

Surfactants as Demulsifiers

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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Approved by,

A handwritten signature in black ink, appearing to read 'Mazlin Bt Idress', is written over a solid horizontal line.

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ABSTRACT

In oil production, the generation of heavy oil/water emulsion can result in significant drop in the production rate due to the high viscosities of the emulsions. The strong agitation and mixing that takes place at the inlet of the well bore together with the presence of the naturally existing emulsifying agents in the crude contribute to the formation of emulsion. Water and oil emulsion formation presents an on-going production issue receiving considerable technical consideration. The formation of emulsion is ultimately cause economics problem, both in terms of expensive chemicals used and due to the daily production losses.

Effective separation of oil and water become an essential operation in order to ensure not only the quality of the crude oil is obtained but also the quality of separated water at the lowest cost. Due to these remarkable issues, there are number of methods that could be applied in order to mitigate these problems such as injection of surfactants into the formation and also surface treatment in order to disrupt the interfacial film and enhance the speed for emulsion breaking (chemical demulsification). Downhole demulsification of crude oil increases well production by reducing vertical flow pressure loss. There are also other major treatments like heating or electrocoalescence but they seem not so practical and effective.

The objective of this project is to identify and compare the results of different surfactants onto the emulsion particles. These will cover lots of samples to be tested during the separation test experiments. The results will show the effect of different surfactants on the rate of separation of crude oil and water from the emulsion. The better the separation, the better the demulsifier is. In spite of the volume of separation, the quality of the crude oil and water also been focused along running the experiments. Results of such trials have been discussed in this project that shows promising success.

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Last but not the least, my family and the one above all of us, the omnipresent God, for answering my prayers for giving me the strength to plod on despite my constitution wanting to give up and throw in the towel, thank you so much Dear Lord.

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CHAPTER 1

INTRODUCTION

1.1 Background of study

1.1.1 Emulsion

An emulsion is a thermodynamically unstable system consisting of at least two immiscible liquid phases, one of which is dispersed as globules in the other liquid phase, stabilized by the presence of emulsifying agent¹. Stable water in oil emulsions can occur at many stages during the production and processing of crude oils. The formation of these emulsions is mainly caused by high shear rates and zones of turbulence encountered at different points of production facilities especially at the wellhead in the choke valve⁵. These emulsions are generally stabilized by the presence of resins, asphaltenes, waxes and solids which play the role of natural emulsifier⁴.

Emulsions are part of a more general class of two-phase systems of matter called colloids¹. Although the terms colloid and emulsion are sometimes used interchangeably, emulsion tends to imply that both the dispersed and the continuous phase are liquid. In an emulsion, one liquid (the dispersed phase) is dispersed in the other (the continuous phase).

There are three types of emulsion which are simple emulsions (macro emulsions), multiple emulsions and micro emulsions³. Simple emulsions can be divided into O/W emulsion (droplets of oil dispersed in water) and W/O emulsion (droplets of water dispersed in oil) while multiple emulsions are W/O/W or O/W/O emulsions. In the oil industry, W/O emulsions are more common and O/W emulsions are sometimes referred as reverse emulsion. Multiple phases like W/O/W or O/W/O are more complex and consist of tiny droplets suspended or trapped in big droplets which suspended in a continuous phase.

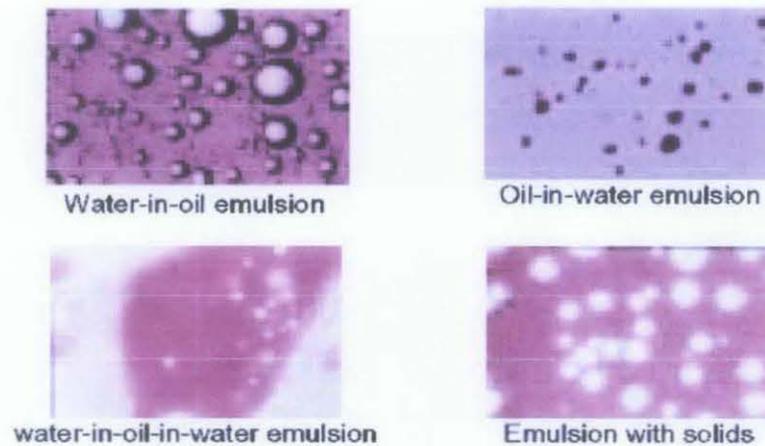


Figure 1.1: Photo Micrographs of Emulsions

Produced oil-field emulsions are classified based on their degree of kinetic stability as follows³:

Table 1.1: Degree of Kinetic Stability

Degree of Kinetic Stability	Descriptions
Loose emulsions	It will separate in short time (few minutes). The separated water is referred as 'free water'
Medium emulsions	It will separate in matter of ten minutes
Tight emulsions	It will fully or partially separate in matter of hours or even days

This kinetic stability is a consequence of small droplet size and the presence of an interfacial film around water droplets³. It is attained by stabilizing agents and these stabilizers will suppress the mechanisms of emulsion formation such as sedimentation, aggregation, coalescence, phase inversion and etc. (*Refer to Literature Review*). The stability of the emulsion is basically related to the ease of water separation (measured in time) and the dosage of demulsifier used.

1.1.2 Surfactants (Chemical EOR)

Surfactant is a surface active agent but do not necessarily lower interfacial tensions significantly. A surfactant will aggregate (self-assembles) in water or other solvent to form various microstructures such as micelles or bilayers⁴.

The usage of surfactant categorized under chemical EOR (tertiary recovery). Tertiary recovery is injection of fluids or chemicals not initially present in reservoir such as polymers and *surfactants*. This type of recovery objectively to increase the amount of oil that can be recovered thus be produced. Generally the main objective of EOR is to increase displacement efficiency. The relative permeability, which in turns depends on saturation, EOR involves mobility control that can change oil and water viscous and interfacial tension.

Each surfactant molecule has a hydrophilic (water-loving) head and a hydrophobic (water-hating) tail that repels water. Hydrophilic consist of nonionic polar groups such as hydroxyl portion of alcohol molecules while hydrophobic consist of nonpolar moieties such as repeating carbon-hydrogen (CH₂) units or carbon fluorine (CF₂) units.

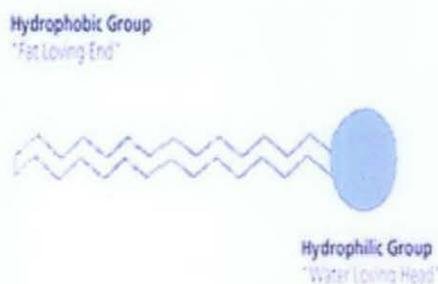


Figure 1.2: Hydrophobic and Hydrophilic Groups of Surfactant

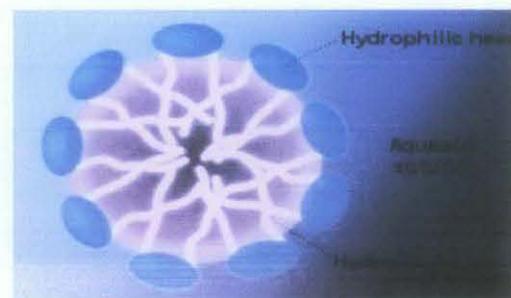


Figure 1.3: Hydrophobic head and Hydrophilic tail

From Figure 1.3, a micelle, the hydrophobic tails of the surfactant molecules remain on the inside of the micelle due to unfavourable interactions. The polar "heads" of the micelle, due to favourable interactions with water, form a hydrophilic outer layer that in effect protects the hydrophobic core of the micelle. The compounds that make up a

micelle are typically amphiphilic in nature, meaning that not only are micelles soluble in protic solvents such as water but also in aprotic solvents as a reverse micelle.

Surfactants may be divided into few groups which are ionic surfactants, zwitterionic surfactants and also nonionic surfactants². These classifications are based solely on the presence of formally charged groups in its head. A nonionic surfactant has no charged group in its head. The head of ionic surfactant carries a net charge whether positive (cationic) or negative (anionic). If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic. Some commonly encountered surfactants of each type include²:

- **Ionic**
- *Anionic*: based on permanent anions (sulfate, sulfonate, phosphate) or pH-dependent anions (carboxylate):
 - Sulfates (Alkyl sulfates, Alkyl ether sulfates)
 - Sulfonates (Docusates, Sulfonate)
 - Phosphates (Alkyl aryl ether phosphate, Alkyl ether phosphate)
 - Carboxylates (Alkyl carboxylates, Sodium lauroyl sarcosinate and Carboxylate fluorosurfactants)
- *Cationic*: based on permanently charged quaternary ammonium cation:
 - Alkyltrimethylammonium salts: cetyl trimethylammonium bromide (CTAB), cetyl trimethylammonium chloride (CTAC)
 - Cetylpyridinium chloride (CPC)
 - Polyethoxylated tallow amine (POEA)
 - Benzalkonium chloride (BAC)
- *Zwitterionic* (amphoteric): based on primary, secondary or tertiary amines or quaternary ammonium cation with:
 - Sulfonates:
 - CHAPS (3-[(3-Cholamidopropyl)dimethylammonio]-1-propanesulfonate);

- Sultaines: cocamidopropyl hydroxysultaine;
- Carboxylates:
 - Amino acids
 - Imino acids
 - Betaines: cocamidopropyl betaine;
- **Nonionic**
 - Fatty alcohols (Cetyl alcohol, Stearyl alcohol, Cetostearyl alcohol and Oleyl alcohol)
 - Polyoxyethylene glycol alkyl ethers
 - Octaethylene glycol monododecyl ether,
 - Pentaethylene glycol monododecyl ether;
 - Polyoxypropylene glycol alkyl ethers
 - Glucoside alkyl ethers (Decyl glucoside, Lauryl glucoside, Octyl glucoside)
 - Polyoxyethylene glycol octylphenol ethers
 - Polyoxyethylene glycol alkylphenol
 - Glycerol alkyl esters:
 - Polyoxyethylene glycol sorbitan alkyl esters

1.1.3 Emulsification

A stable emulsion consisting of two pure liquids cannot be prepared; to achieve stability, a third component, an emulsifying agent must be present. Generally, the introduction of an emulsifying agent will lower the interfacial tension of the two phases. Emulsions are thermodynamically unstable and the droplets have tendency to coalesce. To stabilize the droplets, emulsifying agents or emulsifiers are needed.

Natural occurring emulsifiers in the crude oil include asphaltenes and resins, organic acids and bases. These compounds are believed to be the main constituents of interfacial films which form around water droplets in an oilfield emulsion³. Mechanical stabilizers should also be taken into account because it can lead to the formation of emulsion. The example of mechanical stabilizer is fine solids. These fine solids found in clay

particles, sand, asphaltenes and waxes, corrosion products, mineral scales and drilling muds. Emulsification formation processes are also influenced by fluid mixing, shear, turbulence diffusion, surfactant aggregation, steric stabilization, temperature and pressure¹¹.

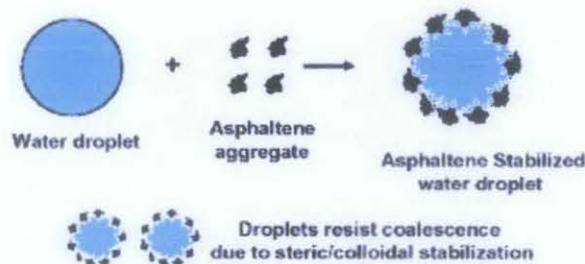


Figure 1.4: Mechanism of emulsion stabilization by asphaltenes

1.1.4 Demulsification

Demulsification is the process of breaking crude oil emulsion into two phases which are oil and water phases³. The process of demulsification is based on modifying the interface properties of the stable emulsion bubbles so as to cause the bubbles to coalesce and form a continuous phase⁷. The oil producer is interested in two aspects of demulsification which are;

- a. The rate or the speed at which the separation takes place
- b. The amount of water left in the crude oil after separation

Demulsifiers also known as emulsion breakers are functionally neutralized the natural surface-active agents. Demulsifiers will break the emulsifying rigid films, promote coalescence and accelerate oil water separation. Demulsifiers are chemicals that contain solvents (benzene, toluene, xylene, short-chain alcohols, heavy aromatic naphtha), surfactants flocculants and wetting agents³. Interfacial tension can be reduced by using

surfactants which enhance stability of emulsion and promote the creation of small droplets. Studies have concluded that emulsion stability is not totally dependent on the interfacial tension value but on the interfacial film properties¹¹.

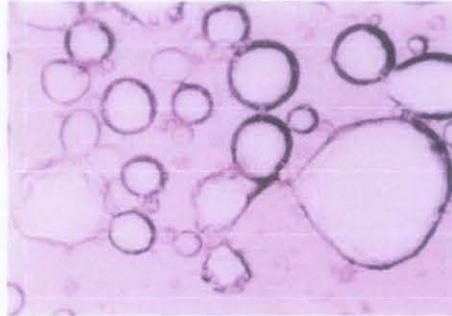


Figure 1.5: Emulsion resolution after addition of demulsifier

In the oil industry crude oil emulsions must be separated almost completely before undergoing transportation process. Emulsion separation into oil and water involve destabilization of emulsifying films around water droplets. This process is accomplished by using any or combination of the methods below:

- Reduce flow velocity that creates gravitational separation of oil, water and gas. (using large volume separators and desalters)
- Add chemical demulsifiers like surfactants
- Increase the temperature of emulsion
- Apply electrical fields that promote coalescence
- Change the physical characteristics of emulsions

(All these methods will be discussed in details in Chapter 2 – Literature Review)

1.2 Problem Statement

Produced water occurs in two ways; some of the water may be produced as free water and other may be produced in the form of emulsions. Emulsions are difficult to treat and will cause many operational problems such as tripping of separation equipment in gas-oil separating plants, production of off-spec crude oil, and creating high pressure drop along the flow lines.

It has always been a challenging task to efficiently break up this emulsion to separate the oil droplet from the water phase or vice versa. The most practical method nowadays are by applying chemical to the wellbore but the result are not sustained in a long period of time and also cause environmental problems. Some chemicals had proven to be a good demulsifier but in future these chemicals will lead to other problems like scale precipitation and paraffins that will cause declining in production.

1.3 Objectives

Due to the problems that stated above, these are the objectives that being drawn throughout this project and hopefully being achieved.

- To obtain the result of the usage of different surfactants and chemicals on the emulsion stability.
- To recommend the best demulsifier by evaluating the performance of different surfactants and chemicals.

1.4 Scope of study

Techniques of emulsion breaker have advanced significantly, over the past few years. There are several methods available currently including thermal, mechanical, electrical and chemical methods. The scope of study will focus on the chemical method which includes research from books and journals on the use of different kind of surfactants and chemicals as demulsifier. After doing some data gathering and analysis, the project will be continued by experiments to obtain the necessary results and findings. These will involve few analytical calculations, theories and literature reviews and laboratory experiments. At the end of these studies, the best combination of chemicals (demulsifier) of handling the emulsions will be recommended.

Chapter 2

LITERATURE REVIEW

2.1 Properties of Emulsions

Oilfield emulsions are characterized by several properties like appearance, basic sediment and water (BSW), size of droplet, bulk and interfacial viscosities, conductivities and etc. Some of the properties are described below³.

- *Drop Size and Drop size Distribution*

Produced emulsions generally have droplet size of greater than $0.1\ \mu\text{m}$ and can exceed up to $50\ \mu\text{m}$. Distribution of droplet size can be viewed in Figure 2.1. Sunil Kokal *et al*³ reported that the droplet size distribution in an emulsion depends on a number of factors including the IFT, shear, nature of emulsifying agents, presence of solids, and bulk properties of oil and water. By rule of thumb, the smaller the average size of the water droplets, the longer the residence time required to separate the emulsions.

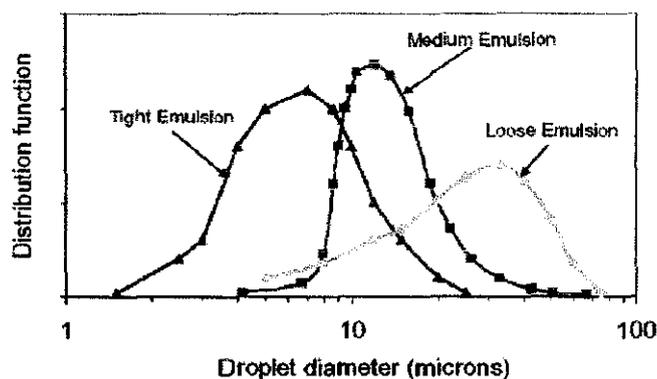


Figure 2.1: Droplet Size Distribution of Petroleum Emulsions

- *Viscosity of Emulsions*

Viscosity of emulsions is higher than either viscosity of oil or water. This is because emulsions show non-Newtonian behaviour due to droplet ‘crowding’ or structural viscosity³.

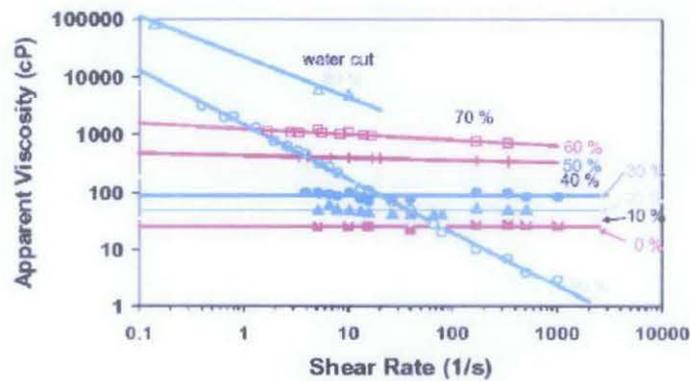


Figure 2.2: Viscosities of very tight emulsions at 125°F at different water cut percentage

This figure indicates that emulsion exhibit Newtonian behavior up to only 30% water cut. Beyond this limit, the slope of the curves starts to deviate from zero indicating non-Newtonian behavior. The behavior of non-Newtonian will result to decline in viscosity with increasing shear rates. From the graph, the very high viscosities achieved as water cut increases up to 80%. Up to 80% water cut, the emulsion is water in oil emulsion, at 80% the emulsion inverts to oil in water emulsion and at last, at water cut above 90% multiple emulsions occur (water in oil in water). The viscosity of emulsion depends on a number of factors³:

- Viscosities of oil and water
- Volume fraction of water dispersed
- Droplet size distribution
- Temperature
- Shear rate
- Amount of solids present

2.2 Factors Affecting Stability of Emulsions

There are few important factors that will affect the stability of emulsions including:

- *Heavy polar fraction in crude oil*

These include asphaltenes, resins and oil soluble organic acids like carboxylic acid. Sunil Kokal *et al* reported that these compounds are the main constituents of the interfacial films surrounding the water droplets that give the emulsions their stability.

Asphaltenes have surface active characteristics that making them as a good emulsifier. The accumulation of asphaltenes at the interface results in the formation of rigid film³. When this rigid film is formed, it will automatically act as a barrier to drop coalescence. For two drops to coalesce together, the film has to be drained and ruptured. The presence of asphaltenes will retard the drainage of the film. The primary mechanism involved in this retardation is the steric repulsion or hindrance caused by the high molecular weight material in the film³.

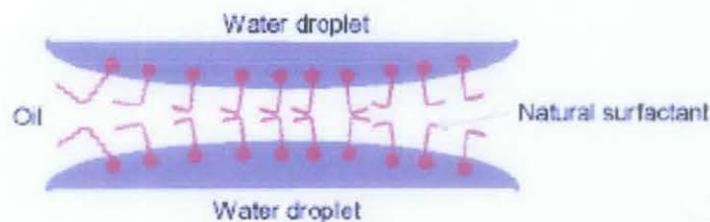


Figure 2.3: Steric repulsion between two water droplets that retards film drainage and coalescence

From the above figure, it shows steric repulsion produced by the interaction between the non-polar or hydrophobic groups (water-love). This steric repulsion will maintain or sustain the interface at a distance to prevent coalescence to be occurred. This will also result in the increment in interfacial viscosity and apparent viscosity of oil in the film between the water droplets.

Resins are complex high molecular weight compounds that are not soluble in ethylacetate but are soluble in n-heptane³. Resins have strong tendency to associate with asphalthenes and they will form a micelle that will stabilize the emulsions well. The asphaltene-resin ratio in crude oil is really crucial and responsible for the stability of emulsions.

Waxes are the high molecular weight paraffin substances present in the crude oil that crystallize out when the oil is cooled below its cloud point³. Waxes itself cannot form emulsions but when it get interact with asphalthenes, it helps to stabilize the emulsions.

- *Solids*

Fine solid particles also contribute to the formation of emulsions. The effectiveness of these solids in stabilizing emulsions depends on factors such as particle size, inter-particle interactions and the wettability of solids³. Solid particles help in formation of emulsions by diffusing to the oil-water interface and prevent coalescence. To act as emulsion stabilizers, the size of the particles should be smaller than the emulsion droplets size.

Regarding the wettability factor, the solid should be wetted by both water and oil phases in order to create emulsion. As example if the solid is oil wet, thus water in oil emulsion will be result. This oil wet characteristic will prevent the water droplet to be coalesced and so do happen to water wet in opposite situation. Examples of oil-wet solids are asphalhenes and waxes while for water-wet solids; inorganic scales, clays and sand.

- *Temperature*

Temperature affects the physical properties of oil, water, interfacial films, and surfactant solubilities in the oil and water phase³. The most important effect of temperature is on the viscosity of emulsions which will be decrease with every single increase in

temperature. Temperature will increase thermal energy of a system, thus will increase the number of drop collisions.

- *Droplet size*

Emulsion droplet sizes range from less than a microns to over 50microns. Basically, the smaller the droplet size, the more stable it will be. For water to separate from emulsions, the water droplets have to coalesce with each other and the smaller the droplet size, more time consuming to reach the separation phase.

- *pH*

pH influences the type of emulsion formed³. Acid or low pH generally produces w/o emulsions whereas high pH will produce o/w emulsions.

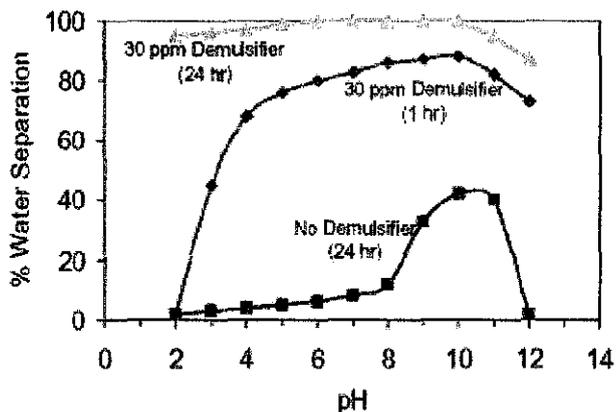


Figure 2.4: Effect of pH and demulsifier concentration on emulsion stability

This figure shows the effect of pH on emulsion stability and it results that the optimum pH for no demulsifier solution is 10 while the addition of demulsifier will promise almost 100% water separation at pH ranges from 2-12. It concludes that demulsifier speed up the demulsification process within one day.

2.3 Demulsification

2.3.1 Destabilizing Emulsions

Produced oil-field emulsions possess a degree of kinetic stability. This stability arises from the formation of interfacial film around the water droplets. To break the emulsion, the interfacial film has to be destroyed and lead to the coalescence of the droplets. The factors that enhance the emulsion breaking include; increasing temperature, reducing agitation or shear, increasing residence time, solids removal, and by controlling of emulsifying agents.

2.3.2 Mechanisms Involved in Demulsification

Demulsification is the separation of an emulsion into its component phases. It can be seen clearly with two step processes which are flocculation or aggregation and coalescence.

- *Flocculation or Aggregation* – the situation when the droplets will clump together and forming aggregates. Coalescence at this stage may be happened if the interfacial film around the water droplets is weak. The rate of flocculation depends on a number of factors including watercut, temperature, viscosity of the oil, and the density difference between the oil and water³.
- *Coalescence* – this is the second step in the demulsification process. During coalescence, water droplets will fuse and coalesce together to form a larger drop. It involves interfacial film thinning leading to film rupture¹¹. This is an irreversible process that leads to a decrease in number of water droplets and eventually to complete demulsification. Coalescence is enhanced by a high rate of flocculation, absence of mechanically strong films, high interfacial tension, low oil and interfacial viscosities, high watercuts and high temperature.

2.3.3 Demulsification Methods

All the methods that have been introduced (*refer to Chapter 1*) can be divided into four different groups which are; thermal methods, mechanical methods, electrical methods and chemical methods. The most common methods for emulsion treatment are the application of heat and appropriate chemical demulsifier³. The author will briefly discuss and explain about all types of methods but the one that will be used throughout this project is chemical methods.

- *Thermal Methods* – by heating the emulsion, it will speed up the breaking and separation process because it reduces the viscosity of oil and increase the water settling rates. Increase in temperature result in the destabilization of the rigid film due to decrease in interfacial viscosity. When the emulsion is been heated, thermal energy of the system will increase, thus the frequency of coalesce to occur also increased.
- *Mechanical Methods* – there are lot of equipments that available as emulsion breaker. These include free water knock out drums, two and three phase separators, desalters and settling tanks. This method is surface based prevention or separation.
- *Electrical Methods* – it is generally theorized that water droplets have a charge associated and when an electric field is applied, the droplets move about rapidly and collide with each other³. This electric field also disturbs the interfacial rigid film by rearranging the polar molecules and weakening the tight film and enhances coalescence.

Electrostatic dehydration is generally used in conjunction with other methods like chemical and heat addition. It is very seldom that this method is used alone in breaking the emulsions.

- **Chemical Methods**

This is the most common method for breaking the emulsions and this method is also called as demulsifiers. These chemicals are designed to neutralize the effect of emulsifying agents that stabilize the emulsions³. Demulsifiers are surface active compounds and when it mixed with emulsion, it will rupture or weaken the rigid film and coalesce will occur.

Sunil Kokal *et al* reported that the optimum emulsion breaking with demulsifier requires; proper selected chemical for the given emulsion, adequate quantity of this chemical, adequate mixing of the chemical in the emulsion, sufficient retention time in emulsion treaters, and addition of heat, electric grids, coalescers to completely resolve the emulsions.



Figure 2.5: Film drainage in the presence of demulsifiers which displace the natural surfactants

Destabilization is accomplished by reducing the interfacial tension at the emulsion interface. In order to destabilize the interfacial film surrounding the dispersed water, a demulsifier should have strong attraction to the interface, have balanced partitioning between the water and the oil phase, be able to diffuse through the emulsion efficiently and be able to promote film thinning¹¹.

After concentrating at the interface, it should weaken the stabilizing agent and attract other droplets strongly to form flocs or aggregates¹⁴. In some emulsions, fine solids such as iron sulfide, silt, clay will act as stabilizing agents, thus in spite of the demulsifier should weaken the interfacial film, it also has to destabilize such emulsions by changing the wettability of the solids to be dispersed either in water or oil phase.

Demulsifiers additives have been developed using organic compounds such as surfactants and solvents and also inorganic materials such as salts and acids¹¹. One of the common chemicals used are from alcohol groups like nonyl phenol and t-butyl phenol. Other than these common demulsifiers, there are also blended chemicals as demulsifier since it is known that a single chemical compound cannot possess all the features to be a good demulsifier and solve any emulsion problems just by using one type of chemical.

Therefore, the industries have come out with blended chemicals as demulsifiers and still running the experiments to obtain the best combination of chemicals. The examples of formulated demulsifiers¹⁴ are A - blend of xylene, toluene, naphthalene and light aromatic naphtha, B - Oxyalkylated alkyl phenol/formaldehyde resin in aromatic solvents in 1, 2, 4 - trimethylbenzene, naphthalene, naphtha with diesel and C - Blend of light aromatic naphtha, 1,2,4 - trimethyl benzene aliphatic alcohols, alkylbenzene sulphonic acid, alkylbenzene and light aromatic naphtha.

In this project, the main components that will be used to become demulsifiers are the surfactants. There are two types of surfactants that will be tested; both from ionic surfactant groups which are from sulfates and sulfonates. These two surfactants are Sodium Dodecyl Sulfate and Alkyl Benzene Sulfonate. In addition, the above chemicals will be taking into consideration since these chemicals have been chosen and proposed by industries, therefore they might be used as minor catalyst in these surfactant solutions.

2.4 Treatment Methods for Surfactants

The use of surfactant in the field can vary from very expensive treatment such as surfactant flooding onto the reservoir, to moderate cost as in stimulation and wettability reversal treatment and to a low cost as in surface injection of surfactant to break down the produced emulsion⁷.

2.4.1 Formation Injection

This is the most practical and common method used worldwide. A typical treatment would be to inject surfactant with diesel as a carrier fluid. However this method has disadvantages in terms of emulsion destabilization and also the incompatibilities with the naturally occurring surfactants in reservoir itself. If using the wrong surfactant or surfactant concentration, it can lead to development of emulsion. This may explain why in some cases of surfactants treatments, the result becomes worsen.

2.4.2 Chemical Injection into Gas Lift Line

Another phase of emulsion formation will be occurred at the entry point of gas lift systems. There will be maximum energy in the form of agitation generated at this point. The formation of the emulsion at this point will increase the weight of fluid and causes backpressure on the formation thus will increase the drawdown and reduce the production rate.

One case study at Bahrain field, the surfactant was injected into the gas-lift stream at the wellhead using high pressure injection pump. As gas enters the tubing through gas lift mandrel, the emulsion occurred is broken down. However, the rate for surfactant injection should be optimized and it is based on trial and error.

2.4.3 Solid Surfactant

There are heavy wax-based surfactant sticks that are 2" diameter and 18" length and can be dropped into the wellbore periodically which will dissolve along the flow from top of tubing to the perforation area. The dissolving process will reduce the interfacial tension between water and oil hence improving oil water separation in tubing.

2.4.4 Surface Treatments

There is also one of the most common methods where surfactants will be injected to the flowing stream at the wellhead or at the well manifold to improve oil-water separation. In wintertime, flowing stream is further circulated into oil heater to improve separation since temperature is one of the accelerated properties. This method is also on trial and error basis.

Chapter 3

METHODOLOGY

3.1 Project Flow Activities

3.1.1 Theoretical Studies and Literature Reviews

From the theoretical studies, facts and theories related to emulsion formation and destabilization will be obtained and collected. Literature sources such as experimental studies, journals and reference books will be the main sources to identify the concept of emulsions formation, diagnosing the different cases of emulsions occurrence, and *different techniques for emulsions prevention*. All the facts that related to the scope of studies will be reviewed and further on will be analyzed. This part is very crucial since this is the kick point of this project that will determine next approaches or procedures.

3.1.2 Data Analysis and Interpretations

In this section, further discussion and analysis will be completed regarding the available techniques to be used as emulsions prevention which will focus more on surfactants treatment. The using of surfactants to the emulsions breaker will be the major concern in this section. The selection of chemicals and surfactants for testing purposes will be done according to the several criteria such as properties of these chemicals, effectiveness and adaptability to the hydrocarbon in the formation or wellbore. With the aid of these theories, the experiments might be continued to obtain the performance of these surfactants.

3.1.3 Experimental Setup and Procedures

The experimental work was performed under constant temperature 28°C (room temperature) and water content approximately 70% volume. The demulsifiers tested will be varies from 1000 to 5000 ppm concentration and 2 to 5 ml of volume. While the emulsion sample per test will be fixed as 5ml in volume. The test will be conducted and the results will be taken in 15minutes, 30minutes, 1hour, 2hours and 24hours. There are six demulsifiers that been tested and the details will be listed in the table below:

Table 3.1: Descriptions of Demulsifiers

Demulsifier A	Toluene
Demulsifier B	Phenol
Demulsifier C	Sodium Dodecyl Sulfate (SDS)
Demulsifier D	Alkyl Benzene Sulfonate (AOS)
Demulsifier E	SDS + 0.05ml toluene + 0.05ml phenol
Demulsifier F	AOS + 0.05ml toluene + 0.05ml phenol

3.1.3.1 Preparation of Emulsion Samples

Emulsion will be made by mixing 70ml of NaOH solution 0.9wt% (emulsion stabilizer) and 30ml of crude oil. This mixture will be agitated by mixer for 5-10 minutes. This sample will be kept in a funnel for 30 minutes to allow the free water to settle. The bottom valve of the funnel was then opened to let the free water out to obtain pure emulsion. At the end of this part, water and crude oil content in emulsion will be calculated by using below formulas.

Volume of NaOH solution (ml) = x

Volume of crude oil (ml) = y

Total mixture (ml) = x + y

Vol of NaOH solution drained off (ml) = a

Vol of crude drained off (ml) = b

Vol of emulsion (ml) = Total mixture - (a + b)

Water content in emulsion (ml) = (x - a) / (vol of emulsion)

Crude oil content of emulsion (ml) = Vol of emulsion - Water content in emulsion

Therefore, from the above calculation we could approximate the volume of water content and also the volume of crude oil content in the pure emulsion. These data are very important to be noted since it will be used at the end of calculation in order to measure water separated and crude oil separated.

3.1.3.2 Preparation of Demulsifier Solution

There are two surfactants from ionic groups will be tested in this project which are Sodium Dodecyl Sulfate (SDS) and Alkyl Benzene Sulfonate (AOS) and the other two chemical bases which are phenol and toluene. These two surfactants have been chosen due to the availability in the market and both surfactants are for testing purposes rather than other surfactants which are not so compatible for testing.

Surfactants solution will be prepared according to specified concentrations which are 1000ppm, 2000ppm, 3000ppm, 4000ppm and 5000ppm. These concentrations have been drawn according to the recent tested surfactants in tertiary recovery whilst for secondary recovery, basically the surfactant concentration will be around hundreds ppm. Meanwhile for toluene and phenol, they will be diluted in a range of 100ppm to 500ppm. Each demulsifier will be prepared in 50ml of volume to ease the retesting purposes later on.

The formulas to prepare the surfactant solutions are like below;

X ppm =

$$\left[\frac{\text{(amount of surfactant/toluene/phenol in grams)}}{\text{(amount of distilled water in ml)}} \right] * (10^6)$$

3.1.3.3 Samples Testing

After the emulsion and demulsifier solution have been prepared, then sample testings can be started. The emulsion approximation of 5ml in volume will be placed in 10ml test tubes and later on the demulsifiers were added to the test tubes according to their concentrations and volumes. The tubes then were put in a centrifuge running at 2000rpm for a period of 10 minutes to ensure fully mixing between emulsion and demulsifiers.

The volumes of each of the separated oil and water phases were measured and taken in periodic of time 15minutes, 30minutes, 1hour, 2hours and 24hours. These periodic of time taking were drawn in order to measure and obtain which demulsifier will give fast reaction result (in 15 minutes) and highest separation result (in 24hours). Finally, all these factors will put into consideration and the best demulsifier will be chosen based on their best performance.

3.1.3.4 Data Calculation and Analysis

The data that will be collected are the final volume of water column and crude oil column in the test tubes. All these volumes will be calculated and the values will be in percentage forms. The details of the calculation will be presented on the next section and they differ according to different demulsifiers. The table below is an example of spreadsheet data obtained;

Table 3.2: Water and Crude Oil Separation

Vol of Emulsion (ml)	5.0
Estimated Vol of Water (ml)	3.5
Estimated Vol of Crude (ml)	1.5
Vol of Demulsifier tested (ml)	5.0

Water Separation					
Sodium Dodecyl Sulfate (SDS)	0.25h	0.5h	1h	2h	24h
1000ppm	5.71%	8.57%	10.00%	11.43%	34.29%
2000ppm	5.71%	7.14%	10.00%	12.00%	34.29%
3000ppm	14.29%	19.43%	21.43%	25.71%	38.57%
4000ppm	14.29%	15.71%	22.86%	28.57%	45.71%
5000ppm	8.57%	14.29%	18.29%	25.71%	51.43%
Crude Separation					
Sodium Dodecyl Sulfate (SDS)	0.25h	0.5h	1h	2h	24h
1000ppm	8.00%	10.00%	10.00%	15.33%	24.00%
2000ppm	8.00%	10.00%	9.33%	16.67%	26.00%
3000ppm	9.33%	9.33%	10.00%	18.00%	28.00%
4000ppm	9.33%	11.33%	12.00%	19.33%	30.00%
5000ppm	10.67%	12.00%	12.67%	20.00%	32.67%

The procedures of getting the volume of the water and crude are by reading from the 10ml measuring cylinder.

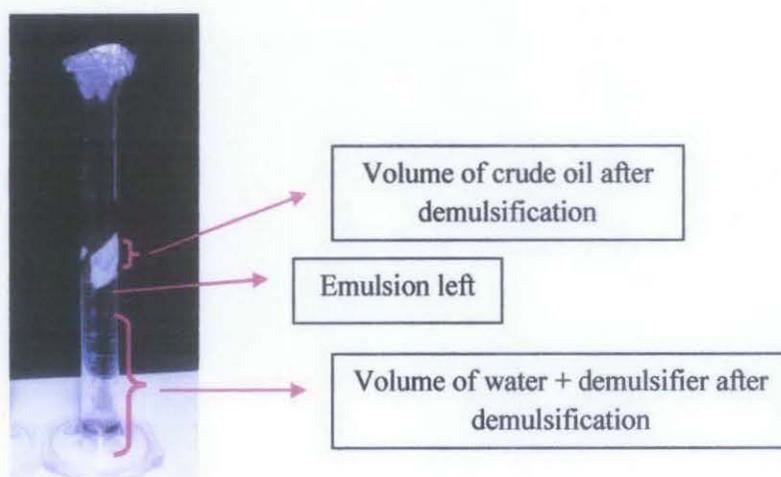


Figure 3.1: Emulsion Sample

Estimation Volume of Crude Oil and Water after Demulsification

When dealing with toluene and phenol (oil based catalysts), there will be addition or errors in volume of crude oil after separation and same goes to volume of water after separation when dealing with SDS and AOS solutions (water based catalysts). Here

initial volume of demulsifier should not be neglected because it will affect final volume of water and crude oil.

Below is an example of calculation for water and crude oil separation using SDS solution. This method of calculation applied to sample testings using SDS and AOS solution.

Before Separation;

Emulsion tested (~70% WC) = 5ml Expected water content = 3.5ml

SDS added = 5ml Expected crude oil content = 1.5 ml

After separation;

Oil column = 1.2ml

Water + SDS column = 7.2 ml

Remaining emulsion = 1.6 ml

Therefore, percentage of water and crude oil separated are;

$$\% \text{ water separated} = (7.2\text{ml} - 5\text{ml}) / (3.5\text{ml}) = 62.86\%$$

$$\% \text{ crude oil separated} = (1.2\text{ml}) / (1.5\text{ml}) = 80.00\%$$

Below is an example of calculation for water and crude oil separation using phenol. This method of calculation applied to sample testings using toluene and phenol.

Before Separation;

Emulsion tested (~70% WC) = 5ml Expected water content = 3.5ml

Toluene added = 1ml Expected crude oil content = 1.5 ml

After separation;

Oil + toluene column (1/2) = 1.80 ml

Water + toluene column (1/2) = 3.65 ml

Remaining emulsion = 0.55 ml

Approx crude oil separated = (1.8ml – 0.5*1ml) = 1.3 ml

Approx water separated = (3.65ml – 0.5*1ml) = 3.15 ml

Therefore, percentage of water and crude oil separated are;

$$\% \text{ water separated} = (3.15\text{ml}) / (3.5\text{ml}) = 90.00\%$$

$$\% \text{ crude oil separated} = (1.3\text{ml}) / (1.5\text{ml}) = 86.67\%$$

3.1.3.5 Modification of Demulsifier Solution

Due to the application of phenol and toluene in a large amount of quantity will cause contamination to the crude oil and also caused environmental problems, thus modification of demulsifier has been made. Combination of demulsifiers will be made in this following order.

Demulsifier E = SDS + 0.05ml toluene + 0.05ml phenol (blended)

Demulsifier F = AOS + 0.05ml toluene + 0.05ml phenol (blended)

For above demulsifiers, the method of calculating for water and crude oil separation is same like SDS and AOS method. This is because the volume of toluene and phenol added are very small and assumes to be negligible.

Below is an example of calculation for water and crude oil separation using Demulsifier F solution. This method of calculation applied to sample testings using Demulsifier E and Demulsifier F solution.

Before Separation;

Emulsion tested (~70% WC) = 5ml

Expected water content = 3.5ml

Demulsifier added = 5ml

Expected crude oil content = 1.5 ml

After separation;

Oil column = 1.28ml

Water + SDS column = 8.10 ml

Remaining emulsion = 0.62 ml

Therefore, percentage of water and crude oil separated are;

$$\% \text{ water separated} = (8.1\text{ml} - 5\text{ml}) / (3.5\text{ml}) = 88.57\%$$

$$\% \text{ crude oil separated} = (1.28\text{ml}) / (1.5\text{ml}) = 85.33\%$$

3.1.3.6 Result Analysis and Finalization

For this section all the data will be analysed and at the end the best demulsifier will be known due to the best capabilities to separate water and crude oil from the emulsion. Each demulsifier tested will give different values and therefore with the aid of graphs we could see clearly which demulsifier promised best results. Some demulsifiers might be good in separating the water from emulsion but not to crude oil separation. Thus, the highest separation obtained for both water and crude oil and also considered about the environmental impact, one demulsifier will be chosen. Example of graph for the results is like below;

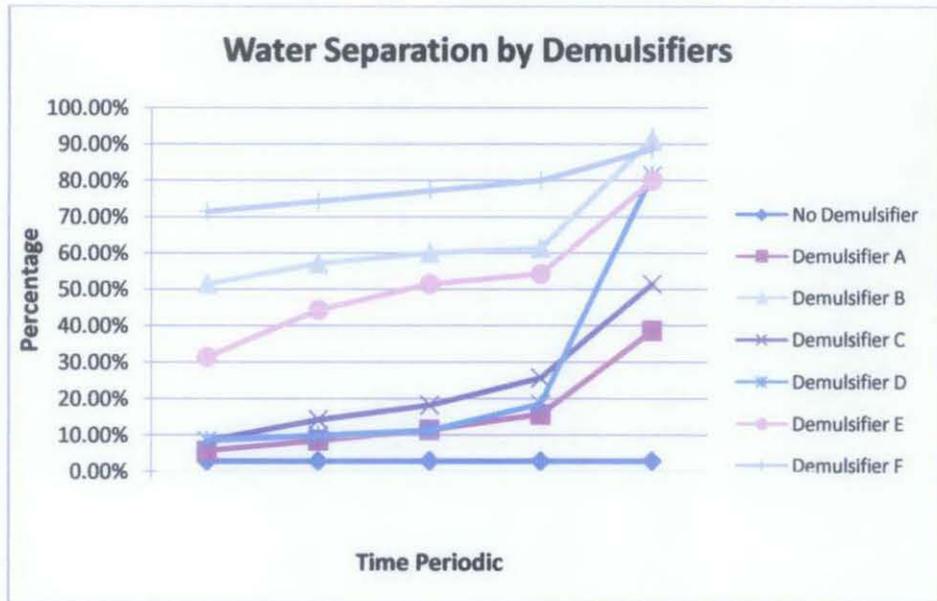


Figure 3.2: Water Separation by Demulsifiers

3.2 Project Flow Chart

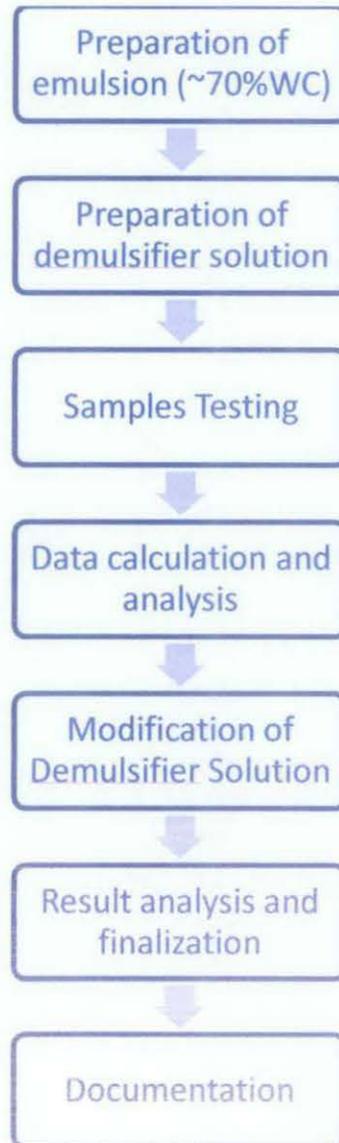


Figure 3.3: Project Flow Chart

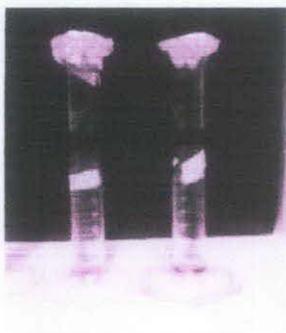
3.3 Gantt Chart

Table 3.3: Gantt Chart

Activities\Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Preparation for emulsion	■	■	■											
Preparation for Demulsifier Solution (SDS,AOS,toluene and phenol)	■	■	■	■										
Samples testing			■	■	■	■	■	■	■					
Data calculation and analysis				■	■	■	■	■						
Modification of Demulsifier Solution					■	■	■	■	■					
Result analysis and finalization						■	■	■	■	■	■			
Progress report								■	■					
Interim Report											■	■	■	
Oral presentation														■

3.4 Tools and Equipments

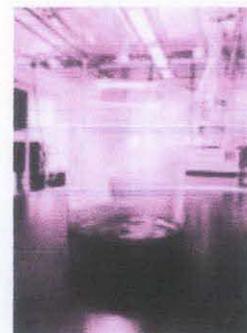
In this experiment, there are only few apparatus and chemicals used. Below are the lists and the pictures of each apparatus and chemicals;



Measuring Cylinder 10ml



Measuring Cylinder 10ml



Beaker 200ml



Mixer



Sodium Dodecyl Sulfate (SDS)



Alkyl Benzene Sulfonate (AOS)



Phenol



Sodium Hydroxide



Toluene

Chapter 4

RESULTS & DISCUSSIONS

During the separation tests, there are six demulsifiers tested and they are labeled as Demulsifier A, Demulsifier B, Demulsifier C, Demulsifier D, Demulsifier E and Demulsifier F. The addition of these demulsifiers will break the interfacial film or in other words it will speed up the interfacial film thinning. The table below presents the details of each demulsifier.

Table 4.1: Details of Demulsifiers

Type of Demulsifier	Description	Volume Tested	Concentration Tested
Demulsifier A	Toluene	1-2ml per 5ml emulsion sample	100-500ppm
Demulsifier B	Phenol	1-2ml per 5ml emulsion sample	100-500ppm
Demulsifier C	Sodium Dodecyl Sulfate (SDS)	2-5ml per 5ml emulsion sample	1000-5000ppm
Demulsifier D	Alkyl Benzene Sulfonate (AOS)	2-5ml per 5ml emulsion sample	1000-5000ppm
Demulsifier E	SDS + 0.05ml toluene + 0.05ml phenol	2-5ml per 5ml emulsion sample	1000-5000ppm
Demulsifier F	AOS + 0.05ml toluene + 0.05ml phenol	2-5ml per 5ml emulsion sample	1000-5000ppm

The demulsifiers have been tested according to certain parameters such as volume, concentration and also time-periodic of taking the data. The first four demulsifiers were tested and some modifications have been made and thus combination of chemicals and surfactants created Demulsifier E and F. The modification has been made due to few purposes; accelerate speed of emulsion breaking, avoid contamination with the crude oil and environmental issues.

Throughout this experiment, the results that will be obtained are amount of water separated and also amount of oil separated. Most of the experiments done in the

industries mainly focus on the water separation but not oil separation. Through development of the demulsifier, some of the chemicals might be able to separate water effectively from the emulsion but not crude oil. Therefore by taking into accounts both rate of separation is the most practical way.

4.1 Volume of Demulsifier

Water and crude oil separation increase with increasing volume of demulsifier (surfactant loading) added to the emulsion. It means that too little demulsifier will leave the emulsion unresolved and partially react with the emulsion. On the other hand, if too high dosages of demulsifier are applied, it also may cause the emulsion become more stable and thus the rate of separation will be low. The graphs below represent water and crude oil separation by Sodium Dodecyl Sulfate (**Demulsifier C**) with 1000ppm concentration.

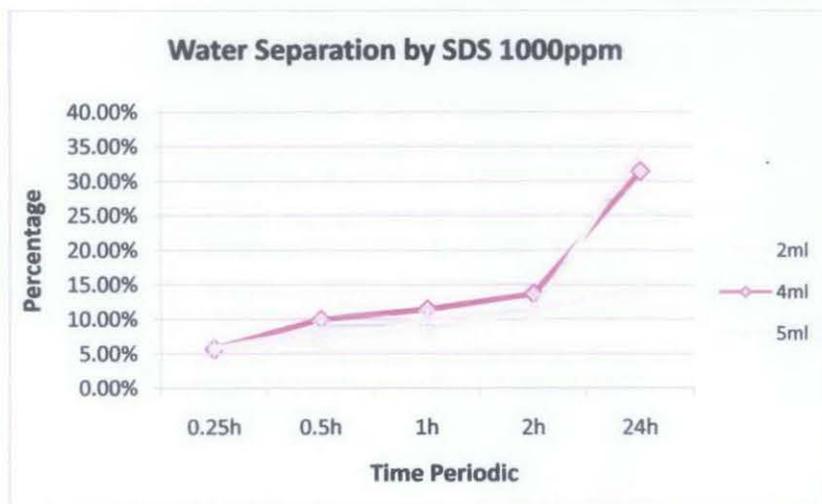


Figure 4.1: Water Separation by SDS 1000ppm

The graph (Figure 4.1 and 4.2) shows the rate of water and crude oil separation increased when the volume of SDS solution change from 2ml to 5ml. However, there is slightly similar effect or result on the water separation by demulsifier loading of 4ml and 5ml. This might be explained through plateau rate which the interfacial films of oil already fully saturated with the demulsifier added.

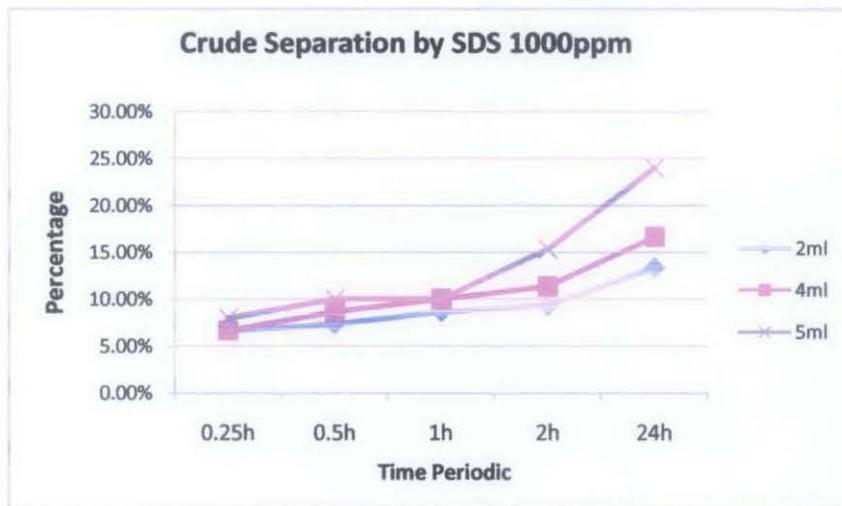


Figure 4.2: Crude Oil Separation by SDS 1000ppm

4.2 Concentrations of Surfactants

Oil film life time decreased with the increasing concentration of demulsifier. This shows that the demulsifier molecules are adsorbed on the oil film, meanwhile film strength and stability decreased and the rate of oil film thinning and the demulsifying efficiency increased with increase of the demulsifier concentration. When the concentration is increased even more, the demulsifiers are saturated at oil–water interface and the oil film life time remains constant (plateau rate).

In this experiment, both surfactants Sodium Dodecyl Sulfate (SDS) and Alkyl Benzene Sulfonate (AOS) have been tested according to five different concentrations which are 1000ppm, 2000ppm, 3000ppm, 4000ppm and 5000ppm. From the graphs below, we can see clearly by increasing the concentration of surfactant, the rate of separation has been increased.

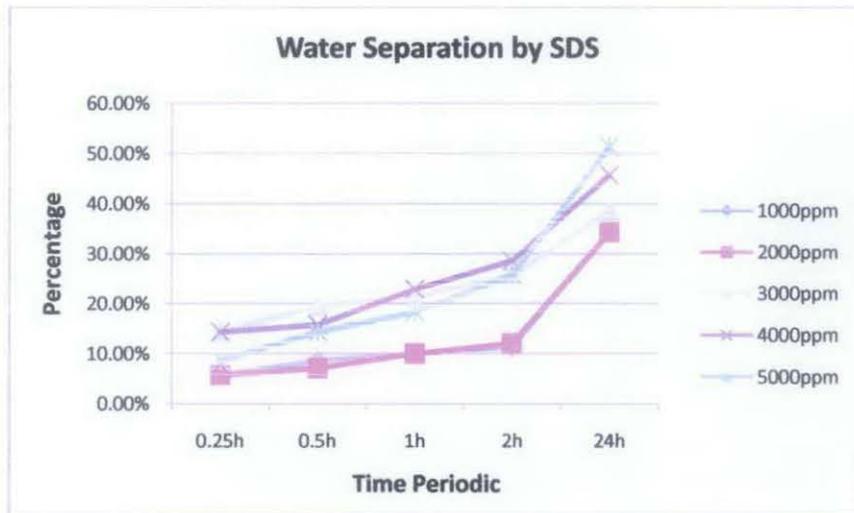


Figure 4.3: Water Separation by SDS

With an increase of demulsifier concentration, the slope of each line has been increased (Figure 4.3 and 4.4). The rate of separation for both water and crude oil are significantly increased when tested from lower to higher concentration.

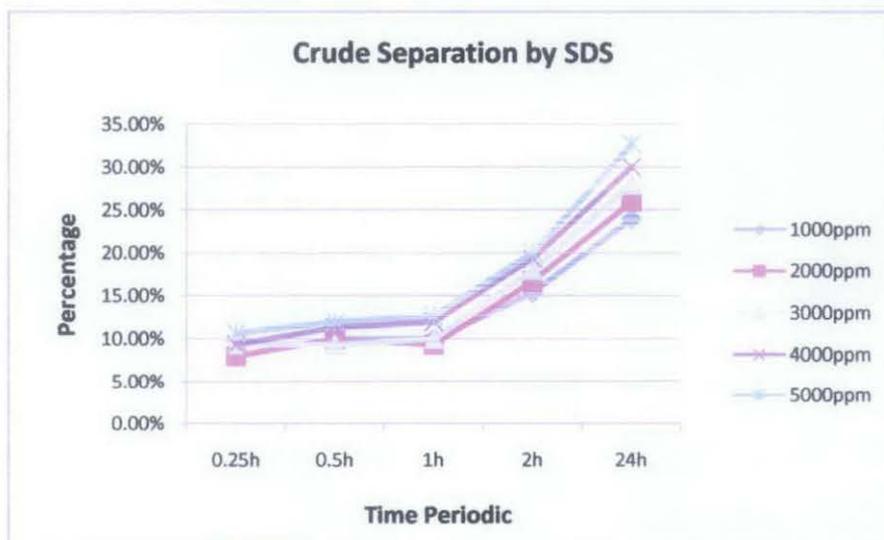


Figure 4.4: Crude Oil Separation by SDS

4.3 Comparison of Surfactants

Analysis of the results from Figure 4.5 and 4.6, both graphs show that the performance of AOS is greater than SDS in terms of water separation and also crude oil separation. Both surfactants are likely produce the same results for the first fifteen minutes and along with time, the rate of separation for AOS had increased gradually and steeply than SDS. From figure 4.5, it can be observed that at 24hours time periodic, both water and crude oil separation for AOS are much greater than SDS; approximately 80% and 70% respectively.

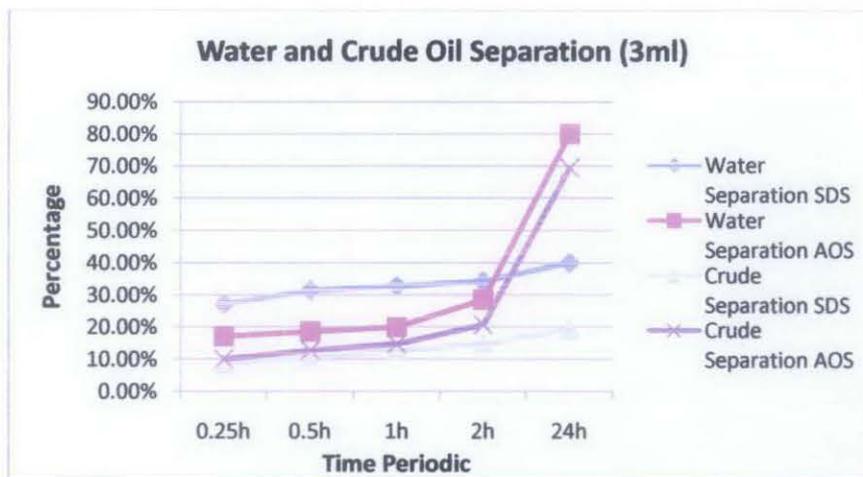


Figure 4.5: Water and Crude oil Separation of 3ml Surfactant Loading

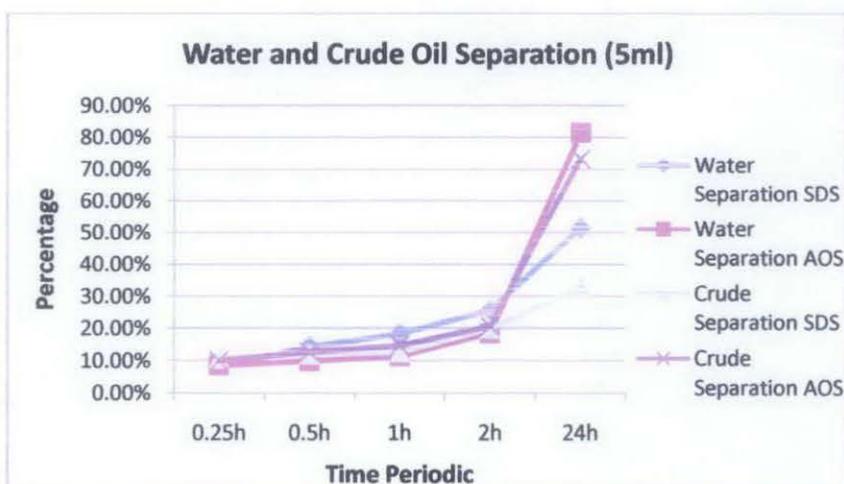


Figure 4.6: Water and Crude oil Separation of 5ml Surfactant Loading

From Figure 4.6, 5ml of surfactant loading shows quite similar pattern with 3ml surfactant loading. At the beginning of test sample, both type of surfactants show same reaction and these results vary towards the end where it can be observed AOS shows better performance than SDS. At 24hours time periodic, both water and crude oil separation for AOS are much greater than SDS; approximately 82% and 75% respectively.

Based on the above results, it can be concluded that Alkyl Benzene Sulfonate (AOS) produce better result compared to Sodium Dodecyl Sulfate (SDS). AOS promised a faster reaction and higher separation at the end of samples testing.

4.4 Comparison of Demulsifiers

Analysis of the results (Table 4.2, Figures 4.7 & 4.8) shows that Demulsifier B gives the highest water separation of approximately 91% followed by Demulsifier F and D. Meanwhile, for crude oil separation, Demulsifier A is the best with 90% separation followed by Demulsifier F, E and B.

Table 4.2: Water and Crude Oil Separation by Demulsifiers

(Details of demulsifiers can be viewed at page 33)

Water Separation	0.25h	0.5h	1h	2h	24h
No Demulsifier	2.86%	2.86%	2.86%	2.86%	2.86%
Demulsifier A	5.71%	8.57%	11.43%	15.71%	38.57%
Demulsifier B	51.43%	57.14%	60.00%	61.43%	91.43%
Demulsifier C	8.57%	14.29%	18.29%	25.71%	51.43%
Demulsifier D	8.57%	10.00%	11.43%	18.57%	81.43%
Demulsifier E	31.43%	44.29%	51.43%	54.29%	80.00%
Demulsifier F	71.43%	74.29%	77.14%	80.00%	88.57%

Crude Separation	0.25h	0.5h	1h	2h	24h
No Demulsifier	6.67%	6.67%	8.00%	8.67%	9.33%
Demulsifier A	66.67%	80.00%	83.33%	86.67%	90.00%
Demulsifier B	60.00%	66.67%	70.00%	73.33%	76.67%
Demulsifier C	10.67%	12.00%	12.67%	20.00%	32.67%
Demulsifier D	10.00%	12.67%	14.67%	20.67%	73.33%

Demulsifier E	40.00%	50.00%	53.33%	56.67%	76.67%
Demulsifier F	46.67%	56.67%	60.00%	63.33%	85.33%

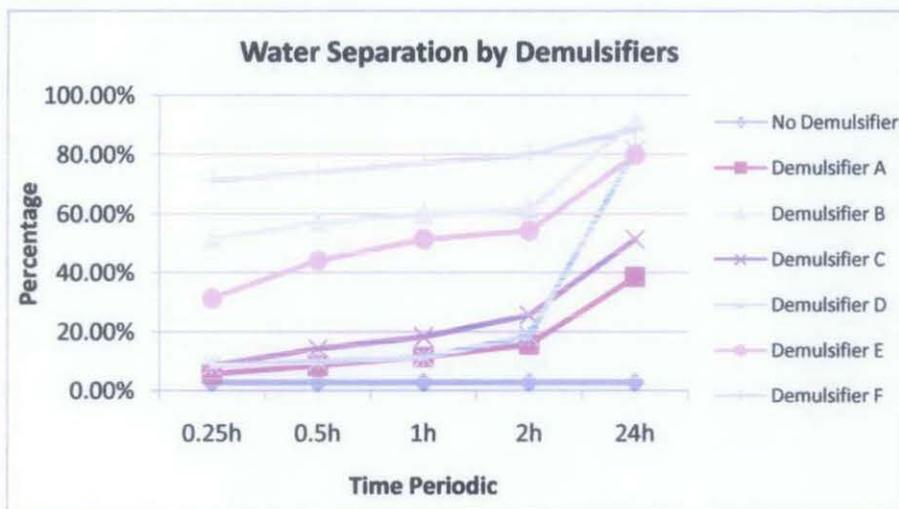


Figure 4.7: Water Separation by Demulsifiers

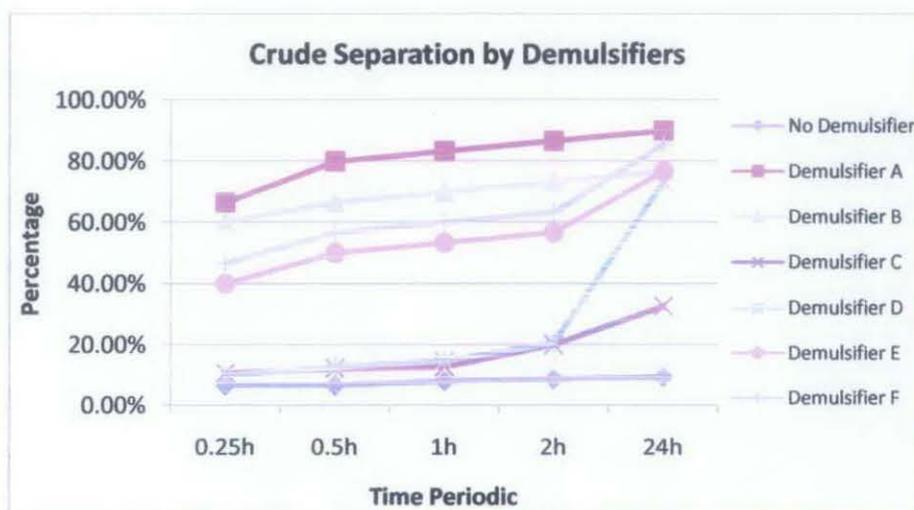


Figure 4.8: Crude Oil Separation by Demulsifiers

Based on the graphs (Figure 4.7 & 4.8), Demulsifier B, E and F are showing good performance either in water or crude oil separation. In spite of high separation of water and crude from the emulsion, these demulsifiers promised fast reaction compared to

others demulsifiers. This characteristic is very crucial in order to shorten the shut in period of the candidate wells and thus can reduce loss due to off-production.

The proposed demulsifier for this emulsion samples is **Demulsifier F** which are blended of AOS and a small portion of toluene and phenol. This proposed demulsifier occupied rate of separation for both water and crude oil; approximately 88% and 85% respectively.

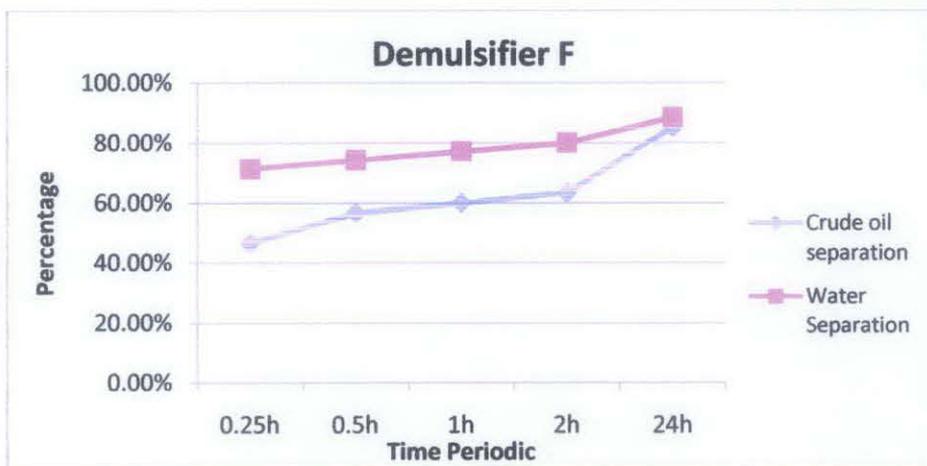


Figure 4.9: Demulsifier F Performance

Chapter 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

Based on the experimental analysis in the results and discussions section, **surfactants can be one of the best demulsifier**. The application of the surfactants can break or destabilize the emulsion particles effectively with the aid of minor catalysts such as phenol and toluene. The results show great value of water and crude oil separation by using Sodium Dodecyl Sulfate (SDS) and Alkyl Benzene Sulfonate (AOS). Among these two surfactants, AOS show more impressive performance by giving higher separation and also reduce the residence time (fast reaction).

The recommended demulsifier is **combination of AOS and very small volume of toluene and phenol**. These minor catalysts will help AOS in accelerating the separation of water and oil while AOS will mainly working on reducing the interfacial tension (film) of the oil and water droplets.

5.2 Recommendation

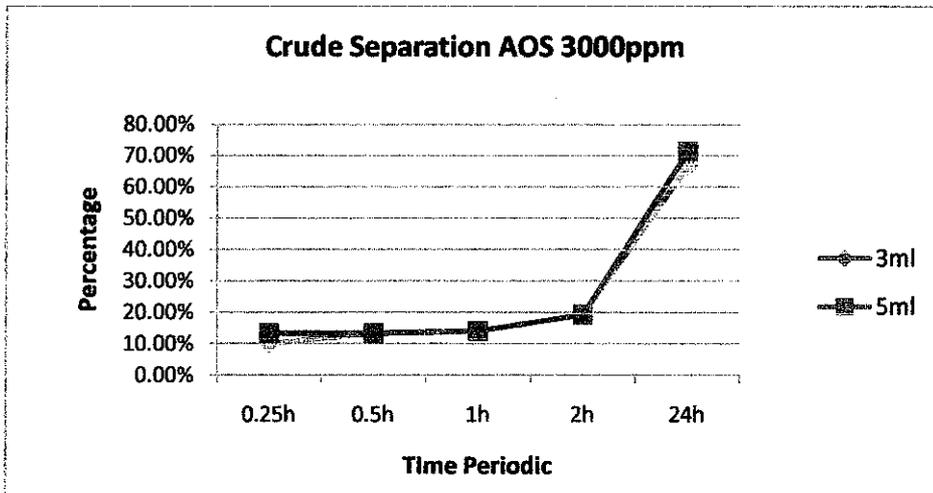
However a wellbore treatment still needs to be carried out to eliminate emulsion from the source. This can be done by diverting the flow mechanism from radial to linear by means of fracturing the formation by proppants. This would avoid the flow from becoming turbulence thus promote emulsion formation.

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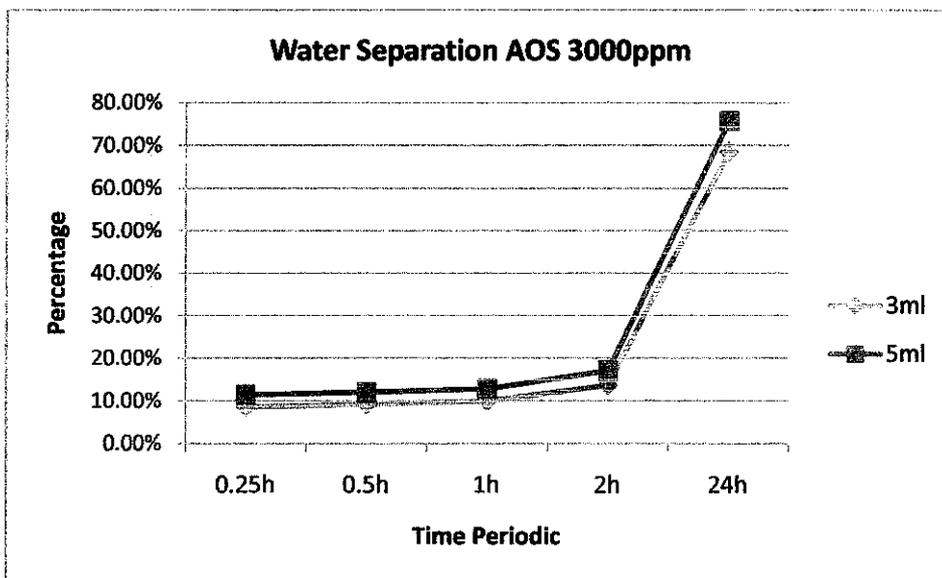
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7 Appendices



Appendix A



Appendix B

Vol of Emulsion (ml)	5				
Estimated Vol of Water (ml)	3.5				
Estimated Vol of Crude (ml)	1.5				
Vol of Demulsifier tested (ml)	2				
Water Separation					
Sodium Dodecyl Sulfate (SDS)	0.25h	0.5h	1h	2h	24h
1000ppm	5.71%	10.00%	11.43%	13.71%	31.43%
2000ppm	17.14%	18.57%	20.57%	21.43%	32.29%
3000ppm	14.29%	17.14%	20.00%	20.86%	33.71%
4000ppm	17.14%	20.00%	21.14%	22.86%	35.14%
5000ppm	22.86%	25.71%	27.14%	28.57%	36.57%

Appendix C

Vol of Emulsion (ml)	5				
Estimated Vol of Water (ml)	3.5				
Estimated Vol of Crude (ml)	1.5				
Vol of Demulsifier tested (ml)	3				
Water Separation					
Sodium Dodecyl Sulfate (SDS)	0.25h	0.5h	1h	2h	24h
1000ppm	20.00%	21.43%	25.71%	28.57%	32.86%
2000ppm	17.14%	22.86%	26.29%	28.57%	32.86%
3000ppm	20.00%	21.43%	24.29%	25.71%	31.43%
4000ppm	22.86%	25.71%	27.14%	28.57%	35.71%
5000ppm	27.14%	31.43%	32.86%	34.29%	40.00%

Appendix D

Vol of Emulsion (ml)	5				
Estimated Vol of Water (ml)	3.5				
Estimated Vol of Crude (ml)	1.5				
Vol of Demulsifier tested (ml)	4				
Crude Separation					
Sodium Dodecyl Sulfate (SDS)	0.25h	0.5h	1h	2h	24h
1000ppm	8.00%	10.00%	10.00%	12.00%	20.00%
2000ppm	8.00%	10.00%	9.33%	12.67%	20.67%
3000ppm	9.33%	9.33%	10.00%	14.00%	22.00%
4000ppm	9.33%	11.33%	12.00%	13.33%	23.33%
5000ppm	10.67%	12.00%	12.67%	14.67%	24.00%

Appendix E