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Decolorization and Characterization of Petroleum Emulsions

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Abstract: The Laboratory tests have demonstrated that, optical microscopic can be an alternative method for characterization of water-in-oil (w/o) emulsions. The 50-50% w/o emulsion was prepared and decolorized by adsorbing in fumed silica to remove its black color. Factors such as stirring speed, emulsification temperature and their effects on emulsion viscosity and droplets size have investigated. Results showed that emulsion viscosity and stability were increased by increasing agitation speed and decreasing temperature, while droplets size decreased with increasing agitation speed.

Key words: Crude oil, decolorization, characterization, W/O emulsion

INTRODUCTION

This research was conducted in UPM laboratory in 2007. Water-in-crude oil emulsions are mainly encountered with in petroleum industries where water is dispersed naturally as droplets in the petroleum crude oil medium, while the opposite systems in which oil is deliberately added to water medium are mostly found in food, drink and cosmetic industries (Nour and Yunus, 2006, 2007; Giribabu and Ghosh, 2007).

The second system (o/w) emulsion is beyond this investigation, while the former is normally submitted to destabilizing process to split it into two distinct phases to recover the pure oil and pure water via a process termed as demulsification (Nour and Yunus, 2006).

Before demulsifying emulsion of whatsoever type, it is necessary to control the coalescence of the drops; one way to do so is to determine the size of droplets versus time and also droplets size have a great effect on emulsion viscosity and stability (Nour *et al*., 2007; Jafari *et al*., 2008; Márquez-Beltrán and Langevin, 2007). Information about droplets is vital to control, predict, measure and report the droplet size of emulsions prepared for different purpose (El-Hamouz *et al*., 2009).

Various studies and techniques have been proposed for drop size measurement including thermogranulometry, optical microscopy, unfortunately not adaptable in compact and concentrated water-in-crude oil emulsion (Nour and Yunus, 2006), add to that the black color of the crude oil which will hinder the observation of droplets under the microscope have lead the researcher to conduct such investigations by using model emulsion, Model-emulsion is a term used to describe a dilute emulsion that prepared by mixing for instance Heptane and Toluene being considered as the Hydrocarbone phase and aqueous phase (McLean and Kilpatrick, 1997). The disadvantage of this process is that it would not reflect the complete behavior of emulsion and as if the original crude oil was used, since crude oil contains thousands of hydrocarbons, heavy metals and clays. That would not exist in the mode emulsion; thus Actual crude oil emulsion characterization is difficult especially when they are concentrated, opaque and highly viscous (Nour and Yunus, 2006), therefore a method of decolorizing the crude oil may contributes tremendously in emulsion characterization in terms of droplets sizes, Zeta potential, Scanning electron microscopy and so forth.

According to Gonglun, various parameters such as stirring speed, diameter of the stirrers, diameter of the container tank, preparation temperature, preparation time, oil viscosity and surfactant dosage are of great impact on emulsion stability, his experimental investigation showed that, emulsion stability increases with increasing stirring intensities, reducing water content and reducing the emulsification temperature (Chen and Tao, 2005). Another researchers reported the effect of Asphaltene and Resin concentration on emulsion stability, he conducted his experiment in jet kerosene-water model emulsion and found the optimal concentration of asphaltene is in the

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range of 0.3 to 0.5% while resin was in the range of 1-2% (Xia *et al*., 2004). Furthermore, other have tested the influence of interfacial active component naturally exist in the crude oil on emulsion stability, they separated the polar component by using silica gel (Sjoblom *et al*.,1990), although they are among the pioneers to mention the effectiveness of this silica in decolorizing the crude oil, yet they used model emulsion for their study, however; they reported the ability of the polar compounds of the crude oil mainly asphaltene in promoting a multilayer at the interface. It is also reported that, emulsion viscosity could vary with temperature and water volume fraction (Farah *et al*., 2005; Colo *et al*., 1934). However, comparative study had carried out to examine the effect of mechanical and Ultrasonic agitations on droplet size distribution and emulsion stability (Abismail *et al*., 1999). Moreover, other group have conducted experimental investigation on emulsion droplet variation with emulsifiers' concentration and average molecular weight on rubber emulsion and concluded that, at lower molecular weight; emulsifiers have produced smaller droplets and high viscosity emulsion over its counter part (Daik *et al*., 2007). The current investigation is aimed to develop a new technique, which could aid to characterize water-in-crude oil emulsion by decolorizing the crude oil prior to it is microscopic analysis so that the emulsified water droplets could be seen under the microscope then followed by viscosity measurement at different stirring speeds and emulsification temperature as stated in the methodology.

MATERIALS AND METHODS

Samples preparation and procedures: This research study was conducted at University Malaysia Pahang-UMP in 2007. The crude oil sample was obtained from Petronas refinery at Malaka city; it was originally from Kuait, then it was decolorized prior to the study.

Decolorization procedure: Ten milliliter of crude oil diluted with 90 mL of n-hexane, 5 g of silica powder was added to the mixture and left to settle until the solvent was transparent above the solution, then the mixture was filtered to remove the adsorbent. The solid silica was washed with hexane with addition of some silica until the filtrate was very light in colour. The solvent was evaporated to recover the pure decolorized crude oil

Emulsion samples preparation: In laboratory, water-in-oil emulsions with water volume fraction of 50% was prepared in 500 mL beaker, the prepared emulsions were examined to identify the type of emulsion (w/o or o/w). All emulsions investigated were type of water-in-oil emulsions. Since all emulsion samples prepared were water-in-oil emulsions, therefore, the continuous phase is oil.

Emulsion was prepared by using the agent in oil technique, emulsifiers were first dissolved in the continuous phase (oil) water was added gradually in a glass beaker (500 mL). Sorbitan Monooleate (SM) commercially known as Span80 was used as surfactant. Emulsions were agitated vigorously using a standard three blade propeller at speed was varied (500- 2000) rpm as well as emulsification temperature (50-90°C) for 7 min. However in the current work Emulsions were characterized by measuring their viscosity and droplet sizes and the volume of water resolution with respect to different processing parameters stated earlier in the objective. Brook field Viscometer and Olympus microscope were used to characterize the emulsions, hence the images were snapped after the completion of the emulsion with a camera installed on an optical microscope at a magnification of 10. Stirring speed, emulsification temperature and emulsifiers concentration are the main parameters considered in this study.

RESULTS AND DISCUSSION

Emulsion characterization is a very important task to choose optimal ways of preparing or breaking. Hence stability of water-in-crude emulsion is defined as the resistance by suspended water droplets against coalescence which is function of various factors as such: presence and amount of surfactants, viscosity, specific gravity, temperature, droplets size and size distribution and aging (Chen and Tao, 2005).

Effect of stirring intensity: Mechanical energy is of paramount importance in preparing an emulsion, since this vigorous agitation breaks the large liquid droplets into smaller ones and reduce the interfacial free energy and that will directly influences the viscosity, droplets size and size distribution and promotes stable emulsion.

Figure 1a-c shows a set of experiment to observe the variation of emulsion droplet diameter, viscosity and water resolution respectively as a function of RPM and it is carried out at room temperature, in a; the mean droplet diameter vs. RPM was plotted, the diameter is reduced with increasing RPM, this evident from the fact that increasing the mechanical energy will hammer the larger droplets and render them fragmented into smaller ones (Chen and Tao, 2005) and that may influences the surface area of the interface and drop-drop interaction which will lead to increase in emulsion viscosity as shown in Fig. 1b; correlates the emulsion viscosity and RPM. It is reported that the intensity of stirring is one of the

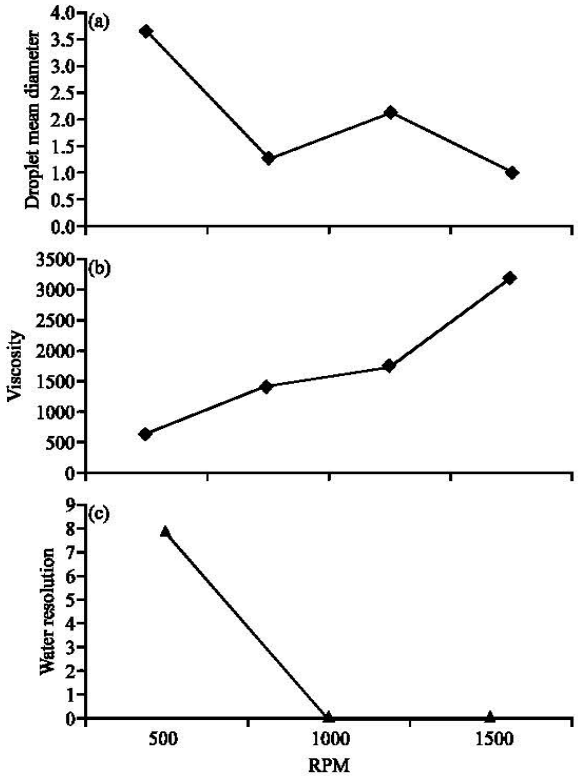

Fig. 1: (a) Droplet mean diameter vs. RPM, (b) viscosity vs. RPM, (c) water separation vs. RPM

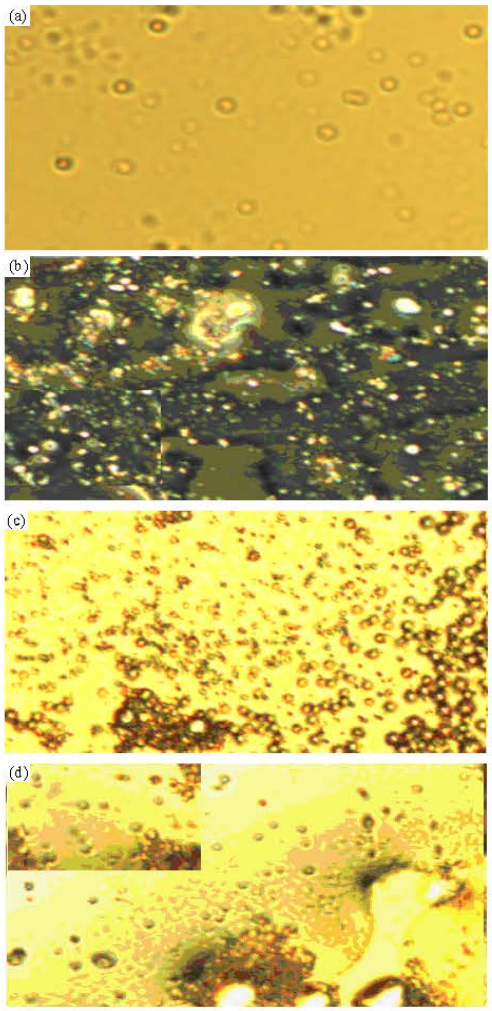

Fig. 2: Mean droplet diameter as a function of RPM, (a) 500, (b)1000, (c) 1600 and (d) 2000

most influential factors requirement in preparing an experimental emulsion, since the rotor will distributes the circulating energy and turbulization energy to the medium being processed, this circulating energy found by using the power consumed to produces circulating flow in the vessel can be used to increase the local dissipation energy in breaking zone (Tropina *et al*., 1996; Chen and Tao, 2005).

The mean water droplet sizes measured by the means of Olympus Microscope apparatus was about 3.6, 1.25 2.11 and 1at 500, 1000, 1600 and 2000 Revolution per Minute (RPM), respectively although at RPM some droplets are in contact with one another and sizes could not be determined accurately but their picture evidenced that there was a decrease in their sizes as RPM increased. In correlating the droplet sizes to the viscosity of prepared emulsion by observing the graphs in Fig. 1a and b in which the same RPM is plotted vs. the emulsion droplet sizes and viscosity respectively, at high droplet sizes of around 3.6 μm (low RPM) emulsion was found to be less viscous of around 600 cp, then increased to around 1700 cp as the droplets reduced to ≈2 μm, then further increased to ≈3000 cp when the droplet diameter was reduced to ≈1 μm wherein emulsion was looked very thick. From this result; obviously there is a direct correlation between the droplets sizes and viscosity. indeed the dependence of emulsion viscosity on droplets diameter which in tern directly related to the stirring intensity all this will straighten the droplets to withstand again coalescence and eventually promote emulsion stability as evidenced by Fig. 1c which show the percentage of water resolution from the aforementioned emulsion as a function of RPM, Knowing the reading was taken for every half an hour interval for 10 h successively. The result was in accordance with the researcher expectation which is; at low RPM the was water separation means less stable emulsion was produced then decreased to zero as the stirring intensity increased.

The similar phenomenon was observed in the pictures in Fig. 2a-d, however; water droplets were observed as they clearly scattered within the continuous

phase as white spots surrounded by some black enclosures that might be the solid particles which cannot transmit light.

At low revolution of 500; the droplets are literally large and spread far away from each other and their size distribution is quite uniform, despite quite long distance is existed between the neighboring droplets. But this reality started to vanish as the stirring intensity is increased and smaller droplets are produced with RPM 1600 and 2000 as observed in Fig. 2c and d as the impeller speed increased; the drops' breakage increased the same results were reported by El-Hamouz *et al.* (2009). Moreover, the most pronounced notice is that the packing density of the small molecules is seemingly increased the surface area, therefore the small droplets might fill the void between the large droplets, despite some agglomeration of the large droplet which in one hand might be attributed to the insufficient amount of surfactant to surround the newly produced droplets or in the other hand it might be due to the high local shear itself could kick the surfactants out of the interface or presumably; the droplet may attained a situation wherein no more fragmentation is possible, however; the agglomeration effect was shown to increase with increasing stirring intensity, therefore, from this experimental investigation one can conclude that although increased stirring intensity is apparently decreases droplet sizes and increases emulsion viscosity and that will consolidates it's robustness and resistance to coalescence; yet it has some intrinsic effect which is inducing some of local droplets to coalesce without being settled out immediately because of elevated bulk viscosity.

Effect of temperature: Usually the liquid viscosity as well as interfacial tension decrease with increasing temperature. The effect of processing temperature on emulsion stability was experimentally tested as depicted by the curve in Fig. 3; reading was taken for each half an hour interval for 10 h at different emulsification temperature varied from 30-90°C, all the other parameters are fixed as the previous emulsion (RPM 1600, span 80 0.5). From the observation the effect of emulsification temperature (EMT) on emulsion stability was apparently pronounced and there was a direct correlation between the temperature and emulsion stability evaluated by both oil resolution and droplet mean diameter measurement (Fig. 3 and 4), from Fig. 3 the maximum oil resolution after 10 h of settling was 1.8, 2, 3.4, 15.4 and 16% at their respective EMT of 30, 50, 60, 80 and 90. The other interesting observation is that at the lowest temperature of 30°C emulsion was very stable with no oil resolution for the first 6 h then started to separate, while all other

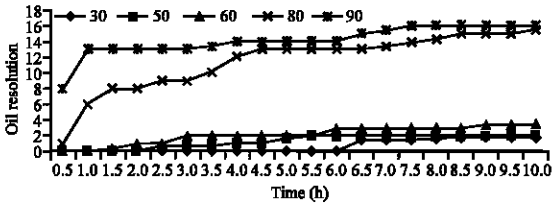

Fig. 3: Effect of processing temperature on emulsion stability

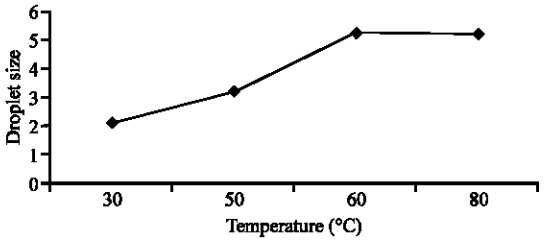

Fig. 4: Effect of temperature on droplet size

emulsions, started to separate at earlier time, for example; 50 and 60°C emulsions started to resolve at 2 and 1 h respectively, furthermore; 80 and 90°C emulsions started to resolve within the first 30 min and that might be due to the viscoelastic pattern of the emulsion and viscosity reduction with elevated temperature may be the main reason, these results were supported by the results plotted in Fig. 4 as the variation of mean droplet sizes as a function of temperature is plotted, at lower temperature of 30°C; the droplet sizes were relatively small around 2 μm and as discussed earlier the emulsion was survived against coalescence for quite long time presumably 6 h, but as temperature increased the droplet behavior has dramatically changed and more bigger droplets are produced accompanied with drastic reduction in emulsion viscosity which caused rapid coalescence to occur and that was evidenced by emulsion picture snapped at different EMT in Fig. 5a-c which showed the evolution of emulsions'droplets as EMT increases this pattern could be considered in such way as just opposed to the trend observed previously in Fig. 2a-d. However, Fig. 5a-c represents the morphology of emulsion at different EMT, the results were in accordance with the researcher's hypothesis and some other previous work as well, at low temperature of 50°C, the droplets were relatively small in sizes and scattered uniformly with minor agglomeration, but as EMT increases to 60°C; more bigger droplet are produced, furthermore at 80°C; even more bigger drops are produced and the agglomerated and partially coalesced droplets could be clearly visible refer to Fig. 5c, the reason behind this behavior is that, as temperature increases; the emulsion viscosity is reduced and the

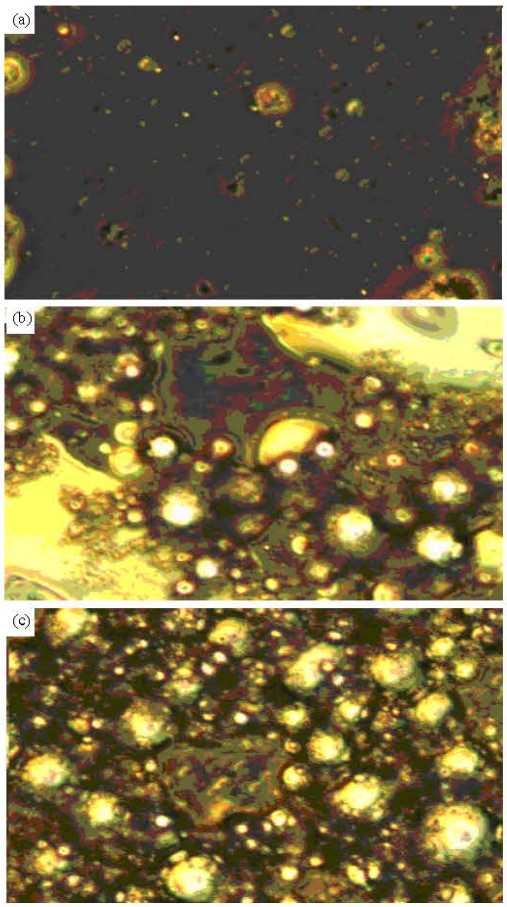

Fig. 5: Effect of temperature on droplet sizes, (a) 50°C, (b) 60°C and (c) 80°C

internal energy of the molecules increased and that may increase the pressure required to induce the interfacial film thinning, drainage, rapture and eventually reduces the coalescence time and ultimately leads to emulsion resolution, thus far it is reasonable to some conclusion about the effect of EMT on emulsion stability, the optimal EMT of water-in-crude oil emulsion stabilized by (SM) emulsifiers lies between 30-50°C and this was in accordance with findings from previous researchers namely: Rusli and coworkers have reported the optimal EMT to prepare Liquid Natural Rubber emulsion is between 28-70°C with respect to some fixed parameters, others have carried out an experimental investigation on coal-oil-water slurry and believed the optimal EMT was 30°C, Abdurahman and coworkers have performed excessive experiments on EMT and concluded that elevated temperature will alter the interfacial tension, affects the adsorption of emulsifiers, reduces its viscosity and affect the vapor pressure of the liquid phase, hence emulsion stability mostly decreases with increasing temperature.

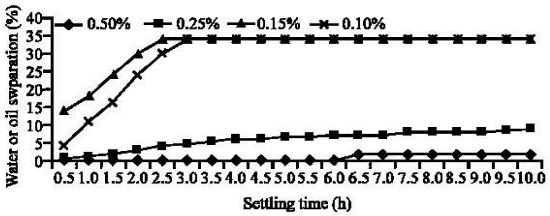

Fig. 6: Effects of emulsifiers' concentration on emulsion stability

Effect of surfactant concentration: Surfactant existence is one of the most influential factors in emulsification, however; their types and dosage are also claimed to be very crucial from efficiency and economical points of view respectively, hence low concentration and high efficiency and preferential and therefore experimental data was presented in Fig. 6 to find out the best concentration of (SM) emulsifiers that needed to prepare water-in-crude oil emulsion knowing most of the previous researchers have done their investigation either in different condition or in model emulsion which will help to considered in this study, however in Fig. 6, four different concentrations were used namely (0.1, 0.125, 0.25 and 0.5), emulsion stability was evaluated by measuring the percentage of water or oil resolution as a function of time, Readings were taken every halve an hours for 10 h successively. From the graph; it is clear that emulsion stability was increased as emulsifiers' concentration was increased; the mast stable emulsion was encountered at 0.5% concentration, at medium concentration of 0.25 the emulsion still could considered stable since the total water resolution after ten hours still less than 10% of total content of the emulsion, on the contrary at low concentration of 0.15 and 0.1%; emulsions were not stable and started to separate into two and even three in some cases immediately. And that is due to low emulsifiers' concentration in which the droplet could not be fully encapsulated therefore agglomeration and coalescence will take place easily. The reverse will hold true for high concentration, similar results were reported by Chen and Tao (2005) and El-Hamouz *et al.* (2009).

CONCLUSIONS

Laboratory tests have shown that optical microscopic can be an effective tool for characterization of w/o emulsions. This study demonstrated the effects of impeller speed, EMT and surfactant concentrations on droplets size, viscosity and stability of w/o emulsions. The optimal impeller speed was found to be in the range 1600-2000 rpm, EMT was 30°C, while emulsifier's concentration was 0.5%.

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