STABILIZATION AND CHARACTERIZATION OF HEAVY CRUDE OIL-IN-WATER (O/W) EMULSIONS

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Abstract

There has been much interest in alternative to transport viscous crude oil from reservoir which is much more abundant than conventional oil. There are many authors hard to find the stable of oil-in-water (o/w) emulsion condition which has been considered as critical analysis. In order to reduce the viscosity, the heavy oil is required to modify for reducing their viscosity. Applying diluent and forming o/w emulsion are the selected as alternative for reducing viscosity. The purpose for this investigation is to study factors that influencing stability and viscosity of o/w emulsion. From the observation, o/w emulsions reduced almost six (6) times less than original heavy oil. However, the addition of 40% of light oil reduced oil viscosity from 478.10 mPa.sto 113.40 mPa.s. Thus, the knowledge and understanding factors that influencing the stability and viscosity of o/w emulsion is important due to avoiding of occurring phase inversion phenomena.

Keywords: *Crude oil, Stability, Heavy oil, Viscosity, Emulsion, Shear Rate, Shear Stress.*

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1. INTRODUCTION

Demanding for crude oil will be increase in the future and this will exert pressure on oil exploration companies throughout the whole world. Indeed, there are various companies that are still focusing on the oil reservoir within their boundaries in the hopes that they might develop and increase their economic growth in the future. The important of crude oil has been focused by developer oil and gas industry. The pipeline transportation by using water and present of surfactant to form oil-in-water emulsion that has been suggested by authors (Zaki 1997; Azodi and Solaimany, 2013; Ashrafizadeh and Kamran, 2010). However, the difficulty to find stability between oil and water which is require knowledge in order to reduce the heavy oil viscosity(Crandall and Wise, 1984; Gillies and Shook, 1992; Hardy et al., 1989; Zakin et al., 1979).Besides, adding light oil as diluent also promotes in reducing viscosity of heavy oil. Unfortunately, the availability of diluent reserves at the production site indicates major difficulties to obtain.

From literature survey, the crude oil world's which has been discover deep in the wellhead is associated with water which is produced as water-in-oil (w/o) emulsion (Steinhauff, 1962; Alvarado and Marsden, 1979). This fact are also mention by Abdurahman et al., (2007) where the hydrocarbon oils are normally present with water or is injected as steam to stimulate oil production. Thus, w/o emulsion is consider as normal emulsion while o/w emulsions indicate reverse emulsion in oil and gas industries.

Shiffert et al., (1984) reported there are three (3) requirements to form or prepare an emulsion; 1) two immiscible liquid, 2) enough agitation to disperse one liquid into small drops, 3) the present of surfactant to stabilize the dispersed drops. The applying of homogenizer forces is to break the dispersed liquid up into many small droplets. According to Dukhin and Goetz (2005), an emulsion are depending on the several factors including liquid properties, surfactant content, temperature, and mixing conditions during preparing the emulsion. In this investigation, there are several variables that influencing preparation of a stable heavy crude o/w emulsion such as, mixing speed, duration time mixing, concentration surfactant, and volume fraction of oil and water. Basically, an emulsion can be categorized into two (2) major phases which is classified as o/w and w/o. The term of o/w emulsion refer to oil as discontinues phase being dispersed in continuous water phase. While term w/o emulsion refer to water as discontinues phase being dispersed in continuous oil phase. In other words, the continuous phase is also referred as the dispersion medium, while the liquid in form of droplets are called as the dispersed phase. The stability of emulsion is an essential valuable knowledge for both academic and industrial points of views. The term of "stability" is defined as the combination between two immiscible liquid which are not separated for long period time and also reduced amount of droplet to be coalescence. Other authors determine the stable emulsions as water droplets are not settle out from oil phase due to their small size and surface tension (Stewart and Arnold, 2009). Besides, emulsions stability is verify by analysis of their drop size, rheological properties, and other factor that effecting stability (Mandal, et al., 2010). This factor has been explained by Mandal et al. (2010) where the stability is dependents on the stirring speed and time during formation. Other than that, Murray et al. (2009) reported the stability of emulsion is effect from small droplet size which has strong interfacial film around oil droplets. In addition, the mixed of oil and water will easily break and form clearly double layer because of different density between oil and water. Besides, Stewart and Arnold (2009) stated that the most stable emulsions often required additional special treatment which is involved the sufficient agitation to disperse the discontinuous phase into continuous phase and the present of surfactant.

2. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

Two types of crude oil samples were used in this study which has been obtained heavy oil from PETRONAS Refinery Melaka and blended with forty per cent (40%) of light crude oil from PETRONAS Kerteh. In order to investigate the most effective surfactant, five (5) different types of emulsifiers willused in this study, namely SDDS, Triton X-100, Span 83, Tween 80, and Coco-Amide. The oil ratio was varied from 50%-70% by total volume. The surfactant concentration is varied from 0.5-1% and homogenized at varied mixing speed from 10,000-15,000 rpm. The oil as dispersed phase was added slowly in water (continuous phase) at 5-10 min. On the other hand, the rheological measurements for all samples were carried out by using Brookfield Rotational Digital Viscometer with UL adaptor and spindles 31 for measuring viscosity, shear rate and shear stress. Figure 1 demonstrated the set-up experiment for this investigation.

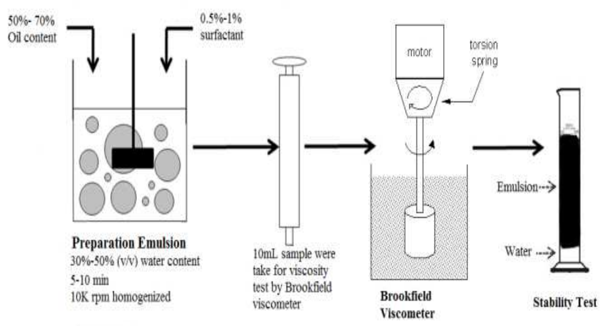

Fig 1: Overview experiment set-up

Table 1 shows the summarizing physical properties for both types of crude oil. Meanwhile Table 2 displayed the chemical properties according to ASTM D-2007 by applying Open Column Chromatography method.

Table 1

Analysis	**Heavy Oil**	**Blend Oil**
Physical Properties		
Density at 25 °C (g/cm^3) [a]	0.9372	0.8977
API gravity (°API) [b]	19.48	26.12
Apparent viscosity at 25 °C, (mPas) [c]	478.1	113.4
Surface tension at 25 °C (mN/m) [d]	33.2	25.7
Interfacial tension at 25 °C (mN/m) [e]	37.7	18.73
Pour Point (^0C) [f]	-12	15
Cloud Point (^0C) [g]	-8.95	20.6

a. Determined by using MicromeriticsPycnometer device in the range 0.9–1.0 kg/m3.
b Calculated according to the relation API = (141.5/Specific Gravity) - 131.5
c. Determined by using Brookfield Rotational Digital Viscometer.
d.&e.Measured using SEO DST30 Tensiometer by applying the du Nuoy ring method.
f&g. Determined by using pour point and clould point device

Table 2

Analysis	**Heavy Oil**	**Blend Oil**
Chemical Properties (wt%)		
Asphaltenes	16.54	10.32
Resin	18.31	7.58
Aromatics	18.63	49.71
Saturates	46.52	32.39

3. EXPERIMENTALRESULTS

3.1 Comparison between Influence Light Oil as Diluent Alternative and Oil-in-Water Emulsion Technique

This interesting idea was apply since only 10-30 % of water used to produce emulsion compared to adding 40% light oil. The diluent required to be recovered at the end of pipe and need to be pumped back to the field hundreds of miles away (Salager et al., 2001). These diluent usually demand high cost and more valuable due to hydrocarbon fractions or light crude oils would be sacrificed in the process (Salager et al., 2001). O/W emulsion can be generating a much better result rather than dilution as illustrated in Figure 2. The low cost commodity is an advantage of this technique. The water is used to reduce viscosity heavy oil by present of surfactant as active agent to produce stable o/w emulsion (Langevin et al., 2004). The o/w emulsion has been proof to reduce viscosity and make it easier delivering oil during transportation. Hence, it is necessary to develop further research and built knowledge about characteristic of crude oil.

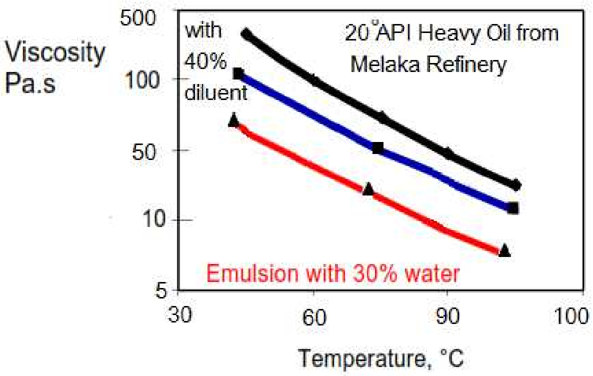

Fig 2: Viscosity as a function of temperature for a heavy crude oil, its mixture with 40% diluent, and its emulsion with 30 % water content.

3.2 Stability of O/W Emulsion

The stability between oil and water phase are very important during pipeline transportation.The highest percentage of stability is selected as the suitable surfactant to form the most stable o/w emulsion. From Figure 3, it's clearly shown that Triton X-100 is the best surfactant to form o/w emulsion. Heavy oil is stable by present of Triton X-100 where the separation indicates less than 3 mL after 14 days. Besides that, Table 3 also demonstrated Triton X-100 promotes highest stability with 94%. Octyl phenol ethoxylate (Triton X-100) is a hydrophilic group where it has a water loving portion with 13.5 value of HLB.

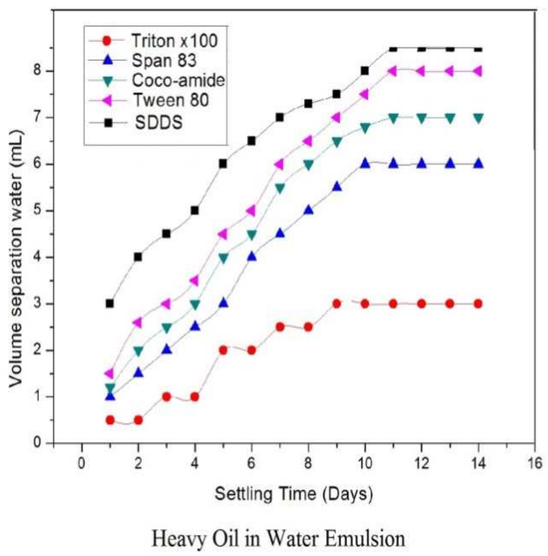

Fig 3: Effect of surfactant type's on the stability heavy o/w emulsion.

Table 3: Stability for different types of surfactant

Types Surfactant	Stability Heavy o/w emulsion
Triton X-100	94%
Span 83	88%
Tween 80	86%
SDDS	85%
Coca-Amide	84%

The stability of emulsion is evaluated according to less amount of water separated. In other word, the high stability of emulsion indicates the minimum percentage of water separation from o/w emulsion. The stability of emulsion was calculated by using Equation 1 as below. This equation is generated by Abdurahman et al. (2012).

$$\text{Emulsion Stability} = 1 - \frac{\text{water separated (\%)}}{\text{water content (\%)}} 100 \qquad (1)$$

The second highest percentage of stability is Span 83 (88 % Heavy) followed by Tween 80 (86% Heavy), Coco-Amide (85% Heavy), and SDDS (84% Heavy). Sodium dedocyl sulphate (SDS) from anionic group obtained the lowest stability compared to other non-ionic group. Besides, non-ionic surfactants can be impart the interactive particles with the steric stabilization mechanism, while anionic surfactants can be provide repulsive force between similarly charged electric double layers to the particles (Chen et al., 1997). The non-ionic surfactant was covered well the thin film droplet to provide less time the emulsion to be coalesce. Therefore, non-ionic surfactant is suitable to use as stabilizer for o/w emulsion.

Generally, non-ionic surfactants such as Triton X-100 indicate a good selection as emulsifiers because they are not afflicted by the salinity of the water, low cost, and not change the oil properties (Rivas et al., 1998). Triton X-100 is the most soluble in water and miscible in most polar organic solvents and aromatic hydrocarbons (Hait and Moulik, 2001). Besides, it is suitable to form o/w emulsion and commercially available in the industry.

3.3 Influence of Surfactant Concentration on Stability and Viscosity of O/W Emulsion

Surfactant concentration promotes significant factors that influence the stability and viscosity of emulsions. An effective technique to reduce the viscosity of heavy oil is the formation of o/w emulsions with the influence of surfactant agents (Martinez-Palou et al. 2011). Other than that, the surfactant concentration strongly influence emulsion stability (Ostberg et al., 1995). As it can be observed from Figure 4 and Figure 5 the increasing of actual emulsifier's concentration in the liquid phase will increases emulsion stability and viscosity, respectively

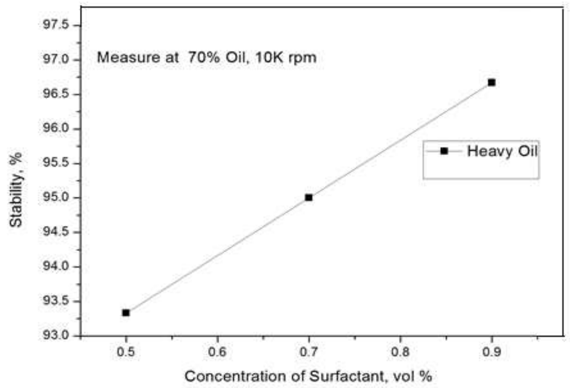

Fig 4: Effect of influence surfactant concentration on the stability of heavy o/w emulsion.

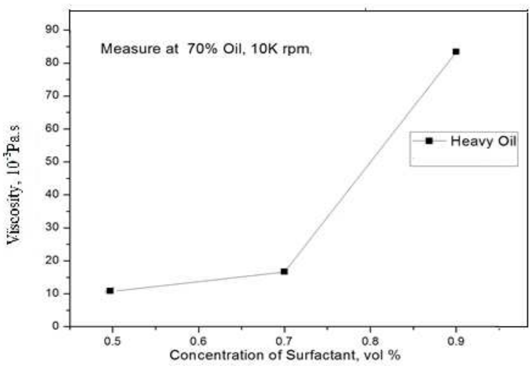

Fig 5: Effect of influence surfactant concentration on the viscosity ofheavy o/w emulsion.

From the graph, emulsion stability is increased as surfactant concentration increased from 0.5% to 0.9%. This observation is explained by Zaki (1997) where the addition of emulsifiers demonstrated in an increase in the amount of emulsifier molecules adsorbed at the oil/water interface. Meanwhile, the viscosity has significantly increased when the concentration of emulsifier increase. Eirong and Lempe (2006) found that the addition of surfactant concentration in the emulsion will increases along the viscosity of the emulsion. The o/w emulsion becomes more stable by increasing the concentration of surfactant. The high amount of surfactant promotes each droplet was covered well to avoid the droplets from coalesce. The adsorbed emulsifier between oil and water molecules because of their non-ionic nature contribute a steric obstacle to droplet oil (dispersed phase) to be coalescence (Singh, 1994; Singh and Pandey, 1991). Furthermore, Ashrafizadeh and Kamran, (2010) reported the increasing of emulsifiers concentration are effect an increments of obstacle between the two phases and promotes a good distribution of oil droplets (dispersed phase) in the water (continuous phase).

3.4 Influence of Mixing Speed and Duration Time of Homogenizer on Stability and Viscosity of O/W Emulsion

The influence of mixing speed on the viscosity and stability of o/w emulsions has been thoroughly studied. The stability of heavy o/w emulsions have been investigated at different mixing speeds of 10,000, 12,000 and 15,000 rpm. Results are shown in Figure 6 and Figure 7 demonstrated relationship speed homogenizer with stability and viscosity for heavy o/w emulsions.

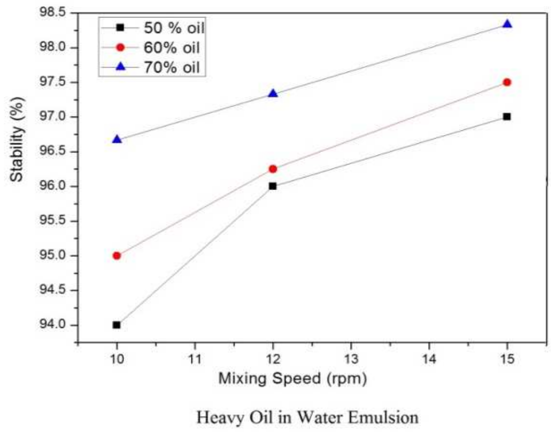

Fig 6: Influence of mixing speed on the stability of heavyand blend o/w emulsion.

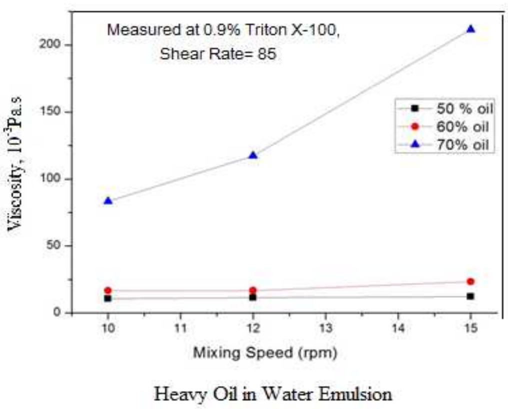

Fig 7: Influence of mixing speed on the viscosity of heavy o/w emulsion.

From the graph illustrated the increasing mixing speed was slightly increased the stability and viscosity. This fact is agreed by Zaki (1997) where the increasing the mixing speed results in an increase in the viscosity of the emulsion. Ashrafizadeh and Kamran, (2010) also agree with the above statement where increasing speed of mixing has a similar effect on the emulsions quality. The stability at 70% oil content showed 100% stable when 15,000 rpm apply during preparing o/w emulsion. The increasing of mixing speed promotes decreasing in the oil droplet size and increasing the viscosity of the emulsion.However, 15,000 rpm is considered very high speed compared to 10,000 rpm. From the observation, the emulsion will require more than 4% of surfactant when mixing speed below than 2,000 rpm was applied and also need more than 20 min to agitate the emulsion. From this condition, the o/w emulsion exhibit low quality in term of stability. Ashrafizadeh and Kamran (2010) has observed when applying mixing speed lower than 3,000 rpm and mixing time less than 10 min, would significantly reduce the quality of the emulsions.

From the observation, there is no separation water or in other word, the emulsion show 100% stable for 70% oil content. Besides, 10K rpm is considered as high speed of mixing and homogenizing for more than 8 min are not efficient because the emulsion become more viscous and creamy. These observations are explained by highly speed homogenized and a longer mixing time will lead an o/w emulsion facing the phase inversion. The observation has been shown that the efficient time for high speed homogenizing at 10,000 rpm is required maximum time at 7 min agitation for 0.9% of Triton X-100. However, the concentration at 0.5% of Triton X-100 require less time of mixing because after 4 min agitated, the emulsion change to w/o emulsion.

3.5 Effect of Temperature on Stability and Viscosity of O/W Emulsion.

Temperature is another factors that is promotes strong influence to reduce of heavy oil's viscosity (Abdurahman et al., 2012; Martínez-Palou et al.; 2011; Ilia and Abdurahman, 2010). Besides, the insulating of the pipeline is usually only a solution for a small distance due to the temperature losses reduction (Martínez-Palou et al., 2011). There are four (4) different studied mixing temperatures, namely, 27, 60, 90, and 96°C while the other parameters are kept constant.Figure 8 shows a plot of the influence mixing speed on the viscosity of o/w emulsions.

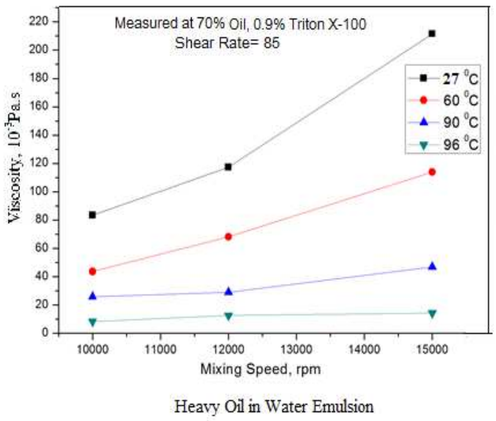

Fig 8: Influence of temperature on the viscosity of heavy and blend o/w emulsion

It is clear from this plot that the viscosity of the emulsion is increased as the temperature is raised (Zaki, 1997; Sanchez and Zakin, 1994; Abdurahman et al., 2012). The increasing of temperature promotes increasing the interfacial tension between oil and water. Consequently, the increase of internal energy of the molecules may increase the pressure required to induce the interfacial film thinning, and eventually reduces the coalescence time (Isaaka et al., 2010). As viscosity decrease with high temperature, the o/w emulsions are available to transport via pipeline.As been discussed previously, the present of surface active agent promotes an increasing of stability and viscosity of the emulsions. However, the solubility of the surfactant normally invert when temperature changes, the stability of emulsion also change. The increasing of temperature cause the flow molecules through the interfaces also increased resulting in a decrease in emulsion stability (Ilia and Abdurahman, 2010). These flow molecules correlated with viscosity where the increasing temperature results in decreasing the viscosity. AccordingStoke's Law theory, the velocity is increase as viscosity decreased. Furthermore, Ilia and Abdurahman (2010) found that the viscosity is very sensitive to temperature due to the high temperature promotes to reduce emulsion stability.

3.7 Oil Droplet Measurement

The droplet size of an emulsion is important variables which are affecting the colloidal stability and rheological properties such as the flow and deformations of the emulsion (Han et al., 2011). The droplet size distribution for the emulsions was determined as a function of different mixing speeds and concentration of surfactant using Carl Zeiss research microscope equipped with the digital camera and AxioVission AC image analysis software. The average of droplet size distribution of emulsion is measured by taking randomly, approximately eight to ten different droplet size images. The influence of average droplet size emulsions on the mixing speed and emulsifier concentration are illustrated in Figure 9 and Figure 10. From both figure, it is clear shown that the average droplet size distribution of the emulsions decreases as the speed of homogenizer and concentration emulsifier is increased.

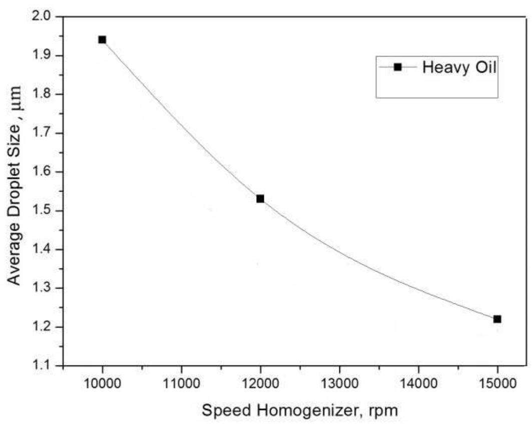

Fig 9: Influence of mixing speed on the average droplet size of heavy o/w emulsion

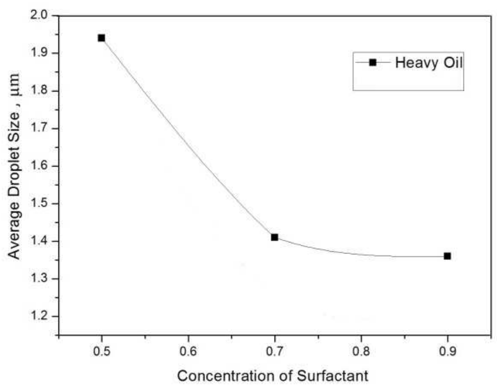

Fig 10: Influence of concentration on the average droplet size of heavy o/w emulsion

This observation has been explained by increasing mixing speed and surfactant concentration will be reducing to droplet oil size. The increasing the surfactant concentration will increase an amount of obstacle between two phases to be separate and improved the distribution of dispersed droplets in the continuous phase (Ashrafizadeh and Kamran, 2010). This findings are also agreed with some authors where the adsorbed molecules of surfactant provide a strong barrier of oil droplet to be the coalescence (Singh and Pandey, 1991; Singh, 1994). Besides, the high surfactant concentration provide well protection to each droplet surface, thus the uncovered droplet surface area with water (continuous phase) is thermodynamically unfavourable (Huda, 2011). The increment of volume surfactant in the emulsion would reduce the interfacial tension which promotes the breakage of droplets into smaller ones and the interaction between particles is increases. Consequently, the droplet between oil and water become more tight relation and hard to break due to high mixing speed and present of high amount of surfactant. At the same time, the increasing mixing speed and mixing time also could cause small droplet size which is finally increase the stability of the emulsion (Ashrafizadeh and Kamran, 2010).

Parkinson et al. (1970) considered the influence of droplet size distribution on the stability and viscosity of the emulsion. This fact are already discussed by Azodiand Solaimany(2013) and Abdurahman et al., (2012) where the increasing of surfactant concentration and mixing speed will reduces average oil droplets size leading to an increase of the viscosity of o/w emulsion. The other author also agree by the decreasing of oil droplets size (dispersed phase) results in a slight increase in the viscosity of the emulsions (Stachurski and MichaŁek, 1996; Zaki, 1997; Pal et al, 1992). This observation is explained by an increase in the mixing speed produced the smaller size of oil droplets, thus influence the increasing of viscosity (Pal et al., 1992; Briceno et al. 2001; Zaki, 1997). The application of homogenizer may cause the formation of oil droplets having a diameter less than 10 µm. According to the droplet result, macro-emulsion and micro-emulsion (2.9 – 0.08 µm) had successfully applied by homogenizer (10,000rpm-15,000rpm). Amorim (2007) also agree by applying homogenizer are produced small size and stabilized the emulsion. However, the droplet size have more than 1.2 µm are found as unstable emulsion due to coalesces process are easy to occur (Jafari et al., 2008).

CONCLUSIONS

According to the result, it can be concluded that, o/w emulsion influence various factor in order to find the stabilize condition. This is due to the physical and chemical properties of type's crude oil which can beaffecting especially need to consider on phase inversion phenomena. The less water separate indicate the most stable o/w emulsion. Applying homogenizer proof the droplet become smallest and displayed tight relation between oil and water.

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