IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

Study on Wax Deposition of Heavy Crude Oil in Pipelines

Abdurahman.HNour*[1], Nadia Eliza NatrahBintiJamaluddin[2]

[*1,2]Faculty of Chemical & Natural Resources Engineering, University Malaysia Pahang, TunRazak Highway, 26300 Kuantan, PahangDarulMakmur, Malaysia

abrahman@ump.edu.my

Abstract

This paper presents wax deposition of heavy crude oil in pipelines study. Pipelines are widely used to transport crude oil.Wax deposition in a pipeline was caused by the high viscosity of the heavy crude oil, particularly if it is left untreated, may have severe consequences on the operational efficiency of a pipeline system. In order to overcome the wax deposition of the heavy crude oil, the crude oil is suggested to mix with water and emulsifier at certain conditions so that it will formed oil in water (O/W) emulsion. In this study, both chemical and physical properties of O/W emulsion that preparedby using three types of emulsifiers,Coca Amide DEA (non-ionic and biodegradable surfactant that synthesis from coconut oil plus diethanolamine), Sodium Dodecyl Sulfate(anionic and biodegradable surfactant that synthesis from coconut oil only) with one type of conventional chemical emulsifier (Span 80) were examined. O/Wemulsions with two different ratios (50-50% and 70-30%) were prepared at 1500 rpm mixing speed with the concentrations (0.3 wt%, 0.5 wt%,1.0 wt% and 1.5 wt%) for each emulsifier to test the stability conditions. Instead of stability; shear rate, shear stress and viscosity were determined by Brookfield Viscometer.On the other hand, the droplet size was carried out by using Digital Carl Zeiss Microscope. Result shows that Sodium Dodecyl Sulfate at 1.5 wt% mixed with 70-30% O/W obtained the most stable emulsion for transportation compared to the other two. Then, properties of heavy crude oil were tested via Fourier Transform Infrared (FTIR). The properties are important to know in order to predict the occurrence of wax deposition during transportation. Next, the determination of Wax Appearance Temperature(WAT) using Koehler Cloud and Pour Point Bath.As the temperature decreases, crystalline structure will start to appear. Cloud and pour point of o/w emulsion using Sodium Dodecyl Sulfate which act as emulsifier are -1˚C and -19˚C respectively.Demulsificationis the process of separation ofwater from the heavy crude oil. Crude oil need to be separate quickly from the water. This is to ensure the crude oil value can be maximized and the operating cost can beminimized. Demulsifiers (Hexylamine and Dioctylamine) with different concentrations (0.2 wt% and0.5 wt%,1.0 wt% and 1.5 wt%) were used for transportation. The relative rates of water separation were characterized viabeaker test. Hexylaminepromotes the best coalescene of dropletscompared with the other demulsifier that used in this study which is Dioctylamine.

Keywords: Wax, heavy crude oil, emulsion, separation, stabilization, WAT, demulsification, destabilization.

Introduction

Pipelines are widely used to transport crude oil. Wax deposition in a pipeline, particularly if it is left untreated, may have severe consequences on the operational efficiency of a pipeline system. Crude oil is an organic mixture containing SARA; saturates (paraffin/waxes), aromatics, resins, asphaltenes(Lee,2008).Deposition of the solid residues may occur in the production facilities at the well head, in pipelines during transportation to the refinery, or in storage tanks at the shipping terminal (Allen and Roberts, 1982). The presence of such solid waxes increases fluid viscosity and its accumulation on the walls reduces the flow line section, causing the blockage of filters, valves and even pipelines, increasing pumping costs, and reducing or even stopping oil production or transport. Their high efficiency makes their use every economic way and attractive to separate oil and water (Staiss et al., 1991).

The temperature gradient occurs between the fluids and flow line when the environment condition outside pipe wall changes. The decreasing of the temperature makes the pipe wall undergo the heat transfer process between itself and the environment to maintain the temperature. Low quality of the crude oil purity during the distillation process makes the contents in crude oil still have clay from the drilling process which help wax producing during the transportation process.

Several methods (Bernadiner, 1993; Hunt, 1996) have been used to enhance the low-temperature properties of crude oil. Pretreatment with pour point depressants (PDD) is an interesting solution for transportation of waxy crude oils through pipelines. Another favorable pipeline approach is the transport of viscous crudes as concentrated oil-in-water (O/W) emulsions(Gregoli et al., 2006; Lappin and Saur, 1989).The technical activity of this approach was showed in an Indonesia pipeline(Lamb and Simpson, 1963)and in a 20 km-long, 0.203-mdiameterpipeline in California. In this approach, with the aid of good surfactants, the oil phase evolved into dispersed in the water phase also stable oil-in-water emulsions are formed. Formation of an emulsion makes an important reduction in the emulsion viscosity. O/W emulsion also might reduce corrosion with acrude oil with large sulfur content; corrosion will appear with the use of an aqueous phase, together with the use of formation water, which is rich in salts. Due to the reduction in viscosity, the transport-assisted and transportation costs problems are shortened. Because of water is the continuous phase, crude oil did not affect pipe wall, which reduces the corrosion of pipe for crudes with high sulfur contents and inhibit the deposition of silts in pipes, as is familiar for crudes with high asphaltene contents (Poynter and Tigrina,1970). Viability of injecting aqueous surfactant solution into a well bore to alter emulsification in the pump forthe production of less viscous O/W emulsions will rise the productivity of a reservoir (Simon and Poynter, 1968; Steinbornand Flock, 1982).

Thus, this research is aims to overcome the wax depositions of heavy crude oil in pipeline transportation by using oil-in-water emulsion technique.

Materials and Methods

In this study, for emulsifiers: Coca Amide DEA, Span 80 and Sodium Dodecyl Sulfate (SDS) were used to form oil-in-water emulsion and for chemical demulsifiers; Dioctylamine and Hexylamine were used to form water-in-oil emulsion. The analyses of physical and chemical properties of emulsion were carried out by Brookfield Viscometer, FTIR, Carl Zeiss Microscope and Koehler Cloud and Pour Point. A 100 ml of graduated cylindrical glass was used as sample container.

Sample preparation and procedures: The crudeoil samples were obtained from Petronas Refinery. The crude oil-in-water emulsions were prepared at room temperature with standard three blade propeller at mixing speed of 1500rpm. 0.3 wt % of SDS was added into the water (continuous phase) and mixed for 5 minutes to achieve homogenous. Crude oil (dispersed phase) is then added slowly to the solution and mixed for 10 minutes. Emulsions were repeated using concentration 0.5 wt%, 1.0 wt % and 1.5 wt%. The volume of water added was calculated based on the ratio of oil to water that needed to prepare: 7:3 and 5:5 by volume. For physical properties determination, Brookfield Viscometer was used to get the viscosity, shear rate and shear stress of the emulsion while Carl Zeiss Microscope was used to measure the droplet size of particles. To check the chemical properties of heavy crude oil, Fourier Transform Infra-red (FTIR) was used. The most stable emulsion was determined and tested for wax appearance temperature (WAT). The first crystal appeared is called cloud point and when the crystalis fully solidified, it is called pour point. Finally, for demulsification performance study, demulsifier was added intothe emulsion prepared at varied concentration (0.3 wt%, 0.5 wt%, 1.0 wt % and 1.5 wt%) and mixed for 15minutes. Destabilization process was same as emulsion stabilization, but this time crude oil will be the continuous phase and water is dispersed phase.

To check whether the emulsions that prepared is oil-in-water or water-in-oil, filter paper was used. For emulsification and demulsification, stability process was carried out and amount of water separated was recorded for every 30, 60, 120, 360, 720, 1440, 2160 and 2880 minutes.

$$\%\text{water separated (e)} = \left(\frac{\text{Volume of separated water,mL}}{\text{Original volume of water in the emulsion,mL}} \right) 100$$

Table 1 : Emulsion prepared at the constant mixing speed, different types and concentration of emulsifiers used

Mixing speed	Emulsifier	Concentration, wt%
1500 rpm	Cocamide DEA	0.3
		0.5
		1.0
		1.5
	Sodium Dodecyl Sulfate	0.3
		0.5
		1.0
		1.5
	Span 80	0.3
		0.5
		1.0
		1.5

Table 2: Demulsificationprepared at different types and concentration of demulsifier used

Mixing speed	Emulsifier	Concentration, wt%
1500 rpm	Hexylamine	0.3
		0.5
		1.0
		1.5
	Dioctylamine	0.3
		0.5
		1.0
		1.5

Results and Discussion

Crude oil-in-water emulsion for ratio 50%-50%

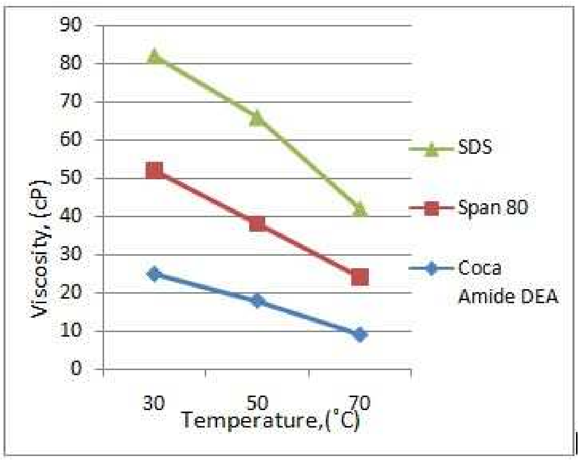


Figure 1:Graph shown the viscosity against temperature using (1.5 wt% concentration) emulsifiers at stirring speed 150 rpm

Crude oil-in-water emulsion for ratio 70%-30%

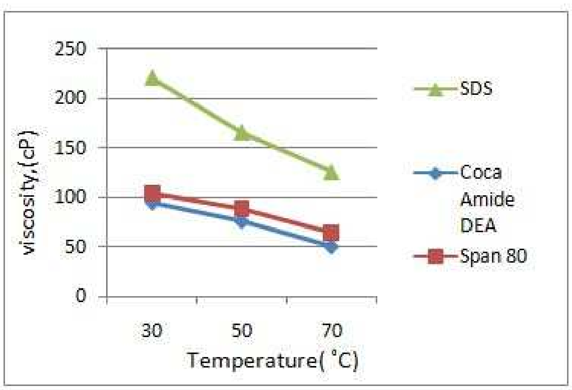


Figure 2:Graph shown the viscosity against temperature using(1.5 wt% concentration) emulsifiers at stirring speed 150 rpm

From Figures 1 and2, it has shown that viscosity decreased when the temperature increased. The solubility of emulsifier is affected by the rising in temperature when it is added to the emulsion and disrupt the interfacial tension at the surface of the disperse droplets. Thus, the flow of molecules through the interfaces will be increased and causes the contraction of viscosity that affects the decrease of emulsion stability. From figure 1, Sodium Dodecyl Sulfate and Span 80 seem like to give the same stability to the emulsion but it is obviously shown at figure 2, this was due to the solubility of the emulsifiers. Sodium Dodecyl sulfate is an anionic surfactant while Span 80 is non-ionic surfactant so at the condition that the emulsion is in the equal ratio of oil and water, it does not clearly shown how effective of it to the emulsion. Thus, at figure 2, it is clearly shown that the Sodium Dodecyl Sulfate is more stable at the condition where the composition of oil is higher compared to the water as it is oil soluble. For Coca Amide DEA that is water soluble, it is shown that its efficiency is lower than Sodium Dodecyl Sulfate and Span 80. The classification of the emulsifiers in terms of decreasing stability of emulsion is therefore the following: Sodium Dodecyl Sulfate>Span 80> Coca Amide DEA. Due to the stability of the emulsion seems better for the ratio of crude oil-in-water ratio of 70%-30%, the discussion is continued by this ratio.

Crude oil-in-water emulsion for ratio 70%-30% for temperature 70˚C

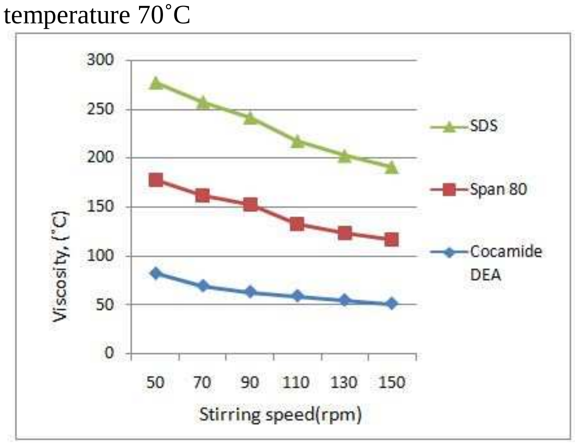


Figure 3:Graph shown the viscosity against stirring speed using(1.5 wt% concentration) emulsifiers at stirring speed 150 rpm

Figure 3 shows the effect of stirring speed on the emulsion viscosity. The emulsion viscosity decreased as the stirring speed increased. This can be explained by the friction occurs during the stirring. As the friction rises, temperature has increased; therefore the emulsion viscosity decreased as the temperature increased. Turbulent flow of emulsion induced as the stirring speed increased. Turbulent

ISSN: 2277-9655
Impact Factor: 1.852

flow will exhibit a drag reduction, and thus lower the viscosity of the emulsion kinetically.

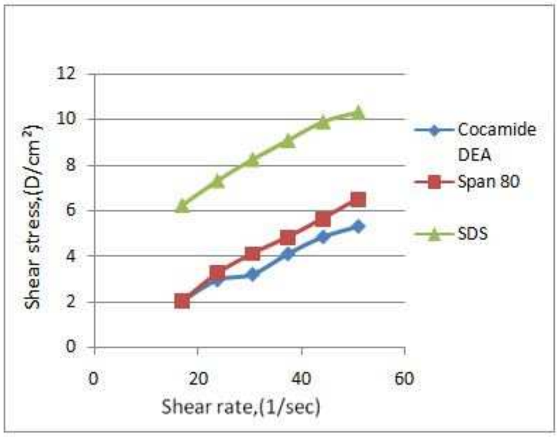


Figure 4:Shear rate against shear stress at 30˚C

Figure 4 showed the relationship between shear stress and shear rate for oil-in-water emulsion 70%-30% at 30°C with 1.5 wt% of varies emulsifiers. Shear stress is directly proportional to shear rate for Newtonian fluid. For non-Newtonian fluid, the behavior would be deviated from that of the Newtonian fluid. The curve line of the graph in figure 4 shows that all the emulsion was non-Newtonian.

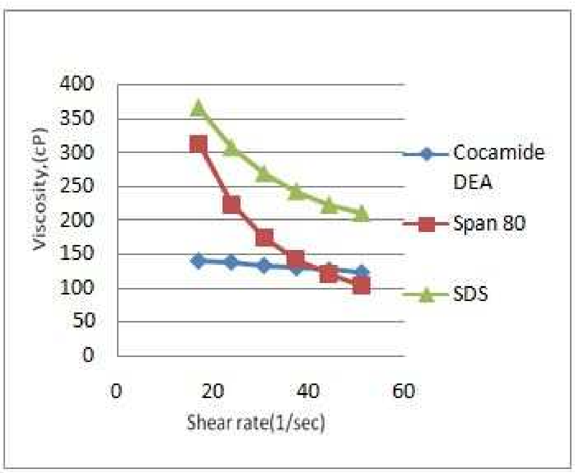


Figure 5: Shear rate against viscosity at 30C

In order to identify the type of non-Newtonian fluid behavior, Figure 5 is plotted. Figure 5 showed that all the emulsions createdare categorized as pseudoplastic non-Newtonian fluid. According to Schramm (2005), pseudoplastic or shear thinning in other word is defined as the fluid that show a decrease of viscosity when the shear rate is increased.

Table 3: Effect of 1.5 wt% of emulsifiers on 50-50% o/w emulsion stability at 1500rpm mixing speed (% water separation, v/v)

Time (min)	Coca Amide DEA	Span 80	Sodium Dodecyl Sulfate
10	0	0	0
30	0	0	0
60	0	0	0
120	0	0	0
360	18	20	22.86
720	20	22.5	24
1440	40	40	50
2160	60	62.86	71.36
2880	70	68.58	97.14

Table 4: Effect of 1.5 wt% of emulsifiers on 70-30% o/w emulsion stability at 1500rpm mixing speed (% water separation, v/v)

Time (min)	Coca Amide DEA	Span 80	Sodium Dodecyl Sulfate
10	0	0	0
30	0	0	0
60	0	0	0
120	0	0	0
360	0	0	0
720	0	0	0
1440	0	0	0
2160	9.5	0	0
2880	19.0	0	0

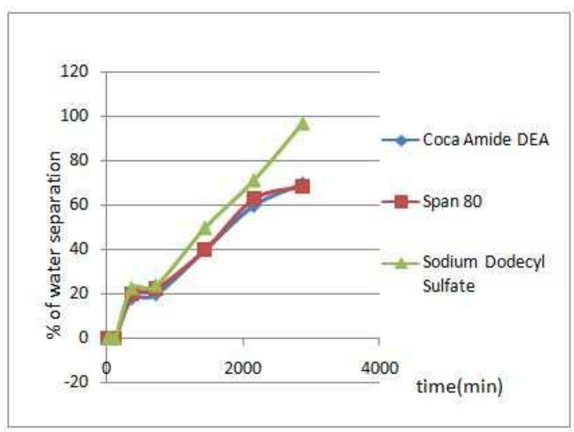


Figure 6: Percentage of water separation for 50%-50% oil in water at 1.5 wt% of emulsifiers

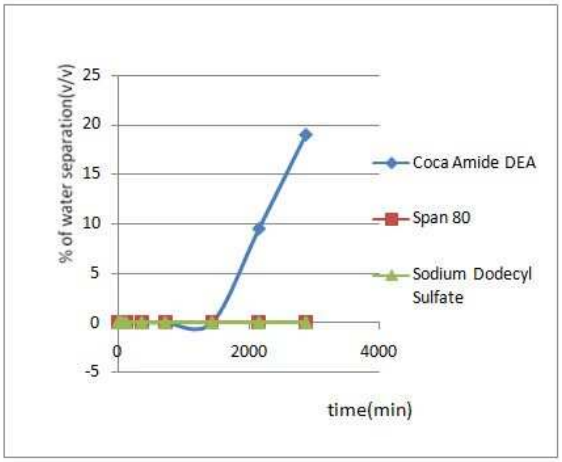


Figure 7: Percentage of water separation for 70%-30% oil in water at 1.5 wt% of emulsifier

If the emulsion is very stable, water will be more difficult to separate out. From Figures 7, it is obviously shows that Sodium Dodecyl Sulfate was the best emulsifiers among the others as it has the least amount of water separated out. Coca Amide DEA showed the highest percentage of water separation at 0.3, 0.5, 1.0 and 1.5 wt% of concentration. Thus, emulsion prepared by Coca Amide DEA was concluded as unstable. While emulsion prepared by Span 80 shows that the percentage water separation is in between Coca Amide DEA and Sodium Dodecyl Sulfate, but its behavior is more towards the Sodium Dodecyl Sulfate compared to Coca Amide DEA. As the conclusion, the classification of emulsifiers in terms of decreasing stability of emulsion is therefore following: Sodium Sodecyl Sulfate> Span 80> Coca Amide DEA.

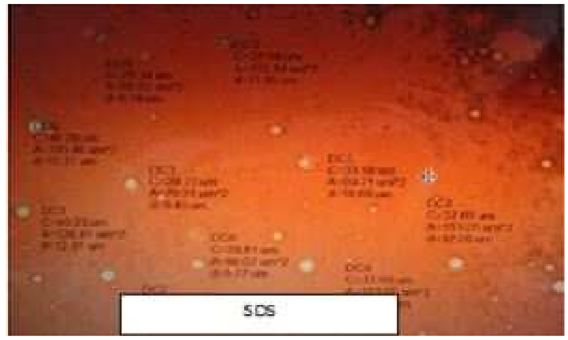


Figure 8: Droplet size with 1.5 wt% Sodium Dodecyl Sulfate

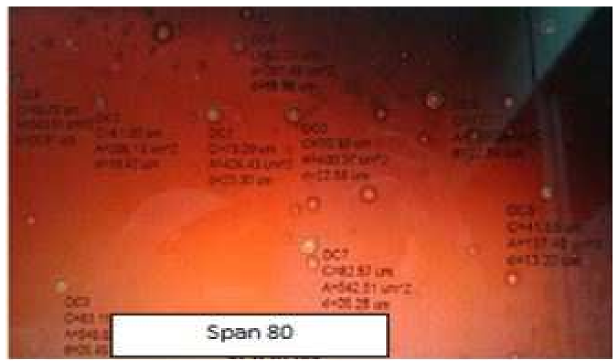


Figure 9: Droplet size with 1.5 wt% Span 80

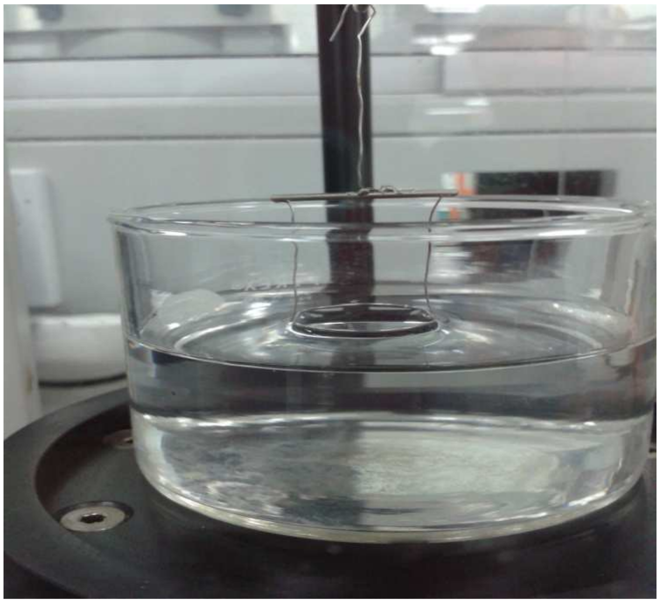
Table 6: Average Droplet size of the emulsions

O/W Ratio	Concentration (wt %)	Emulsifier used	Droplet size(micro meter)
			13.23
			19.42
			19.80
			20.91
		Span 80	22.58
			22.84
			23.30

 ISSN: 2277-9655
Impact Factor: 1.852

70-30%	1.5		26.28
			26.45
		Sodium Dodecyl Sulfate	9.17
			9.34
			9.46
			10.69
			11.93
			11.95
			12.00
			12.00
			12.81
			15.37

Average droplet size of each emulsion that was examined through Carl Zeiss Research Microscope was shown in Table 6. The droplet dispersion formed by the shear stress in the region near the impeller and the coalescence of droplets in the area of fluid circulation are held for dispersion (Duran and Salanger, 1989; Morel et al., 1991; Becher and McCann, 1991; Lachaise et al., 1996). Droplet size distribution of the dispersed phase also has a vital effect on the viscosity of emulsions, particularly for high concentrations of dispersed phase (Pal, 1998). The droplet size distribution of an emulsion is effected by the interfacial tension between the crude oil and the water, emulsifying agents, presence of solids and shear (Kokal, 2005). The huge difference in droplet size distribution profiles between two types of emulsion may be attributed to the difference in interfacial tension



The surface tension between air and water is 30.968 N/m. The interfacial tension between crude oil and water is 70.746 N/m.

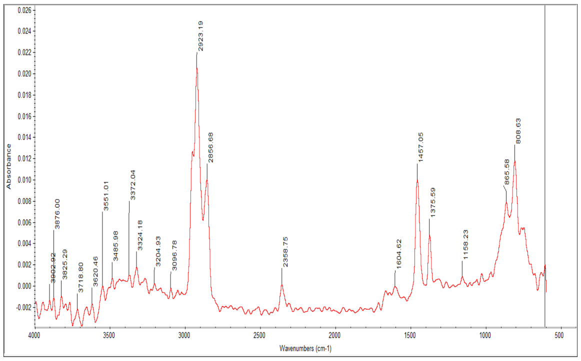


Figure 10: Absorbance versus Wave number of heavy crude oil from FTIR

From the graph above, there are 5 peaks found in the screened out which have the highest frequency, 808.63, 865.58, 1457.05, 2856.68 and 2923.19. The peak within the range of 800-850 is categorized as aromatics (strong), 1000-750 as sulfonates, 1090-810 as phosphines, 1500-1400 as aromatics (medium) and 2800-2950 as alkanes.

Therefore, it can be conclude that the alkanes and aromatics as the major compounds of the heavy crude oil screened out.

Table 7: The wax appearance (WAT) and precipitance temperature (WPT)

Emulsifier used	Cloud point	Pour point
No emulsifier	3˚C	-5˚C
Sodium Dodecyl Sulfate	-1˚C	-19˚C
Span 80	3˚C	-7˚C

Wax appearance temperature (WAT) is the temperature at which crude oil appear as crystallization which depend on the concentration and molecular weight of the waxes and the chemical nature of the non-waxy part of the crude oil, termed the hydrocarbon matrix (Mustafa et al., 1996).Crude oil comprises of n-paraffin waxes that tend to be separated from oil when the temperature of crude oil falls below the wax appearance temperature. When dropping temperature, thewaxes normally crystallize as an interlocking network of the sheets, therefore entrapping the remaining liquid fuel in cage-likestructures. When the temperature getting nearto the pour point, the oil may gel totally causing the flow lines problems such as clothing of flow pipes or production lines. The pour point isthe minimum temperature at which oil will flow freely under itsparticular weight under certain test conditions.(Abdurahman et al., 2012).Based on the results, it show that the cloud and pour point of the emulsion using Sodium Dodecyl Sulfate as emulsifier are much lower than pure crude oil and emulsion using Span 80 as emulsifier. As the crude oil forming the emulsion, the settling time for the crude oil to be waxy was reduced. So it will enhance the flow of crude oil in pipelines.

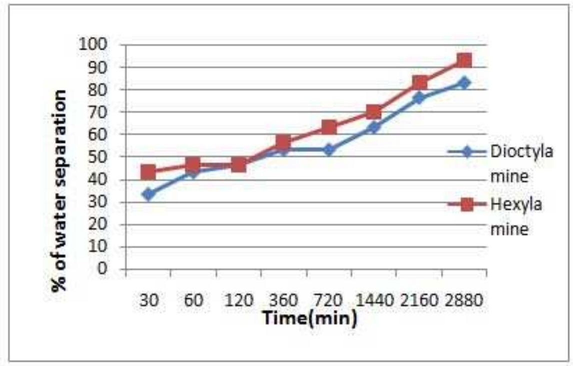


Figure 11: Water Separation versus time for Hexylamine and Dioctylamine at 1.5 wt% concentration

For 70-30 wt% of crude o/w emulsion (which contain Sodium Dodecyl Sulphate), emulsion with 1.5 wt% Hexylamine showed the highest water separation compared to others. There is less water being separated by using Dioctylamine compared to Hexylamine. Efficiency of demulsifier is increasing when the concentration of demulsifier is higher. The classification of demulsifiers in term of decreasing efficiency is therefore the following: Hexylamine>Dioctylamine.

Conclusions

The oil-in-water (O/W) emulsions were successfully prepared using heavy crude oil. Based on the beaker tests and the experiment results that carried out by using Brookfield Viscometer, the most stable emulsion was o/w 70-30% prepared by mixing speed of 1500rpm and 1.5 wt% of Sodium Dodecyl Sulfate. Thus, emulsion prepare undergo chemical analysis. Results obtained from For 70-30% of o/w emulsion at mixing speed of 1500 rpm with 1.5wt% Sodium Dodecyl Sulfate, Dioctylamine and Hexylamine is used for the demulsification process. Hexylamine show the high efficiency of water separation. Therefore, the classification of demulsifiers in term of decreasing efficiency is Hexylamine>Dioctylamine.

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ISSN: 2277-9655
Impact Factor: 1.852

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