SCALE UP PRODUCTION OF NS-16-1 SURFACTANT

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CHAPTER 1

SCALE UP PRODUCTION OF NS-16-1 SURFACTANT

I. PART 1 (SURFACTANT SYNTHESIS)

1.1 Background

An attempt was made to produce and test local nonionic surfactants for petroleum-based emulsions. The surfactant was produced by reacting a polyol with carboxylic acid in the presence of base NaOH catalyst. The reactants and catalyst were charged in laboratory reaction flask equipped reflux condenser, stirrer and thermometer/thermocouple. The content was heated gradually from 120 to 220 ᵒC for five hours. The produced surfactants were cured with some additives then tested directly without purification. The test was conducted on different aspects including, droplet sizes, viscosity and stability (water resolution). Based on these results, the experimental emulsifiers were found to reduce the sizes of the droplets and produce more uniform and stable emulsions than the commercial ones. Furthermore, the stability study also proved the effectiveness of the emulsifiers. After 7 days of stability test, emulsion fuel with experimental surfactants had 3% oil resolved and 7% lower layer“ll”, while emulsion fuel sample with commercial surfactants had 2% oil resolved and 29% lower layer. Hence, stable emulsion fuel could be obtained with the current locally produced experimental surfactants when their concentration reaches 4.5%.

1.2 Summary of research findings:

This research is aimed to synthesis as well as formulates emulsion stabilizers based on affordable raw materials. Thence, in order to produce polyol and fatty acid based stabilizers, some cooking oils (sunflower and canola) were tested and found to perform well as the saturated fatty acid, the oleic acid, which is normally used in the production of sorbitan fatty acid based stabilizers.

Beside D-sorbitol, other polyol was also performed well up on testing, and can be used as limiting reactants to produce polyol based stabilizers. These include polyethylene glycol (PEG 600) and Glycerol. However, glycerol can produce good surfactants while PEG 600 can produce good co-surfactants when reacted with fatty acid (sunflower or canola cooking oil)

1.3 Introduction

Sorbitol, also known as glycerol is a sugar alcohol, that is normally obtained by reduction of glucose (changing the aldehyde group to hydroxide group). it is synthesized by sorbitol-6-phosphate dehydrogenase, then converted to fructose by succinate dehydrogenase and sorbitol dehydrogenase enzymes. The most commonly used sorbitol is the white powder D-sorbitol (Kodayshi et al., 2011).

Sorbitol based emulsifiers

Sorbitol based surfactants are commonly used in many daily life products such as food, pharmaceutical, detergent, agricultural, fine chemicals, personal care industries and beverage industries, in several commercial names such as Span, Triton, tween and so on. Technically speaking, a good surfactant must meet certain characteristics, first of which, it should process the ability to position itself at interface in the solution of two immiscible liquids. Secondly, must process the ability to lower the interfacial tension between the two phases, that is strongly related to their hydrophilic lipophilic balance (HLB). Thus, the two immiscible phases can mix and form what so called emulsion. Depending on the HLB number, the type of the resulting emulsion could be estimated, since high HLB emulsifiers tend to produce oil-in-water type emulsions, while low HLB emulsifiers tend to produce water-in-oil emulsions. Famodan and Gill (Julie louise Humpherey 2007, Yan Xu et al., 2008), (Jasminka et al., 1996), (Rakmi abdulrahman and Tjahjono Heranan, 2000).

Sorbitol based surfactants are reported to be test less, colorless, non-toxic, non-irritant biodegradable and hence they are very safe to be used in household and environmental friendly as well (G. L. Hansenhuett and R.W. Harted 2008).

Sorbitol based emulsifiers are esters that synthesized by reacting Sorbitol and fatty acid in the presence of catalyst at elevated temperature of around 215 ^{o}C, the product obtained by this process are normally mixture of sorbitan ester of fatty acid, together with some sorbitol and sorbide esters (George J. Stock burger 1981).

Three types of fatty acids are in common use which captive tallow based oleine, vegetables based oleine, Vegetable based oleine and coconut based fatty acid (IPPE 2009).

Besides being well known sustainable food stabilizers, sorbitol based emulsifiers are also characterized by being good solibilisers, dispersants, foaming agents. They are completely biodegradable under both aerobic and anaerobic conditions, nontoxic, non-harmful to skin contact, odorless, test less, wetting agents, electrolyte donors, and stable over wide range of pH (Rakmi abdulrahman and Tjahjono Heranan, 2000) (croda europ LTD).

It was also reported that the sorbitol based fatty acid ester surfactants are naturally nonionic lipophilic type surfactants but they could be modified to hydrophilic via ethoxilation process (George J. Stockburger, 1981)

Some previous literature on sorbitan production

In contrast to their simple names, Sorbitol based emulsifiers are complex mixture of molecules that are reacted under high temperature to yeild many many desired product as well as byproducts such as sorbitan, sorbitol and isosorbate (G. L. Hasenhuett, R. W. Harted 2008).

The reaction mixture consists of carboxilic acid, sorbitol and a catalyst that is heated under an inert atmosphere to stimulate both esterification and cyclization simultaneously ((Paul Mcgrane 2006).

However, the general mechanism of their function as stabilizers relay heavily on the fact that they are amphiphilic, means the sugar based heat group (sorbitol) functions as polar part of the molecule which naturally attracted to aqueous phase, and the nonpolar long hydrocarbon chain tail group of the fatty acid functions as lipophilic group. although thy are classified as nonionic because of the absence of the formally charged ions at the sugar heat part, but they are proved to position themselves very well at the interface promoting long stability to most of the personal care, beverage and pharmaceutical products (G. L. Hasenhuett, R. W. Harted 2008).

Elsewhere sorbitan ester was prepared via dual stage procedure, in the first stage sorbitol was initially dried to sorbitan at temperature of 180 ^{0}C via Phosphoric catalyst then in the other stage this produced sorbitan was further esterified to at 220 ^{0}C using sodium hydroxide as catalyst however after analyzing the product quality they reported that the properties of the produced ester was function of initial ratio of the fatty acid to sorbitol fed to the reactor (Jan Smidrkal, Radka Cerrenkova and Valdmir Philip 2004).

Elsewhere, the sugar fatty acid ester was synthesized in series of steps including, firstly reacting the fatty acid with methyl or ethyl alcohol in the presence of sulfuric acid catalyst to produce fatty acid ester and water, the fatty acid ester then reacted with sugar that is dissolved in dimethyl sulfoxide in the presence of metal carbonate catalyst to get the sugar ester. Reaction time was reported to be 8-24 hours, at 105-125 ^{0}C (Nikhil Kumar, 2012).

The amount of the fatty acid in the feed supposed to be in excess of the stoichiometric quantity when monoester formation is desired. However, the ratios of the fatty acid to the sorbitol is usually varies from 1:1 to produce sorbitane monolaurate, to 1:33 if sorbitan monoestearate is to be synthesized, authors also reported that the average reaction time is about 2.5 to 5 hours, then reaction can be terminated by cooling the reaction products mixture and adding little amount of acid to neutralize the alkali present, also reaction should be carried out in inert and anhydrous media, indeed, the amount of sodium hydroxide used should not exceed 1% w/w based on the weight of the products (George J. Stockburger, 1981).

The enzyme catalyzed synthesis of sorbitol based fatty acid ester was also reported in so many articles, for instance, Douglas and coworkers had synthesized their sorbitan ester via first dehydrating the sorbitol, then followed by lipase catalyzed esterification. However, they used an azeotropic mixture of test-butanol hexane as a reaction medium and no specific temperature or pressure and time were reported (Douglas B. Samey et al., 2000).

Others had investigated the enzyme catalyzed synthesis of several sorbitol dieters. Their experimental method was based on adding polyol to a solution of fatty acid. Aceton was used as solvent because of their low toxicity character. However, their process had given complete conversion of sorbitol (Jose A. Acros, Manuel Bernabe and Christina Otero 1998).

The commonly used fatty acids could be either saturated or unsaturated, having chain length ranging from C_8 to C_{24} , also the sorbitol or polyol group is reported to be esterified at the most lateral hydroxyl group available, hence for sorbitol that should be the two primary hydroxyl groups, and ultimately the mono and di ester would predominate.Overall, sorbitan could produce mono, di, tri up to hexa ester, since it contains six hydroxyl groups, but the formation of tri to hexa sorbitan esters are seldom to happen due to its rapid dehydration to iso sorbides.

The sorbitol fatty acid reaction mechanism and the subsequent side reaction are described in the next series of reaction equations (D. Mukesh et al., 1993). **Figure 1** shows the esterification reaction mechanism of the surfactant production.

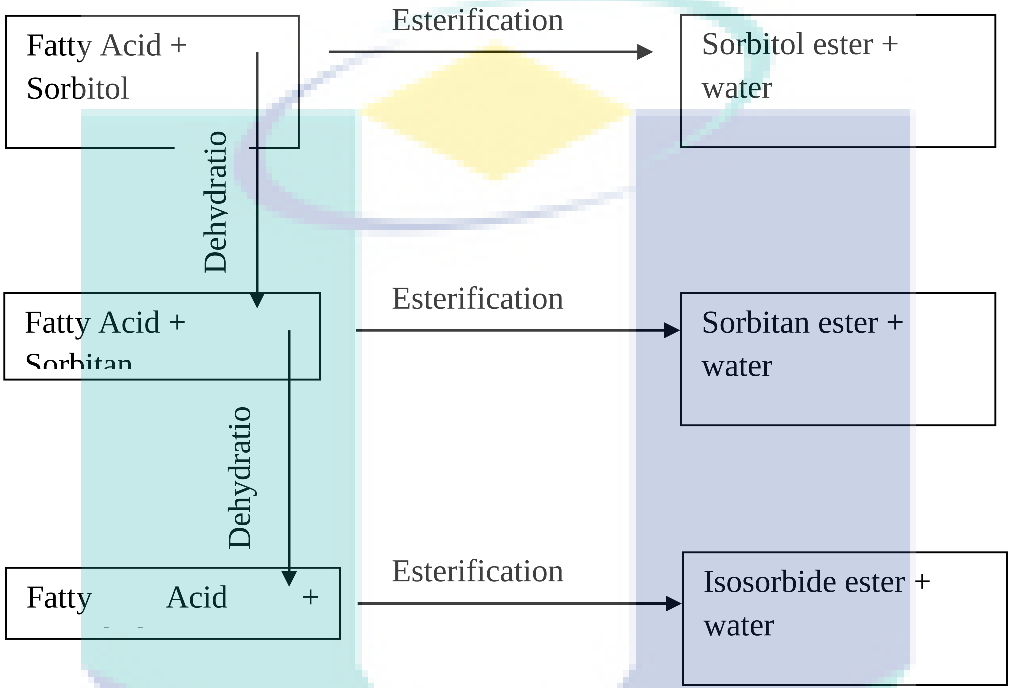

Figure 1: esterification Reaction mechanism (modified from Julie Louise Humphery 2007)

From this figure the fatty acid ester produced depends on the raw materials used, for instance if sorbitol is used it would produce sorbitol ester, if iso-sorbate is used it would produce isosorbate ester and so forth.

According to international process plant model, they set their sorbitan ester plant by first heating the raw materials in a preheating reactor befor being fed to the main reactor Vessel. The fatty acid they used were captive tallow based oleine, vegetable based oleine and coconut fatty acid. The sorbitol used was in the form sorbidex, and their catalyst was a mixture of phosphoric acid and sodium hydroxide (WWW.ippe.com , 2009)

Elsewhere the lopozyme catalysed esterification of isosorbide and sorbitol was investigated comparatively, and the result showed that, isosorbide only produce monooleate, whereas, sorbitol can produce both mono and dioleate. However, their reaction is reportrdely lasted for 13 hours (D. Mukesh et al., 1993).

Elsewhere, the enzymatic esterification reaction between sorbitol and esteric acid via *Aspergillus terrus* lipase as a reaction catalyst was studied. However, the optimal yield was obtained when the ratio of the steric acid to sorbitol was 1 to 4, at reaction time of 24 hours. Indeed, they also mentioned the effect of organic solvent and water activity together with the temperature (Ruchi Gullati et al., 2003)

Jasminka and co-researchers have observed the path of the esterification reaction of hexitols (sugar alcohols) and some long chain fatty acids at different temperatures, they have had specifically studied the reaction between sorbitol and lauric acid to produce sorbitol ester of lauric acid at a molar ratio of (1:1), with P-toluenesulfunic acid being used as a catalyst, besides that, the reaction temperature was varied from 140 to 180, also the reaction path was followed by taking samples intervals after 15, 30, 45, 60, 90, 120, and 150 minutes to determine their acid values, however their results proved that the optimal conversion of the lauric acid could be attained if the sorbitol is previously converted to either of its cyclic forms (sorbitan or iso-sorbide) . (Jasminka et al., 1996).

The reaction temperatures were observed to decrease whenever enzymatic catalyst were used, as reported by rakmi in what he referred to as “bio surfactant”. He reacted fructose and palm oil fatty acid by using the of Lipozyme as biocatalyst (Rakmi abdulrahman and Tjahjono Heranan, 2000).

Similar results were obtained by Ducret, who had produced the biosurfactants by esterifying sugar and sugar alcohols via enzymatic catalyzation, from which they produced several nonionic surfactants one of which was Sorbitol monooleate (Mucret et al., 1995).

CHAPTER 2

Product Characterization

2 Production methods

Normally, sorbitol based surfactants are synthesized by direct esterification of sorbitol or intermolecular condensate of sorbitol with fatty acids in the presence of acid or alkali catalyst and that is called one step process.

In two steps process method, sorbitol is first dehydrated to sorbitan and then esterified with acid or alkali catalyst.

2.1 Materials and Methods

2.2 Materials

Two samples of heavy crude oil utilized for the experiment was acquired from the refinery of Petronas located at Melaka-Malaysia. The two samples of the crude oil were labelled A (Tapis) and B (a combination of Mesilla and Tapis) with ratio 60:40, respectively. A new surfactant of non-ionic (NS-16-1) was formulated. The surfactant was produced by reacting polyol with carboxylic acid in the presence of base catalyst (NaOH). The reactants and catalyst were charged in laboratory reaction flask equipped reflux condenser, stirrer and thermometer. The content was heated gradually from 120 °C to 220 °C for four hours, with purity more than 99%. The emulsifying instrument for the preparation of oil-in-water (o/w) emulsions was produced surfactant.

2.3 Characterization of crude oil

2.3.1 SARA Distribution

An analytical technique that brings about separation of the components of crude oil with regard to crude oil ability to polarize is Saturate, Aromatic, Resin and Asphaltene (SARA). The saturate section is made up of materials that are nonpolar, such as branched, linear and hydrocarbons that are cyclically saturated (paraffins). The aromatics' section is to some extent polarizable because it is made up of at least single aromatic rings while resins and asphaltenes sections are made up of polar substituents. What distinguishes the asphaltenes from the resin is that the insolubility of the asphaltenes are manifested when there is excess heptane (or pentane) while resins have the ability of forming homogenous mixture with heptane (or pentane).

In this regard, after preliminary heating of the heavy crude oil at 60°C for two hours, there was an addition of n-heptane (making the ratio of the crude oil/solvent equal to 1/30 (wt/v)) and then a stirring of the mixture was done for 20 min; thereafter, it was kept for four hours at a normal room temperature. The filtering of the mixture was done, and then quickly washed by hot toluene inside soxhlet. After taking away the solvent, the remainder of the asphaltenes was weighed. The simulation of the maltene (filtrate) was carried out by means of a n-heptane saturated column triggered by silica (100 °C), and the elution (of saturates) was later done by using 100 ml of the following elements: n-heptane, toluene, (elution of aromatics), toluene – methanol (50:50) solution, methanol-chloroform (50:50) solution, chloroform, and acetonitrile (elution of polar/resins). The elutes were put into another container. After each solvent was removed by means of soxhlet, the remainder of the aromatics saturates and resins were weighed in order to identify the percentage of each in the entire crude (Jha et al, 2014). Table 2.1 presents the results. Table 2.1 depicts the crude oils' physical properties, and Table 2.2 presents data about the level of influence that the oil content has on both the viscosity and quantity of separated water in the O/W emulsion.

Table 2.1

Crude oil chemical properties (Crude A and B)

Crude oil sample No.	Saturates (%)	Asphaltenes (%)	Resins (%)	Aromatics (%)
A	55.83	2.93	14.57	26.67
B	51.58	1.65	16.89	29.78

Table 2.2

Crude oils physicochemical, surface and interfacial properties (Crude A and B)

Crude oil	Crude A	Crude B

API gravity	19.40	22.50
Density (gm cm^{-3})	0.968	0.875
Viscosity (Pa s)	0.036	0.024
Surface tension (mNm^{-1}) at 30 °C	31.20	25.50
Interfacial tension (mNm^{-1}) at 30 °C	27.90	21.70

Table 2.3

Viscosities of crude oil A, obtained blends B, and water separated (% water separated after 10 days at 30 °C) as a function of oil contents.

Oil content	**Viscosity**		**Separated water (%)**		**Surfactant**	**Pour point**
(vol. %)	**Crude A**	**Crude B**	**Crude A**	**Crude B**	**conc. (wt. %)**	**(°C)**
	(Pa. s)	**(Pa.s)**	**(%)**	**(%)**		
30	1.84	1.78	44	55	2.5	+ 6
40	1.88	1.75	38	50	2.5	+ 7
50	1.92	1.84	20	25	3.0	+ 9
60	1.97	1.92	12	16	3.5	+ 9
67	**2.20**	**1.96**	**9.0**	**13**	**3.5**	**+ 9**
70	2.00	1.98	7.0	10	3.5	+ 9

73 13	**2.51**	**2.44**	**4.0**	**7.0**	**3.5**	**+**
80 13	2.62	2.40	0.0	0.0	3.5	+
100 18	2.68	2.48	0.0	0.0	-	+

2.3.2 Wax precipitation

The procedures stated by Burger et al. (1981) was utilised in carrying out the precipitation of wax; after the dissolving of crude oil in n-pentane, it was mixed for 30 minutes. acetone (acetone/n-pentane ratio 3:1) was put into the blend and it was left for it to cool down to 253 K for 24 hour. A separation of the existing solid phase in the oil was done by means of filtrating it in a Buchner funnel that utilises a glass microfiber Whatman filter N^{o} 934. A re-dissolving of the solid phase was carried out inside the n-hexane so that the asphaltenes can be removed. When the removing of the solvent was done, the final product was weighed. In determining the Wax Appearance Temperature (WAT), the observation of the noticeable crude oil viscosity was done in the rheometer test at 5 ^{o}C temperature intermissions (from 30 to 80 ^{o}C) as it shown in Fig. 2.1. The utilised shear rates were 240 sec^{-1}, 700 sec^{-1} and 1000 sec^{-1}. The observation of the temperature was done where the viscosity deviated from the straight line because of the solid wax drops described as the value of the WAT (Dantas et al., 2009).

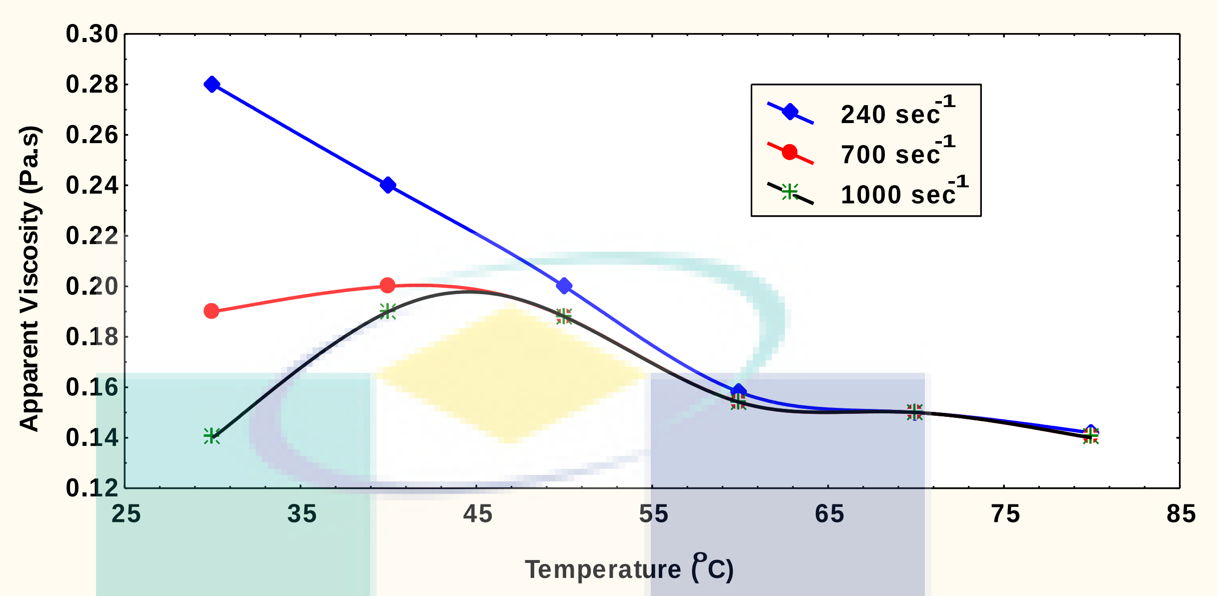

Fig.2.1: Wax appearance temperature of heavy crude oil

2.3.3 Pour point measurement

In measuring both the samples of emulsion and the crude oils' pour points, the standard technique called ASTM was utilised (ASTM D1480-15, 2015). The set-up of a pour point device is made up of a jacket, test jar, water bath, and thermometer. After initial heating was done on the samples, the crude oils were allowed to become cool in the device. The movement of the crude oils was examined by means of horizontally tilting the jar at each drop of 3 ^{o}C temperature. A report of the specific lowest temperature indicating the stop in the flow point was taken.

2.3.4 The severity of API and the sampled crude oil water content

The significance of the crude oil's water content cannot be undermined in the process of producing and classifying scheme. In this regards, toluene was applied as solvent as specified in the method of Dean and Stark (ASTM D95-13e1, 2013). The collection of two distinct stratums of solvent and water was done and the measurement of the water capacity was done at the bottom. At first, the heating of the crude oil was done for 20 minutes at 65^{o}C so as to disrupt the wax crystals stickiness. The removal of water out of crude oil required the use of hexylamine as demulsifier. Afterwards, 3% (v/v) of hexylamine was added to the crude oil, and for another four hours, heating and stirring of the crude oil was done. Another heating process with no stirring for one hour was repeated. Thereafter, a separation of the water was done by the use of separating funnel, and the unadulterated crude oil was utilised for supplementary experiment.

2.4 Characterization of Emulsion

2.4.1 Sample preparation and procedures

Two samples of heavy crude oil utilised for the experiment was acquired from the refinery of Petronas located at Melaka-Malaysia. The two samples of the crude oil were labelled A (Tapis) and B (a combination of Mesilla and Tapis) with ratio 60:40, respectively. Abdurahman et al., (2006) have already given a report about the comprehensive procedure involved in preparing crude oil-in-water (o/w) emulsions. The steps involved in the experiment will be briefly explained in this section. The preparation of various samples of oil-in-water emulsions (o/w) was carried out in 300 mL regulated beakers having different water and oil phase capacities. Made up of the distilled water is the water phase. The stirring of the emulsions was actively done by means of a standardised MLW research laboratory prototype MR 25 which is made of stainless steel stirrer, having four fan blade type. The formulated emulsion was utilised in testing out either w/o or o/w emulsions. The studied emulsions were o/w emulsion, which is known as the water-continuous phase.

2.4.2 Particle size distribution of emulsion droplets

In distributing the droplets size of the formulated emulsions, an instrument, Zetasizer Nano S90 which analyses particle size, was obtained from Malvern at 30 ^{o}C. Dispersing angle by means of Dynamic Light Scattering, the device assessed, at a 90 ^{o}C, the emulsions' particle size. In actual time, the instrument(Zetasizer) did an analysis of the Brownian particles motion and then calculated the intensity of the scattered light; in addition, in order to present the distribution of the globule size, a correlation of the intensity was done by means of a suitable formerly documented light scattering theory.

2.4.3 Stability measurement of the prepared emulsions

In measuring the stability of the formulated emulsions, two successive experimentations were carried out on two separate crude oil samples. The measurement of the emulsion's stability was determined by the quantity of water that is taken out of the formulated emulsions after twenty-four hours. The preparation of O/W emulsions was done in diverse situations and the stability of the emulsion was verified by transporting the emulsions into set-up beakers in the research laboratory. The separated water's volume (which is the stability of the emulsion) was documented applying Equation 2.1. The tabulation of the results is presented in Table 2.4.

$$Emulsion\ stability = 1 - \frac{water\ separated\ (\%)}{water\ content\ (\%)}\ (100) \tag{2.1}$$

2.4.4 Surface tension of O/W measurement

The following are the three discovered things while assessing the tension of the surface: first, the least achieved level of surface tension; second, the least consistent CMC; and thirdly, the shielded capacity every surface-active molecule. The tension-meter by Kruss Easy Dyne was utilised, by means of Du Nuoy Ring method, in measuring the surface of the formulated O/W emulsion samples using.

2.5 Methodology

- Excess reactants (Sunflower or canola cooking oils)
- Limiting reactants (polyols (D-Sorbitol, Glycerol and polyethylene glycol 600))
- Catalyst (Sodium hydroxide pellets)

The surfactants were synthesized via esterification of either fatty acid (Oleic acid) or cooking oils mainly Sunflower oil and canola oils, with polyols (D-sorbitol as well as Glycerin and PEG 600) in the presence of sodium hydroxide catalyst in a four necked reaction flask equipped with stirrer, condenser and thermocouple. The ratio of limiting reactant (D-sorbitol) to excess reactant (Fatty acid) was fixed at 1:5, while the amount of catalyst was fixed at 2.5% based on the weight of sorbitol. In the beginning of the reaction, catalyst and fatty acid were charged in the reactor and stirred to melt the catalyst pellets and mix with the reactant at 190 °C for one hour, after that the limiting reactant (D-sorbitol) was added and stirred for 30 minutes, after that temperature was increased to 220 °C for 3.5 hours. The product was left to cool overnight then collected and used to prepare emulsions, Figure 2.2 shows the lab scale experimental reactor used in this research while Fig. 2.3 shows the commercial (left) and experimental (right) reactants. Figure 2.4 depict the emulsions produced using the commercial (number 2) and experimental (number 1) surfactants, after 1 hour after preparation, 2% concentration of each surfactant, 2000RPM, and 8 minutes stirring time

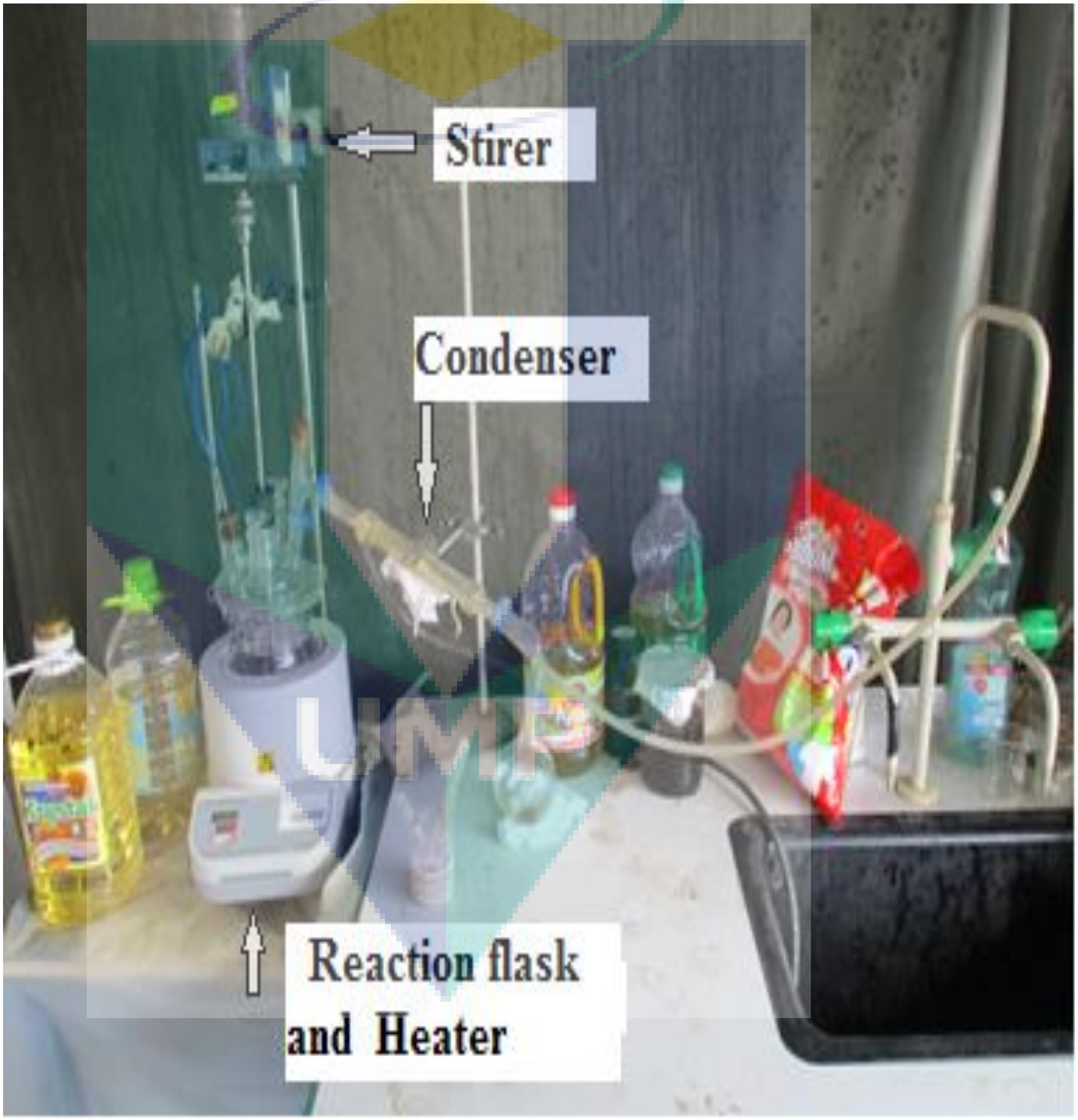

Figure 2.2: picture of reactor set-up

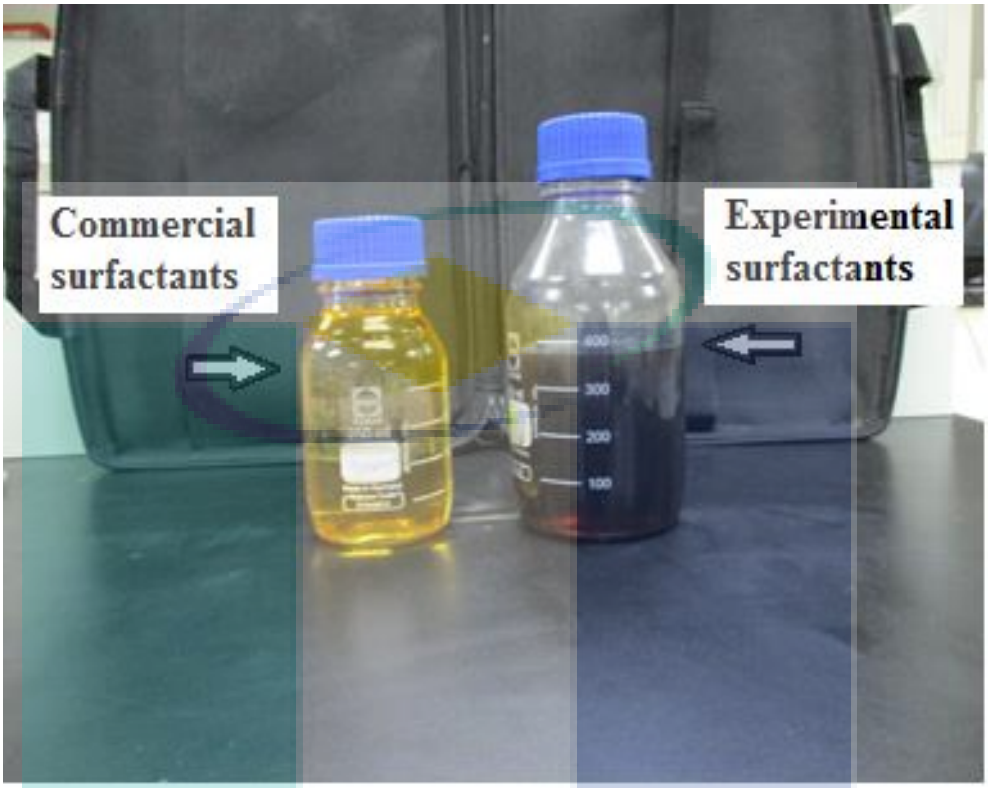

Figure 2.3: picture of the commercial (left) and experimental (right) reactants

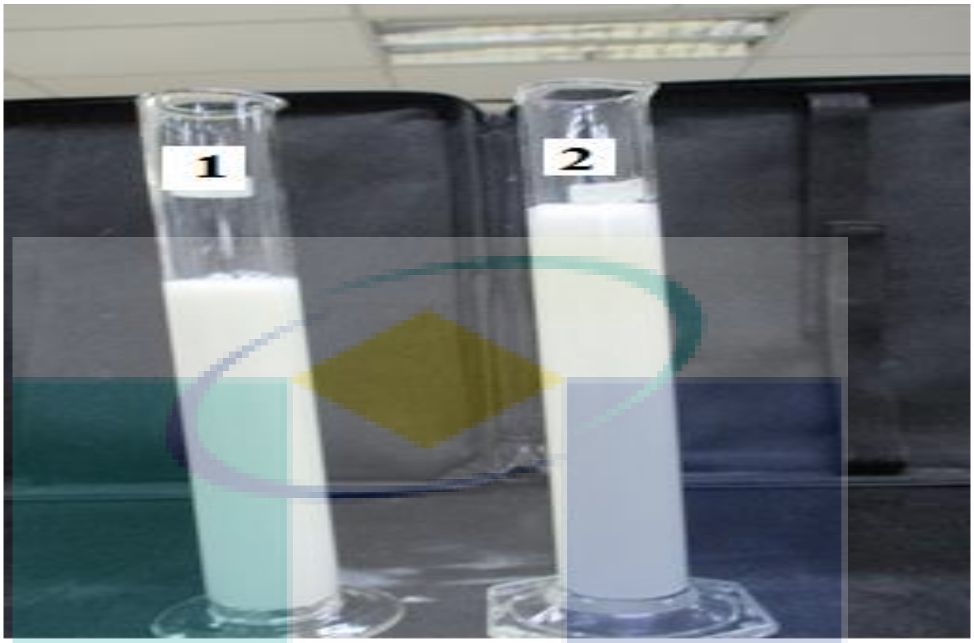

Figure 2.4: Picture of the emulsions produced using the commercial (number 2) and experimental (number 1) surfactants, after 1 hour after preparation, 2% concentration of each surfactant, 2000RPM, and 8 minutes stirring time.

2.6 Reaction procedures

1- Set-up an esterification reactor provided with condenser, receiver, temperature probe and heating mantle.

2- Put the excess reactant (Oil) and catalyst (NaOH), and heat them up with gentle stirring until the palates are thoroughly melted and mixed, this is normally requiring about an hour at temperature range of 170-190 °C.

3- Add the limiting reactants (sorbitol), and wait until it is dissolved and mixed thoroughly, this requires about halve an hour.

4- Increase the mixture temperature to 220 °C and maintain for 4 hours.

5- Switch off the heater and let the sample cool to ambient temperature

6- Test the sample (emulsion stability test).

Note: when tested on emulsion fuel samples this sunflower oil based surfactant was found to have the effect as the commercial oleic acid based surfactants (in terms of diesel based emulsion fuel stability).

2.7 Other new surfactants

Two new surfactants were synthesized by following the method described above. However, the sorbitol portion was replaced by another polyol namely, Glycerol and Polyethylene glycol (600). These new surfactants are synthesized by the same method above; just the D-sorbitol was replaced by these two polyols (Glycerol and PEG 600).

The glycerol and sunflower oil based surfactant is good emulsifiers, while the PEG 600 and sunflower oil based surfactants are good co-emulsifiers.

Emulsion samples produced with these two surfactants and Octadecanol was found to be very uniform and stable. Some pictures are shown next.

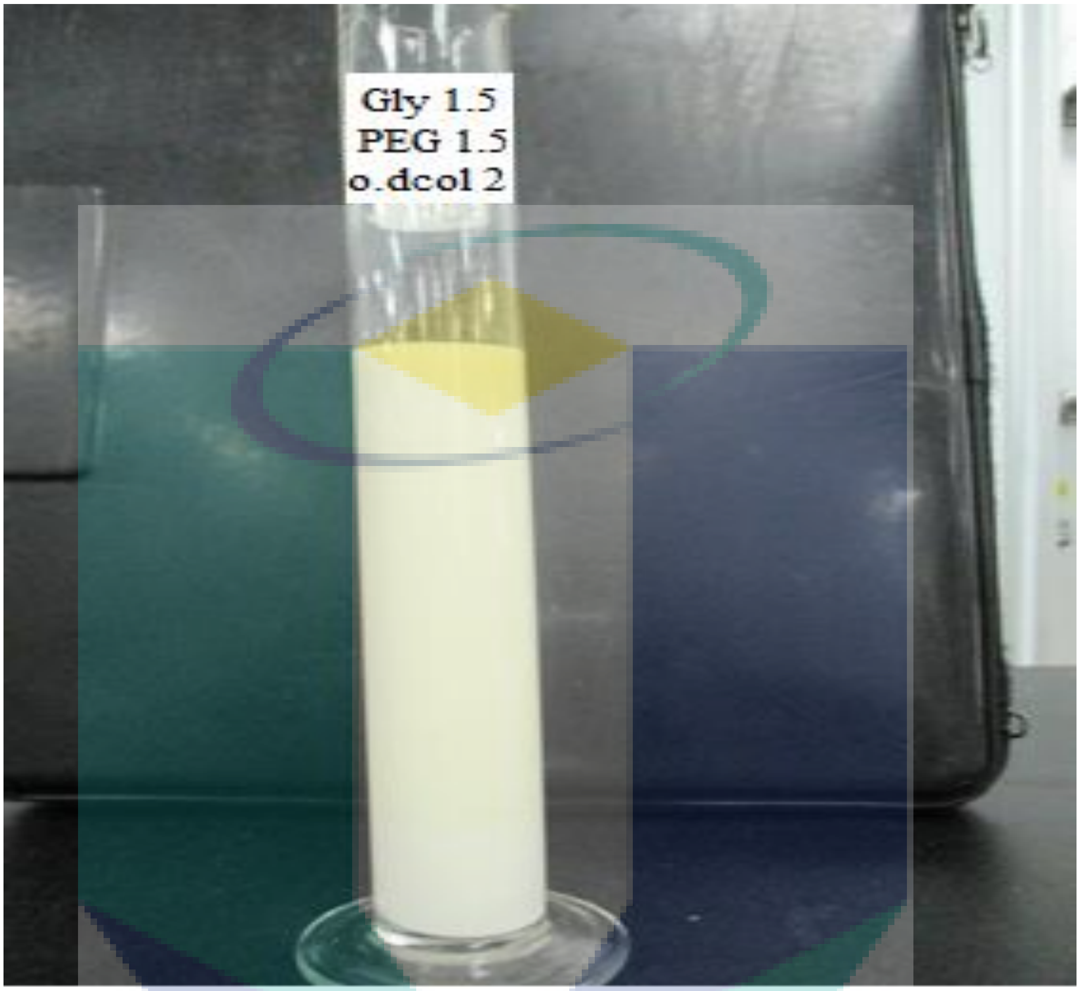

Figure .2.5: stable emulsion fuel sample prepared of glycerol, PEG based surfactants and octadecanol (1.5%,1.5% and 2% respectively), picture taken after two days from preparation

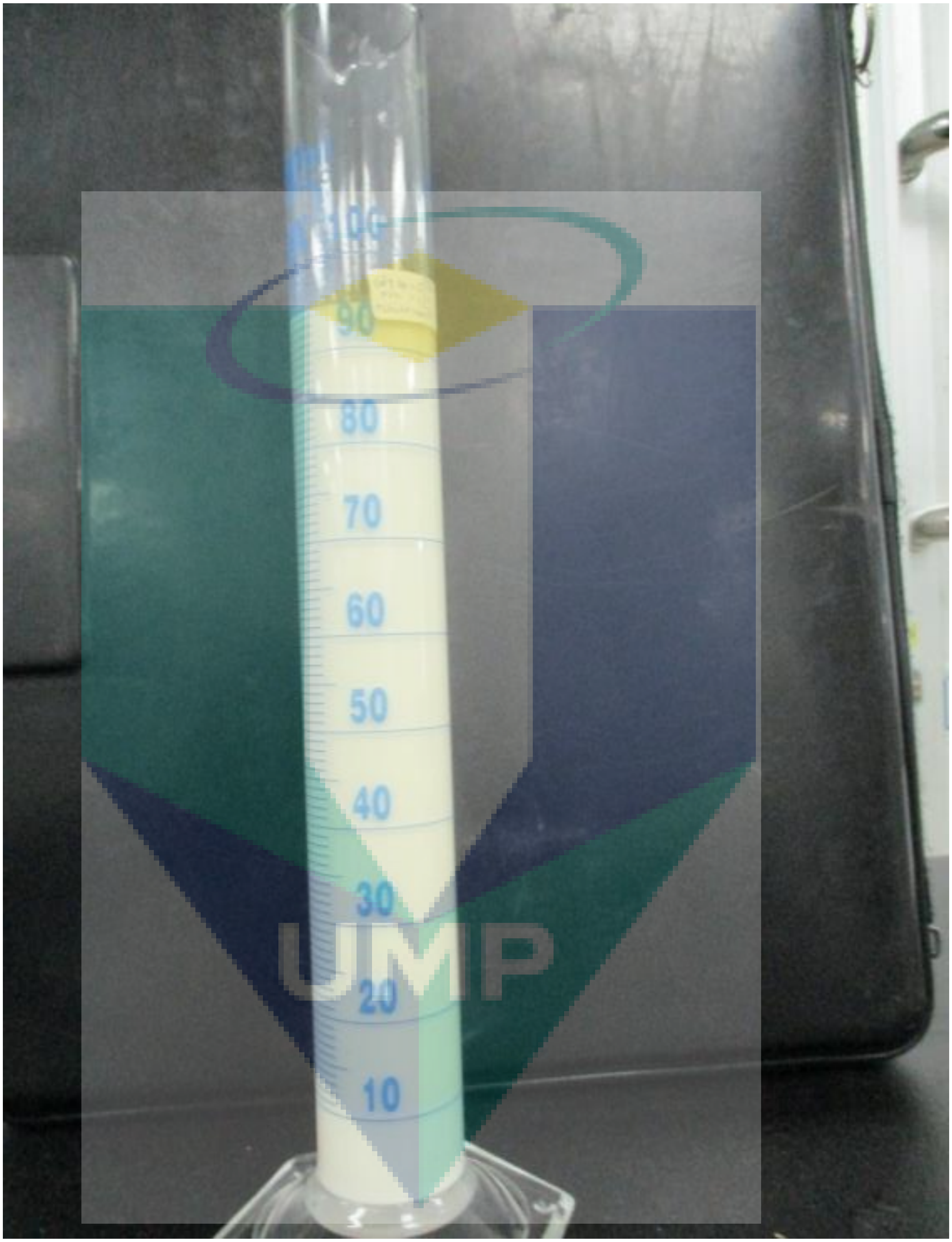

Figure 2.6: Same formulation as in sample Figure 2.4, after four days

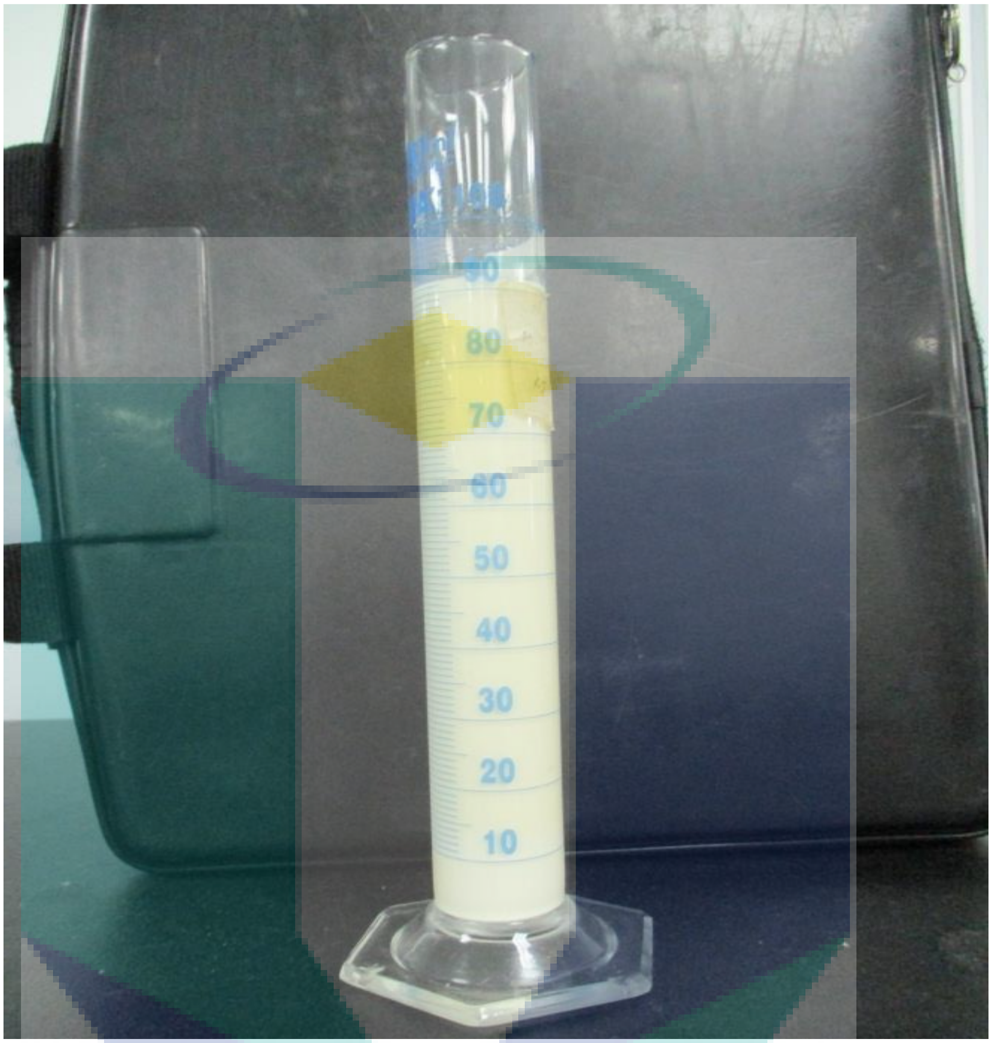

Figure 2.7: Sample composed of Glycerol and PEG 600 based surfactants, Octadecanol, and ethanol (1.5,1.5, 2 and 0.5% respectively)

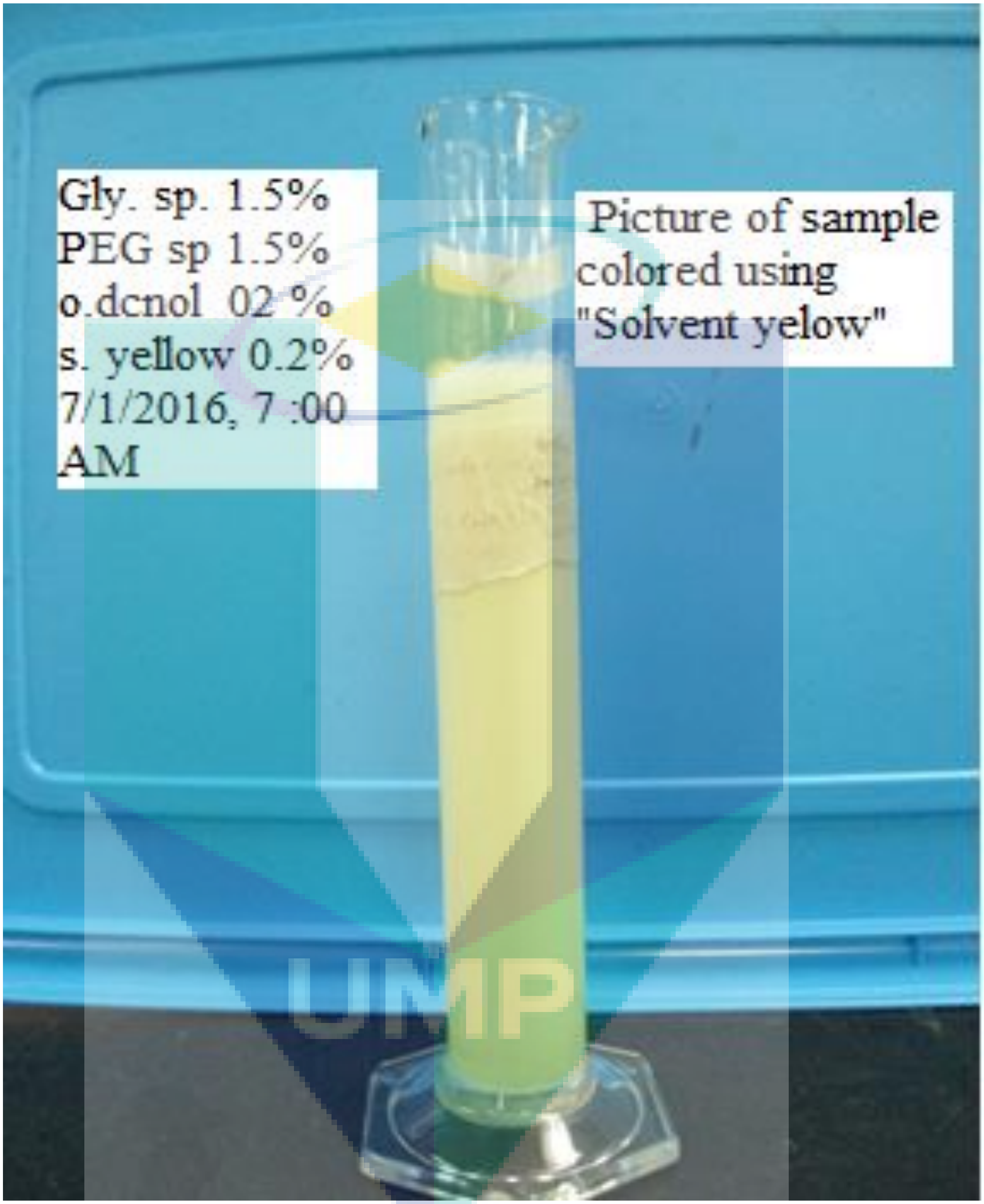

Figure 2.8: emulsion sample colored with solvent yellow

Based on samples in figure seven, it is proofed that solvent yellow is a good color to change the color of the emulsion fuel, for instance, emulsion fuel that looked pure white in figure 6 turned lemon yellow when as little as 0.2% solvent yellow was added.

2.8 Long term stability and co-surfactants

For long term stability concerns, various types and amount of affordable and ecofriendly co-surfactants were used. Some of which are: short chain alcohols (methanol, ethanol, and propanol) mono-ethanol amine, long chain alcohols (Octadecanol), PEG fatty acid ester (prepared by the same method of sorbitan), Shower foam (Shukubushu) as well as dish washing detergent (Depex).

2.9 The Best combination of Alcohol co-surfactants with surfactants

Among alcohol group co-surfactants, results showed that the efficiency of alcohol as co-surfactants increase with increasing the alcohol chain, hence from this experimental investigations, Octadecanol was found to produce stable emulsion in which the usual two phases in the emulsion fuel are very similar and almost undetectable with visual observation for 24 hours and even beyond. Pictures of these stable emulsions which aged from two to three days are shown next.

2.10 The Best combination of shower foam and dish washing detergent co-surfactants with surfactants

The other cosurfactants used in this research were, shower foam (with brand name Shukubushu), and Dish washing detergent with brand name (Depex) together with fractions of triton X-100 and ethanol. These co-surfactants were very efficient when specific amount of each was added to the polyol based surfactants. Some sample some selected formulations produced emulsion fuels that were stable for two months.

Some selected combinations that produced long term stable emulsions (two months and beyond) are:

1) Sample consisting of sunflower oil based surfactants, triton-x100, shower foam (shukubushu), and dish washing detergent (dipex) as given in Table 1.

Table 1: Selected surfactants and co-surfactants formulations

Surfactants and co-surfactants	Ratios
a) Sunflower oil surfactants	0.5% dissolved in Diesel
b) TritonX-100	0.2% dissolved in water
c) Shower foam (Shukubushu)	1% dissolved in water
d) Dish washing detergent (Depex)	1% dissolved in water

Note: this sample is light and low viscosity.

2) Sample consisting of sunflower oil based surfactants, shower foam (Shukubushu), and ethanol as given in table 2.

Table 2: Selected surfactants and co-surfactants formulations

Surfactants and co-surfactants	Ratios
a) Sunflower oil surfactants	1% dissolved in Diesel
b) Shower foam (Shukubushu)	2% dissolved in water
c) Ethanol	3% added emulsion completed

Note: this sample is heavy and high viscosity.

Table 3: Selected surfactants and co-surfactants formulations

Surfactants and co-surfactants	Ratios

a) Glycerol and sunflower oil surfactants	1.5 % dissolved in Diesel
b) PEG and sunflower oil surfactants	1.5 % dissolved in Diesel
c) octadecagon	2 % Dissolved in Diesel

Note: this sample is light and produced very uniform emulsions.

Pictures of Products and raw materials

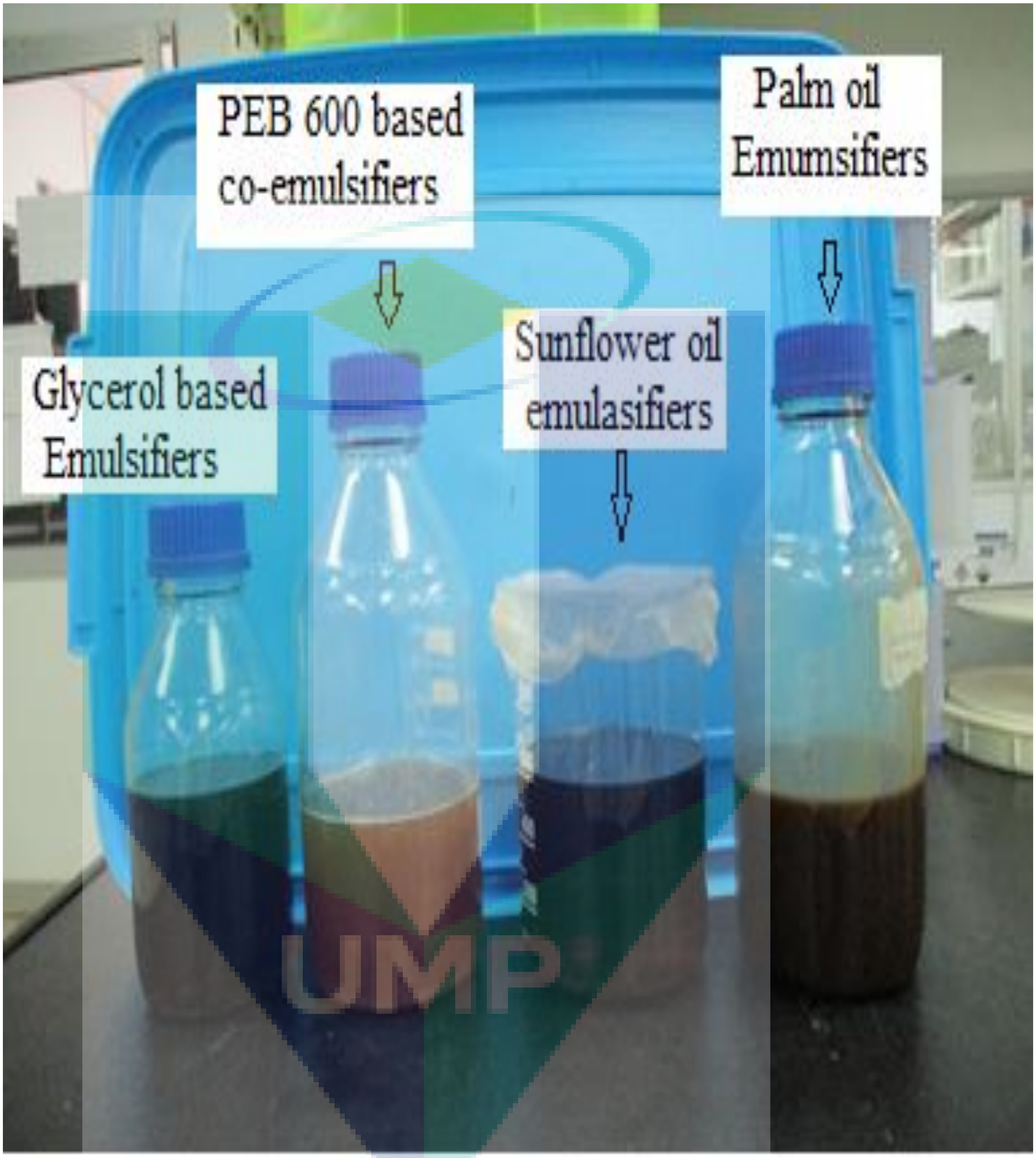

Figure 9: Samples of the surfactant and co-surfactants produced in this research

Figure 10: Sample of the different raw materials used to produce the surfactants

Figure 11: Picture of the commercial co-surfactants used for the long term stability

Product Scaled-up

Fig.12 Reactor set-up

Fig.13 Reactor set-up and sampling

Fig.14 Reactor set-up and sampling

Fig.15 Reactor set-up and sampling

Fig.16 Reactor set-up and sampling

Fig.16 UMP Surfactant

CHAPTER 4

CRUDE OIL EMULSION FORMATION AND STABILITY

4.1 Introduction

This chapter describes studies done on the crude oil emulsion formation and stabilization based on four crude oil types namely, A (Tapis crude oil), B (Masila + Khafji), C (Iran crude oil), and D (Miri). These crude oils were collected from Petronas Refinery Melaka. The primary focus of this chapter is to understand the factors that influence the stability of emulsions as well as characterization of emulsions. While chapter 3, describes and compare the demulsification of water-in-oil emulsions between microwave heating technology and the conventional heating methods.

Emulsions have wide ranging importance in the chemical technological field as well in everyday life. The success of emulsion preparation is determined by the process of manufacturing, the processing conditions, the additives and active ingredients and by the selection of an efficient emulsifier or emulsifier combination. Main destabilizing processes are creaming, flocculation, coalescence, ripening, and phase separation. The stability and performance of the emulsions is further determined by the emulsion type and the rheology of the emulsions. The stability of an emulsion is predominately determined by the stability of the liquid films that separate individual drops. In the absence of surfactants, viscous resistance is the primary reason for the slow drainage of such films; London-van der Waals forces provide attraction between interfaces, so the film thins slowly until rupture. The presence of surfactant creates repulsive forces (electrostatic or steric) that offset the attractive force to create a metastable film which promotes emulsion stability. All emulsions have in common that they are thermodynamically unstable.

4.2 Stability Characteristics of Crude Oil Emulsions

This section studied in detail the formation, production and stabilization of water-in-oil (w/o) emulsions where distilled water was used as the water phase (dispersed phase), and crude oil as oil phase (continuous phase). The stability measurement was carried out by preparing the emulsion from four different crude oils namely, A (Tapis crude oil), B (Masila + Khafji), C (Iranian Crude oil), and D (Miri) which designated as (COE-A, COE-B, COE-C, and COE-D) respectively. The formation of emulsions is very important, so how emulsions can form; well, to disperse droplets of one of the liquids into the other, this means a large increase in interfacial area and thus interfacial energy. From the literature point of view, emulsions thermodynamically were unstable; therefore, the presence of the emulsifying agent must help to stabilize the interfacial regions. It does this by (1) reducing interfacial tension between the two liquids so that the increase in energy associated with the increase in area is reduced, (2) by decreasing the rate of coalescence of the dispersed liquid droplets by forming mechanical, steric, and/or electrical barriers around them. Steric and electrical barriers prevent the droplets from getting close enough to coalesce. A mechanical barrier increases their resistance to coalescence upon shock/shear. Stability is actually fairly complex to accurately define, since in different applications it may be different. The difference in specific gravity between the two liquids will cause a gravitational settling in many cases, but for some applications at least, this is not considered as coalescence since the droplets will still be dispersed. From above mentioned, the stability measurement is very crucial, the only real way to deal with it (stability) is to look at the rate of coalescence. It is sometimes done by measuring under a microscope the number of droplets per volume as a function of time.

As mentioned above, stability of emulsion depends on many parameters. The importance of understanding the mechanisms governing water-in-crude oil stability has been recognized for some time and has precipitated publication of a number of papers on the subject; Oil composition in terms of surface active molecules (Ahmed et al., 1999), (Elgibaly et al., 1997), salinity and pH of water (Plegue et al., 1997), (Plegue et al., 1985), oil/water volume ration (Sun et al., 1996), droplets size and polydispersity (Ahmed et al., 1999: Sun, et al 1996), temperature (Sun, et al 1996), surfactant type and concentration (Sun et al., 1996: Zaki et al., 2000). A large number of studies, mostly experimental in nature have been carried out on oil/water emulsions (Ahmed et al., 1999), and (Zaki, 1997). However, the results of these studies are not always consistent. The reason is that the behavior of emulsions is complex and as mentioned above, depends on many factors.

The water-in-crude oil emulsion has great importance in the oil industry. The stability of water-in-crude oil emulsion is investigated over a wide range of parameters. In the following section, the effect of processing conditions, emulsifier polarity, phase ratio water-oil (10-90 %), centrifugal acceleration (800-1800 rpm), surfactant concentrations, and temperature on emulsion stability is covered. Mostly the ratio of the total liquid separated (water and oil phase) was used as measure of emulsion stability. The physicochemical properties of water-in-crude oil emulsion in terms of density, viscosity, interfacial tension, surface tension, pour point, and pH were measured. The investigation shows that the presence of the emulsifying agent is necessary for stable emulsion, and stability gradually decreases with water concentration. The study also showed the processing time was greatly affecting the emulsion stability.

4.2.1 Effect of Surfactant Concentration Ratio on Stability of Emulsions

Emulsions were made as described in the materials and methods section of chapter four using a variety of surfactants namely, low sulphur wax residue, (LSWR), (poly-ethylene glycol-octylphenol ethers) its trade name (Triton X-100), sodium dodecyl-sulphate (SDDS), sorbitan monooleate (Span 83), and sorbitan monooleate Span 80. The purpose of these surfactants is to provide stability for water-in-oil emulsions. The concentrations of surfactant and dye varied depending on the application. In this regard, the composition of W/O emulsion formulations and their corresponding stabilities are given in Table 4.1 which shows the surfactants used for this study, while Table 4.2 shows the effect of surfactant concentration. Table 4.3 summarizes the results and description of emulsion formation and stability. The stability of the formulations was also assessed via microscopic observation of the emulsion structure and measurement of volume of water separated. This study provided some practical ideas as to how surfactants and mixing affected emulsions stability.

Table 4.1: Emulsion descriptions. Most emulsions made in 900ml beaker.

Emulsion	Stabilizer	Wt % Stabilizer In Ext. Phase (oil)	Emulsion Type	% Internal Phase
1	LSWR	0.50	w/o	50
2		0.75	w/o	55
3		2.00	w/o	60
4		5.00	w/o	70
5	Triton X-100	0.75	w/o	50
6		0.90	w/o	55
7		1.50	w/o	60
8		3.00	w/o	70
9	SDDS	1.00	w/o	65
10		1.50	w/o	70
11		3.00	w/o	75
12		3.50	w/o	80
13	Span 83	4.50	w/o	50
14		6.00	w/o	55
15		1.50	w/o	60
16		6.80	w/o	70
17	Span 80	1.50	w/o	60
18		3.00	w/o	65
19		6.00	w/o	70
20		10.0	w/o	75

According to Table 4.1, LSWR and Triton X-100 water-in-oil (w/o) emulsions were made with 50, 55, 60, and 70 % (v/v) internal phase. For the 50 and 55 emulsion, a higher solids concentration was found (6 mg/ml oil versus 2 mg/ml) allowed easier emulsification and slowed the settling process. The 60 % and 70 % emulsion appeared fairly stable with little settling. The LSWR and Triton X-100 stabilized emulsions exhibited only slight coalescence over two weeks. Some globule formation was observed and settling occurred. In contrast, the Span 83 is a sesquiester of monooleate and dioleate at a 2:1 molar ratio and has an HLB of 3.7. It is commonly used in pharmaceuticals because of its low toxicity; its structure is shown in Figure 4.1. Span 83 emulsions were different from LSWR and Triton X-100 emulsions, even at similar dispersed phase volume fractions. Emulsions were made at 50 and 55 % (v/v) internal phase with surfactant concentrations in the oil phase of 1.5 % and 4.5 % (w/w), at 60 % (v/v) (3 % w/w), and at 70 % (v/v) (6.8 % w/w). The different between surfactant concentrations for the 50 % and 55 % emulsions made by Span 83 appeared very significant on emulsions stability. High Span 83 concentrations increased emulsion stability; therefore, for high concentration of Span 83, the viscosity of w/o emulsion increased considerably and the emulsion droplets lost their shape.

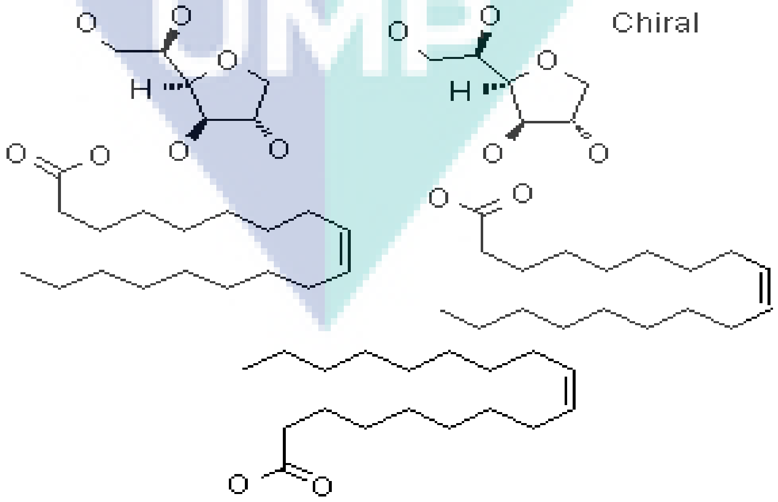

Figure 4.1 Chemical structure of Span 83

The effect of the disperse phase on the stability of emulsion systems was also examined with sodium dodecyl sulphate, (SDDS) as the emulsifying agent. In this regards, the SDDS emulsions were made with 65, 70, 75, and 80 % (v/v) (1 to 3.5 w/w in oil) internal phase.

Span 80 (sorbitan monooleate, its HLB = 4.3) was used to stabilize emulsions at 60, 65, 70 and 75 % (v/v) (1.5 to 10 % w/w in oil). At low Span 80 concentrations (1.5 % and 3 % wt), rapid coalescence occurred within a short period of time. It was observed that, the water-in-oil (w/o) emulsions was significantly more viscous at the percentage of the surfactant reached up to 10 %. At higher surfactant concentrations (6 % and 10 % wt) of Span 80, the droplets were smaller compared to formulations with (1.5 % and 3 % wt) and became very thick early in the dispersion process. As a result, the water did not disperse easily. The final product was thick rheologically. The emulsion appeared less stable compared with those emulsions made with SDDS, LSWR, Span 83 and Triton X-100, in which their emulsions were more stable, as evidenced by lower volume of water separated. Emulsion made at lower surfactant concentrations were less stable than those made at higher surfactant concentrations. The surfactant concentration on emulsion stability was investigated through emulsion viscosity. The concentration of surfactant mainly affects the viscosity of emulsion; this study shows that the viscosity of emulsion increases as surfactant concentration increases (Table 4.2.)

Table 4.2: Effect of Surfactant Concentration

Surfactant Concentration C_s (wt %)	Emulsion Viscosity μ (cp)
1.0	20.6
2.5	24.8
3.5	29.3
5.0	36.7
5.5	39.4

7.0	47.2
7.5	54.8

Table 4.3 depicted the effect of emulsifiers on the stability of four different authentic crude oil emulsions with different concentrations (ppm). It's obviously at temperature 26.5 C^o, the effect of the emulsifiers was significant on the crude oil emulsion stability, especially for the crude oil emulsion C and B. In this regards, COE-C and COE-B completely stabilized by LSWR, Triton X-100, Span 83 and SDDS there were no separation obtained. Table 4.3 shows the emulsions made by emulsifier (sorbitan monooleate-Span 80) were the least stable emulsions. On the other hand, emulsions of Span 83 (sorbitan monooleate) were the best in terms of stabilization. Stability increased with an increase in the concentration of the surfactants. Table 4.3 also showed that as concentration increases (ppm), the emulsion stability decreased.

Table 4.3: The effect of emulsifiers on the stability of four different authentic water-in-crude oil emulsions. The separation of distilled water is recorded.

Crude oil	Conc.(ppm)	LSWR	Span 83	Triton X-100	SDDS	Span 80
	Temperature:26.5C					
A	60	5	5	4	0	20
	80	18	9	6	8	26
	100	28	11	10	11	37
	120	35	18	15	16	40
B	60	0	0	0	0	8
	80	0	0	0	0	10
	100	0	5	0	0	12
	120	5	8	0	0	16

C	60	0	0	0	0	6
	80	0	0	0	0	8
	100	0	3	0	0	10
	120	0	0	0	0	13
D	60	24	10	12	20	28
	80	32	15	24	26	39
	100	36	24	33	31	43
	120	46	40	38	37	50
	Temperature:50C					
A	60	20	18	0	24	30
	80	35	24	7	30	39
	100	46	40	10	46	47
	120	52	47	15	54	75
B	60	22	0	0	0	37
	80	28	0	0	9	45
	100	32	10	0	26	53
	120	40	25	0	37	64
C	60	0	0	0	0	35
	80	0	0	0	8	41
	100	6	0	0	10	50
	120	15	9	0	15	58
D	60	36	10	0	40	50

	80	40	11	0	52	66
	100	52	20	14	56	77
	120	58	47	20	60	80

4.1.1 Effect of Stirring time and Emulsifier on Emulsion Stability

The emulsion stability for the four crude oils were examined as function of processing time and emulsifier applied. Stability evaluated via the ratio of the total water separated. The evaluation was carried out with centrifugal at 1800 rpm at 30 minutes at 26.5 ^{o}C. As demonstrated in Figures 4.2, 4.3, 4.4, 4.5 and 5.6 in most cases stability of emulsion increases with processing time.

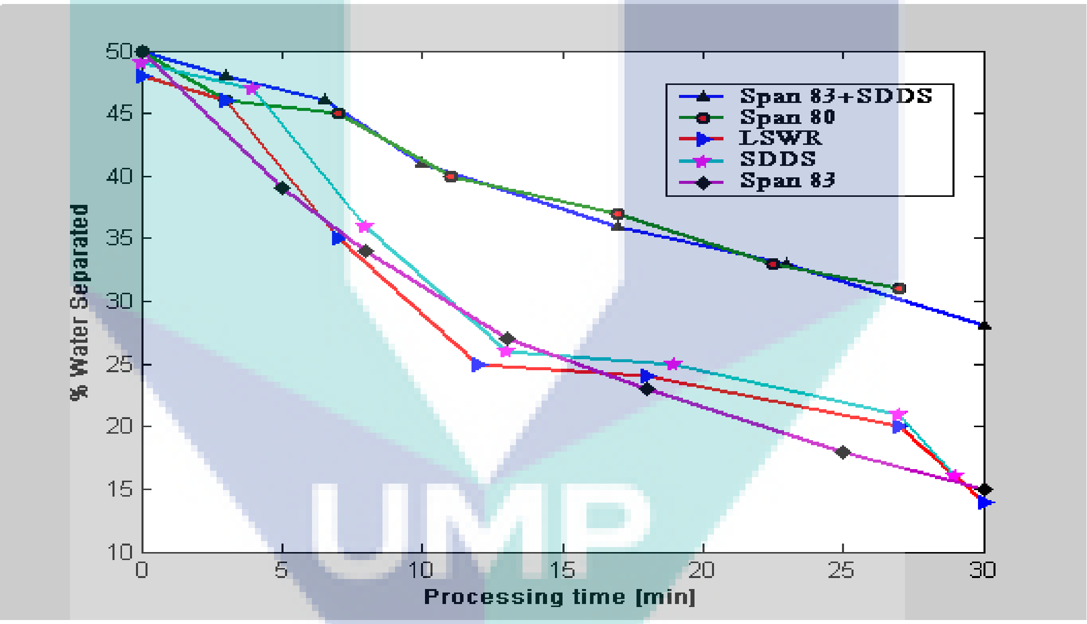

Figure 4.2 Change of emulsion stability for Iranian oil emulsions (50-50 % w/o), as function of processing time and emulsifier applied.

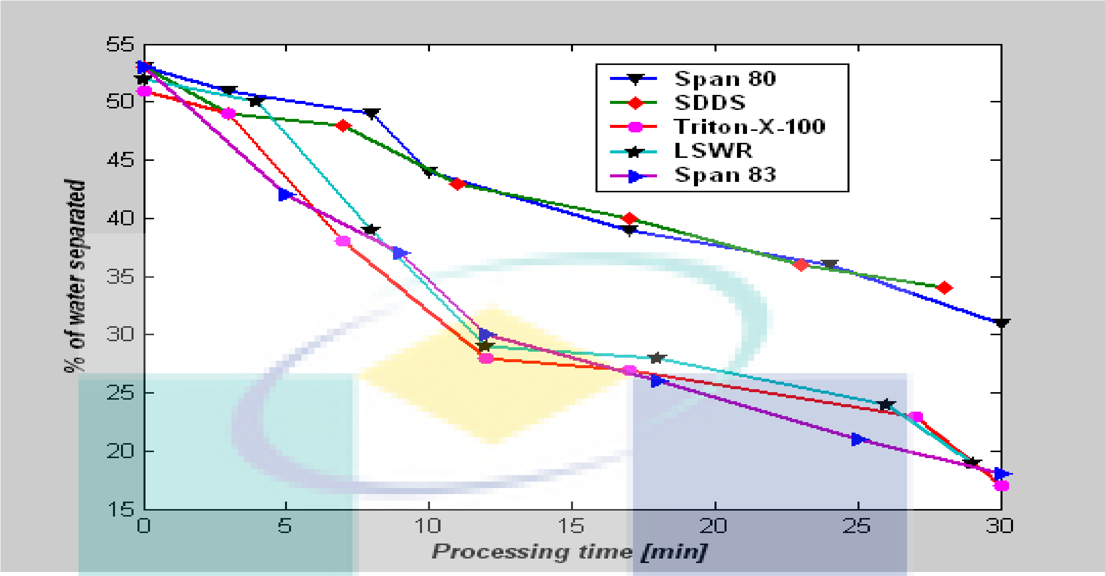

Figure 4.3 Change of emulsion stability for Iranian oil emulsions (50-50 % w/o), as function of processing time and emulsifier applied.

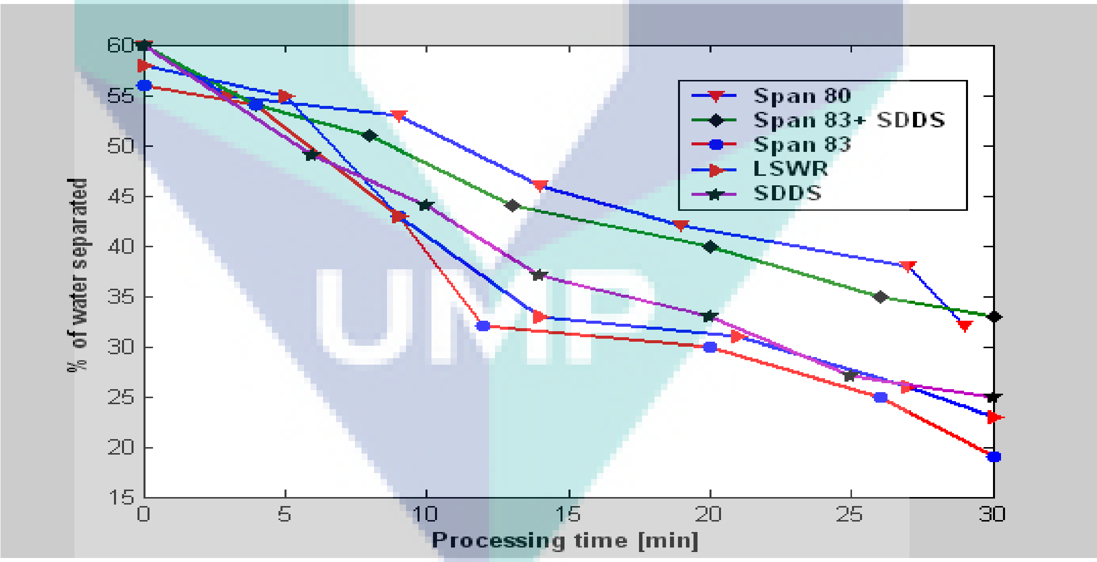

Figure 4.4 Change of emulsion stability for (Tapis) oil emulsions (50-50 % w/o), as function of processing time and emulsifier applied.

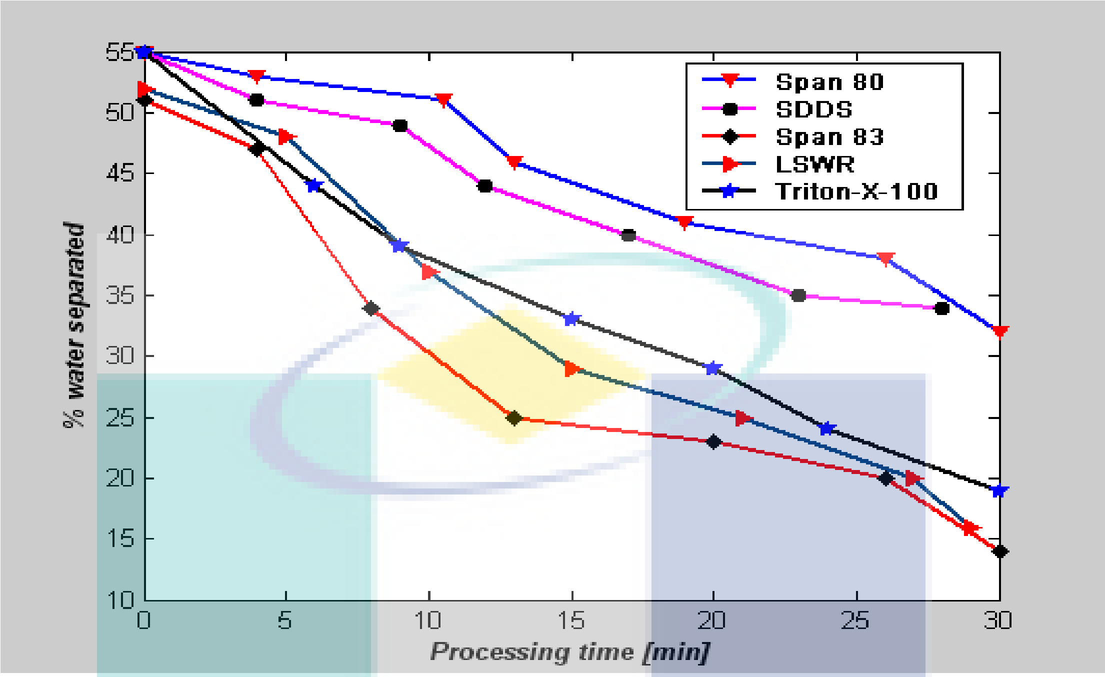

Figure 4.5 Change of emulsion stability for (Masila + Khafji) oil emulsions (50-50 % w/o), as function of processing time and emulsifier applied.

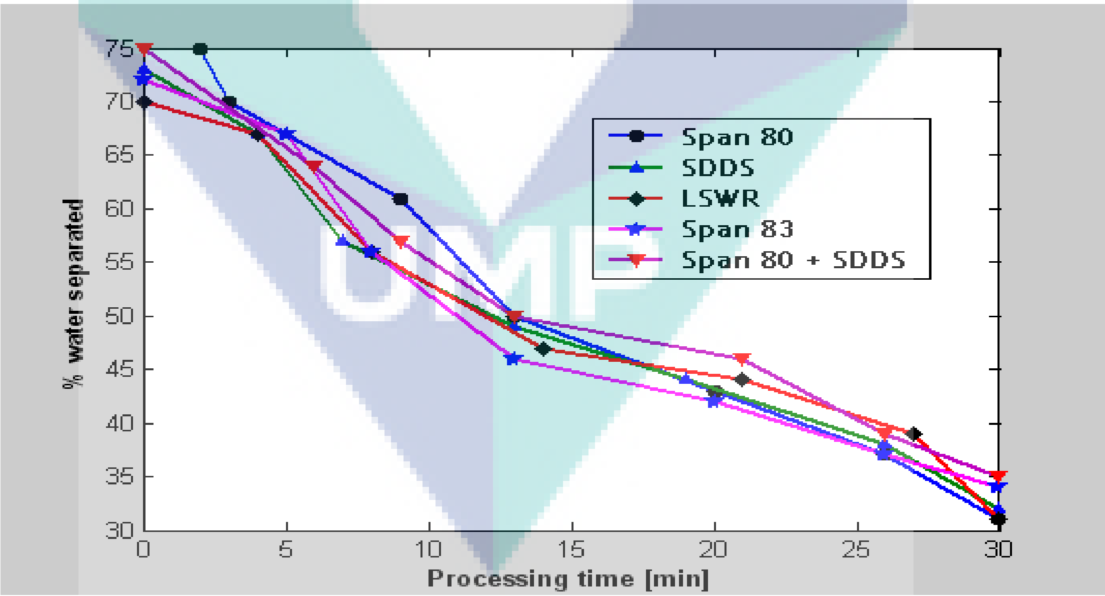

Figure 4.6 Change of emulsion stability for (Miri) oil emulsions (50-50 % w/o), as function of processing time and emulsifier applied.

It is worth noticing that all surfactants, except Span 80 permit a very long time for separation of the water phase (emulsion more stable). However, the maximum amount of water separated from Iranian crude oil was (50 %) followed by Masila +Khafji (55 %), Tapis (60 %), and finally Miri (75 %). From these observations, the classification in terms of decreasing stability efficiency is therefore the following; Span 80 > SDDS > Triton-X-100 > LSWR > Span 83 respectively.

The specific behavior of Span 80 (less emulsion stable) encouraged performing some tests on Span 80 with combination to the other surfactants, this was performed with 1800 ppm for all tests. Figure 2.7 shows the efficiency of the stability of blends Span 80 +Span 83, Span 80 + LSWR, Span 80 + Triton-X-100, and Span 80 + SDDS (50-50 % v/v) for the Iranian crude oil emulsion. The presence of the Span 80 emulsifier with some surfactants strongly increased the emulsion stability compared to each surfactant used alone. The maximum amount of water separated from Iranian crude oil emulsion was found to be 47.5 %. While for Tapis crude oil emulsion found was 55 %.

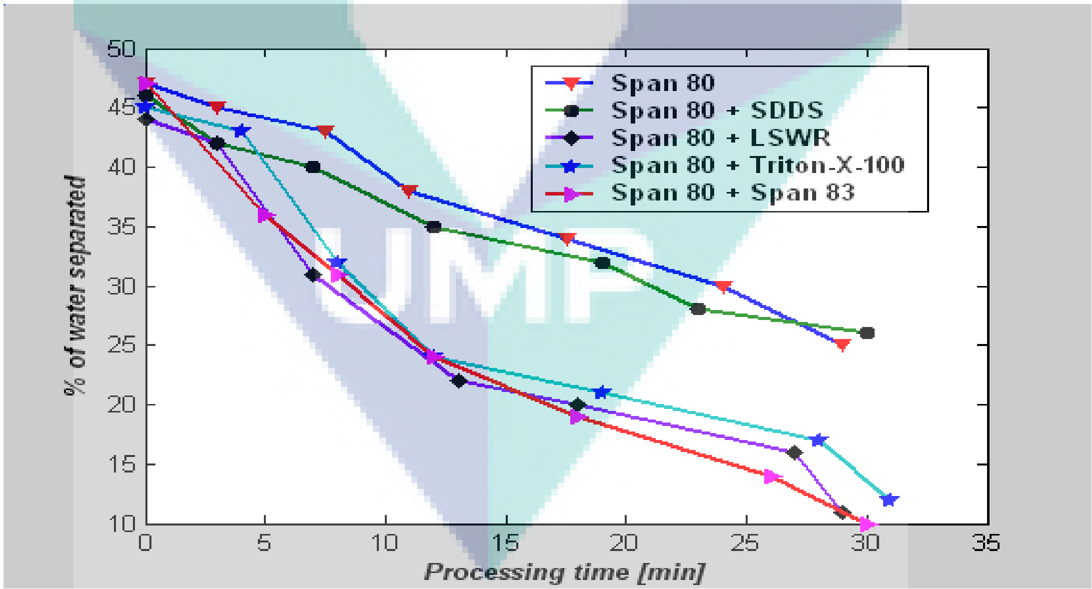

Figure 4.7 Change of emulsion stability for Iranian oil emulsions modified of Span 80 with blends (Span83, LSWR, Triton X-100, and SDDS), (50-50 % w/o) as function of processing time and emulsifier applied.

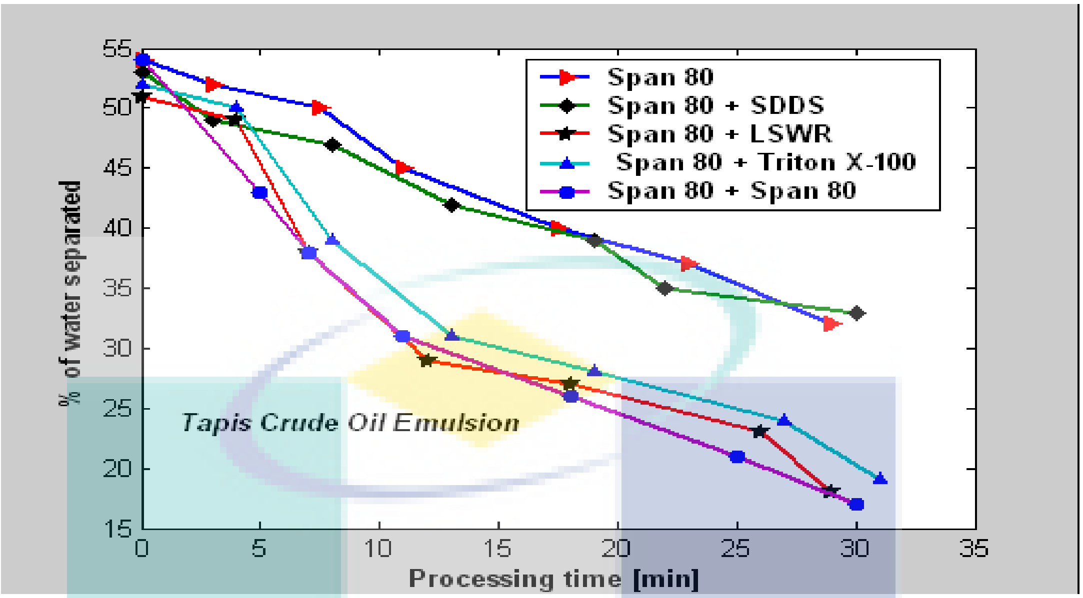

Figure 4.8 Change of emulsion stability (Tapis Crude) modified of Span 80 with blends (Span83, LSWR, Triton X-100, and SDDS) (50-50 % w/o), as function of processing time and emulsifier applied.

4.2.2 Effect of Stirring time and Phase Ratio (water/oil) on Emulsion Stability

The effect of stirring time and phase ratio on emulsion stability was investigated in this section. Water-in-oil emulsions were prepared with various volume ratios as shown in Figure 4.9. At low phase ratio water/oil (10/90 %) only low stability was obtained, the increment of the volume continued till (75/25 %). It's interesting to observe that, increasing the phase ratio, surfactant availability increases accordingly leading to highly stable emulsion (75/25 %). The variation in stability of the emulsions with phase ratio of 75/25 % is very difficult to explain its behavior, especially during the first 8 minutes of processing. When the volume of dispersed phase reached to (90/10 %), the emulsion behavior completely changed as shows in Figure 4.9. the emulsion changed from w/o to o/w. from these measurements and observations, it can be deduced that the phase inversion point should be in the range of 68-72 % water. The oil-in-water emulsion with a phase ratio of 90/10 % is very instable emulsion.

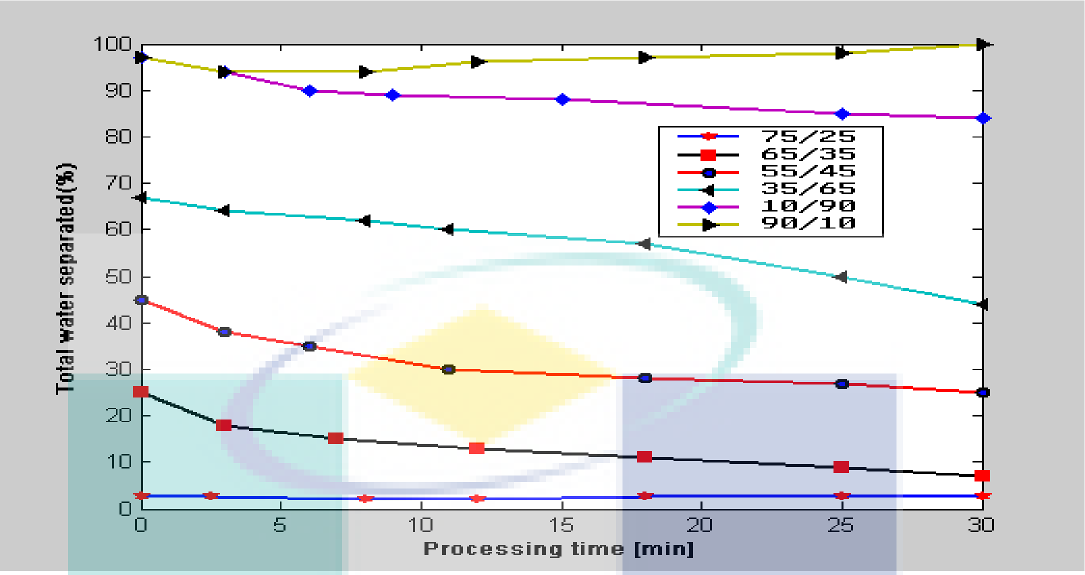

Figure 4.9 Change of (w/o) emulsion stability for crude oil emulsions (stabilized with Span 83 surfactant) as function of processing time. Stability evaluated via the ratio of total water separated.

As the volume of the dispersed phase increases, the continuous phase must spread out farther to cover all of the droplets. This causes the likelihood of impacts to increase, thus decreasing the stability of the emulsion. This means that, the emulsion might not break in the event of increasing the volume of the dispersed phase.

In fact, this increment caused an emulsion to invert from one phase (w/o) to another (o/w). Stable w/o emulsions have very strong films, and this is believed to be in the solid-condensed phase region. Stronger films are necessary in w/o emulsion systems because the water droplets carry no net charge and thus have little resistance to coalescence. To confirm the effect of stirring time and phase ratio on emulsion stability, an oil-in-water (o/w) emulsions were prepared with varied phase ratios. For oil-in-water emulsions, at low phase ratio of oil/water, again only low stability was observed as shown in Figure 4.10 with the polar emulsifier (Triton-X100 water soluble molecule) due to its high content of highly water soluble molecules and therefore, relatively low surfactant concentration at the interface. As the phase ratio increases, the stability of emulsion was increased.

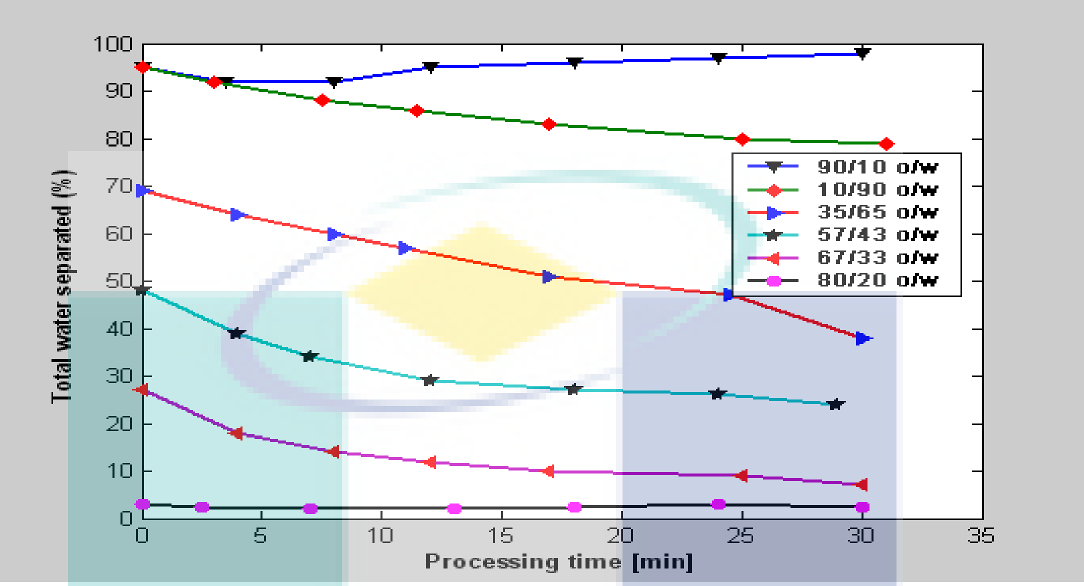

Figure 4.10 Change of (o/w) emulsion stability for crude oil emulsions (stabilized with Triton X-100 surfactant) as function of processing time

The variation in stability of the emulsions with phase ratio of (80/20 %) oil/water is difficult to explain, due to the linearity of the line. There was no clear answer for this phenomenon currently. It can be deduced that the phase inversion point must be in the range of 70-77 % oil. The water-in-oil emulsion with a phase ratio of 90/10 % is very instable. Emulsions are very susceptible to changes in conditions. One of things that can happen, as mentioned earlier, is that the emulsion may go through inversion, that an o/w emulsion may change to a w/o, or vice versa.

The effect of volume fraction of internal phase (water) on emulsion stability was also studied with emulsion viscosity. In this regard, Table 4.4 illustrates the viscosity of emulsion increases greatly as internal volume fraction (Φ) increases, the result leads to emulsion stability. An interesting and surprisingly, when the volume fraction reached (Φ =0.885) the emulsion converted from w/o to o/w as shown in Figure 4.11.

Table 4.4: Effect of Volume Fraction on Emulsion Viscosity

Volume fraction Φ (w/o)	Emulsion Viscosity μ_e (cp)	Oil viscosity μ_o (cp)	$\ln \frac{\mu_e}{\mu_o}$
10/90---------0.087	9.8	9.41	0.041
15/85---------0.131	15.6	14.63	0.064
35/65---------0.315	26.3	22.21	0.169
55/45---------0.511	37.8	27.67	0.312
65/35---------0.613	45.6	30.12	0.415
75/25---------0.719	58.4	36.14	0.48
*90/10---------0.885	48.8		

*** Note**: when the volume fraction of emulsion reached (0.885), the emulsion was inverted from water-in-oil (w/o) to oil-water (o/w) emulsions (Figure 4.11).

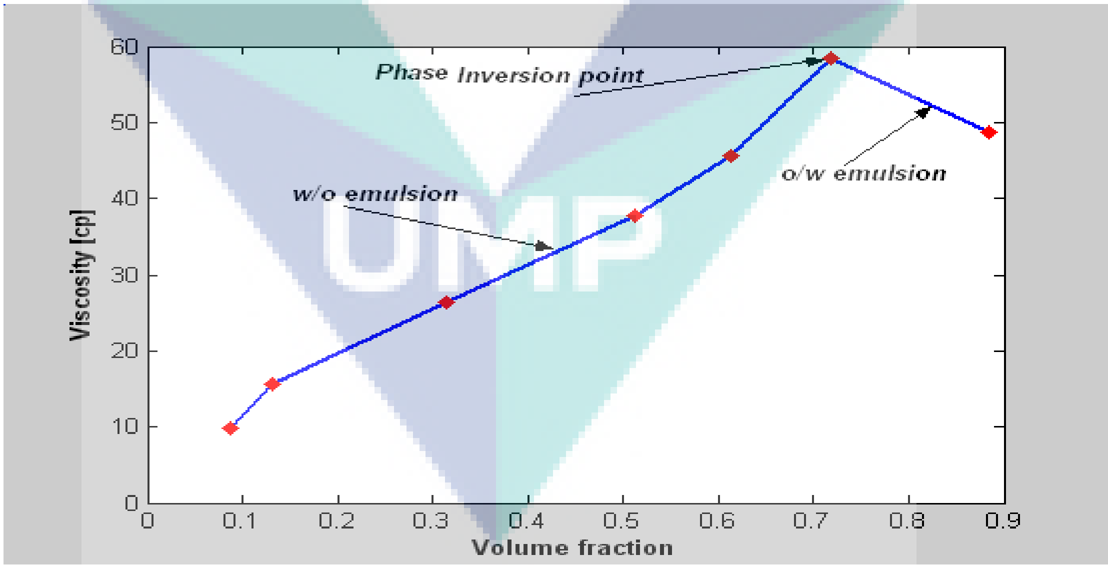

Figure 4.11 Effect of Volume Fraction on Emulsion Viscosity.

Again the effect of the emulsified volume fraction of water studied with both pure crude oil and emulsion viscosities as illustrated in Table 4.4. Figure 4.12 shows that there seems to be a linear relation between the logarithm of the ratio between the viscosity of the emulsion and the crude oil, and the volume fraction of the water content in the emulsion.

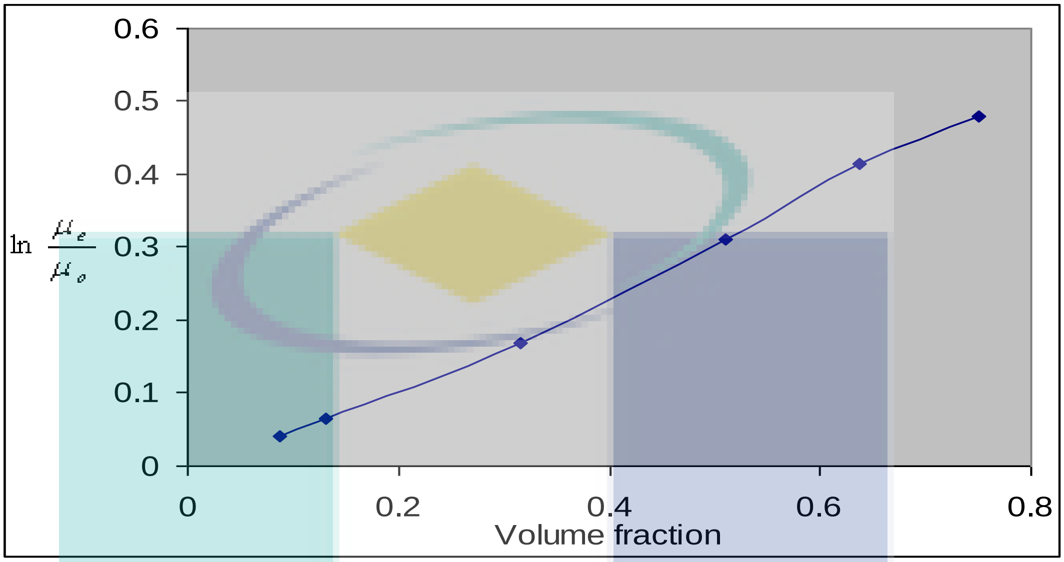

Figure 4.12 The logarithm of ratio of the viscosity of the crude oil emulsion to that of the pure crude oil as a function of the content of water in the emulsion

The effect of surfactant concentration and volume fraction on emulsion stability is studies by two ratios of water-in-oil emulsions that's; 50-50 % and 20-80 % water-in-crude oil emulsions. It found that as the volume fraction (ϕ) decreases, the separation time for water to separate from the emulsion decreased. In this regard; the volume fraction (ϕ) for 50-50 % w/o is 0.459 while for 20-80 % is 0.175. The concentration of surfactant mainly affects the viscosity of emulsion. Experiments show that the viscosity of emulsion increases as surfactant concentration increases, Figures 4.13, and 4.14 show the effect of surfactant concentrations 50-50 % w/o and 20-80 % w/o on emulsions stability respectively.

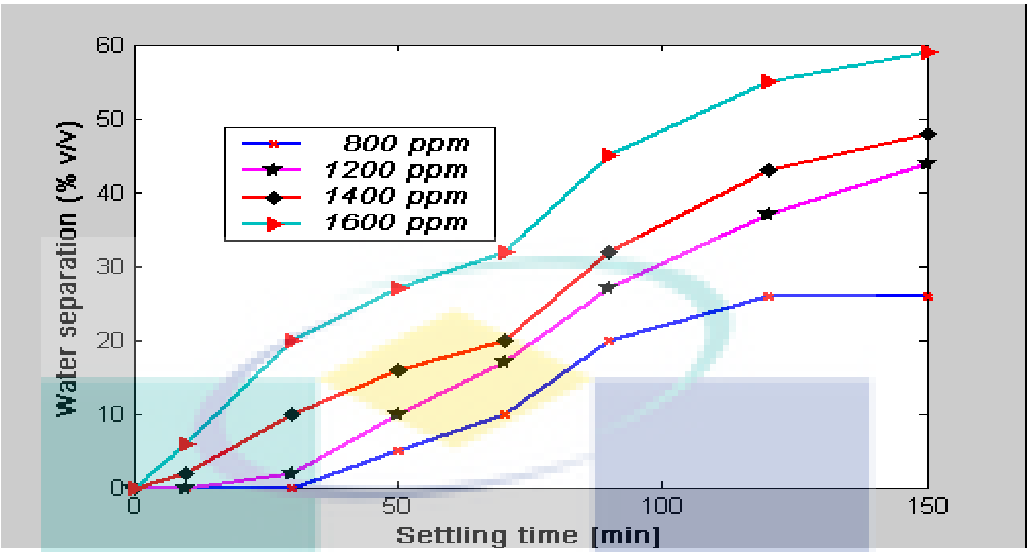

Figure 4.13: Effect of Surfactant concentration (ppm) on emulsion stability (50-50 % w/o)

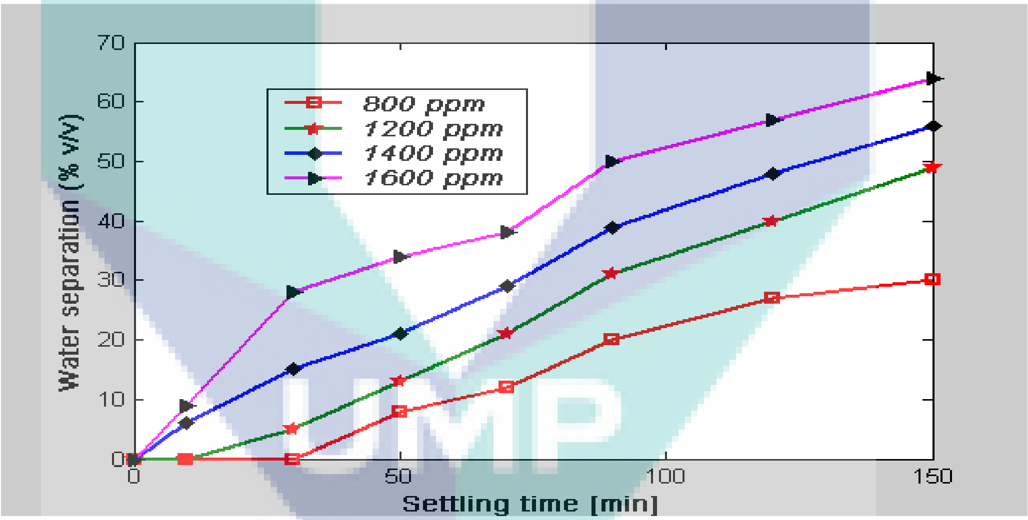

Figure 4.14: Effect of Surfactant concentration (ppm) on emulsion stability (20-80 % w/o)

4.2.3 Effect of Surface Active-Agents On Emulsion Stability

The stability of emulsions was again determined by measuring the water separation from the emulsions at constant temperature (28.5 °C) using surface-active agents (asphaltene and resin). The four Sara-Fractions are saturates (S), aromatics (A), resins (R), and asphaltenes (A). The interfacially active fractions such as asphaltene and resins used in these experiments were extracted from the different oils collected from petronas refinery. The separation of asphaltene and resins were described in chapter 4, section 4.4. When the surface-active agents added to the emulsion, the interfacially active agents were adsorbed or deposited at the interface of the oil/water system. The process takes place over a period of time until the system attains equilibrium. Plots describing the stabilities of emulsion system for the four crude oils emulsion with asphaltene and resins as interfacially active components are shown in Figures 4.15, 4.16, 4.17, and 4.18 for the crude oils Tapis, Masila+Khafji, Iranian, and Miri respectively.

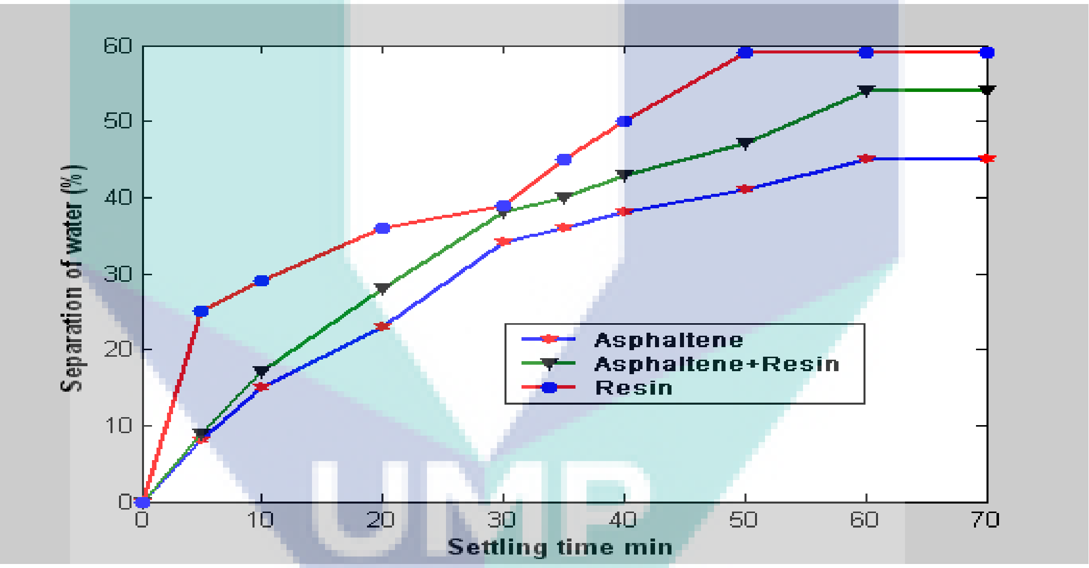

Figure 4.15 Stability of (w/o) emulsions with asphaltenes, resin and a mixture of asphaltenes and resins of (Tapis) crude oil.

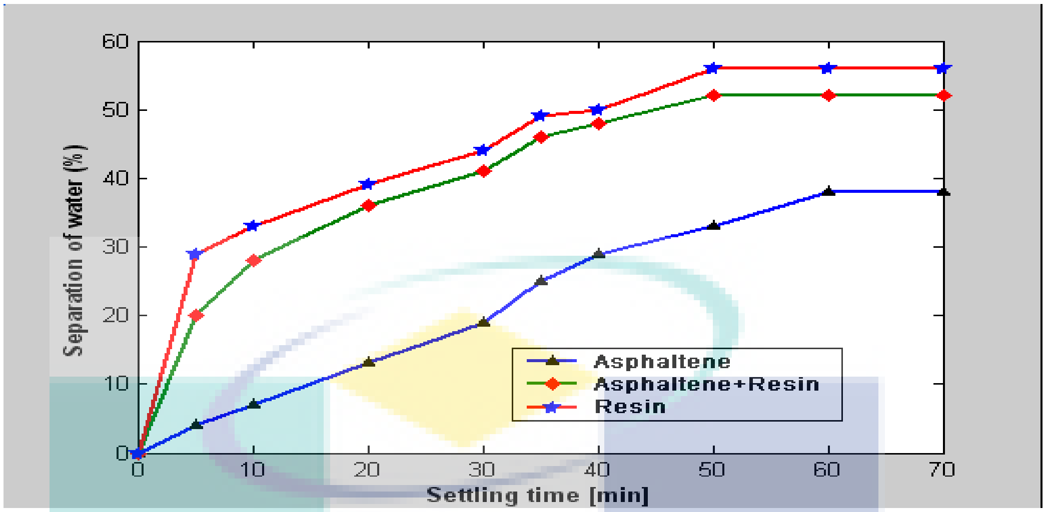

Figure 4.16 Stability of (w/o) emulsions with asphaltenes, resin and a mixture of asphaltenes and resins of (Masila+Khafji) crude oil.

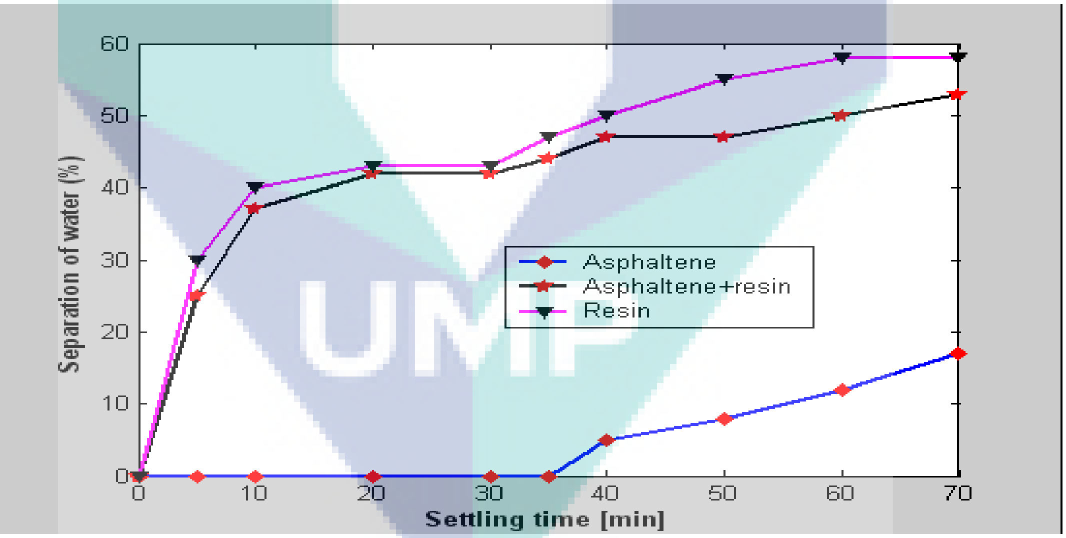

Figure 4.17 Stability of (w/o) emulsions with asphaltenes, resin and a mixture of asphaltenes and resins of Iranian crude oil.

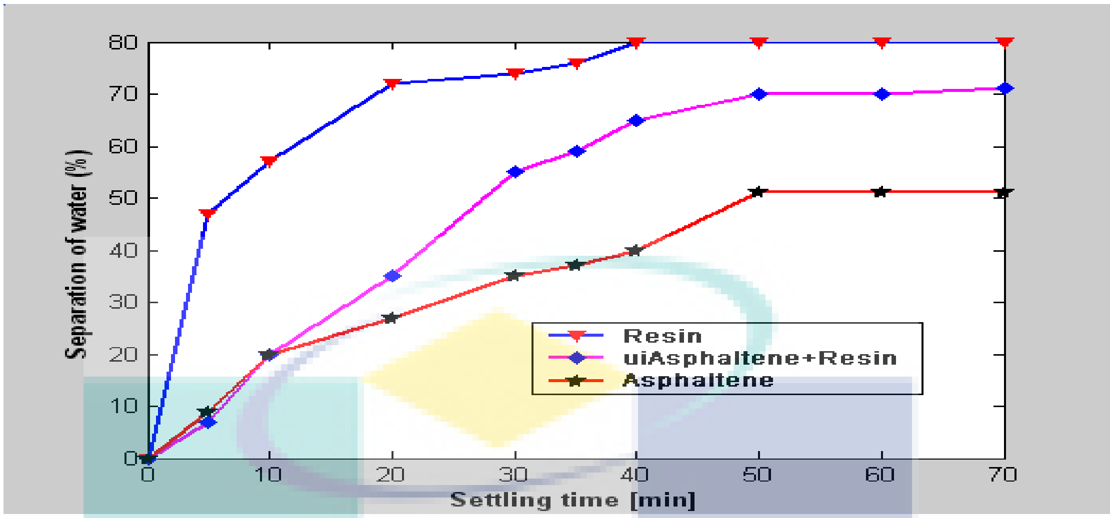

Figure 4.18 Stability of (w/o) emulsions with asphaltenes, resin and a mixture of asphaltenes and resins of (Miri) crude oil.

From these figures, crude oil C (Iranian crude oil) was more stable among the four crude oils and crude oil D (Miri) emulsions less stable. These figures also shown that the emulsions made by asphaltenes were more stable than those made by resin or mixture agents (asphaltene + resins)

4.2.4 Effect of Temperature On Emulsion Stability

In ordinary emulsification, a change of temperature has only an indirect effect as result of altering the interfacial tension, adsorption of emulsifier, and viscosity. However, significant changes in temperature cause changes in interfacial tensions, viscosities, nature (hydrophilicity-hydrophobicity) of the surfactants, vapor pressures of the liquid phases, and in the thermal agitation of the molecules. Thus, emulsions tend to be very sensitive to temperature changes. Emulsions are more stable when the temperature is near the point of minimum solubility of emulsifying agents. Emulsion stability decreases when temperature is increased. Figure 4.19 depicted the effect of HLB-value and temperature on stability of water-in-oil (w/o) emulsions, while Figure 4.20 shows for oil-in-water (o/w) emulsions. These emulsions were prepared with (50-50 %) oil/water ratio using a mixture of oil and a water soluble emulsifier. The temperature dependence of emulsion stability can easily be assessed by centrifugation at different temperatures. Near the optimum HLB

(Hydrophilic-Lypophilic Balance) value, (Figures 4.19 and 4.20) stability is less dependent on temperature. At higher temperatures, the optimum HLB moved to higher values.

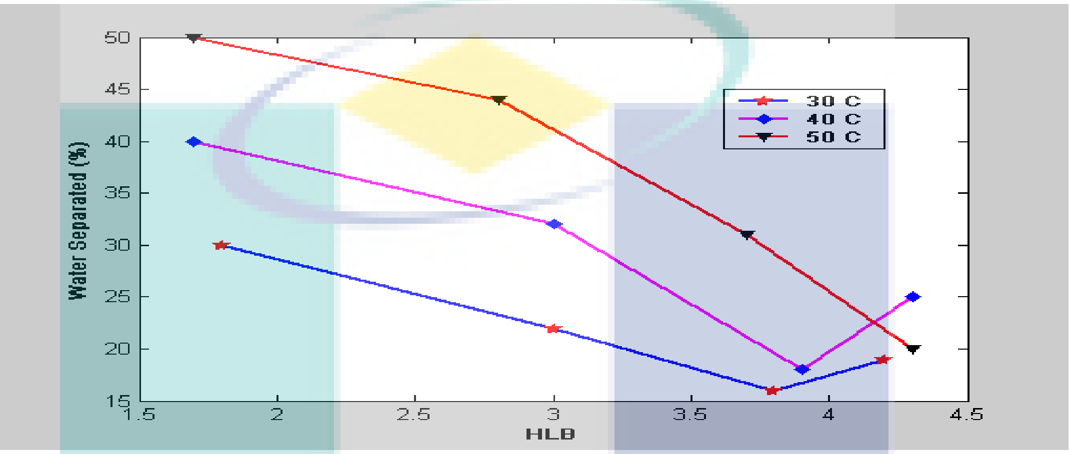

Figure 4.19 Effect of Temperature on (w/o) Emulsion Stability for 50-50 % w/o emulsions

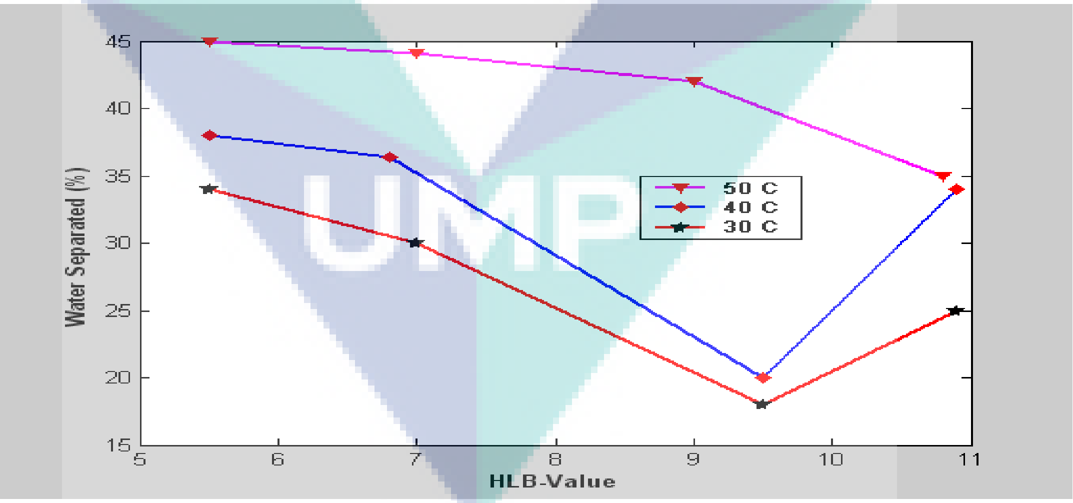

Figure 4.20 Effect of Temperature on (o/w) Emulsion Stability for 50-50 % w/o emulsions

The effect of temperature on emulsion stability was also investigated through the emulsion viscosity. As mentioned earlier the separation of water from oil in water-in-oil emulsion involves two processes: coalescence of emulsified water droplets and sedimentation of coalesced water droplets. Both processes are affected by temperature. The rate of water separation in sedimentation depends on the settling velocity of water droplets in the emulsion (Fang et al, 1995). If the concentration of water droplets is low, droplets move without interaction with others and the settling velocity is given by Stoke's law (Bird. et al., 1960). According to the force balance and Stoke's law, if oil is the continuous phase, the settling velocity of water droplets through oil is given by:

$$v_w = \frac{(\rho_w - \rho_o) g D^2}{18\mu_o} \tag{4.1}$$

As illustrated in Equation (4.1), the settling velocity is proportional to the density difference, square of droplet diameter, and the reciprocal of the oil viscosity. The viscosity of oil and water were very sensitive to temperature, much more than density difference. Therefore, as temperature increases, viscosity decreases much faster than the density difference and the rate of coalescence increases. The diameter of water droplets plays an important role, since the settling velocity depends on the square of diameter as indicated in the above equation. The results show a higher settling velocities and faster separation of emulsified water from oil. In this regard; Table 4.5 shows the viscosity of four crude oils against temperature. Figure 4.19 shows the relation of temperature versus viscosity of four crude oil emulsions.

Table 4.5: Effect of temperature on emulsion viscosity

Temperature T, °C	Viscosity of various crude oils (μ , cp)			
	COE-A	COE-B	COE-C	COE-D
28.5	45	74.5	100.6	30
40	30.6	62.3	88.7	18
50	21.3	47.4	55.1	13
60	16.3	26.0	30.0	10
70	10.0	16.0	19.2	7.0
80	8	11.0	12.1	3.5

Table 4.5 depicts the effects of temperature on emulsion viscosity; it is clear that the viscosity decreases very fast when temperature increases, the result leads to acceleration of coalescence processes which cause emulsion unstable.

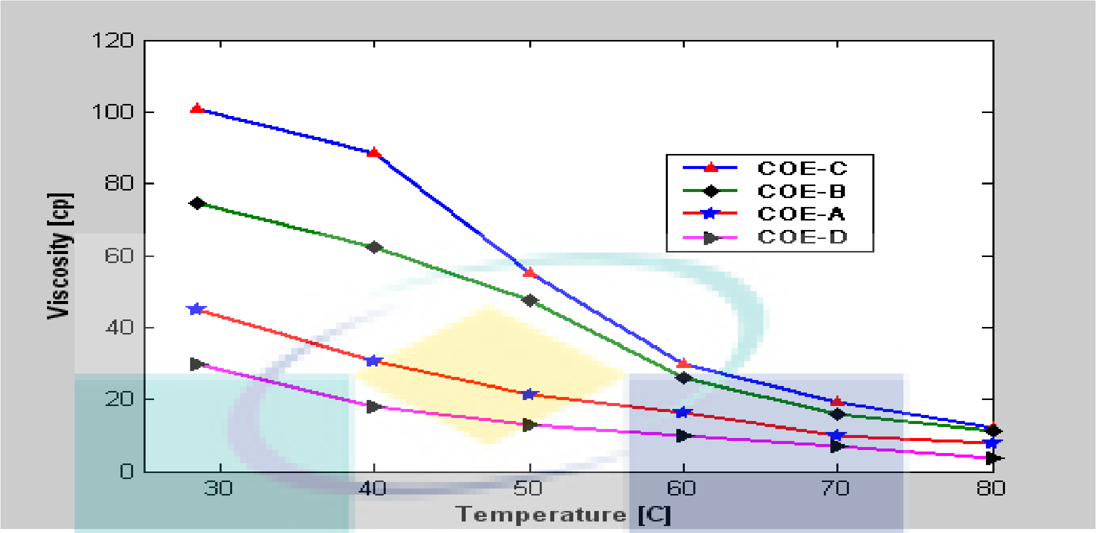

Figure 4.21 Temperature versus viscosity for four crude oil emulsions.

Characterization of an emulsion as stable or unstable is required before other properties can be considered, because properties change significantly for each type of emulsion. The emulsion stability and four water-in-oil states are: stable emulsions, meso-stable emulsions, unstable emulsions (or simply water and oil), and entrained water (Fingus, 2000; Schramm, 2000). These four states are distinguished by perseverance through time, visual appearance, and by rheological measurements. Meso-stable emulsions, can be red to black in appearance, have properties between stable and unstable emulsions. Meso-stable emulsions lack sufficient asphaltenes to render them completely stable, although the viscosity of oil may be high enough to stabilize some water droplets for a period of time. Meso-stable emulsions many degrade to form layers of oil and stable emulsions. Unstable emulsions are those that largely decompose to water and oil after mixing, generally within a few hours. Some water, usually less than about 10 percent may be retained by the oil, especially if the oil is viscous.

An important measurement to characterize water-in-oil states is forced oscillation rheometry (Fingas et al., 2000). From this measurement, the presence of significant elasticity is clearly defined whether a stable emulsion has been formed. Viscosity by itself can be an indicator, under some conditions, of the stability of the emulsion. Color is also used as an indicator, but it may not be definitive. All stable emulsions are usually reddish, although some meso-emulsions also have a reddish color, but unstable emulsions are always the color of the starting oil.

Based on above mentioned, the ability of each category of crude oil to form stable emulsions is shown in Table 4.6 and Figure 4.22. Table 4.6 illustrates water-in-oil emulsion states of four crude oils; Iran crude, Miri, Masila + Khafji, and Tapis. Obviously, one can based on a visual inspection as in Figure 4.22, classify the emulsions as; stable, meso-stable, and unstable on a time scale of minutes, hours, and weeks (or months), respectively. In this regard, Iranian crude oil and Masila + Khafji are classified as stable emulsion, Tapis crude oil is categorized as meso-stable emulsion, while Miri crude classified as unstable emulsion.

Table 4.6 Examples of water-in-oil emulsions (Spindle no: 31 at room temperature)

Oil type	w/o emulsion state formed	Viscosity at Starting (cp)	Viscosity after formation (cp)	viscosity after one week (cp)	Ratio of starting/formation
Tapis crude oil	Meso-stable	30	180	110	6
Masila+Khafji Crude oil	Stable	41	369	450	9
Iranian crude oil	Stable	15	200	200	13
Miri crude oil	Unstable	60	100	810	2

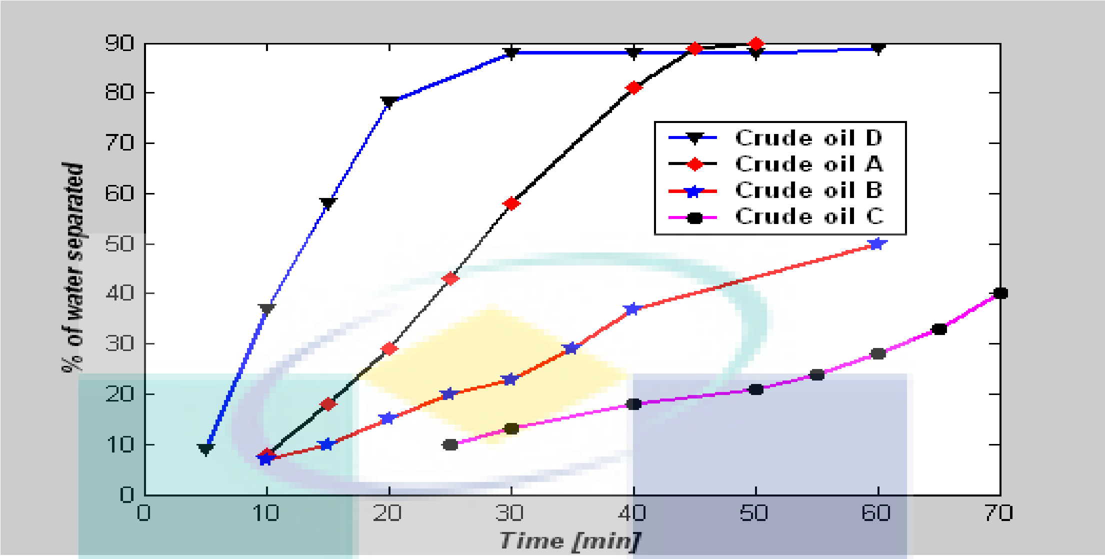

Figure 4.22 Separation of water from (w/o) emulsions based on different crude oils.

Again the effects of temperature on emulsion stability and its effects with temperature changes were investigated. In this regards, the emulsion stabilized with SDDS, Span 83, and LSWR surfactants were found to be a water-in-oil (w/o) emulsion at high temperature, but the same emulsion converted to oil-in-water (o/w) emulsion at low temperature. The phase inversion (PIT) in the emulsion takes place at some medium temperature (Figure 4.23 shows the phenomena). The existence of a phase inversion temperature (PIT) indicates appreciable changes of the hydrophilic-lipophilic balance (HLB) of a nonionic surfactant with temperature. In this regards, it found that the effect of phase volume on the phase inversion may be smaller than that of temperature, (Figure 4.23), the phase inversion temperature (PIT) stays almost constant over a wide volume fraction range, indicating the strong type determining tendency of the adsorbed monolayer of nonionic surfactant. The emulsion is water-in-oil (w/o) type below the (PIT) curve and oil-in-water (o/w) type above the (PIT) curve.

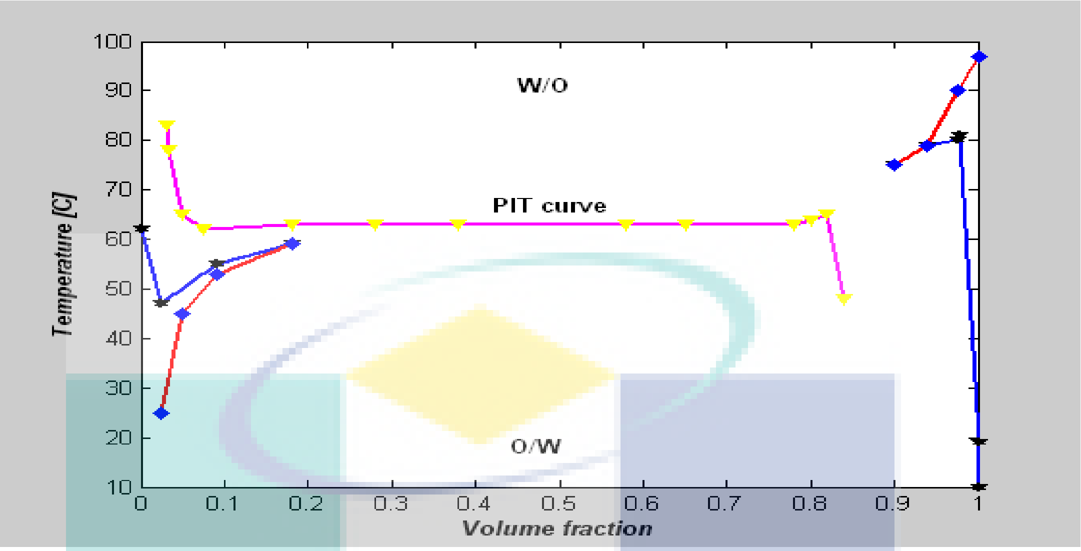

Figure 4.23 The effect of phase volume on the phase inversion temperature (PIT).

4.3 Analyzing Other Factors Controlling Crude Oil Emulsion Stability

In the previous sections, the stability of the four crude oils emulsion was investigated through many parameters. In this section, some other parameters such as the chemical and physical properties are discussed.

4.3.1 Effect of Physicochemical Properties of Crude Oil Emulsions

The above section discussed the formation of emulsions, while this section outlined the physico-chemical properties of emulsion. In the most cases the crude oil is characterized by some physico-chemical and chemical properties. The fundamental physico-chemical properties of the crude oil comprise of two parts: water phase and oil phase. The oil physical properties like density, surface tension, interfacial tension, viscosity, pH, conductivity, pour point, while water physical properties include density, surface tension, pH, and conductivity. Table 4.7 shows the physico-chemical properties of four crude oil samples used for this study. The physico-chemical properties in Table 4.7 at 26 ^{o}C, 40 ^{o}C, and 60 ^{o}C show that the densities values vary between 0.793 and 0.852 g/cm^{3}, the viscosities values at 26 ^{o}C, 40 ^{o}C, and 60 ^{o}C vary between 14.54 to 44.75, 10.20 to 38.68 and 6.22 to 30.62 cp, respectively. The values of surface tensions vary between 23.3 and 28.2 mN/m, and the interfacial tensions vary between 25.6 and 27.3 mN/m. It has been observed that in two specific cases of COE-A and COE-D, the interfacial tension exceeds the values of surface tension, this may due to high content of waxes for COE-A, and COE-D. The pH values vary from 6.45 to 7.06, while pour point values in the range -15 to 13 ^{o}C. Based on results given in Table 4.7, there is a correlation between the crude oil viscosity and surface tension. The higher viscosity of crude oils gives the higher surface tension. This may attribute to the existing of concentrated polymer film at the interface which may show elastic or viscous properties, and hence make it difficult to break the emulsion. The difference of density ($\Delta\rho$) between the continuous and dispersed phase influences the emulsion stability. In this regard, the higher ($\Delta\rho$), causes the molecules move faster, increasing the velocity of water droplets which cause emulsion unstable. The settling velocity of water droplets can be calculated as mentioned earlier from Stoke's law (Schubert and Armbruster, 1992), Equation 4.1.

Table 4.7: Physicochemical properties of some crude oil samples at 26 oC , 40 oC, and 60 oC.

Crude Oils / **Physicochemical Properties**	**Decreasing Order of Stability**			
	COE-C	**COE-B**	**COE-A**	**COE-D**
Density, ρ_c (g/cm^3), @26 ^{o}C	0.852	0.834	0.811	0.793
Viscosity, (cp), @26 ^{o}C	44.75	30.42	20.73	14.54
Viscosity, (cp), @40 ^{o}C	38.68	24.54	16.21	10.20

Viscosity, (cp), @60 ^{o}C	30.62	17.46	11.68	6.22
Surface tension, (mN/m), @26 ^{o}C	28.2	26.2	24.6	23.3
Interfacial tension (mN/m), @26 ^{o}C	27.3	24.0	28.3	25.6
pH, @26 ^{o}C	7.00	7.06	6.87	6.45
Pour Point, ^{o}C	13	9	2	-15
Density, ρ_d (g/cm^3), @26 ^{o}C	1.00	1.02	1.03	1.01
$\Delta\rho = \rho_d - \rho_c$ (g/cm^3), @26 ^{o}C	0.148	0.186	0.219	0.217

There is also a correlation between the viscosity and the pour point; the higher viscosity of crude oil gives the higher pours point and vice versa. The variation of crude oil viscosities shown in Figure 4.24, it is obviously, the viscosity decreases at increasing temperature increases. Figure 4.25 shows the viscosity of crude oil and viscosity of crude oil emulsions as a function of temperature. It is clear that, the viscosity of crude oil emulsions always higher than viscosity of crude oil (using COE-C for comparison).

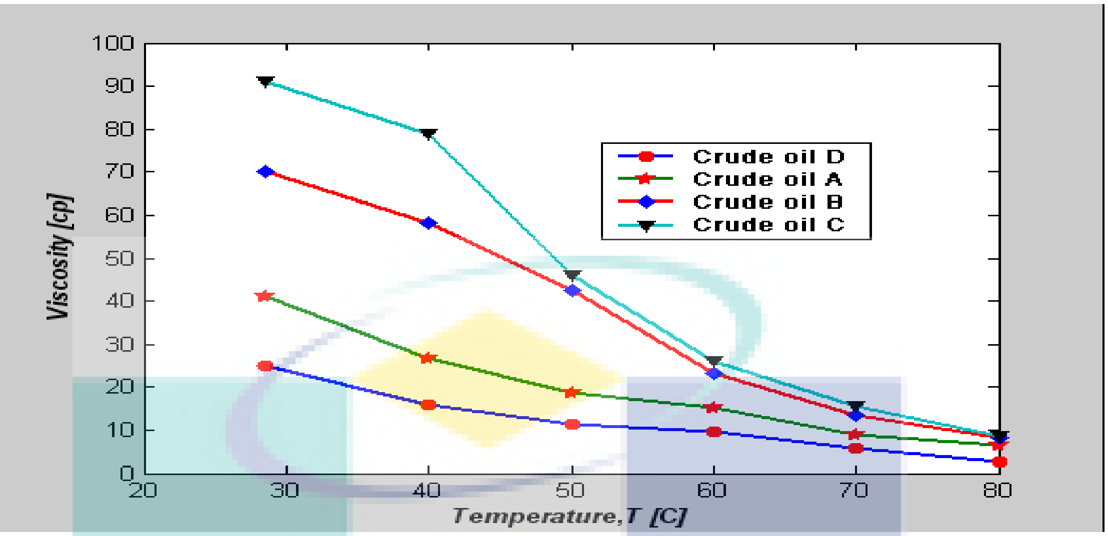

Figure 4.24 Viscosity of crude oils as function of temperature (Crude oil A, B, C, and D)

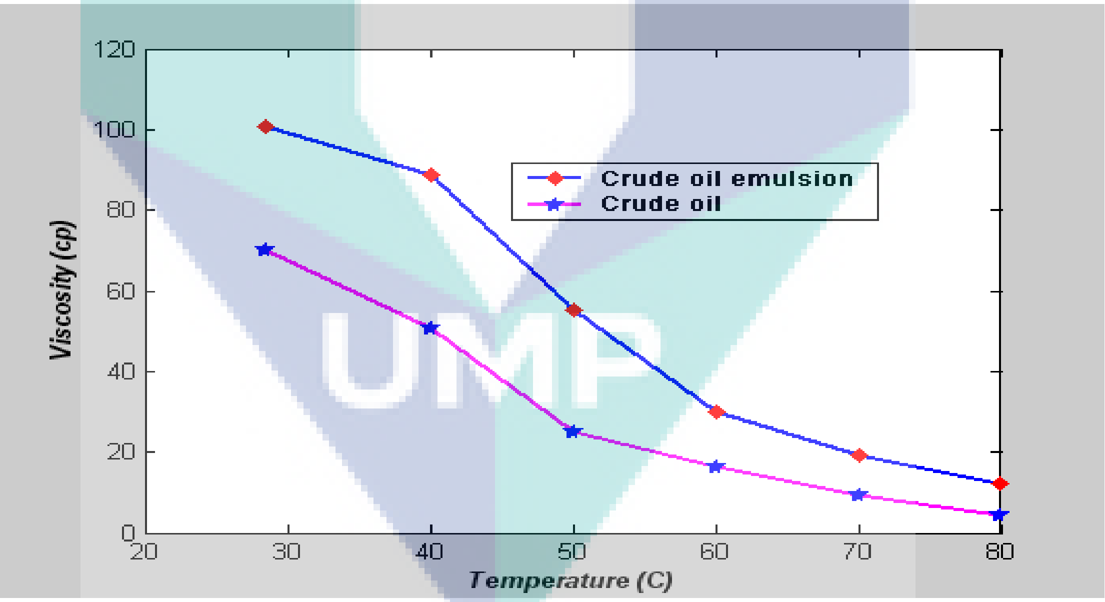

Figure 4.25 The viscosity of crude oils and crude oils emulsion as a function of temperature.

4.3.2 Rheological Properties of W/O Emulsions at Different Internal Volume Fractions

In terms of emulsion characterization, this study used a variety of surfactants to get a high stability for water-in-oil emulsions. Coalescence needs to be minimized to obtain any useful rheological information. Emulsions were produced by gradually dispersing the water in the external phase (oil) in a 900 ml glass beaker. The shear stress and shear rate behavior of emulsions has been thoroughly examined. However, at low internal phase volume fractions, below 20 vol. % or ((5 %, 10 %, and 15 % (v/v)), most of the emulsions show Newtonian behavior in all the range of shear rate. It was found that the viscosity is independent of shear rate or shear stress. The behavior of emulsions is Newtonian with a viscosity that depends largely on the external phase viscosity and the internal phase volume fraction Figures 4.26, 4.27 and Table 4.8 show the Newtonian phenomenon. Above 20 % (v/v) internal phase, emulsions exhibit non-Newtonian, pseudo- plastic behavior and the viscosity of emulsion is highly dependent on both shear rate and shear stress. This behavior is illustrated in terms of shear stress versus shear rate in Figure 4.28. As shown shear rate increases with increasing shear stress. Figure 4.29 gives the shear rate dependency on the viscosity for emulsions at various volume fractions. As revealed by the figure, beginning with 30 %, viscosity decreases like having the yield stress at low shear rate and then at high shear rate it becomes constant. The presence of a yield stress in water-in-oil emulsions has been reported experimentally by Yan et al. (1992). When the volume fraction is increased up to 70 %, the emulsions show shear-thinning behavior.

Table 4.8: Shear rate, shear stress, viscosity, and apparent viscosity for emulsion at (5-90 %, 10-90 %, and 15-85 %)

Shear rate γ (sec^{-1})	Shear stress τ (dyne/cm^2)	Viscosity (μ) at (5-95 %)	Viscosity (μ) at (10-90 %)	Viscosity (μ) at (15-85 %)	Apparent viscosity $\eta = \frac{\tau}{\gamma}$
12	5	70	89	108	0.42
20	8.4	61	79.5	98	0.42
26	11	55	71	92	0.42
30	12.6	49	66	80.4	0.42
40	16.8	38	53	72	0.42
45	18.9	32	47	64	0.42
50	21.1	27	40	50	0.42
58	24.4	18	30	42	0.42

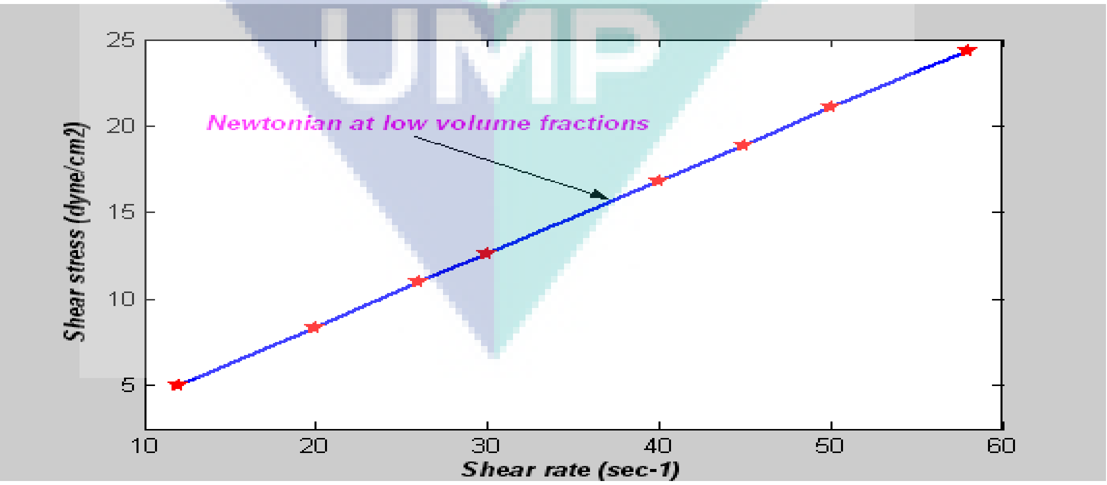

Figure 4.26 Emulsion behaviors at low volume fractions (shear rate versus share stress)

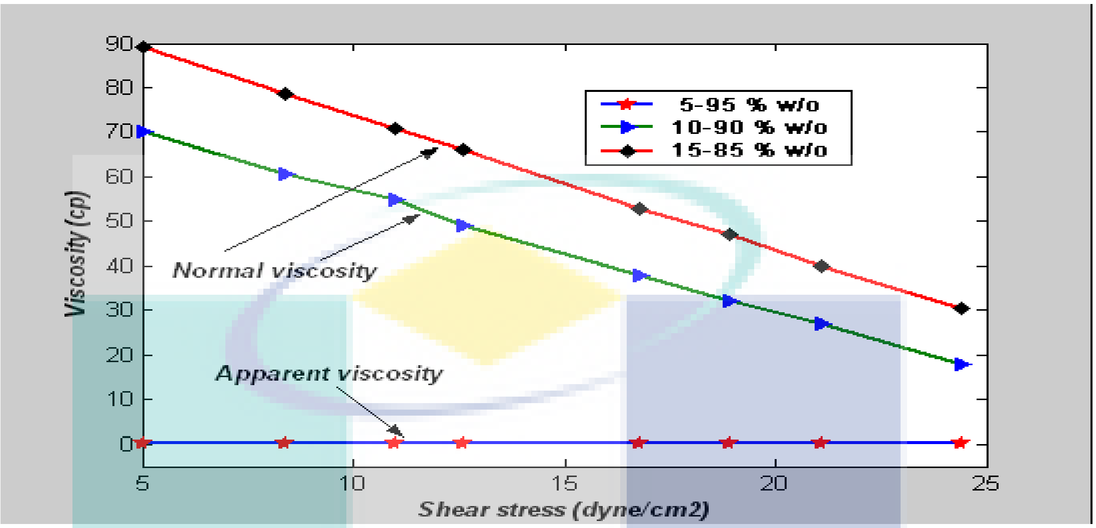

Figure 4.27 Emulsion behaviors at low volume fractions (viscosity versus shear stress)

The apparent viscosity is defined by the shear stress divided by shear rate. (The drop in volume fraction is increased; the drops are forced closer together until they become close and coalesced).

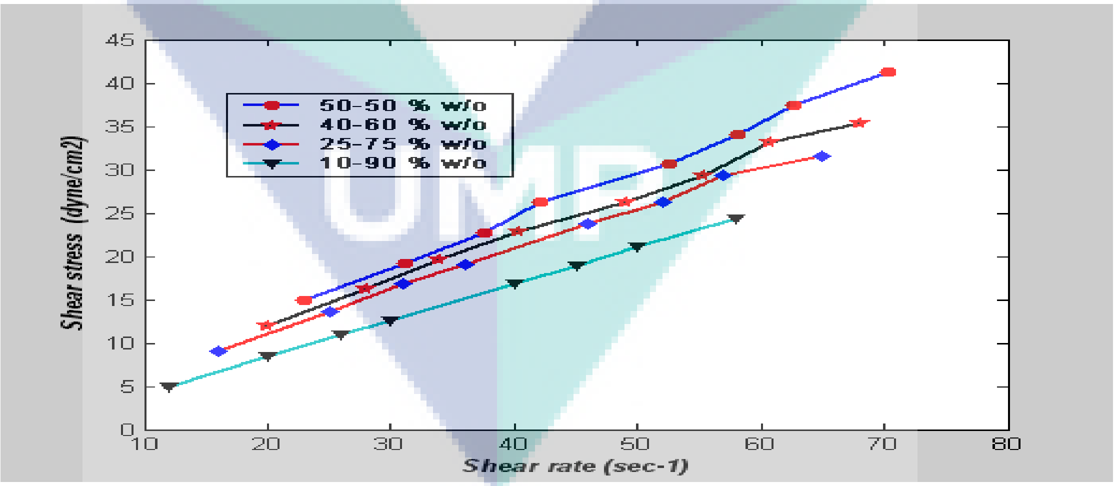

Figure 4.28 Shear rate versus shear stress for different emulsion dispersed volumes

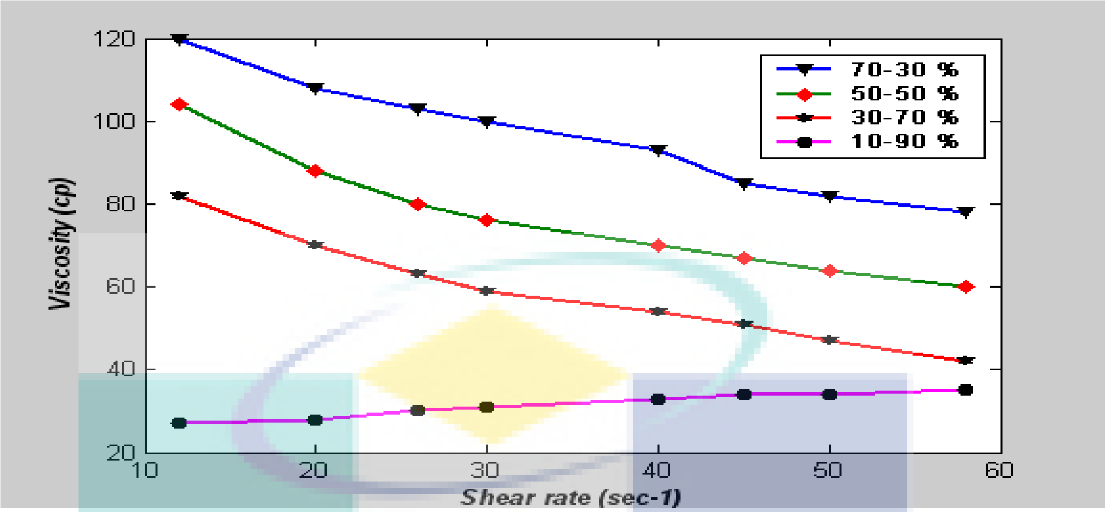

Figure 4.29 Viscosity versus shear rate for various emulsion dispersed volumes.

Table 4.9 shows the comparison of physicochemical properties from various crude oil fields. There are eight crude oils from different countries (Johansen et al., 1989; Sharma et al., 1982; Bhardwaj and Hartland, 1998; Koots and Speight, 1975; Chanda et al., 1998). The data in range values, which was obtained from several values in the literature. In general, the physicochemical properties of crude oil samples are not far different from each other's. For example, the density and viscosity of the crude oil samples are similar to Norwegian Continental Shelf crude oils, which vary from 0.79 to 0.89 g/cm^3 and 23.0 to 27.7 mNm^{-1}, respectively (Johansen et al., 1989). All of the crude oils show a correlation between the viscosity and pour point. The lower viscosity will give the lower pour point, and vice versa. The Norwegian Continental Shelf crude oils which have low viscosity (2.2 cp), obtained very low pour point (-50 ^{o}C). In contrast, the crude oils that have viscosity (Assam crude) give a high pour point (40 ^{o}C).

Table 4.9: Comparison of physicochemical properties from various crude oils.

Crude Oil	**Physicochemical Properties**					
	Density (g/cm^3)	**Viscosity (cp)**	**Surface tension (mNm^{-1})**	**Interfacial Tension (mNm^{-1})**	**Pour Point (°C)**	**Reference**
Indian waxy Crude oil	-	17.5-37.5	-	-	27.0-30.0	Chanda et al., 1998
Alberta crude oil (Canada)	0.81-0.96	-	-	-	-	Koots et al., 1975
Velden (Germany)	0.902	35	-	-	-	Bhardwaj et al., 1998
Norwegian Continental Shelf	0.79-0.89	2.2-42.0	23.0-27.7	21.0-28.0	-50.0-24.0	Johansen et al., 1989
Assam Crude Oil (India)	0.88-0.92	25.0-55.0	29.0-32.5	-	28.0-40.0	Sharma et al., 1982
Malaysian Crude Oil	0.78-0.87	3.0-8.8	25.0-30.0	27.0-36.0	-6.0-27.0	Bambang, P 2005

Tapis Crude Oil	0.811	11.68-20.73	24.6	28.3	2	This study (Table 5.7)
Masila + Khafji Crude	0.834	17.46-30.42	26.2	24.0	9	This study (Table 5.7)
Iranian Crude Oil	0.852	30.62-44.75	28.2	27.3	13	This study (Table 5.7)
Miri Crude Oil	0.793	6.22-14.54	23.3	25.6	-15	This study (Table 5.7)

4.4 Surfactant and Emulsion Stability

This section outlines observations on the ability of various surfactants to stabilize water-in-oil (w/o) emulsions. The earlier sections of this chapter discussed the studies of emulsion stability for those emulsions made in large quantities (900 ml). However, this section, on the other hand, reports on the related studies done on a smaller scale using a number of different surfactants (short chain and polymeric) surfactants. Table 4.10 shows descriptions of emulsions made by short chained surfactants, while Table 4.11 illustrates emulsions stabilized by polymeric surfactants. As shown in tables 4.10 and 4.11, it turns out that only very few of these surfactants provide emulsion stability compared to previous surfactants (Span 83, LSWR, Triton X-100, SDDS, and Span 80) which were used for the same purpose (emulsion stability), despite the common chemical attributes among all the surfactants including a large hydrophobic group and a smaller hydrophilic group.

The main reason for this is that surfactants that stabilize water-in-oil (w/o) emulsions rely on steric repulsion between interfaces by creating well-packed adsorbed layers at the interfaces. From results of tables 4.10 and 4.11 it appears that surfactants that can provide these well-packed layers are not so common.

Table 4.10: Emulsion Stability Using Short-Chained Surfactants

Emulsion	Surfactant	Oil phase	Water phase	Emulsion type	Emulsion stability
1	**Igepal DM-430**	Crude oil	Distilled water	w/o	low
2	-	Crude oil	Distilled water	w/o	low
3	-	Crude oil	Distilled water	w/o	low
4	**Arlacel 186**	Crude oil	Distilled water	w/o	high
5	-	Crude oil	Distilled water	w/o	high
6	-	Crude oil	Distilled water	w/o	high
7	**Igepal CA-210**	Crude oil	Distilled water	o/w	poor
8	-	Crude oil	Distilled water	o/w	poor
9	-	Crude oil	Distilled water	o/w	low
10	**Igepal CA-210**	Crude oil	Distilled water	w/o	high
11	-	Crude oil	Distilled water	w/o	med
12	-	Crude oil	Distilled water	w/o	med

Low = w/o emulsion formed but mostly coalesces in minutes or hours
High = w/o emulsion persists for 2 weeks with some coalescence noticeable
Poor = water drops not formed or o/w emulsion formed
Med = w/o emulsion persists for days

Table 4.11: Emulsion Stability Using Polymeric Surfactants

Emulsion	Surfactant	Oil phase	Water phase	Emulsion type	Emulsion stability
1	**Hypermer 2296**	Crude oil	Distilled water	w/o	high
2	-	Crude oil	Distilled water	w/o	high
3	-	Crude oil	Distilled water	w/o	high
4	**Tetronic 901**	Crude oil	Distilled water	w/o	low
5	-	Crude oil	Distilled water	w/o	med
6	-	Crude oil	Distilled water	w/o	low
7	**Pluronic 31R1**	Crude oil	Distilled water	o/w	poor
8	-	Crude oil	Distilled water	o/w	poor
9	-	Crude oil	Distilled water	o/w	low
10	**Hypermer B246 SF**	Crude oil	Distilled water	w/o	high
11	-	Crude oil	Distilled water	w/o	med
12	-	Crude oil	Distilled water	w/o	high

CONCLUSIONS:

It can be concluded that, this research was able to synthesis as well as formulates an environmentally friendly surfactant based on affordable raw materials. These raw materials include: some cooking oils (sunflower and canola), sorbitan fatty acid, polyol and fatty acid. Results of this study enabled the produced surfactant (NS-16-1) been tested as stabilizer. Results of NS-16-1 was compared with the current commercial surfactants. Finally, the NS-16-1 was scaled up its production from 60 Litre per day into 100 Liter per day. 2000 Liter from produced NS-16-1 was delivered into Scinomiq Company. NS-16-1 ready for fully commercialization.

The water-in-crude oil emulsions have great importance in the oil industry. The formation, production and stabilization of water-in-crude oil (w/o) emulsions are investigated over a wide range of parameters. These parameters are surfactant concentrations, temperature, stirring time, volume fraction of dispersed phase, phase ratio water-oil (10-90 %), and centrifugal acceleration (800-1800 rpm). The physical properties of water-in-crude oil emulsions in terms of density, viscosity, surface tension, and interfacial tension, pour point, pH were also measured. The SARA-Separation analysis was used to measure the surface-active molecules. The four SARA fractions are the Saturates (S), Aromatics (A), Resins (R), and the Asphaltenes (A).

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