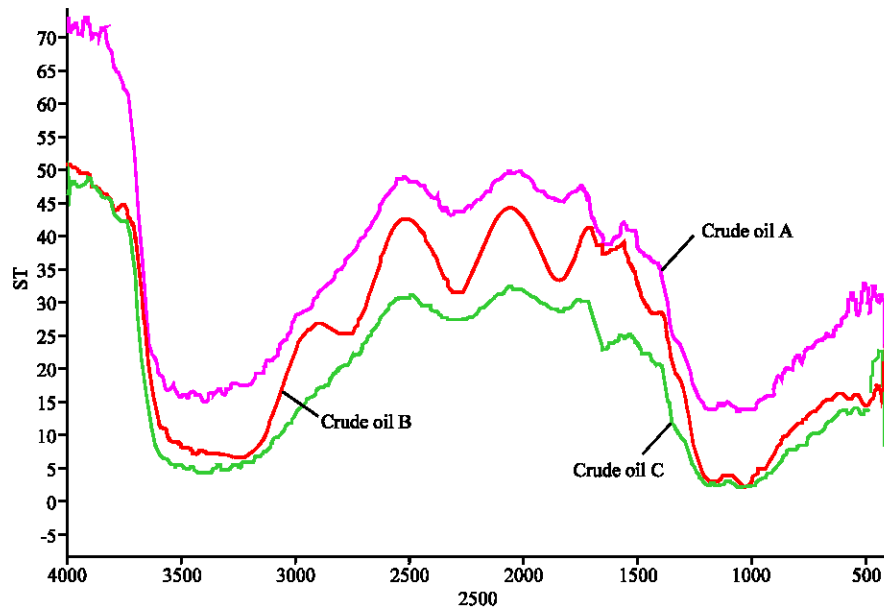


Fig. 3: FTIR spectra for resin crude oil A, crude oil B and crude oil C

OH due to the presence of hydrogen bonding between OH groups and various hydrogen bonding acceptors such as ether oxygen and pyridinic nitrogen.

Figure 2 shows the strongest absorption  $\sim 3300\text{ cm}^{-1}$  that OH-ether oxygen was the main hydrogen bonds in all the types of crude oil studied. These types of crude oil also contained large amounts of water, characterised by the large broad band at  $3400\text{ cm}^{-1}$ . At  $\sim 1600\text{ cm}^{-1}$ , the crude oil contain of aromatic group. However this functional group indicates stronger peak in crude oil B compared to other crude oil. The stronger peak of aromatic performs lower asphaltenes (Ariany, 2004).

Resin is a component in crude oil that has dark color in liquid or semisolid. The functional groups of resin are also indicated in crude oil A, B and C. Figure 3 displays the spectra of resin analyze using FTIR. The overall trend of spectra has similarity with asphaltenes because resin also has polar group. As same as perform in asphaltenes, the hydrocarbon group (OH) shows in broad stretch for all the crude oil. Crude oil B displays the presence of aldehydes group at  $2775.85\text{ cm}^{-1}$  which the presence of this functional group quite different with crude oil A and B.

**Transitional phase inversion:** Temperature often has indirect factors that affect the emulsion stability as results of altering the interfacial tension and viscosity of emulsion. The effect of temperature was examined at 20-80 and 50-50 w/o% emulsion. For both ratios, viscosity of w/o emulsion is strongly augmented by decreasing

temperature. According to the ideal Stoke’s Law for the creaming rate of emulsion, the gravitational instability rate of emulsion is directly proportional with density different of continuous and dispersed phases ( $\rho_o - \rho_w$ ):

$$v_m = \frac{gD^2(\rho_o - \rho_w)}{18\mu_o} \quad (3)$$

If viscosity, (cP) is lower, the density different of continuous and dispersed phases increased. Thus, lead the higher velocity of droplets. As temperature increased, the movement of droplets (velocity) also higher thus enhances the droplets to coalescence.

Figure 4a and b show decreasing of viscosity as augmented temperature. However for crude oil B, at  $90^\circ\text{C}$  the deformability limit for the droplets is over and the viscosity abruptly increased. The drastic increasing of viscosity in crude oil B is believed because of the phase inversion occurs from w/o to o/w emulsion. Temperature is one of factor changing the surfactant Hydrophile-Lipophile Balance (HLB) in systematically varied from predominantly oil-soluble to water soluble. At lower temperature, Span 83 is mainly soluble in oil phase and as temperature increased at  $90^\circ\text{C}$  (crude oil B), the surfactant is preferentially soluble in water phase.

Crude oil B obtained the lower viscosity compared to crude oil A and C. At inversion point, the interfacial tension decreases favor the breaking process thus, produced smaller droplets size and associated higher viscosity.

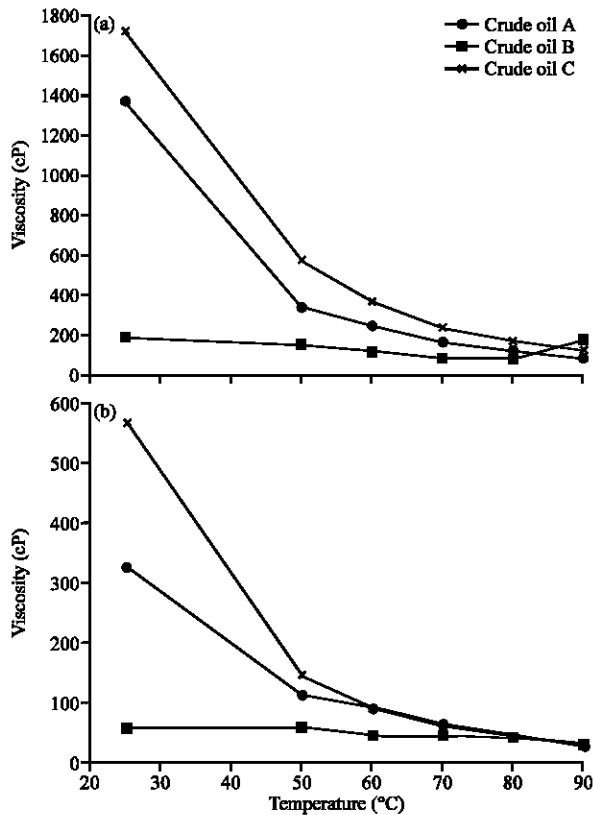


Fig. 4: Effect of temperature on emulsion stability at (a) Higher 50-50% w/o and (b) Lower 20-80% w/o emulsion

Mean diameter of emulsion droplets for 50-50% and 20-80% w/o emulsion for crude oil B were investigated closely and display in Fig. 5. At lower temperature, emulsions rheology property changed from viscous to elastic state and at higher temperature the interaction of droplets is lower due eliminated rigid film surround the droplets.

From Rusli *et al.* (2007), as droplet size increased, the specific surface area of oil/water interface also increased and resulting in stronger interaction between droplets. However, at temperature increased, the droplets decreased to 7.5 μm because of viscosity have no longer effects to temperature.

The emulsion which have relatively large droplet size (>10 μm), the relative temperature is independent of the droplet size. As temperature increased, the viscosity decreased thus the viscosity of emulsion is no longer independent factor. This result is correlated with Zaki (1997) which, at higher droplet size, the hydrodynamic forces (hard-sphere interaction) are dominant. While for smaller droplet size (>10 μm), the colloidal surfaces and Brownian motion can be dominant as proven from Fig. 5 at 90°C.

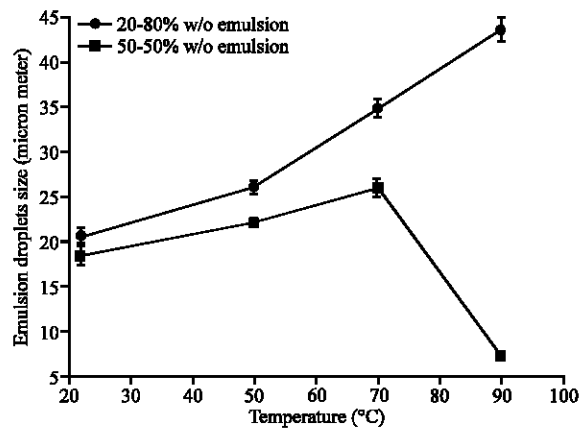


Fig. 5: The mean diameter of emulsion as function of temperature ranging from 22-90°C

If investigated the size distribution, at lower temperature, the size distribution quite uniform compared to higher temperature. This is expected because the stability of emulsion is reduced and coalescence process is begun.

**Catastrophic phase inversion:** The emulsion was prepared and varied the phase ratio within 10-90 to 60-40% w/o emulsion. Viscosity can be thought as resistance of fluid to flow. The affecting factors are numerous and viscosity is one of the expected. If the internal phase in an emulsion has a sufficiently high volume fraction, the emulsion viscosity increased due to droplet crowding or structural viscosity become non-Newtonian until achieved to the critical volume fraction. This expected result is proven by investigated the effects of viscosity when changing the volume fraction of emulsion.

The effects of volume fraction and maximum volume fraction on viscosity are described using the Krieger-Dougherty equation:

$$\eta = \eta_c \left( \frac{1 - \phi}{\phi_m} \right)^{-2} \quad (4)$$

where,  $\eta$  is viscosity of emulsion;  $\eta_c$  represents the viscosity of the crude oil;  $\phi$  is phase volume of dispersed phase and  $\phi_m$  denotes the maximum phase volume.

Effect of the viscosity on the volume fraction is shown in Fig. 6 for all the types of crude oil used in this study. At low volume fraction (~0.15), the viscosity increased linearly but as the volume fraction increased the viscosity increase is steeper. However, when the droplets are closed enough and exceed the limitation, the viscosity decreased drastically due in changing the phase inversion

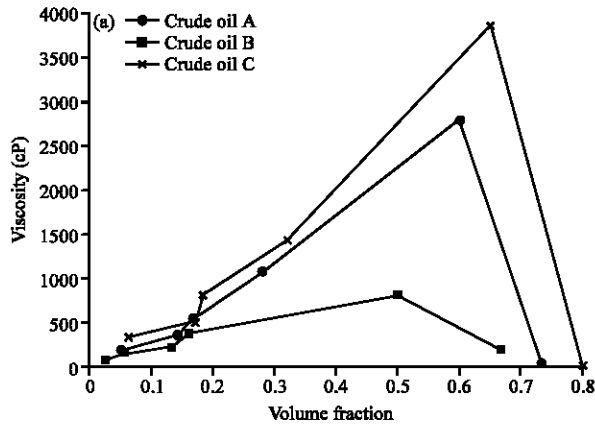


Fig. 6: An influence of phase volume fraction on the emulsion type and viscosity

of emulsion to oil-in-water. From figure, the critical volume fraction point for crude oil A, B and C are 0.5, 0.6 and 0.68. This result is supported by Tadros (2009) which, random packing droplets might start being in contact at a lower volume fraction. Earlier assumptions of phase inversion were based on packing parameters. When volume fraction exceeds of maximum packing (~0.64 for random packing and ~0.74 for hexagonal packing of monodisperse), critical point of volume fraction reached. However, these assumptions are not adequate because there are still emulsion invert at volume fraction values below than the maximum packing.

**Rheological properties of W/O emulsions at varied phase ratio:**

The rheological behavior of emulsion also can be determined either Newtonian or non-Newtonian behavior. The effect of shear stress on shear rate at lower and higher phase ratio are presented in Fig. 7a and b. Results show the shear stress is no longer linear as increasing the dispersed phase composition which at 20-80% w/o emulsion, a straight line graph observed from shear stress versus shear rate. While, as increased the composition, crude oil B and C obtained non-Newtonian behavior. This is expected as increasing dispersed phase composition, the emulsion behavior more on non-Newtonian as same as previous researchers (Lee *et al.*, 1997; Chhabra, 2006).

As revised from Lee *et al.* (1997) in generally at low to moderate concentration of dispersed phase, the emulsion tends to exhibit Newtonian, but at higher concentration, the emulsion behaves as shear-thinning fluids. However, at 50-50% w/o emulsion for crude oil A, the emulsion follows Newtonian behavior which as shear stress is applied, the crude oil is flow continuously. This is due to the lower content of wax precipitated (0.42

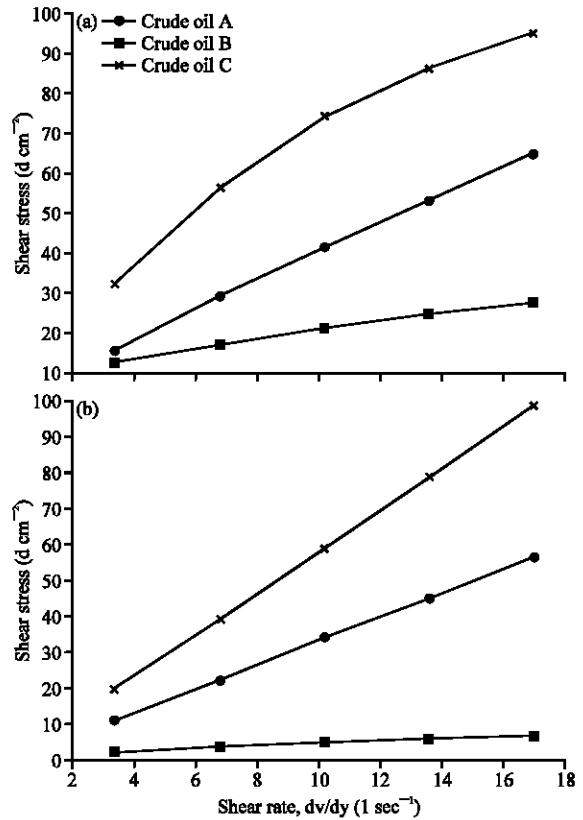


Fig. 7: Effect of shear stress on shear rate with varied phase ratio (a) 50-50% w/o emulsion and (b) 20-80% w/o emulsion

compared to other crude oil. The higher content of wax precipitated exhibited crude oil to exist as non-Newtonian behavior.

The crude oil A was investigated closely by increasing the composition of water-crude oil to 55-45% w/o and 60-40% w/o emulsion as shown in Fig. 8. As increasing the phase composition, the emulsion behavior as pseudoplastic which emulsion was stretched and alignment while being sheared due to increasing the droplet content into the crude oil. This result also verified that higher composition is required in crude oil A to behave as non-Newtonian due to the content of wax-precipitated.

The behavior of emulsion by affected from its composition is confirmed by plotting apparent viscosity versus shear rate. Figure 9 show the plots of apparent viscosity at different phase ratio (a) 50-50% w/o emulsion and (b) 20-80% w/o emulsion. At higher phase ratio, the apparent viscosity of crude oil B and C clearly decreased as increasing shear rate thus confirmed the emulsion pursued pseudoplastic behavior. The gradual break-up of interparticles structure may be primarily responsible for

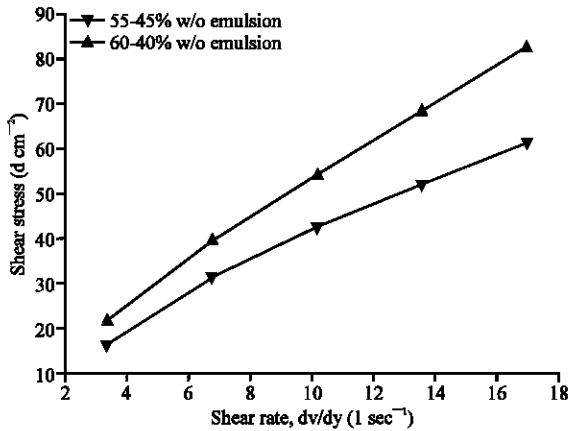


Fig. 8: Effect of shear stress on shear rate in crude oil A by increased the composition

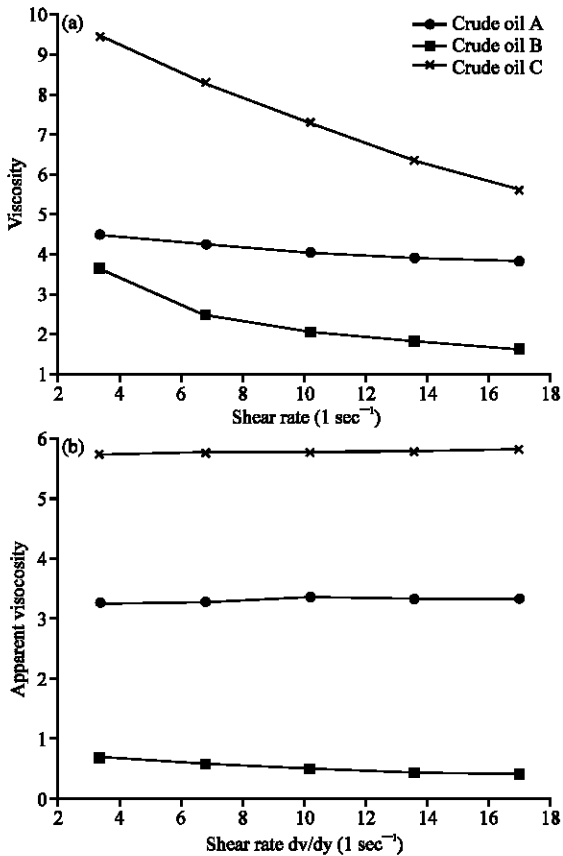


Fig. 9: The shear rate dependence on viscosity of emulsion with varied phase ratio (a) 50-50% w/o emulsion and (b) 20-80% w/o emulsion

this behavior. While, crude oil A obtained a slightly decreased of apparent viscosity at lower shear rate and begun to be constant at higher shear rate.

However, at lower phase ratio, all the crude oil confirmed act as Newtonian behavior whereas the apparent viscosity is independent with shear rate. At lower phase ratio, the flocculation of droplets does not take place because of the little droplet present in the emulsion.

**CONCLUSION**

The results presented in this study identify the effect of crude oil physico-chemical characteristics in the phase inversion and rheological of emulsion. The critical volume fraction,  $\Phi$  was correlated with wax content which crude oil C obtained the higher volume fraction (0.68) before emulsion inverted to o/w. Then followed by crude oil B (0.6) and crude oil A (0.5). For transition phase inversion, crude oil B displayed phase inversion from w/o to o/w at  $90^\circ\text{C}$  because obtained the lowest viscosity compared to others crude oil.

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