OIL-IN-WATER EMULSION TECHNIQUE ENHANCEMENT FOR VISCOUS CRUDE OIL FLOW IN PIPELINES

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MUHAMMAD FAWWAZ BIN ABDUL WAHAB

Thesis submitted in partial fulfillment of the requirements
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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Gas Technology).

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Dedication

I am dedicating this thesis to my parents who have meant and continue to mean so much to me. Although my father is no longer of this world, his memories continue to regulate my life. To my father Abdul Wahab bin Jantan who has loved me and showed me that love has no boundaries and who taught me the value of hard work. Thank you so much, I will never forget you.

Next is for sure I dedicated this thesis for my mother, who has raised and has always been by my side most of the time, her support, her encouragement and her constant love have sustained me throughout my life. May Allah (S.W.T) grant you Jannatul Firdaus.

Amin.

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ABSTRACT

The production of heavy crude oil is limited due to its high viscosity. It is expected to increase in the future as low viscosity crudes are depleted. The high viscosity lead to the increasing of pump energy as it creates high pressure drop. In order to reduce the viscosity of the heavy crude, it is suggested to mix it with water and optimum emulsifiers to create a lower viscous fluid, oil-in-water (O/W) emulsions. In this study, both chemical and physical properties of O/W emulsion that is prepared by using cocoamide DEA (non-ionic and biodegradable surfactant that synthesis from coconut oil) and two types of conventional chemical emulsifiers (Span 80 and Triton X-100) were investigated. O/W emulsions with three different ratios (50 - 50% and 65 - 35% and 80 - 20%) were prepared at a mixing speed of 2000 rpm with the concentrations of (1.0 wt%, 1.5 wt% and 2.0 wt%) of each emulsifier. These emulsions were tested for relative rates of water separation (stability test), viscosity, shear stress and shear rate at room temperature and stirring speed of Brookfield viscometer. While the droplet size was carried out by using Carl Zeiss Research Microscope and its software. Result shows that Span 80 at 1.0 wt% mixed at each ratio of 50 - 50%, 65 - 35% and 80 - 20% O/W with 2000 rpm mixing speed obtained the most stable emulsions for transportation compared to the other emulsifiers. Demulsification is the process of separation of water from crude oil. Crude oil needs to be separated efficiently and quickly from the water to allow further treatment. This is to ensure the crude oil value can be maximized and the operating cost can be minimized. Demulsifiers (Hexylamine, Cocamide MEA and Dioctylamine) with different concentrations (1.0 wt%, 1.5% and 2.0 wt%) were used for demulsification. The relative rates of water separation were characterized via beaker test.

Keywords: Transportation, demulsification, o/w stabilization, biodegradable, coco-amine.

ABSTRAK

Pengeluaran minyak mentah adalah terhad disebabkan kelikatan yang tinggi. Ia dijangka meningkat pada masa akan datang kerana minyak mentah kelikatan rendah berkurangan. Kelikatan yang tinggi membawa kepada peningkatan tenaga pam kerana ia mewujudkan penurunan tekanan yang tinggi. Dalam usaha untuk mengurangkan kelikatan minyak mentah, ia dicadangkan untuk bergaul dengan air dan pengemulsi optimum untuk mewujudkan bendalir likat yang rendah, emulsi minyak dalam air (O/W). Dalam kajian ini, kedua-dua sifat-sifat kimia dan fizikal emulsi O/W yang disediakan dengan menggunakan Cocoamide DEA (bukan ionik dan surfaktan terbiodegradasi disebabkan ia disintesis dari minyak kelapa) dan dua jenis pengemulsi kimia konvensional (Span 80 dan Triton X-100) disiasat. Emulsi O/W dengan tiga nisbah berbeza (50 - 50%, 65 - 35% and 80 - 20%) telah disediakan di satu kelajuan percampuran iaitu 2000 rpm dengan kepekatan (1.0%, 1.5% dan 2.0%) pengemulsi masing-masing. Emulsi ini telah diuji untuk kadar relatif pemisahan air (ujian kestabilan), kelikatan, tegasan ricih dan kadar ricih pada suhu yang pelbagai dan kelajuan kacau menggunakan Brookfield viskometer. Selain itu, pengukuran saiz titisan telah dijalankan dengan menggunakan Mikroskop Carl Zeiss dan perisian. Keputusan menunjukkan bahawa Span 80 pada 1.0% dicampur dengan 50 - 50%, 65 - 35% dan 80 - 20% O/W dengan kelajuan 2000 rpm percampuran memperoleh emulsi yang paling stabil. Demulsifikasi adalah proses pengasingan air dari minyak mentah. Minyak mentah perlu berasingan dengan cekap dan cepat dari air untuk membolehkan rawatan lanjut. Ini adalah untuk memastikan nilai minyak mentah boleh dimaksimumkan dan kos operasi dapat dikurangkan. Demulsifiers (Hexylamine, Cocamide MEA dan Dioctylamine) dengan kepekatan yang berbeza (1.0% berat, 1.5% berat dan 2.0% berat) telah digunakan untuk pengangkutan. Kadar relatif pemisahan air dicirikan melalui ujian bikar.

Kata Kunci: Pengangkutan, demulsification, O/W penstabilan, terbiodegradasi

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

O/W	Oil-in-water
W/O	Water-in-oil
DEA	Diethanolamine
MEA	Monoethanolamine

Executive Summary

Heavy crude oil resources are greater than double the conventional light oil reserves worldwide. Heavy crude oils creation is generally twice as capital and vitality concentrated as the generation of conventional oil. This is a result of their greatly low portability because of high consistency at reservoir conditions close by the vicinity of undesirable segments, for example, substantial metals, asphaltenes and sulfur making it additionally difficult to create, transport and refine. The transportation of heavy and extra heavy crude oils from the head-well to the refinery is getting to be critical since their production is right now expanding everywhere throughout the world. The blended of the downfall of the conventional oils and an expand request in world vitality, crude oils was one of the rundown hydrocarbons assets that pertinent for utilization later on. One of the good pipeline techniques in the transportation of viscous crude oil is the transportation of it as concentrated oil-in-water (O/W) emulsions. In past studies, there were three general methodologies for transportation of heavy and extra heavy crude oils, which are consistency diminishment, drag minimization and in-situ oil enhancement. This 3 conventional method required high cost. Hence, in order to minimize the cost of the transportation, our aim of research is to convert the 95% of w/o in pipeline to o/w technique by using the advantage of water to carry the oil. An emulsion is formed when two immiscible liquids are mixed together. The main aims for this research are to develop a generic but efficient and sustainable O/W stabilization method, to recognize the characterization of O/W emulsions in term of physic-chemical properties and to investigate the various factors affecting the preparation of a stable crude O/W emulsion. There are several methods that we need to use in order to achieve the aim of this research, first is the use of various stabilizers such as Span 80, Triton X-100 and Cocamide DEA as the surfactants in order to find the best surfactant to stabilize the emulsion, the gravitational test, the Brookfield test, the tensiometer and also the use destabilizers to determine which one is the best in order to destabilize the emulsion. The expected result of this research is to achieve emulsions that are stable for long term. The previous methods of transportation crude oils have its own side effects to the environment, so the result that are expected from this research is that the while the process of transporting the crude oils is ongoing, there will be no side effects to the environment or it is called an environmental friendly method.

1 Introduction

1.1 Motivations and Statement Problem

Hydrocarbon resources are very important regarding the fact that they include about 65% of the world's overall energy resources (Langevin, 2006). Nowadays crude oil is the most important hydrocarbon resource of the world and heavy crudes account for a large fraction of the world's potentially recoverable oil reserves (Chilingar & Yen, 1980) (Langevin, 2006). With the combination of an increase in world energy demand and the decline of conventional oils, heavy crude oils have been presented as a relevant hydrocarbons resource for use in the future (Lanier, 1998). However, heavy crude oils only account for a small portion of the world’s oil production because of their high viscosities, which cause problems in the transportation of these oils via pipelines (Plegue, 1989). Generally, interest for heavy and extra heavy crude oil has been minimal as a result of their high viscosity and composition complexity that make them troublesome and lavish to deliver, transport and refine. Nowadays, Alberta in Canada and Orinoco Belt in Venezuela are good examples of regions producing extra heavy oil. However, an increase in production of heavy and extra heavy crude oil will take place in several regions like the Gulf of Mexico and Northeastern China, as it will be needed over the next two decades to replace the declining production of conventional middle and light oil.

The production of heavy crudes is expected to increase significantly in the near future as low viscosity crudes are depleted (Plegue, 1989). Several alternative transportation methods for heavy crudes have been proposed and employed, including preheating of the crude oil with subsequent heating of the pipeline (Layrisse, 1998) (Saniere, 2004), dilution with lighter crude oils (Iona, 1978), partial upgrading (MacWiliams & Eadie,W, 1993), and injection of a water sheath around the viscous crude. All the above-mentioned methods experience logistic, technical, or economic disadvantages, however. Currently, there are three general approaches for transportation of heavy and extra heavy oil: viscosity reduction, drag minimization and in-situ oil upgrading (Rafael, 2010).

Although it is often mentioned that the field of hydro processing catalysis is mature and there are not much compasses for researcher, the increasing demand of heavy oil has made hydro processing a challenging task for refiners as well as for researchers (Rana, 2007). Paraffin wax deposition costs the oil industry billions of dollars worldwide for anticipation and remediation. Paraffin precipitation and disposition in crude oil transport streamlines and pipelines is an expanding test for the improvement of profound water subsea hydrocarbon stores. There are a few paraffin wax treatment methods. The most widely recognized removal methods are mechanical heat application utilizing hot oil or electrical heating, application of chemicals (e.g., solvents, pour-point dispersants) and the utilization of microbial products. Crude oil contains paraffin waxes that have a tendency to be separated from oil when the temperature of crude oil falls underneath the wax appearance temperature. With decreasing temperature, the waxes for the most part crystallize as an interlocking system of the sheets, along these lines entangling the staying fluid fuel in enclosure like structures. At the point when the temperature approaches the pour point, the oil may gel totally bringing on the cold flow problems, for example, blockage of flow pipes or production lines. The pour point is the most reduced temperature at which oil will flow openly under its own weight under particular test conditions.

1.2 Research Background

One of the newest pipeline techniques is the transport of viscous crudes as oil-in-water (O/W) emulsions (Lappin & Saur, 1989) (Gregoli, 2006). In this method, by the aid of suitable surfactants, the oil phase becomes dispersed in the water phase and stable oil-in-water emulsions are formed. The result causes a significant reduction in the oil viscosity, i.e. the produced emulsion has a viscosity in a range about 50 – 200 cP, and therefore in the transportation costs and problems. This method can be very effective in the transportation of crude oils with viscosities higher than 1000 cP especially in cold regions. Besides, since water is the continuous phase, crude oil has no contact with the pipe wall and this reduces the pipe corrosion (e.g. in the crudes with high sulfur content) and prevents forming of sediments in pipes (e.g. in the crudes with high asphaltene content) (Poynter & Tirgrina, 1970).

The technical viability of this method was demonstrated in an Indonesia pipeline (Lamb & Simpson, 1963) and in a 20-km-long, 0.203-m-diameter pipeline in

California. In this method, with the aid of suitable surfactants, the oil phase becomes dispersed in the water phase and stable oil-in-water emulsions are formed. The formation of an emulsion causes a significant reduction in the emulsion viscosity; even O/W emulsion might reduce corrosion with a crude oil with high sulphur content; corrosion may also appear with use of an aqueous phase, even with the use of formation water, rich in salts. The produced emulsions have viscosities in the range of approximately 0.05 – 0.2 Pa·s. Because of this reduction in viscosity, the transportation costs and transport-assisted problems are reduced. This method can be very effective in the transportation of crude oils with viscosities higher than 1 Pa·s especially in cold regions. In addition, because water is the continuous phase, crude oil has no contact with the pipe wall, which reduces pipe corrosion for crudes with high sulfur contents and prevents the deposition of sediments in pipes, as is common for crudes with high asphaltene contents (Poynter & Tirgrina, 1970). The possibility of injecting aqueous surfactant solution into a well bore to affect emulsification in the pump or tubing for the production of less viscous O/W emulsions will increase the productivity of a reservoir (R. Simon & Poynter, 1968). The main aims of this research are to investigate the factors affecting both the stabilization and the destabilization of oil in water emulsion of crude oils.

1.3 Objective

The objectives of this research are as follow:

1) To develop a generic but efficient and sustainable oil/water stabilization method.
2) Characterization of o/w emulsions in terms of physic-chemical properties.
3) To investigate the various factors affecting the preparation of a stable crude o/w emulsion.

1.4 Scope

In general, this study is about finding the best stabilizer and destabilizer for the oil-water-emulsion. In order to achieve that, surfactants such as Span 80, Triton X-100, Cocamide DEA, Cocamide MEA and MSDS are used and their reactions or behaviors are studied during the experiments. The concentration of the surfactant varies as well as the ratio of water-in-oil emulsion so that we can determine the perfect concentration for the emulsion to be at its best stabilization. Besides that, the brook's field is also studied to get the measurement of the viscosity, density, sheer rate, sheer stress and RPM. Surface tension and interfacial tension are very important elements in this study which need to take into account, in order to get these measurements, the using of tensiometer is in need. Finally, to get the best destabilizer, the highest amount of water content in any emulsions is measured. Hexylamine, octylamine, dioctylamine, PEG 600 and PEG 1000 are taken as destabilizers, which will then be compared to get the best one.

2 Literature Review

2.1 Overview

This research signifies the experimental study of transporting viscous crude oils as oil in water emulsions. The experiments that will be held are through few methods, which are gravitational stability test; Brook's field, tensiometer and finally it will go through the demulsification. In gravitational stability test, the emulsion stability is measured based on the amount of separated water from the prepared emulsions after 24 hours. Different surfactants are used in this test with different concentrations and different ratio of oil in water. In the brook's field test, viscosity, torque, rpm, sheer rate and sheer stress are measured. The measurement of surface tension and interfacial tension are important in this study so the tensiometer is used to get its measurements. After obtaining the most stable emulsifier agent, samples of emulsion will be futher experimented for demulsification part, which is known as a breakdown process. Few demulsifiers, each with varieties of concentrations are used in this experiment to determine which demulsifier demulsifies the emulsion best.

2.1.1 Heavy Crude Oils

Highly viscous oil is heavy crude oil or extra heavy crude oil; these oils will not flow easily or effortlessly to production wells under ordinary reservoir condition. The density and specific gravity of these oils are higher than the light crude oils, which make them called heavy crude oils. Having higher viscosity, higher specific gravity and heavier molecular composition contrast them from the light crude oil. Production, transportation and refining of heavy crude oil display an extremely exceptional difficulty contrasted with light crude oils. For the most part, a diluent is included at normal separations in a pipeline convey heavy crude oil to facilitate or smoothen the stream.

2.1.2 Emulsion

An emulsion is a mixture of two or more liquids that are ordinarily immiscible. In an emulsion, one fluid (the scattered stage) is scattered in an (continuous stage). Two liquids can structure diverse sorts of emulsions which case in point, oil and water can structure oil-in-water emulsion where oil is the scattered stage and water is the scattering medium, second is water in oil emulsion where in water is the scattered phase and oil is the outside phase. Multiple emulsions are additionally conceivable which are water-in-oil-in-water emulsion and an oil-in-water-in-oil emulsion. Emulsion stability is characterized as the ability of an emulsion to oppose change in its property after some time. The four sorts of instability in emulsion are flocculation, creaming, coalescence and Ostwald ripening. At the point when there is an alluring compel between droplets, they will structure flocs and that is called flocculation. Coalescence happens when droplets hit into each other and consolidate to structure bigger droplet so the size extends over the long run. Emulsions can likewise experience creaming, where the droplets climb to the highest point of the emulsion affected by buoyancy, or affected by the centripetal power actuated when a centrifuge is utilized. A fitting "surface active agent" (surfactant) can build the kinetic stability of an emulsion with the goal that the extent of the droplets does not change fundamentally with time.

2.2 Previous Work on the Techniques of Transporting of Viscous Crude Oil

To transport heavy oils economically, the pressure drop in the pipeline must be lowered to minimize the pump power required to push the oil over a long distance. However, because of their high viscosity at reservoir conditions compared to conventional light crude oils, conventional pipelining is not adequate for transporting heavy crude oil and bitumen to refineries without reducing their viscosity (Ahmed & Nassar, 1999). The methods used for transporting heavy oil and bitumen through pipelines are generally grouped into three as shown in Fig 2.1: (a) viscosity reduction [e.g. preheating of the heavy crude oil and bitumen and subsequent heating of the pipeline, blending and dilution with light hydrocarbons or solvent, emulsification through the formation of an oil-in-water emulsion and lowering the oil's pour point by using pour point depressant (PPD)]; (b) drag/friction reduction (e.g. pipeline lubrication through the use of core-annular flow, drag- reducing additive); and (c) in situ partial upgrading of the heavy crude to produce a syn-crude with improved viscosity, American Petroleum Institute (API) gravity, and minimized asphaltenes, sulphur and heavy metal content. In Fig. 2.2, the pressure drop versus the flow rate for the several methods of transporting heavy crude oil and bitumen is presented.

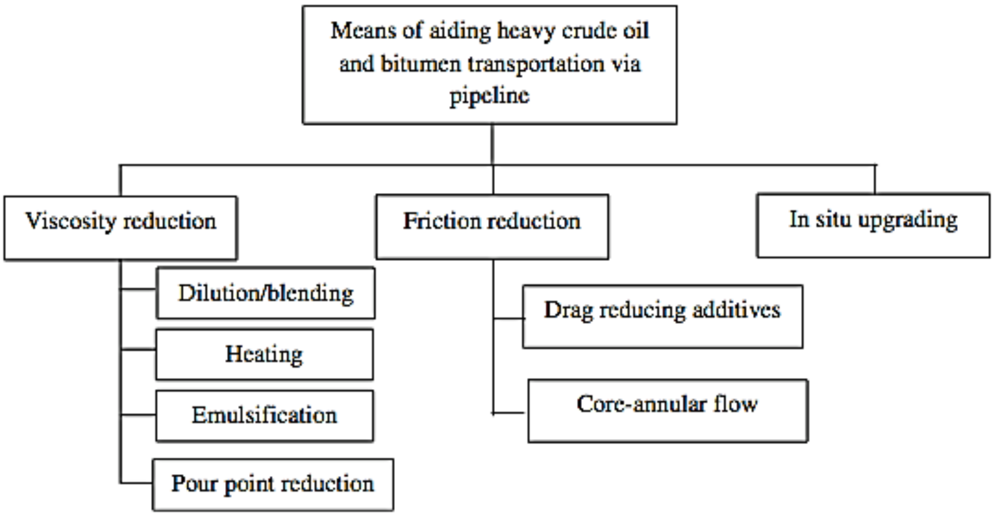


Figure 2.1: Diagrammatic Display of Methods in Improving the Transportation of Heavy Crude Oils and Bitumen via Pipelines

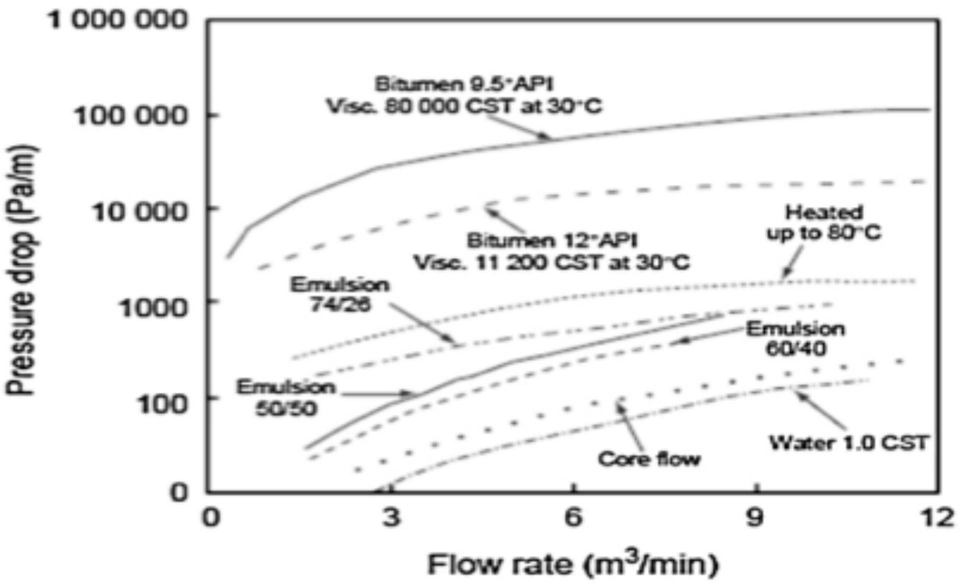


Figure 2.2: Pressure Drops against Flow Rate for the Different Heavy Crude Transport Mechanism

*(**Source:** Guevara & Gonzales, 1998)*

High viscosity at reservoir conditions is a major setback to heavy crude oil and bitumen recovery and transportation by pipelines. Therefore, mixing or dilution of heavy crude oil and bitumen to reduce viscosity is one of the few methods to improvise transportation via pipelines that is a most commonly used technique in the petroleum industry since the 1930s. The mixing fluid or diluents is always less viscous than the heavy crude and bitumen. Generally, it is well known that the lower the viscosity of the diluents, the lower is the viscosity of the blended mixture of heavy crude and bitumen (Gateau, 2004). The widely used diluents include condensate from natural gas production, naphtha, kerosene, lighter crude oils, etc. However, the use of organic solvents such as alcohol, methyl tert-butyl ether, tert-amyl methyl ether has been investigated (Anhorn & Badakhshan, 1994). The use of these solvents is prompted based on their use in improving the octane number of gasoline. Subsequently, a mixture of hydrocarbons and organic solvents with polar group in their molecular structure has shown some effectiveness in viscosity reduction of heavy crude oil at constant dilution rate (Gateau, 2004). The use of diluents allows the transportation of large quantity or volume of heavy crude oil and bitumen.

Furthermore, the viscosity of the blended mixture is determined by the dilution rate as well as the viscosities, densities of the heavy crude oil and bitumen and the use diluents. The resulting blend of heavy crude oil and diluents has lower viscosity and therefore it is easier to pump at reduced cost. The dilution of heavy crude oil and bitumen to enhance transportation by pipelines requires two pipelines, one for the oil and another for the diluents. The use of diluents to enhance the transportability of heavy crude oil and bitumen in pipelines would be cost-effective, if the diluents are relatively cheap and readily available.

The increasing utilization of vast heavy oil and bitumen resources to meet global energy demand and the apprehension for the environment have led to the incorporation of in situ upgrading with enhanced oil recovery. These processes trust on the reduction of heavy crude oil viscosity by heat to improve its flow from the oil reservoir to the production well. The upgrading is due to the heavy molecules splitting into smaller molecules thermally. This thermal cracking reactions in situ reduces the viscosity of the heavy oil and bitumen to a high order of magnitude, thereby improving flow and production.

2.3 Emulsion Stability

Crude oil emulsions have a wide variation in both physical and chemical properties, and also stability of emulsion. Emulsion presences in industry normally performed the stable emulsion due to the existence of natural surfactant in crude oil. The rheological properties such as emulsion composition and viscosity have been a great interest in understanding the concept of emulsion stability. Therefore, it is necessary to study the composition and properties of crude oil before further with the factors effect stability and rheological properties in emulsion. In this chapter, the characterisation of crude oil, the formation of emulsion and the factors affect stability of emulsion will be reviewed. Then, the demulsification methods will be touched in generally by explaining the application of chemical demulsifiers, conventional thermal heating and electric current in treating the emulsion.

2.3.1 Crude Oil Emulsion Composition

Crude oil varies greatly in appearance depending on its composition. As postulated from Auflem (2002), crude oil is the complex mixture of hydrocarbons, with small amount of sulphur, oxygen and nitrogen, as well as various metallic constituents, particularly vanadium, nickel, iron and copper. Crude oils consist of light hydrocarbon such as gasoline, asphaltenes, resins, waxes and napthenic acid. Crude oils, especially heavy crude oils contain large quantities of asphaltenes (high molecular weight polar components) act as natural emulsifier or also called surface-active agent. Besides, the other crude oil components such as resins, fatty acids, waxes and napthenic acid also act as surface-active agent but cannot action alone in producing stable emulsion. The other particles in crude oils such as silica, clay and iron oxides naturally hydrophilic but they can become oil-wet (hydrophobic) due to long term exposure to the crude oil in the absence of water (Langevin, 2006).

The method of dividing crude oil into four major fractions: saturates (including waxes), aromatics, resins and asphaltenes is called SARA fractionation, based on their polarity and solubility in the solvent. Based on Hannisdal (2005), briefly, saturates are defined as the saturated hydrocarbons ranging from straight-chained paraffins to cycloparaffins (naphthenes) while the aromatic fraction includes those hydrocarbons containing one or more aromatic nuclei which may be substituted with naphthenes or paraffins. Asphaltenes are defined as the solubility class of crude oil that precipitates in the presence of aliphatic solvents while the resin fraction is defined as the fraction soluble in light alkanes, but insoluble in liquid propane. Both are the most aromatic and most polar compounds of petroleum with the greatest amount of sulphur, nitrogen, and oxygen. The method of dividing crude oil into these four fractions is illustrated in Figure 2.3. Crude oils from different regions have different properties. The physical properties that mainly affect the behaviour and persistence of crude oil are specific gravity, viscosity and pour point (Hannisdal, 2005).

2.4 Emulsion Formation

There are two-stage processes formation of emulsions, which are formation of new droplets and stabilisation of the droplets (Figure 2.3). For the formation of emulsion, at least two immiscible liquids are required (Ariany, 2004). The first process, formation of new droplets involves disrupting the stable bulk liquid to form dispersed phase by apply mechanical energy. The second process is the tendency of the droplets to coalesce and reform the stable bulk liquid must be overcome (Jennifer, 1999).

Emulsions form more readily as the interfacial tension between the oil and water phases is reduced, and theoretically, when the value of interfacial tension is zero, the emulsion will form spontaneously. According to the emulsion theory, the formation of emulsion is easier when the interfacial energy is low but this is not a crucial factor for emulsion stability (Wanli et al., 2000). In the formation of an emulsion, the surface area or interfacial area between the dispersed and continuous phases increase to a very great extent, and the properties of the interface are important in determining the ease of emulsion formation and its stability. This increase in surface area increases the free energy and thermodynamic instability of the system. Emulsifiers have the property of adsorbing at the interface, thus reducing the interfacial free energy, and this influences the ease with which the emulsion forms.

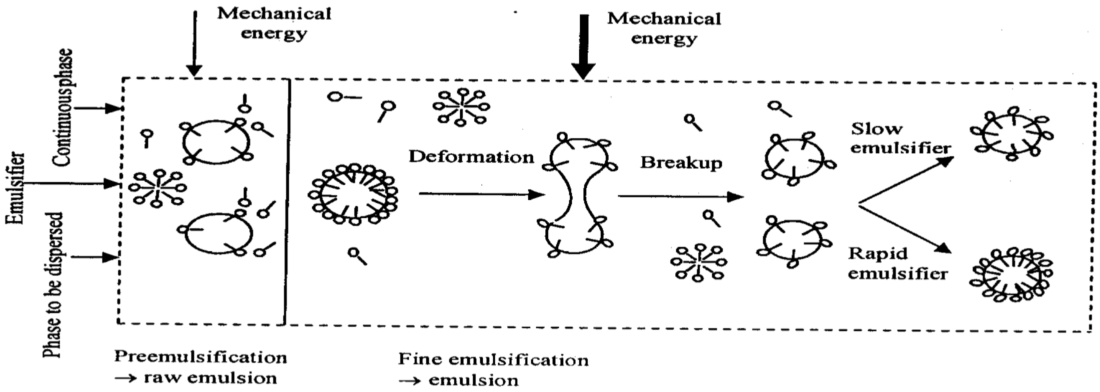


Figure 2.3: Processes of the Crude Oil Emulsion Formation

*(**Source:** Ariany, 2004)*

2.4.1 Physico-chemical Factors Affecting the Formation of Emulsions

Emulsion is part of liquid-liquid dispersion that can be affected by the formation of emulsion. The more important one are: (a) Concentration, (b) stability, (c) particle size, (d) viscosity, of the emulsion. Sometime other properties, like dielectric strength, electrical conductivity, or the colour may be specified, but these are relatively special features.

2.5 Types of Emulsion

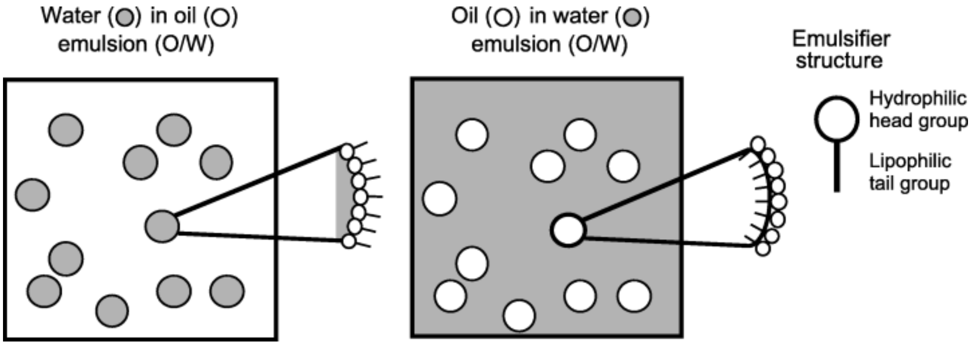


Figure 2.4: Types of Emulsions

Commonly, there are two basic types of emulsion that depend on the kind of liquid that perform as continuous phase. Still, the very general formulation by Bancroft (1912) is states that the "*continuous phase of an emulsion will be in which the surfactant (emulsifier) is most soluble"*. The common types of emulsions in the petroleum industry are oil-in-water (O/W) and water-in-oil (W/O).

2.5.1 Water-in-Oil Emulsion (W/O)

In industry, typically W/O emulsion is existed. Water dispersed in crude oil, therefore water act as dispersion phase and continuous phase is crude oil. As claimed by Fingas (2001), W/O emulsion can be classified in four types, which stable emulsion, mesostable emulsion, unstable emulsion and entrained water. Stable emulsion is brown material with about 80% of average water content. While mesostable emulsion is brown or black viscous liquid with average water content of 62% on the day of formation and 38% one week later; entrained water is black liquids with average water content 42% in on the first day of formation and about 15% after one week.

2.5.2 Oil-in-Water Emulsion (O/W)

In general, O/W is displayed if the surfactant (emulsifying agent) is more soluble in water than oil. Emulsions are normal colloidal frameworks in numerous modern items, for example, cosmetics, beauty care products, and pharmaceutical or agrochemical arrangements. O/W emulsion is frequently used to convey practical particles and wholesome profits, or to make a certain surface to the buyer. Oil-in-water emulsions are made of oil droplets, which are scattered in a aqueous continuous phase and stabilised by surface-active molecules.

2.5.3 Differences Between W/O and O/W Emulsions

Not all emulsions exhibit the classical "milky" opaqueness with which they are usually associated. A tremendous in range of appearance of emulsion is depending on the droplets sizes and difference of refractive index between the phases. Physically, the texture of an emulsion frequently reflects to the continuous phase. W/O emulsion feel more “oily or greasy” compared to O/W which this types of emulsion are considered more “watery or creamy” (Schramm, 2005).

2.6 Tests for Emulsion Types

Several tests can be used to identify the emulsion types. In general, three tests are usually used as listed below: -

2.6.1 Dilution Method

This method is based on the fact that an emulsion can be diluted freely with a liquid as same as continuous phase. Typically, a small amount of the emulsion is added to a relatively large volume of water and the mixture is stirred. If the emulsion disperses in water, it is considered to be on O/W type emulsion. However, the emulsion remains undispersed is opposite type, W/O emulsion.

2.6.2 Electrical Conductivity

Measurement of electrical conductivity with conductivity bridges using platinum electrodes fused into glass tubing was proposed many years ago as a way differentiating between O/W and W/O emulsions. The concept of this method based on the ability of the emulsion to conduct electrical current. Thus, when a voltage is applied across a liquid, a significant amount of electric current will flow only when the path of the current is through water as continuous phase. W/O performed insignificant current flow when applied under electric current since oil is a non-conductor of electricity.

2.6.3 Staining the Continuous Phase

Another method to determine the type of emulsion is to use Sudan III or Scharlach R, red dyes soluble in the oil but not in the water (Bancroft, 1912). A small portion of the finely powdered dye is dusted over the surface of the emulsion. If oil is the external phase the colour gradually spreads throughout the emulsion. But if water is the external phase the colour does not spread but is confined to the oil with which it comes in contact on the surface. An example of such a dye is scarlet red, which is an oil soluble dye. When added to an O/W type emulsion, followed by observation under the microscope, bright red coloured oil drops in an aqueous phase can be seen clearly.

2.7 Emulsion Stability

Emulsion stabilized with particles is called “pickering emulsions”. It is generally considered that since the size of stable emulsion drops is generally 10 µm or less, the particles contributing to emulsion stabilization should not be more than 1 µm in size (Langevin, 2006). Usually emulsions made by mixing together two pure liquids are not very stable. The stability of emulsion is determined by the interaction between the particles during the collisions. As studied from previous researchers (Sullivan and Kilpatrick, 2002; Ariany, 2004; Abdurahman et al., 2007) there are at least four mechanisms by which emulsions are stabilized; electrostatic repulsion, steric repulsion, the Marangoni- Gibbs effect, which retards film drainage and thin film stabilization.

2.7.1 Electrostatic Forces

The collision of emulsion droplets to another may be resisted by electrostatic forces. Sullivan and Kilpatrick (2002) as saying that electrostatic forces in emulsions arise from a surface charge on the droplet and then electric double layer may form around disperses phase droplet (Figure 2.5). Electrostatic forces do not play a significant role in the stabilization of water-in-oil emulsion because of the low dielectric constant of continuous phase.

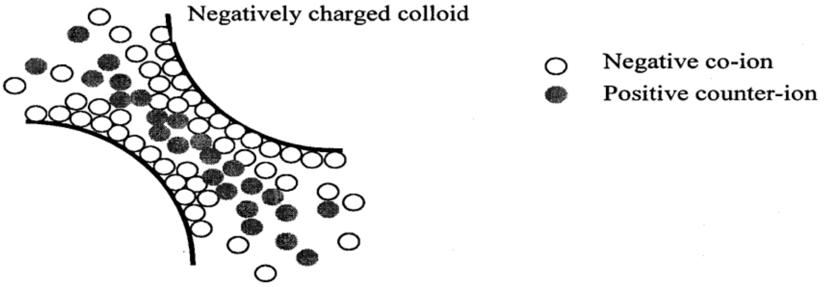


Figure 2.5: Electrostatic Forces

*(**Source:** Ariany, 2004)*

2.7.2 Steric Repulsion

Steric repulsion is one of the mechanisms in emulsion stability. Steric repulsion is the resistance of adsorbed species on droplet interfaces to interactions with adsorbed species on other droplets as shown in Figure 2.6 (Sullivan and Kilpatrick, 2002). This mechanism occurs when it is energetically favourable for the adsorbed material to interact with the solvent in the continuous phase rather than other adsorbed material. Steric repulsion is commonly found in systems stabilized by nonionic where salvation energies can be high as result of hydrogen-bonding interactions.

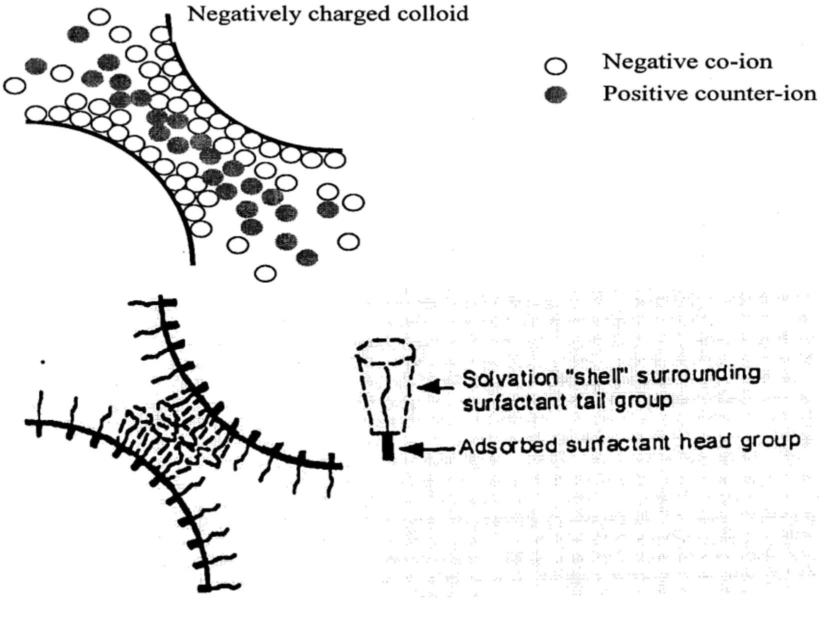


Figure 2.6: Steric Repulsion

*(**Source:** Ariany 2004)*

2.7.3 Marangoni-Gibbs Effect

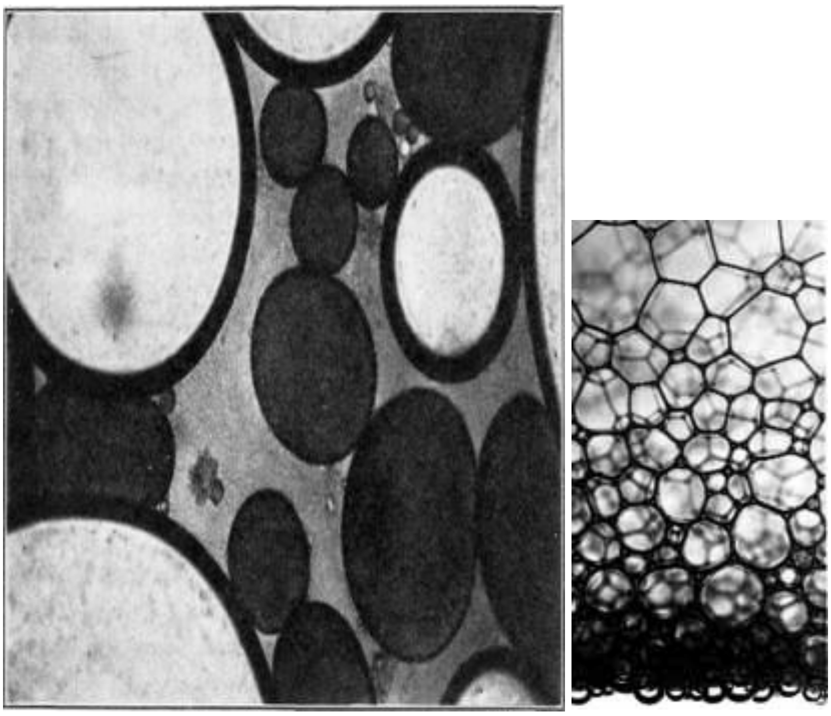
The effect on the surface tension by surfactant adsorption from the bulk solution (Gibbs effect) and by diffusion along the interface (Marangoni effect) is often referred to as combined Marangoni-Gibbs effect. The critical thickness for rupture of a thin film depends on the adsorption kinetics and interfacial activity of added demulsifiers. As the film thins, the continuous phase drains out from between the droplets and an interfacial tensions gradient is formed as the surfactants at the droplet interface are dragged out with the liquid. Because of the depletion of surfactant at the centre of the thin film interface, a diffusion flux is generated in the opposite direction of the drainage which cause the slowing fluid drainage (Sullivan and Kilpatrick, 2002)

2.7.4 Thin Film Stabilization

The formation of a mechanically rigid, viscoelastic and stagnant film around the droplets provides a physical barrier for droplet-droplet coalescence. Crude oil varies greatly in appearance depending on its composition. As postulated from Auflem (2002), crude oil, especially heavy crude oils contain large quantities of asphaltenes (high molecular weight polar components) act as natural emulsifier or also called surface-active agent. Besides, the other crude oil components such as resins, fatty acids, waxes and napthenic acid also act as surface-active agent but cannot action alone in producing stable emulsion (Langevin, 2006).

2.8 Emulsions and Foam

As mention above, emulsion is colloidal dispersion in which a liquid is dispersed in a continuous liquid phases. Foam is also deal with the colloidal dispersion. However, foam involve with gas is dispersed in a continuous liquid phase. Liquids foams and emulsions in general, unstable thermodynamic (Wilde, 2000). The creation of foams and emulsion essentially requires the formation of fine bubbles and droplets. Foam can be created by liquid, which, the surface area of liquid is expand to form a thin film around gas bubbles. The liquid must be able to posse the correct rheological and surface properties to retard thinning of the lamellae which lead to bubble coalescence and also diffuse the trapped gas from small to large bubbles or to the surrounding atmosphere. Figure 7 illustrated the general foam and emulsion image. Bubbles in persistent foams are polyhedral and not spherical. In fact foam bubbles usually have diameters greater than 10 μm and may be larger than 1000 μm (Schramm, 2005).



(a) (b)

Figure 2.7: Illustration of a Generalised (a) Foam (b) Emulsion

*(**Source:** Schramm 2005)*

2.9 Emulsion Destabilisation

The break-up of droplets depends strongly on the type and intensity of the flow, which is determined by the rotational speed, and geometry of the impeller, geometry of the vessel and material properties of the continuous phase such as viscosity and mass density (Hannisdal; 2005). The phenomenon of emulsion separation can be broadly categorized into four mechanisms for demulsification which are sedimentation/ creaming, aggregation coalescence and Ostwald ripening. Sedimentation or creaming occurs when there is density different between dispersed and continuous phase. Aggregation is when two or more droplet species are aggregated and clump together but separated by a thin film of continuous phase. While coalescence occurs when thin film between the droplets break and they fuse together to form single larger unit. From Figure 2.8, at low interfacial coverage of the stabilizing units, collision of the emulsion droplets (a-b) usually terminated their coalescence (b-c). The flocculation or aggregation (d) takes place before proceed with coalescence process.

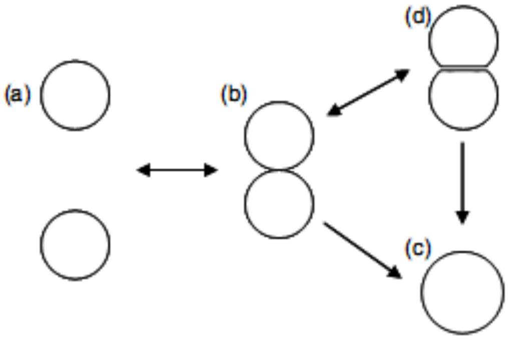


Figure 2.8: Possible Consequence from Collisions between Two Droplets

***(Source:** Hannisdal, 2005)*

2.9.1 Sedimentation

This is the phenomenon by which emulsions separate into two emulsions, one richer other is poorer in the dispersed phase. The more concentrated emulsion is commonly referred to as cream. The separation of cream from unhomogenised milk is very common example of cream phenomenon. The mechanism of creaming appears to be due to the slow sedimentation of the emulsified droplets (Paul and Daniel; 1985).

2.9.2 Aggregation

Flocculation is the process in which emulsion drops aggregate, without rupture of the stabilizing layer at the interface. Flocculation of emulsions may occur under conditions when the van der Waals attractive energy exceeds the repulsive energy and can be weak or strong, depending on the strength of inter-drop forces (Hannisdal, 2006). The rate of flocculation can be estimated from the product of a frequency factor (how often drops encounter each other) and the probability factor (how long they stay in contact).

2.9.3 Coalescence

As two emulsified drops approach each other, liquid flows out of the film and thinning occur. According to Wanli et al. (2000), the drainage velocity of thinning film is dependent upon the forces acting at the interface of the film then, the droplets fuse together to form a single larger unit.

2.9.4 Ostwald Ripening

Ostwald ripening is a long-term effect in destabilisation process of emulsion. This step occurs when dispersed phase is soluble enough within the continuous phase and consists of a gradual coarsening of emulsion (Hannisdal, 2005). Ostwald ripening caused by the diffusion of monomers from smaller to larger droplets due to greater solubility of a single monomer molecules in the larger monomer droplets.

2.10 Methods of Emulsion Breaking

The breaking of emulsion is necessary in emulsion treatment. Methods currently available for demulsification can be classified as chemical, electrical and mechanical (Abdurahman et al., 2007). In generally, methods to induce phase separation for water-in- oil emulsions can be applied using chemical or heating the emulsion. Chemical demulsifiation is common method used and since the 1930s, demulsifier has been used in treating emulsion (Wu et al., 2003). Conventional thermal heating involved the breaking of emulsion due to reduction of viscosity of continuous phase. However, currently microwave has been studied an alternative method to treat the emulsion.

2.10.1 Application of Chemical

Chemical demulsifier is a conventional method widely used in industry. However, the problems of using this method are environment problematic which involve with waste water stream and the cost of using chemical in large quantities volume could be enormous and may outweigh the benefits realized (Countinho et al., 2008; Rajaković and Skala , 2006; Arnoud, 2004). This method involves the use of chemical additives to accelerate the emulsion breaking process. As studied by Kang et al. (2006), the breaking through this method is based on the rupture of interfacial film and surfactant adsorption mechanisms. The dispersed phase (water droplets) approached each other and flattens to form a thin film of continuous phase between them. Demulsifier molecules and natural surfactants (asphaltenes) then compete each other to adsorb onto voids created because of the difference of interfacial tension inside and outside film (Figure 10). The outward drainage flow of the film can create gradients in the interfacial tension, which then oppose and slow down to drainage (Djuve et al., 2001). In this way, the adsorption of demulsifier is continuous exponentially until the films become very thin and it ruptures due to close proximity of adjacent dispersed phase surfaces and local absence of surfactant molecules.

Most commercial demulsifiers that are used to break up water-in-oil emulsions are oil soluble. The interfacial activity of these oil soluble demulsifier molecules is controlled by the rate of the bulk diffusion process from bulk phase to the interface and adsorption barrier at the water/oil interface. As reviewed by Djuve et al. (2001), the efficiency of the demulsifier is related to the hydrophile-lipophile balance (HLB) behaviour.

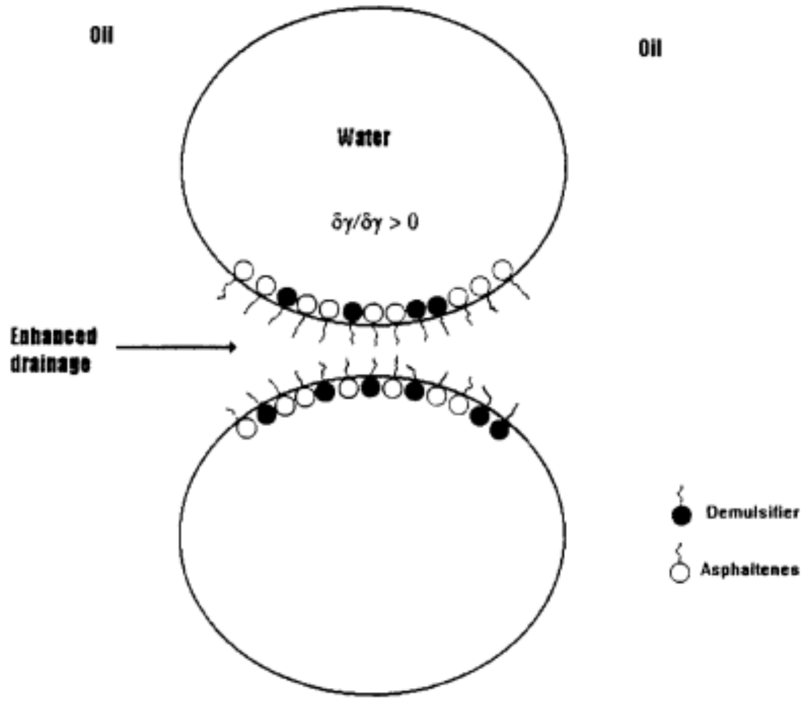


Figure 2.9: Process of Chemical Demulsification

*(**Source:** Djuve et al., 2001)*

2.10.2 Application of Thermal Heating

Thermal heating method is the addition of heat to enhance the emulsion breaking. Heating an emulsion usually causes a slight reduction in the interfacial tension between oil and water phases. Heat is applied in breaking the emulsion because it is characterised by rates in temperature (Coutinho et al., 2008). The thermal heating is affected on the emulsion due to reduction of viscosity of emulsion. This is agreed from previous researchers (Strom-Kristiansen et al., 1995; Hannisdal, 2005; Yang et al., 2009) the viscosity of emulsion is reduced as increasing temperature due to the elimination of protective rigid film surround the droplets.

Temperature and viscosity have significant factors in heating. Indeed, microwave irradiation also occupied with heating but in different way. In microwave irradiation, electromagnetic is transfer to energy and energy will be conversed. But, for thermal heating the heat transfer is transfer using thermal gradient from conduction to convection (Yanniotis and Sundén, 2006). Microwave irradiation is widely used in food industry because demonstrates significant advantages over conventional methods in reducing process time and improving food quality. The idea of using this microwave heating in food industry leads of using this method in demulsification. As studied by Xia et al. (2004), conventional heating could be used in demulsification due to the reduction of viscosity; however this process takes long time in separation.

2.10.3 Effects of Electric Current

Electric is applied to demulsified across an emulsion that causes the charged droplets to move toward the oppositely charged. Electric field produced disturbs the surface tension of each droplet, possibly by causing polar molecules to reorient themselves. This reorientation weakens the film surround the droplets because the polar molecules are no longer concentrated at the droplets surface. A mutual attraction of adjacent emulsion particles receives induced and oriented charges from the applied electric field. This mutual attraction places oppositely charged particles in close proximity to each other. Therefore, the droplets are electrically attracted to each other and lead coalescence process.

In microwave irradiation, electric current is applied due to the combination of electric and magnetic wave from penetration of electromagnetic through the materials. Information of using this method in demulsification has been developed in last 30 years. This method was firstly introduced by Klaika and Wolf since 1970s in their patent application to remove hydrocarbon fuel from geological substrates such as coal, shale, tar sand and existing oil wells (Klaika, 1978). Abdurahman and Rosli (2006) studied the efficiency of microwave irradiation by comparing gravity sedimentation, conventional heating and microwave irradiation by using light crude oil. They concluded that microwave irradiation can be tool to demulsified emulsion. In a related study, Ngai and Wu (2005) investigated the efficiency of microwave mixed with solvent in stabilising the microemulsion polymerisation. These combination solvent and microwave could be able to produce narrowly distributed small emulsifier-free polystyrene latex particles due to volumetric heating in microwave. Rajaković and Skala (2006) also proved the efficiency of microwave irradiation in demulsification method by combination freeze-thaw and microwave and metalworking oil has been used as emulsion sample.

The development of microwave irradiation as an alternative method for heating heavy crude oil in reservoirs may be economically viable alternatives to steam in certain situation. From Mutyala et al. (2010), the application of microwave in petroleum industry could be used as pre-heating tools where the temperature effect on viscosity is significant.

2.11 Surfactants

Surfactants are widely used and find a very large number of applications because of their remarkable ability to influence the properties of surfaces and interfaces. A surfactant, also called surface-active agent is a substance that has the property of adsorbing onto the surfaces of interfaces of the system at low concentration and alter to a marked degree the surface or interfacial free energies of those surfaces (Rosen, 2004). Previous researchers (Rosen, 2004; Schramm, 2000), agreed that surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for solvent, known as hydrophilic group, together with a group that has strong attraction for solvent, and known as hydrophobic group. This is known as an amphiphilic structure.

The adsorption of surfactant from a bulk phase to a surface or interface occurs at any concentration. As studied by Homberg (2001), the surface concentration increased gradually as soluble surfactant in water increased until reaches a maximum level at specific bulk concentration. Beyond this concentration, individual surfactant monomers begin to aggregate with their hydrophilic heads pointing outwards towards the solution and the hydrophobic tails pointing inwards away from the water in order to minimise the free energy of the system. The effects of association between adjacent hydrophobic or hydrophilic section of surfactant molecules are enhanced in aggregate structures such as micelles (Biresaw and Mittal, 2008). Hence, the concentration at this aggregation occurs is called the critical micelle concentration (CMC) as shown in Figure 2.10:

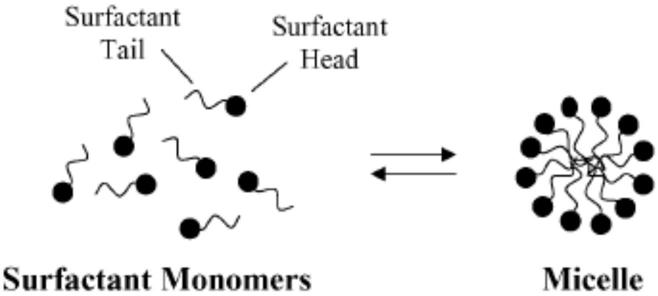


Figure 2.10: Typically Surfactant Structure

*(**Source:** Carlota et al. (2005)*

By adding surfactant such as surface-active emulsifiers or demulsifiers that affect the molecular confirmation and arrangement at the interface, would alter the interfacial tension and changed the stability of the formed emulsions (Wang et al., 2004). The selection of surfactant in preparation of either W/O or O/W emulsions is often made by hydrophilic-lipophilic balance (HLB). This method was first introduced by Griffin (1954) to scale the relative percentage of hydrophilic to lipophlic (hydrophobic) groups in the surfactant molecules. For an O/W emulsion, droplets the hydrophobic chain exists in the oil phase, while the hydrophilic head resides in aqueous phase and vice versa for W/O emulsion.

2.12 Summary

In the petroleum industry, the present of emulsion is undesirable because of problems caused by the formation of emulsions, for example in the pipelines, which can cause too many problems for the transportation. Essentially breaking of emulsion is to improve the quality of emulsion. The stability of emulsion is the most important part in this research, determining the factors the affect the stabilization of emulsion should be investigated thoroughly. This stability of emulsion depends on the properties of crude oil and factors affected on emulsion characteristics such as viscosity, temperature and concentration of dispersed phase.

3 MATERIALS AND METHODS

3.1 Chemicals

Chemicals were obtained sources namely Sigma-Aldrich (Span-80, Triton X-100 and Cocamide DEA) for the emulsifiers. The demulsifiers are also gotten from Sigma-Aldrich (Hexylamine, Cocamide MEA and Dioctylamine).

3.1.1 Crude Oil

In order to achieve the aim of this study, the crude oi samples were obtained from Petronas Refinery Kerteh. The preparation of oil-in-water (O/W) is described in few main steps. Distilled water were dispersed in the crude oil at room temperature with standard three blade propeller at 2000 rpm speed. The emulsifying agent was used as received without any futher dilution.

3.2 Samples Preparation

The general idea of emulsion preparation is by adding dispersed phase (oil) little by little to the continuous phase (water with stabilizer) in a plastic beaker (100 ml). The emulsions were prepared at room temperature with standard three-blade propeller at mixing speed of 2000 rpm at room temperature (28-30℃). 1.0 wt % of emulsifier (Span 80, Triton X-100 and Cocamide DEA) was added into the water (continuous phase) and mixed for five minutes to achieve homogenous. Crude oil (dispersed phase) is then added slowly to the solution and mixed for ten minutes. The sample procedure is repeated respectively for different concentration of emulsifier, which is 1.0 wt%, 1.5 wt% and 2.0 wt% with same ratio of oil to water. The samples started with 50-50% ratio of O/W emulsion as tabulated in table 3.1 below.

Table 3.1: Type of Emulsifiers Used with Different Concentrations

Emulsifiers	Weight percentage, wt% (concentration)
Span-80	1.0
	1.5
	2.0
Triton X-100	1.0
	1.5
	2.0
Cocamide DEA	1.0
	1.5
	2.0

Next, the ratio of water to oil is change to 65-35% and the same procedure is repeated for 80-20% O/W ratio..To make sure the samples prepare are in our niche area, we check the sample using filter paper either the sample in O/W or W/O emulsion.

3.2.1 Gravitational Stability Test

The emulsion stability was measured based on the amount of separated water from the prepared emulsions after 30 minutes. O/W emulsions prepared at different conditions were tested for their stability by transferring the emulsions into test tube, the latter were left at room temperature to rest for a while. The volume of separated wate rwas recorded after 30 minutes after the time homogenization was performed. By dividing the amount of water separated from the emulsion to the initial amount of water in the emulsion, the percentage of separated water from the prepared emulsions was achieved. The amount of water separated was noted at 30 minutes, 1 hour, 2 hour, 6 hour, 12 hour and 24 hour for the first day and every 6 hours after that for 5 days. The water separation in percentage was calculated as separation efficiency (e) from volume of water observed in the measuring cylinder as follow:

$$\%\ \text{Water separated} = \frac{\text{Volume of separated water, mL}}{\text{Original volume of water in the emulsion, mL}}$$

3.2.2 Brook’s Field

The brook’s field are studied to measure the viscosity, torque, rpm, sheer stress and sheer rate. The most stable emulsifier base on the result gravitational stability test will be taken for demulsification test.

3.2.3 Carl Zeiss Research Microscope

The instrument used is the Carl Zeiss Microscope and a digital camera before connected with Dino Capture 2.0 software. All size measurements were done in duplicates and averages of size were reported in this study. The effect of temperature on emulsion stability was investigated by measuring the droplet sizes (after emulsification).

3.2.4 Tensiometer

There are many method proposed to measure surface or interfacial tension. Major methods are: ring method, hanging plate method, drop weight method, maximum bubble pressure method, capillary rise method, sessile drop method and pendant (hanging) drop method. The studies prefer to use the ring method. For surface tension measurements, the emulsion sample was placed on the sample platform. Then the sample platform was raised by adjusting the screw until the ring was just submerged. The platform was lowered slowly at the same time applying torsion to the wire by means of dial- adjusting screw. These simultaneous adjustments were performed carefully proportioned, while the ring system remained constant at its zero position. As the breaking point was approached, the adjustment was made more carefully. The experiment was repeated and four measurements were recorded for the accuracy. The general procedures followed for determination of interfacial tension is the same as the surface tension determination with some modifications. Since oil is lighter than water, the aqueous solution (water) was first placed in the sample vessel and the ring was immersed therein. The oil on top of the water solution was then poured to form the two-layer system (emulsion). Contact between the oil and the ring was avoided during the operation. After allowing sufficient time (5 minutes) for the interfacial tension to come to its equilibrium value, measurements were made.

The summaries of the usage of the equipment are tabulated in Table 3.2.

Table 3.2: Summary of usage of Equipment

Equipment	Usage
Brookfield viscometer	To measure the physiochemical properties of O/W emulsion
Digital Tensiometer	- To measure the surface tension of water and crude oil - To measure the interfacial tension between the crude oil and water
Propeller	To prepare emulsion by mixing the crude oil (dispersed phase) and water (continuous phase).
Carl Zeiss Research Microscope	To determine the droplet size of the emulsion

3.2.5 Demulsification

After obtaining the most stable emulsifier agent, samples of emulsion will be further for demulsification part, which is known as a breakdown process. The samples will be mix with the demulsifier as shown in Table 3 below.

Table 3.3: Type of Demulsifiers used with different concentrations

Demulsifiers	Weight Percentage, wt% (concentration)
Hexylamine	1.0
	1.5
	2.0
Cocamide MEA	1.0
	1.5
	2.0
Dioctylamine	1.0
	1.5
	2.0

Demulsification has been defined by Fan (2009) as a process of breaking emulsions in order to separate water from oil, which is also one of the first steps in processing the crude oil.

4 RESULT AND DISCUSSION

4.1 Emulsification

Table 4.1.4: Result of Emulsification for 50 - 50% O/W Ratio

Type of Emulsifier	Concentration (wt %)	50-50% O/W Ratio		Percentage of Water Separation (%)	Date	Time (hr)
		Oil	Water			
Span-80	1.0	69	31	62	28/3/2015	15:04
	1.5	67	33	66	29/3/2015	15.06
	2.0	65	35	70	29/3/2015	15:36
Triton X-100	1.0	68	32	64	8/4/2015	13:30
	1.5	66	34	68	8/4/2015	21:30
	2.0	68	32	64	8/4/2015	09:35
Cocamide DEA	1.0	68	32	64	8/4/2015	03:35
	1.5	66	34	68	13/4/2015	15:00
	2.0	69	31	62	13/4/2015	15.30

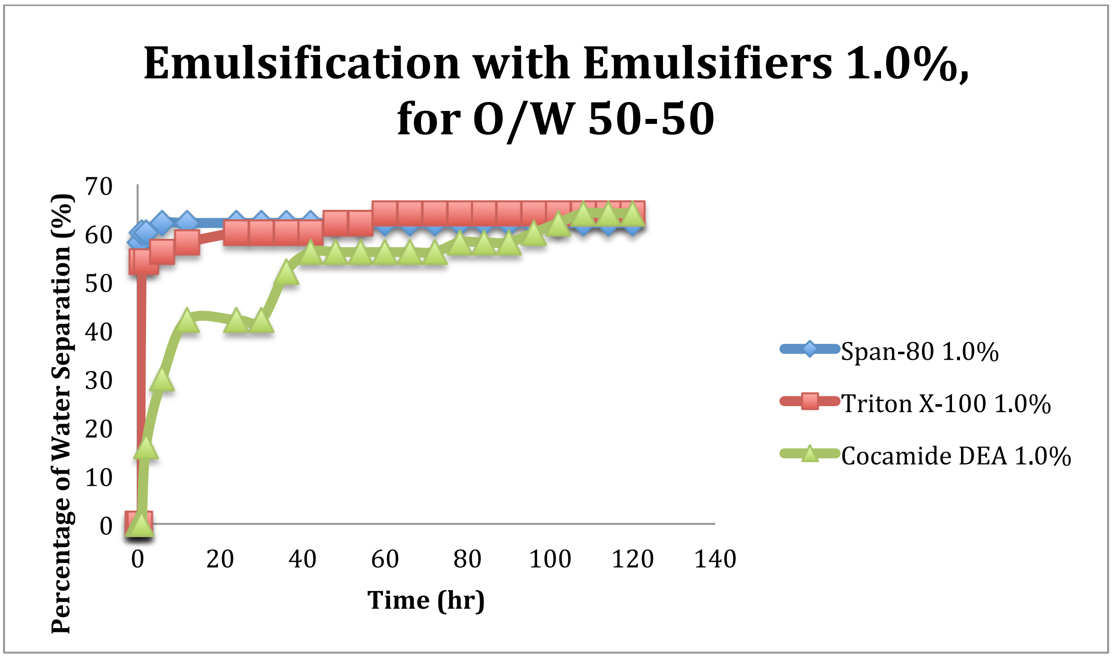


Figure 4.1.11: Percentage of Water Separation for O/W Ratio 50-50 Using Emulsifiers with 1.0%

Based on the result gained in Table 4.1.4, the graph of percentage of water separation against time is showed in Figure 4.1.11. Based on the figure 4.1.11 above, the least percentage of water separation between these 3 prepared emulsions with emulsifiers is Span-80. Therefore we can conclude that the emulsion prepared with Span-80 is the most stable emulsion compared to emulsions prepared with Triton X-100 and Cocamide DEA. While the emulsions prepared with these two emulsifiers share the same amount of separation, which is at 32 ml, equivalent to 64%. This result was expected because due to the increased entropy for the effective collisions between the droplets, the coalescence rate is reduced for the increasing dispersed phase volume fractions (N.H. Abdurahman, 2013). However, phase inversion will occur due to over limit of concentration of oil, which leads to the increasing of viscosity. (N.H. Abdurahman, 2013).

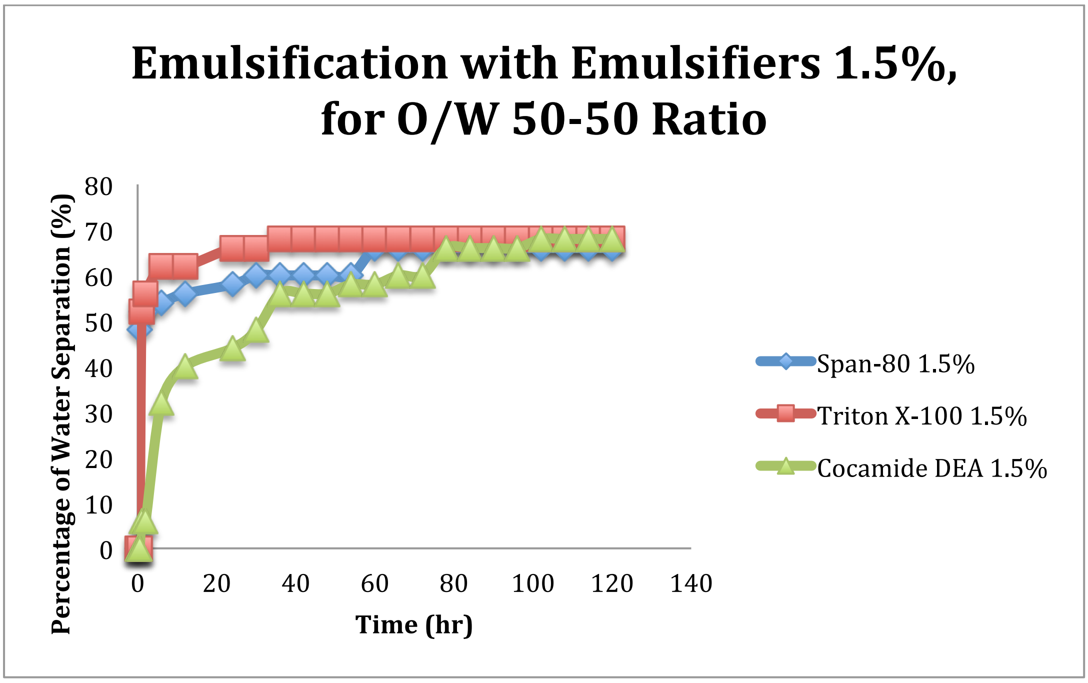


Figure 4.1.12: Percentage of Water Separation for O/W 50-50 using Emulsifiers 1.5%

For emulsification using emulsifiers with weight percentage of 1.5%, the result is shown in Figure 4.1.12. The separations of water for all the three emulsifiers are in range of 33ml to 34ml, which Span-80 has the least water separation, which is at 33 ml, and both Triton X-100 and Cocamide DEA share the same amount of separation, which is at 34ml. We can conclude here with the same conclusion that based on the result of emulsification using 1.0% emulsifiers which is that Span-80 provided the most stable emulsion at 50-50 O/W ratio using emulsifiers with weight percentage of 1.5%. But comparison between the weight percentages used for this ratio, as we increase the surfactant, the amount of separation increases by 4% to 5%.

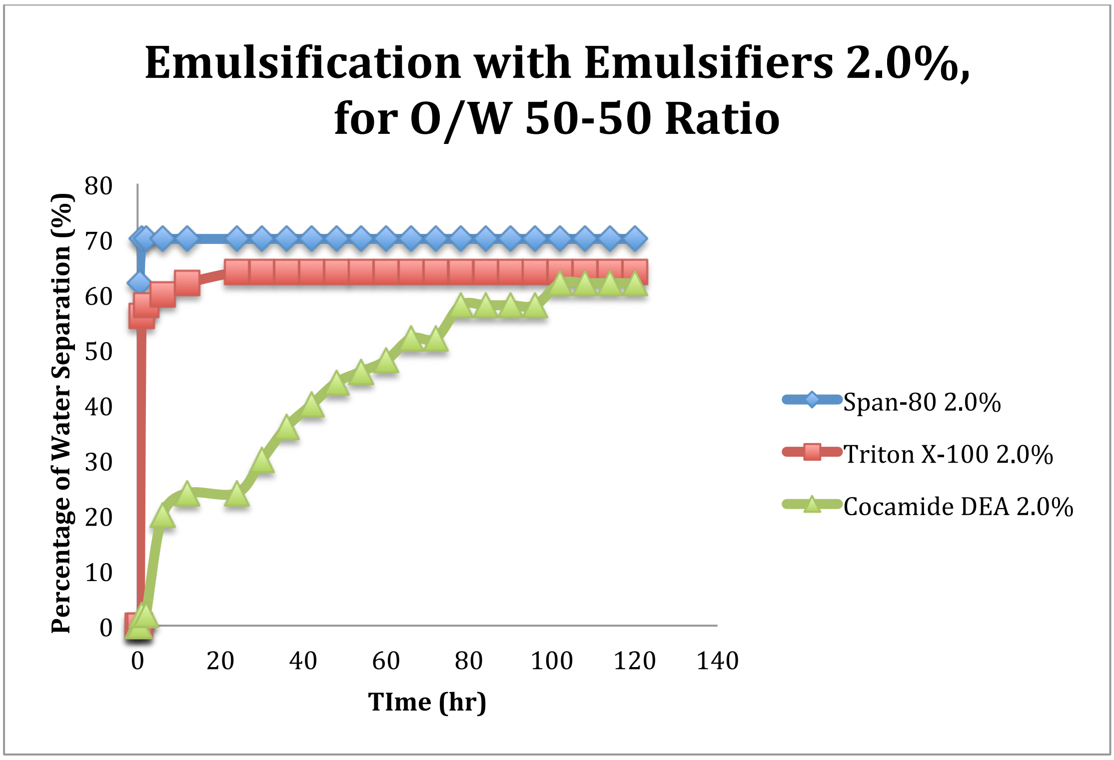


Figure 4.1.13: Percentage of Water Separation for O/W Ratio 50-50 using 2.0% Emulsifiers

Based on Figure 4.1.13, we have figured out the percentage of water separation for 50-50 O/W ratio with the concentration used, which is 2.0%. The result for Span-80 differs from the two earlier concentrations because based on the result, Span-80 has the highest amount of separation which is at 35ml, equivalent to 70%. For Triton X-100 and Cocamide DEA the amount of separation is 32ml and 31ml respectively, which in this case, Cocamide DEA is the best emulsifier that can be used if they were to used 2.0% as the weight percentage. For all the three concentrations used, we can conclude that as we increased the amount of surfactant would result in decreasing the stability of the emulsion for emulsifier Span-80, but increases the stability of emulsion for Triton X-100 and Cocamide DEA by increasing the concentration from 1.5% to 2.0%. In this case, for Triton X-100 and Cocamide DEA it is expected because increasing the surfactant concentration would affect in lowering the interfacial tension, which would assist in the breakage of droplets into smaller ones. The sample would result in a more stable emulsion because of a higher viscosity emulsion is produced (Sakka, 2002).

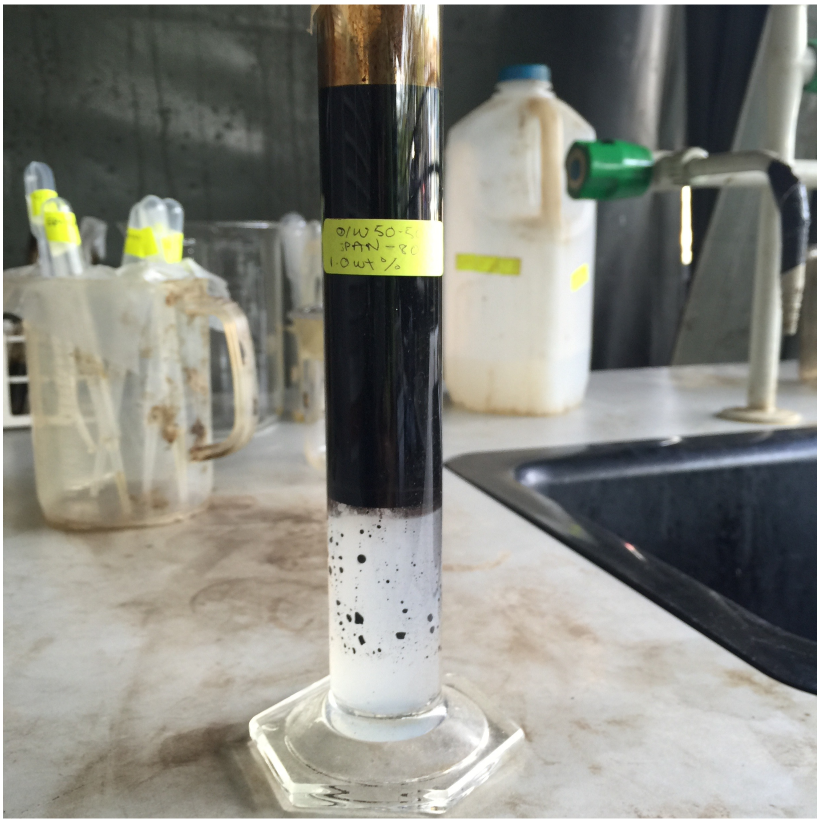


Figure 4.1.14: Emulsion of O/W Ratio 50-50 with Span-80 1.0%

Based on the experiment of this parameter which is O/W 50-50 ratio, we can conclude that the best surfactant that can be used to produce a stable emulsion for this particular ratio is Span-80 with 1.0% of concentration. The reason behind this surfactant being chosen is that the emulsion made with it has the least separation compared to the other emulsifiers being used except for Cocamide DEA with 2.0% concentration. Despite the emulsion with 2.0% Cocamide DEA has the same amount of separation with Span-80 1.0%, the amount of surfactant concentration being used higher that would make the emulsion more expensive. So reducing the cost of the emulsifiers and emulsion in transporting the heavy crude oil is also one of the main factors to be considered.

Table 4.1.5: Result for Percentage of Water Separation for O/W 65-35 Ratio

Type of Emulsifier	Concentration (wt %)	65-35% O/W Ratio		Percentage of Water Separation (%)	Date	Time (hr)
		Oil	Water			
Span-80	1.0	100	0	0	13/4/2015	15:49
	1.5	100	0	0	13/4/2015	16:10
	2.0	100	0	0	13/4/2015	16:30
Triton X-100	1.0	82	18	51.4	16/4/2015	14:30
	1.5	85	15	42.9	16/4/2015	14:46
	2.0	88	12	34.3	16/4/2015	14:59
Cocamide DEA	1.0	89	11	31.4	18/4/2015	16:35
	1.5	91	9	25.7	18/4/2015	17:00
	2.0	96	4	11.4	18/4/2015	17.30

Based on the result shown in Table 4.1.5, there are no separations for Span-80 for all the three concentrations used after five days. While for Triton X-100 and Cocamide DEA, the percentage of separation ranged from 10% to 52% for all concentrations used. Details of discussion are discussed further below.

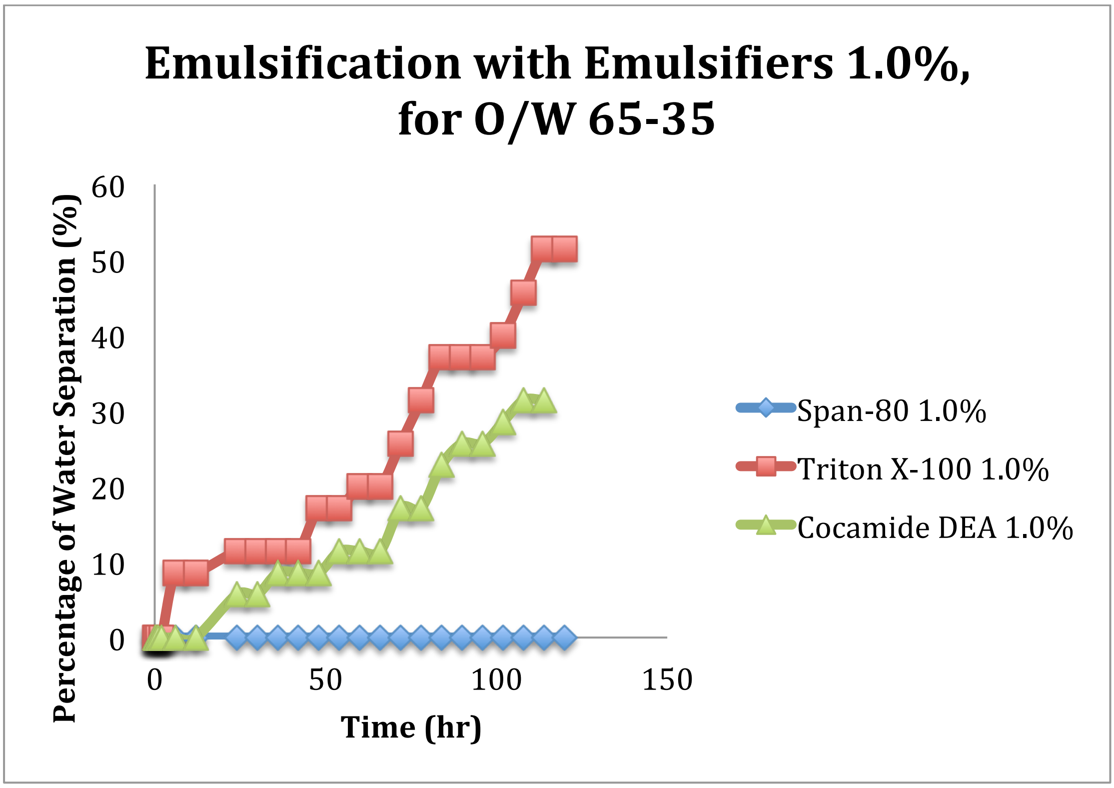


Figure 4.1.15: Percentage of Water Separation for O/W 65/35 Ratio with Emulsifiers 1.0%

The stability of the emulsions largely increased when the ratio is changed to 65-35%. Maximum oil content limit plays a very important role in designing the emulsion transport system. Obviously, it is desirable to reduce the water content to enhance the efficiency of the transportation system so that the pipe will be less occupied with water. For Span-80, there is no separation until the fifth day which result by the stability of the emulsion is too high. Over a certain limit of concentration, a critical enhancement in viscosity would occur when increasing the oil content due to the occurrence of the phase inversion (Ashrafizadeh, 2010). For Triton X-100 and Cocamide DEA, a change in stability can be seen from the 50-50 O/W ratio used, as the amount of separation became much less. The decrease of the water separation depends strong on the droplet size distribution.

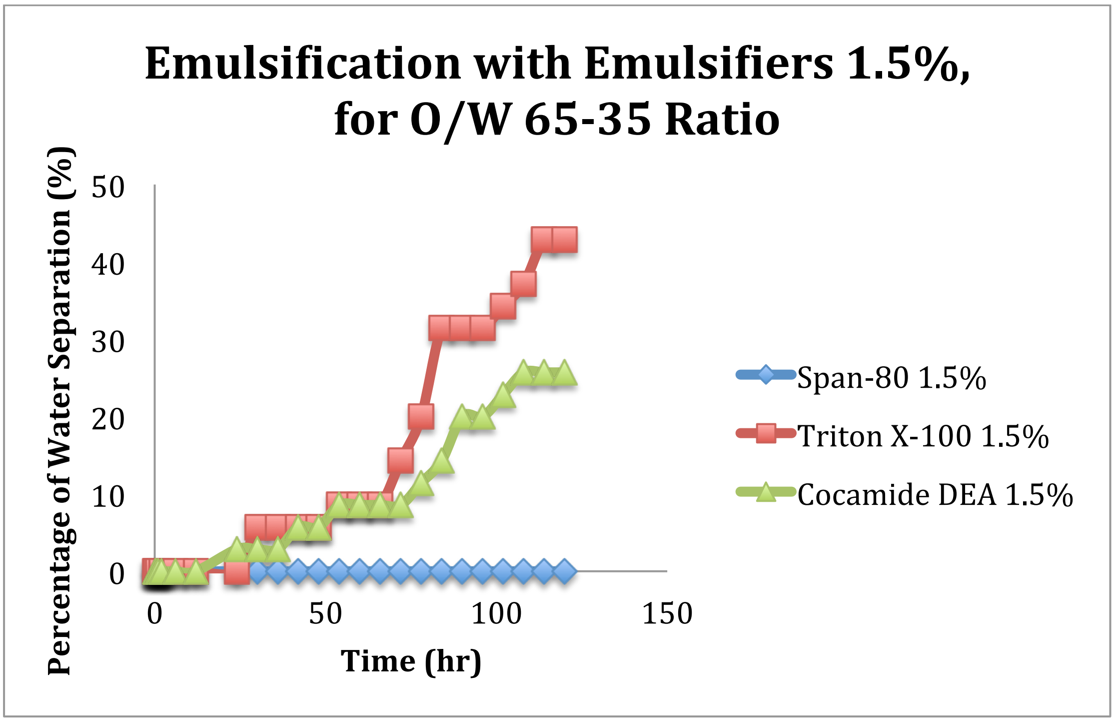


Figure 4.1.16: Percentage of Water Separation for O/W Ratio 65-35 for Emulsifiers 1.5%

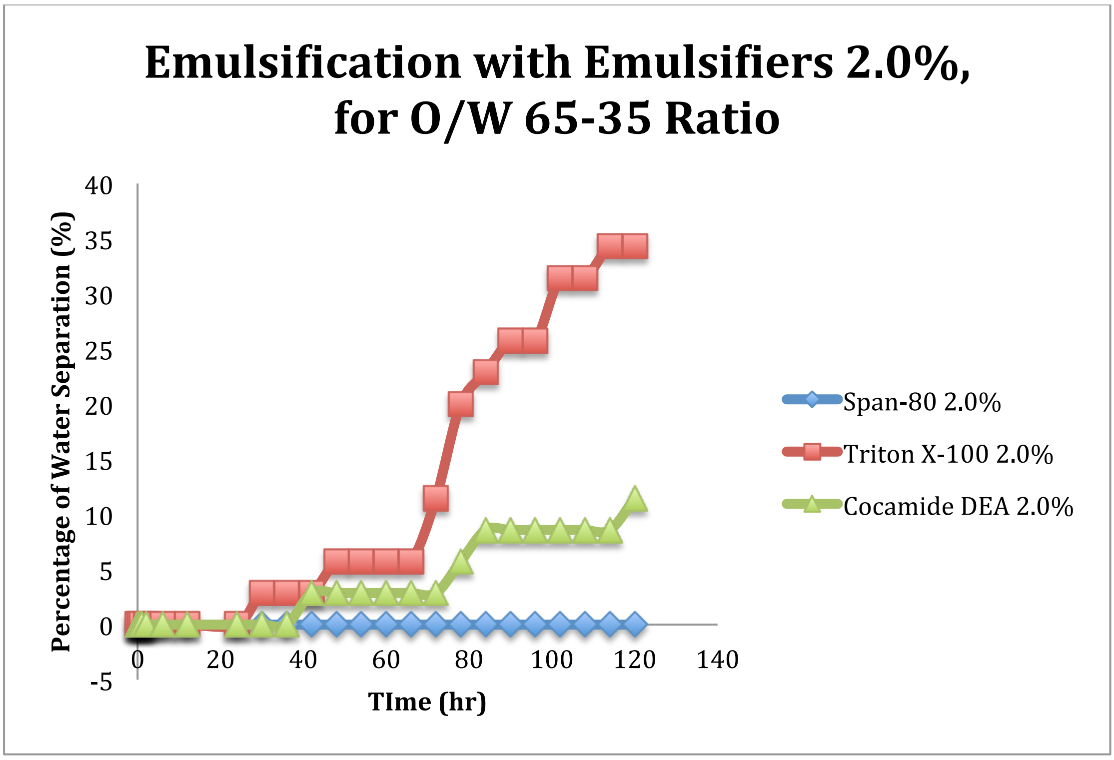


Figure 4.1.17: Percentage of Water Separation for O/W Ratio 65-35 for Emulsifiers 2.0%

The stability of emulsions increases when the concentrations are increased. An effective method to reduce the viscosity of heavy oil is the formation of O/W emulsions with the facilitate of emulsifiers (Martinez-Palou et al. 2011). There are still no separation for Span-80 after 5 days when 1.5% and 2.0% concentrations are used. These result are expected because the surfactant concentration strongly influence emulsion stability (Otsberg, 1992). As it can be observed from Figure 4.1.16 and Figure 4.1.17 the increasing of actual emulsifier’s concentration in the liquid phase will increases emulsion stability and viscosity, respectively. From the graph too the stability of emulsions increase when the concentrations of surfactant Triton X-100 and Cocamide DEA are increased, emulsion stability is increased from 1.5% to 2.0%. This observation is explained by (Zaki, 1997) where the addition of emulsifiers is explained in an increase in the amount of emulsifier molecules adsorbed at the oil/water interface. Meanwhile, the viscosity has significantly increased when the concentration of emulsifier increase. (Eirong, 2006) found that the addition of surfactant concentration in the emulsion will increases along the viscosity of the emulsion. The O/W emulsion becomes more stable by increasing the concentration of surfactant. The increase amount of surfactant promotes each droplet was covered well to avoid the droplets from coalesce. The adsorbed emulsifier between oil and water molecules because of their non-ionic nature contribute a steric obstacle to droplet oil (dispersed phase) to be coalescence (Singh, 1994; Singh and Pandey, 1991). Furthermore, Ashrafizadeh and Kamran, (2010) reported the increasing of emulsifiers concentration are effect an increments of obstacle between the two different phases and provides a good distribution of oil droplets (dispersed phase) in the water (continuous phase).

Figure 4.1.18: 65-35 O/W Ratio with Span-80 1.0% Emulsifier

Based on the research on O/W ratio 65/35 ratio, the best surfactant among the three surfactants used is also Span-80, the separations for all the three concentrations used are non after five days. To select the best Span-80 emulsion among the three concentrations used, it has to be the least one which is the 1.0%. The same reason stated in the O/W 50/50 emulsion as reducing the concentration would reduce the cost of it. Based on (Eirong, 2006), there will be a significant change for the viscosity when the concentration of the surfactant is increased. Which result in increasing the stability, but in this case, reducing the concentration will not change the stability of the emulsion as after 5 days, no separated water can be seen for the three samples which proves that for all the three concentrations, the emulsion prepared are stable.

Table 4.1.6: Result for Percentage of Water Separation for O/W 65-35 Ratio

Type of Emulsifier	Concentration (wt %)	80-20% O/W Ratio		Percentage of Water Separation (%)	Date	Time (hr)
		Oil	Water			
Span-80	1.0	100	0	0	23/4/2015	15:41
	1.5	100	0	0	23/4/2015	15.55
	2.0	100	0	0	23/4/2015	16:05
Triton X-100	1.0	100	0	0	23/4/2015	16:20
	1.5	100	0	0	25/4/2015	14:30
	2.0	100	0	0	25/4/2015	14:40
Cocamide DEA	1.0	100	0	0	25/4/2015	14:55
	1.5	100	0	0	25/4/2015	15:17
	2.0	100	0	0	25/4/2015	15:30

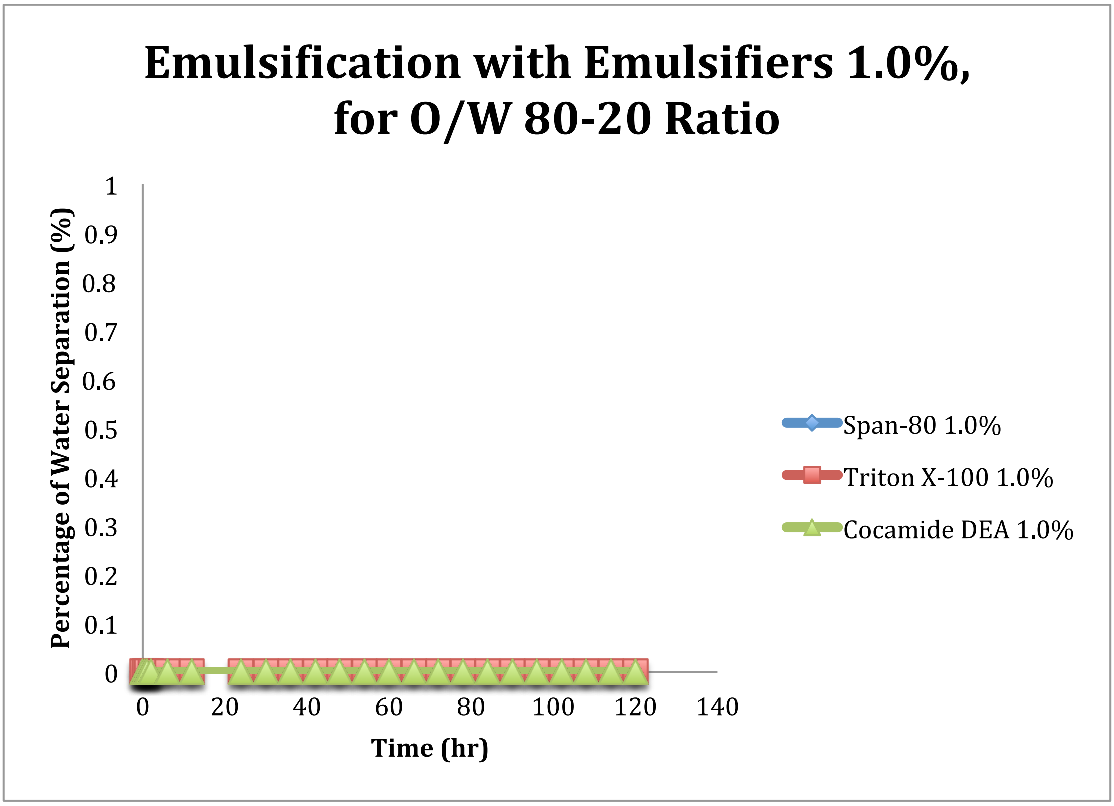


Figure 4.1.19: Percentage of Water Separation for O/W Ratio 80-20 for Emulsifiers 1.0%

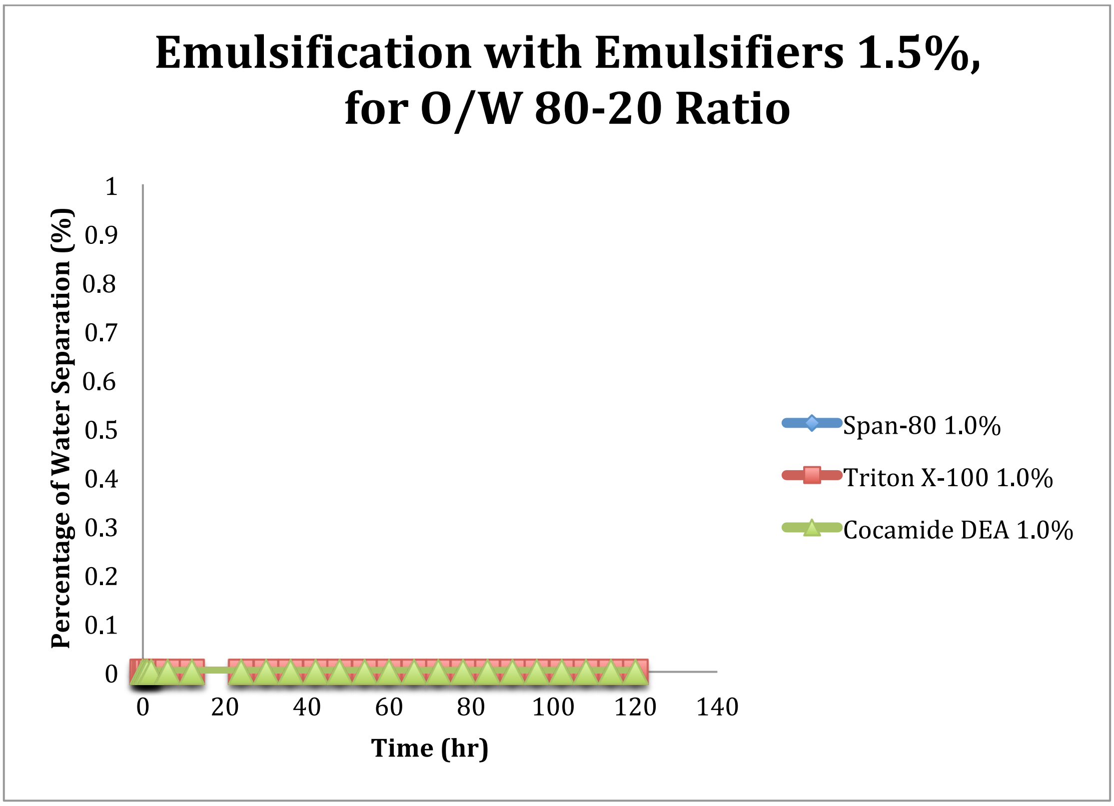


Figure 4.1.20: Percentage of Water Separation for O/W Ratio 80-20 for Emulsifiers 2.0%

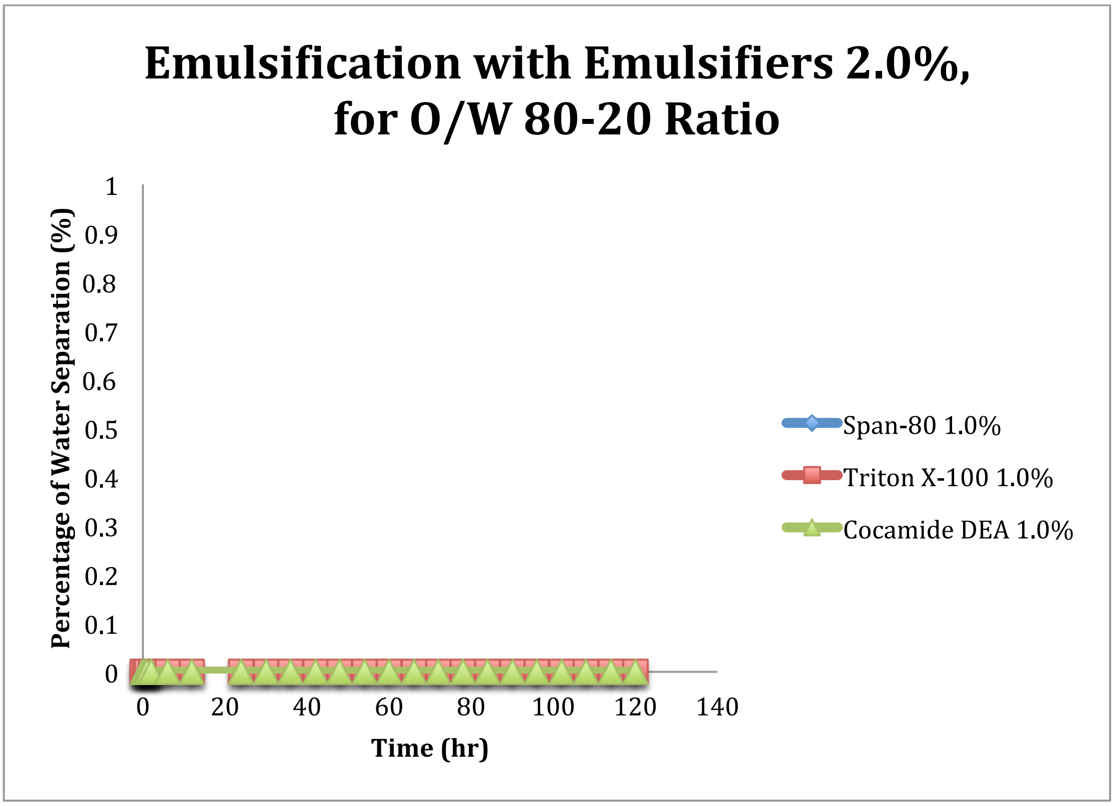


Figure 4.1.21: Percentage of Water Separation for O/W Ratio 80-20 for Emulsifiers 2.0%

The stability of O/W emulsion rapidly increased when the ratio is changed to 80-20%. Maximum oil content limit plays a very important role in designing the emulsion transport system. Obviously, it is desirable to reduce the water content of the emulsions as much less as possible to enhance the efficiency of the transportation system as less pipe space will be occupied by water. On the other hand, beyond a certain limit, increasing the oil content of the emulsion would result in a significant enhancement in its viscosity due to the occurrence of the phase inversion (Ashrafizadeh, 2010). The homogeneous of emulsion sample were obtained by using high speed of mixing with longer the time of mixing. There are no separations at all after being left for 5 days, the samples were left for an extra of 7 days and still no separation were observed. The decrease of the water separation depends strongly on the droplet size and droplet size distribution.

Figure 4.1.22: Emulsion for Ratio O/W 80-20 with Emulsifiers Span-80 1.0%

For this particular ratio of O/W 80/20, there are no separations for all the three emulsifiers used with all three different concentrations used after a period of 5 days. The difficulty on selecting the best emulsifier for this particular ratio is higher compared to the previous ratios as it can be selected by comparing the separation of water. For this ratio, Span-80 with 1.0% concentration has been chosen as the best emulsifier among the other emulsifiers because of the cost of the emulsifier itself compared to Triton X-100 and Cocamide DEA. In addition the concentration selected is 1.0% because least concentration used can contribute to reducing the cost in preparing the emulsion.

4.2 Effect of Speed (rpm) on Viscosity

Based on the gravitational stability test, result shows that Span-80 with 1.0% weight percentage concentration provided the best stability for the emulsions with ratio O/W ratio 50-50, 65-35 and 80-20. Therefore three of these samples are taken for Brookfield test to find out their viscosity, sheer stress, sheer rate, and torque based on certain speed.

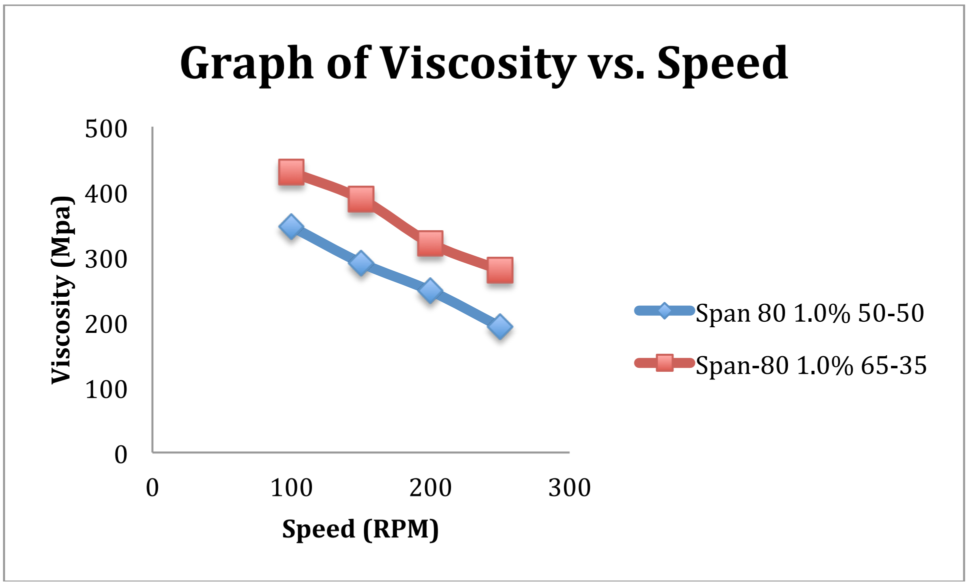


Figure 4.2.23: Effect of Speed on Viscosity

Based on the result using the Brookfield, it shows that the viscosity of the emulsion sample 80 1.0% for O/W ratio 50-50 is decreases as the rpm is being increased. Increasing either speed or time of mixing has a similar effect on the emulsions quality. Their increase has a decreasing effect on the viscosity of the emulsions while increases the stability of the emulsions up to a desirable level. On the other hand, increasing the speed from range 100 to 250 rpm result in decreasing the viscosity of the emulsion. But, the span 80 for ratio O/W 80-20 has the highest viscosity compared with others emulsifier while increasing the speed, but it is not stated in the graph because of its too high viscosity, it is immeasurable by the Brookfield machine, but it is detected at 5 rpm, the viscosity is 3527 Mpa. Thus increasing its concentration in the emulsion increases the viscosity of the emulsion (Eirong J. L., 2006). At the same time, increasing the surfactant concentration would lower the interfacial tension, which would facilitate the breakage of droplets into smaller ones. The latter would result in a more stable emulsion of higher viscosity (Sakka, 2002).

4.3 Effect of Shear Rate on Viscosity

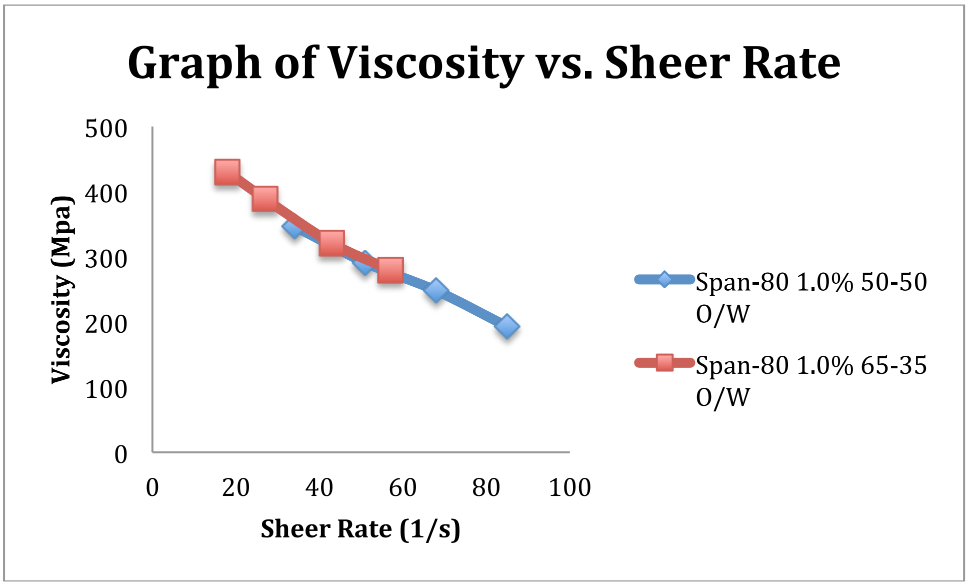


Figure 4.3.24: Effect of Sheer Rate on Viscosity

For the samples of emulsions that are emulsified with span-80 at 50-50 and 65-35 O/W ratio, it shows non-Newtonian shear thinning behavior over the range of shear rates from 34 to 85 in which the apparent viscosity decreases considerably with viscosity. The viscosity differences were larger at low shear rates than at high shear rates. The rheological behaviour of an emulsion may be either Newtonian or non-Newtonian depending upon its ratio. When shear stress is applied, Newtonian liquid flows as long as stress is applied even after stress is removed (McClements, 2005).

4.4 *Effect of Shear Rate and Shear Stress*

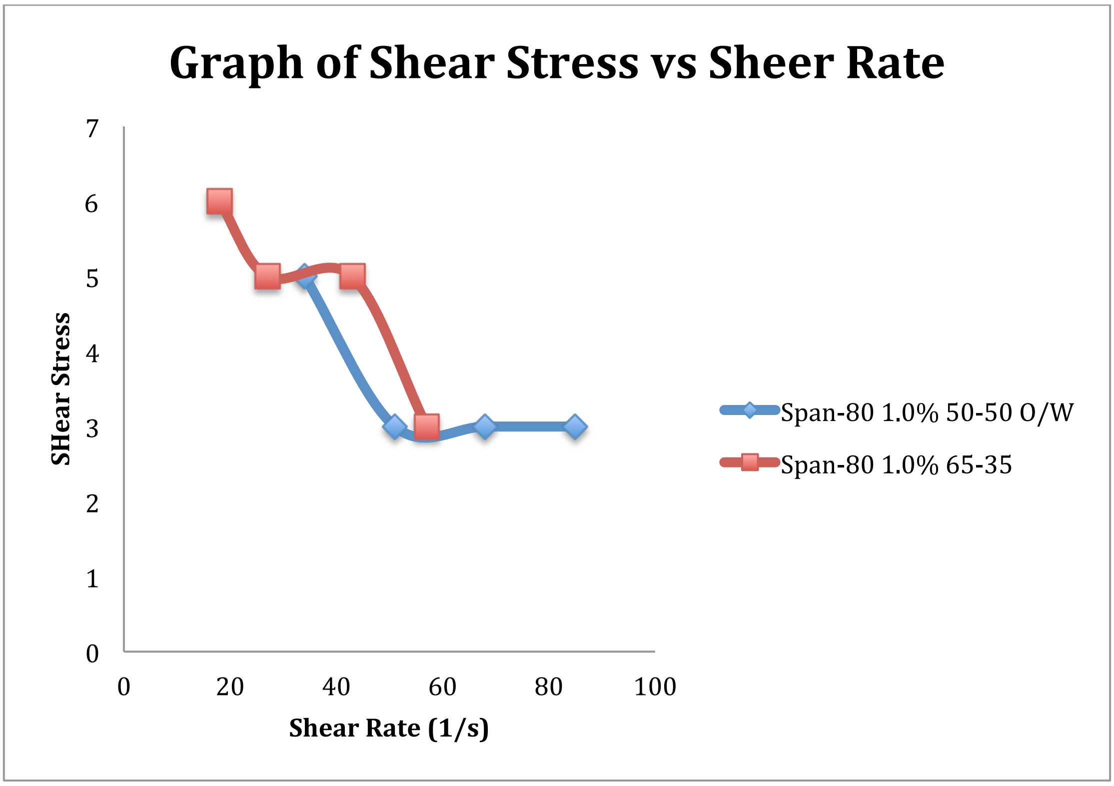


Figure 4.4.25: Result on Shear Stress vs. Shear Rate

The shear stress versus shear rate profile is presented in Figure 4.4.25. The rheological behaviour of an emulsion may be either Newtonian or non-Newtonian depending upon its ratio. When shear stress is applied, Newtonian liquid flows as long as stress is applied even after stress is removed (McClements, 2005). When increasing the dispersed phase ratio which is the oil, both the emulsion for the ratio of 50-50 and 65-35 with emulsifier of Span-80 1.0% obtained non-Newtonian behaviour. As proposed from Chhabra, (2007) and Lee et al. (1997), as increasing dispersed phase ratio, the emulsion behaviour more on non-Newtonian due to the alteration of rheological properties of fluid flow condition.

4.5 Effect of Interfacial Tension and Surface Tension

Surface tension is a measure of the force at a boundary between condenses and gas phase. If these attractive forces are between two immiscible liquids, which boundary between two condensed phases, like oil and water, they are referred to as interfacial tension. The interfacial tension of crude oil are important because they are also indicative the ease of formation and emulsion stability. Surfactants are special classes of molecules, which are both hydrophobic and hydrophilic; hence the most stable configuration for these molecules is at the crude oil and water interface. These molecules are generally injected in order to reduce the interfacial tension between crude oil and water. The interfacial tension plays a fundamental role in conventional and enhanced oil recovery (EOR) methods (Amir et al., 2012). The tensiometer was set up with value is 0.997 and at temperature of 25 °C. From the tensiometer testing, the average result from 3 repeated data obtained for surface tension of air and water is 57.11 N/m. For interfacial tension between heavy crude oil and air is 27.14 N/m. Meanwhile, for interfacial tension between heavy crude oil and water is 11.93 N/m. Refer to A.N. Ilia Anisa et al. (2010), at the inversion, the interfacial tension decreases favour the breaking process thus, produced smaller droplets size and associated higher viscosity.

4.6 Demulsification

After the emulsification process of the emulsions, the 3 of the best samples out of 27 of all the ratios were taken for the demulsification process. The emulsion selected to proceed with the demulsification for the ratio of O/W 50/50 is Span-80 with 1.0% concentration.

Table 4.6.7: Result on Demulsification for the Ratio of O/W 50-50 emulsion

Type of Demulsifier	Concentration (wt %)	50-50% O/W Ratio		Percentage of Water Separation (%)	Date	Time (hr)
		Oil	Water			
Hexylamine	1.0	9	41	164	29/4/2015	15:01
	1.5	14	36	144	29/4/2015	15.10
	2.0	36	14	56	29/4/2015	16:20
Cocamide MEA	1.0	50	0	0	29/4/2015	16:30
	1.5	50	0	0	29/4/2015	16:40
	2.0	30	20	80	29/4/2015	16:55
Dioctylamine	1.0	36	14	56	29/4/2015	17:06
	1.5	30	20	80	29/4/2015	17:14
	2.0	50	0	0	29/4/2015	17:24

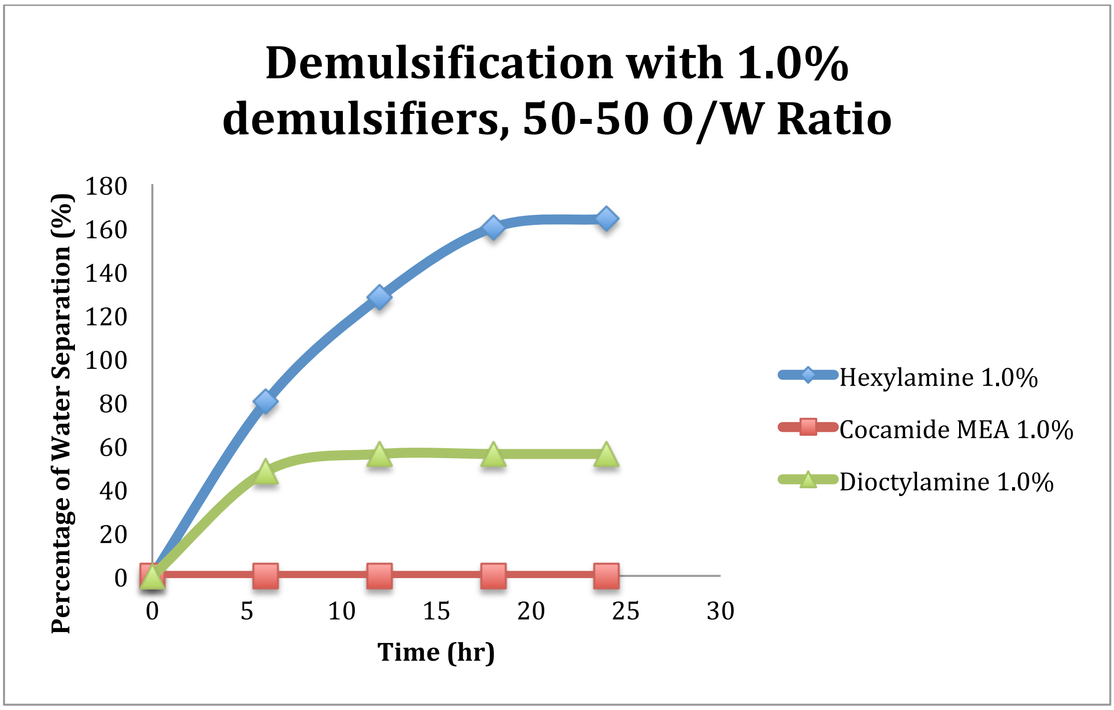


Figure 4.6.26: Demulsification with 1.0% Emulsifiers, 50-50 O/W Ratio

According to the previous study done by (Abdurahman, 2007), the descending sequence of amine demulsifier efficiency was due to high molecular weight factor which acts as flocculants in adsorption and interaction activities. Based on the figure 4.6.26, the emulsion with the highest percentage of separation is Hexylamine which is at 164%. The error which lead to the high percentage of error is because the method of preparing the emulsion with the demulsifier. Supposed that the water content in the emulsion is only 25ml as the total volume of the emulsion is 50 ml. But based on the result it shows that the hexylamine is able to separate most of the water content which make the emulsifier the most suitable in destabilizing the emulsion.

Figure 4.6.27: Ratio of O/W 50-50 Emulsion with Hexylamine 1.0%

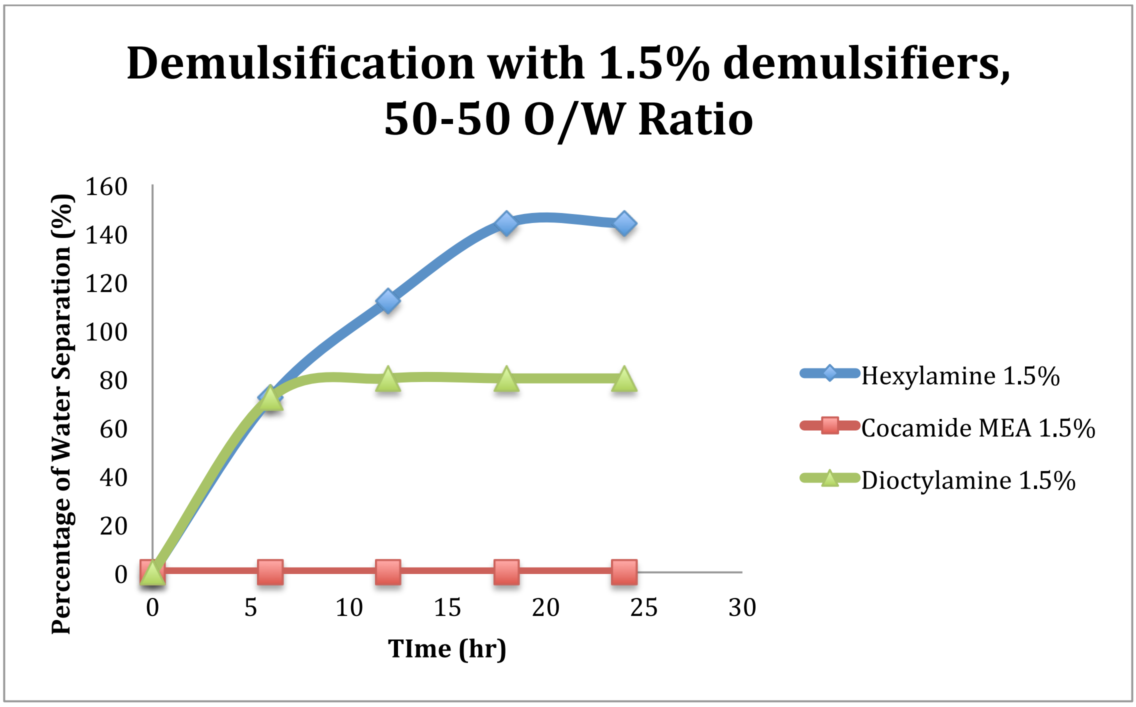


Figure 4.6.28: Demulsification with 1.5% Emulsifiers, 50-50 O/W Ratio

Based on the graph obtained in Figure 4.6.28, the highest percentage of separation is still hexylamine which is at 36ml, but the percentage of separation is slight less than when using hexylamine 1.0% which is at 144%, less 20% from the 1.0% of concentration of hexylamine. The result for Cocamide DEA for both concentrations remained the same with no separation after 24 hours. Dioctylamine with 1.5% concentration is tested with the ratio and the result for it is a moderate one as the percentage of water separation is at 80%, obviously more than Cocamide DEA and less than Hexylamine.

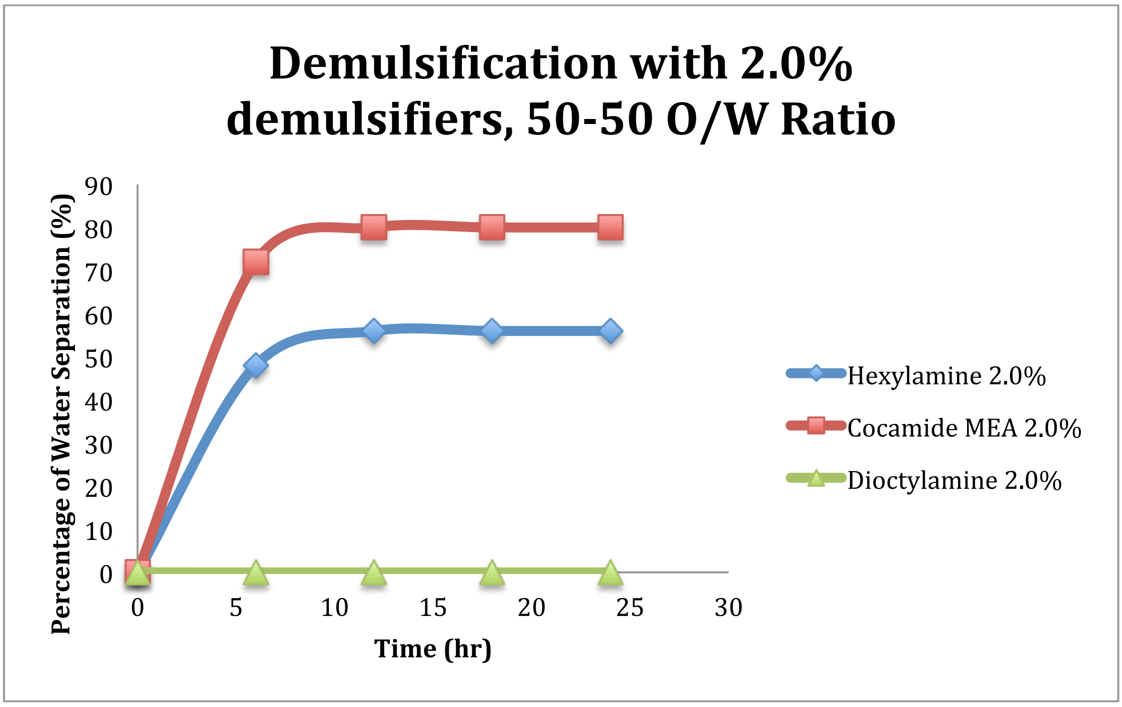


Figure 4.6.29: Demulsification with 2.0% Emulsifers for 50-50 O/W Ratio

Total change can be seen when the concentration of demulsifiers are increased to 2.0% as Cocamide DEA provided the best separation which is at 80% while emulsion with dioctylamine with 2.0% concentration did not have any separation at all after 24 hours.

Conclusion can be made that the best demulsifier to destabilize the emulsion of Ratio O/W is Hexylamine 1.0% as it provided the highest percentage of separation.

Table 4.6.8: Result of Demulsification with Demulsifiers for Ratio of O/W 65-35

Type of Demulsifier	Concentration (wt %)	65-35% O/W Ratio		Percentage of Water Separation (%)	Date	Time (hr)
		Oil	Water			
Hexylamine	1.0	50	0	0	1/5/2015	14:01
	1.5	50	0	0	1/5/2015	14.15
	2.0	50	0	0	1/5/2015	14:25
Cocamide MEA	1.0	50	0	0	1/5/2015	14:40
	1.5	44	6	34.3	1/5/2015	14:55
	2.0	50	0	0	1/5/2015	15:07
Dioctylamine	1.0	50	0	0	1/5/2015	15:25
	1.5	50	0	0	1/5/2015	15:37
	2.0	50	0	0	1/5/2015	15:51

Based on the Table 4.6.8, the results for emulsions with demulsifiers for the ratio of O/W 65-35 were obtained. There was only separation for the emulsion with demulsifier of Cocamide MEA while no separation can be viewed for other emulsifiers after 24 hours.

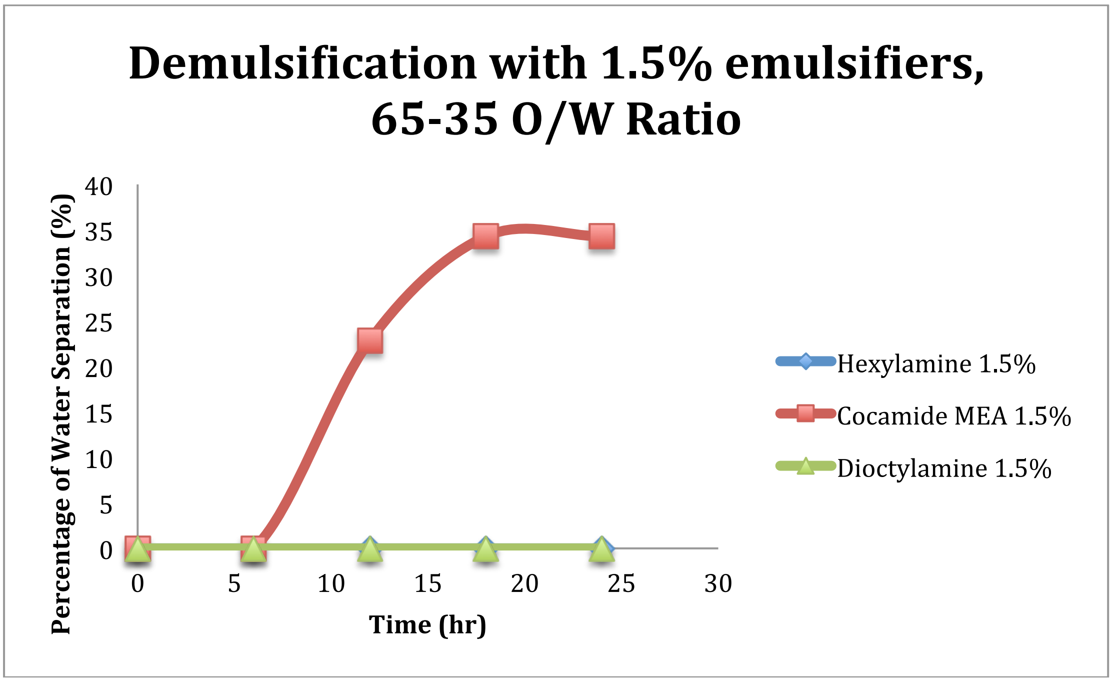


Figure 4.6.30: Demulsification with 1.5% Emulsifiers for 65-35 O/W Ratio

Emulsion with Cocamide MEA 1.5% has the highest percentage of separation which is at 34.3%, According to (Souleyman et al., 2007) a good and effective oil soluble demulsifier usually reduce the interfacial tension gradient and the interfacial viscosity which causes an increase in the rate of film thinning and a decrease in the time it takes the film to reach a certain thickness as shows by Hexylamine, Cocamide MEA and Dioctylamine.

Figure 4.6.31: Ratio of 65/35 Emulsion with Demulsifier MEA 1.5

Table 4.6.9: Result of Demulsification with Demulsifiers for Ratio of O/W 80-20

Type of Demulsifier	Concentration (wt %)	80-20% O/W Ratio		Percentage of Water Separation (%)	Date	Time (hr)
		Oil	Water			
Hexylamine	1.0	50	0	0	04/05/2015	16:41
	1.5	50	0	0	04/05/2015	16.55
	2.0	50	0	0	04/05/2015	17:05
Cocamide MEA	1.0	50	0	0	04/05/2015	17:20
	1.5	50	0	0	04/05/2015	17:30
	2.0	50	0	0	04/05/2015	17:40
Dioctylamine	1.0	50	0	0	04/05/2015	17:55
	1.5	50	0	0	04/05/2015	18:17
	2.0	50	0	0	04/05/2015	18:30

Based on Table 4.6.9, no separation can be seen after 24 hours. The result behind the result is probably because of few reasons, first is that the emulsion made from the emulsifiers were very stable, second is that the emulsifiers used were very suitable for this particular ratio and third is that the emulsion has achieved phase inversion where the amount of continuous phase was reduced beyond its limit. The logical reason that can be made is also that the demulsifiers used are not suitable for the emulsion.

4.7 Droplet Size

The droplet size of an emulsion is important variables which are affecting the colloidal stability and rheological properties such as the flow and deformations of the emulsion (Han et al., 2011). The droplet size distribution for the emulsions was determined as a function of surfactant using Carl Zeiss research microscope equipped with the digital camera and AxioVission AC image analysis software. The average of droplet size distribution of emulsion is measured by taking randomly, approximately eight to ten different droplet size images.

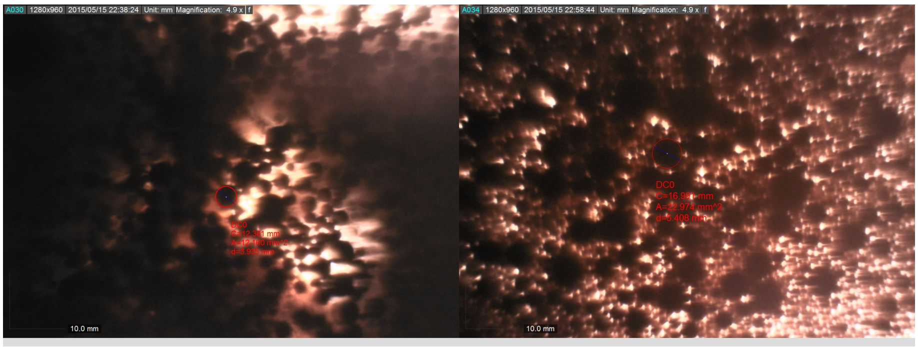


Figure 4.7.32: Droplet Size Measurement for Emulsion of Span-80 for 50-50 ratio (left) and then demulsified with Hexylamine 1.0% for the ratio of O/W 50-50 (right)

Based on the result gained on Figure 4.7.32, the droplet size diameter before it was being demulsified is 3.935 µm, after it was being demulsified was 5.408 µm. Clearly that adding the demulsifier increases the droplet size which contribute to the destabilization of the emulsion as the viscosity is reduced. The droplet between oil and water become more tight relation and hard to break due to high mixing speed and present of certain amount of surfactant. At the same time, the increasing mixing speed and mixing time also could cause small droplet size which is finally increase the stability of the emulsion (Ashrafizadeh, 2010). Parkinson et al. (1970) considered the influence of droplet size distribution on the stability and viscosity of the emulsion. This fact are already discussed by Azodiand Solaimany(2013) and Abdurahman et al., (2012) where the increasing of surfactant concentration and mixing speed will reduces average oil droplets size leading to an increase of the viscosity of O/W emulsion.

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The research has been successfully done after a period of time. Oil-in-water emulsions were successfully prepared by the heavy crude oil provided by Petronas Refinery Kerteh. The emulsions were prepared using three emulsifiers, which are Span-80, Triton X-100 and Cocamide DEA. Using oil-in-water emulsion and water as the continuous phase benefits the transportation of the heavy crude oil in pipeline by reducing the viscosity, which lead to the reducing of energy usage as it will ease the pumping of the oil, and less erosion and precipitation will occur inside the pipelines. As the continuous phase content decreases in the emulsion, the stability of the emulsion is increased. By referring to the result of the gravitational test, by comparing the ratio of 50-50%, 65-35% and 80-20%, we can conclude that 80-20% ratio has the best stability of O/W emulsion as no separation occurred after a week of observation. The most stable emulsifier for all the ratios that were being experimented was Span-80, followed by Triton X-100 and the last one is Cocamide DEA.

Demulsification process or the process of destabilization of the emulsion after the best emulsion being determined has been performed in order to determine the best demulsifier in order to separate the water from the oil. Three demulsifiers used in this research are Hexylamine, Cocamide MEA and Dioctylamine. The best demulsifier has been found out which Hexylamine as it provided the highest volume of separation for the ratio of 50-50% and 65-35%. All the demulsifiers were concluded as not suitable for the emulsions of 80-20% ratio as no separations occurred after 24 hours of observation.

Besides, the effect of interfacial tension between crude oil and water was investigated. The interfacial tension obtained by using the tensiometer is 11.193 N/m, while the surface tension of air and water obtained was 57.11 N/m. Meanwhile, the surface tension of heavy crude oil is 27.141 N/m.

On the other hand, no environmental drawbacks would occur by discharging the effluent. Moreover, since no surfactant remains in the oil phase, the problems encountered in the refining process of the crude oil such as foaming etc. are also prevented.

5.2 Future Work

The final year student supervised under Prof. Abdurahman Hamid Nour has continued this research with different emulsifiers and demulsifiers. The ratios also have been changed in order to vary the result on this research as the possibilities of the characterizations of heavy crude oils are wide.

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APPENDICES

EMULSIFICATION FOR RATIO O/W 50-50

Time (hr)	Volume of water separated for Span-80 1.0% (ml)	Percentage of water separated (%)	Volume of water separated for Triton X-100 1.0% (ml)	Percentage of water separated (%)	Volume of water separated for Cocamide MEA 1.0% (ml)	Percentage of water separated (%)
0	0	0	0	0	0	0
0.5	29	58	0	0	0	0
1	30	60	27	54	0	0
2	30	60	27	54	8	16
6	31	62	28	56	15	30
12	31	62	29	58	21	42
24	31	62	30	60	21	42
30	31	62	30	60	21	42
36	31	62	30	60	26	52
42	31	62	30	60	28	56
48	31	62	31	62	28	56
54	31	62	31	62	28	56
60	31	62	32	64	28	56
66	31	62	32	64	28	56
72	31	62	32	64	28	56
78	31	62	32	64	29	58
84	31	62	32	64	29	58
90	31	62	32	64	29	58
96	31	62	32	64	30	60
102	31	62	32	64	31	62
108	31	62	32	64	32	64
114	31	62	32	64	32	64
120	31	62	32	64	32	64

Time (hr)	Volume of water separated for Span-80 1.5% (ml)	Percentage of water separated (%)	Volume of water separated for Triton X-100 1.5% (ml)	Percentage of water separated (%)	Volume of water separated for Cocamide DEA 1.5% (ml)	Percentage of water separated (%)
0	0	0	0	0	0	0
0.5	24	48	0	0	0	0
1	26	52	26	52	3	6
2	26	52	28	56	3	6
6	27	54	31	62	16	32
12	28	56	31	62	20	40
24	29	58	33	66	22	44
30	30	60	33	66	24	48
36	30	60	34	68	28	56
42	30	60	34	68	28	56
48	30	60	34	68	28	56
54	30	60	34	68	29	58
60	33	66	34	68	29	58
66	33	66	34	68	30	60
72	33	66	34	68	30	60
78	33	66	34	68	33	66
84	33	66	34	68	33	66
90	33	66	34	68	33	66
96	33	66	34	68	33	66
102	33	66	34	68	34	68
108	33	66	34	68	34	68
114	33	66	34	68	34	68
120	33	66	34	68	34	68

Time (hr)	Volume of water separated for Span-80 2.0% (ml)	Percentage of water separated (%)	Volume of water separated for Triton X-100 2.0% (ml)	Percentage of water separated (%)	Volume of water separated for Cocamide DEA 2.0% (ml)	Percentage of water separated (%)
0	0	0	0	0	0	0
0.5	31	62	0	0	0	0
1	35	70	28	56	1	2
2	35	70	29	58	1	2
6	35	70	30	60	10	20
12	35	70	31	62	12	24
24	35	70	32	64	12	24
30	35	70	32	64	15	30
36	35	70	32	64	18	36
42	35	70	32	64	20	40
48	35	70	32	64	22	44
54	35	70	32	64	23	46
60	35	70	32	64	24	48
66	35	70	32	64	26	52
72	35	70	32	64	26	52
78	35	70	32	64	29	58
84	35	70	32	64	29	58
90	35	70	32	64	29	58
96	35	70	32	64	29	58
102	35	70	32	64	31	62
108	35	70	32	64	31	62
114	35	70	32	64	31	62
120	35	70	32	64	31	62

EMULSIFICATION FOR RATIO 65-35

Time (hr)	Volume of water separated for Span-80 1.0% (ml)	Percentage of water separated (%)	Volume of water separated for Triton X-100 1.0% (ml)	Percentage of water separated (%)	Volume of water separated for Cocamide MEA 1.0% (ml)	Percentage of water separated (%)
0	0	0	0	0	0	0
0.5	0	0	0	0	0	0
1	0	0	0	0	0	0
2	0	0	0	0	0	0
6	0	0	3	8.571428571	0	0
12	0	0	3	8.571428571	0	0
24	0	0	4	11.42857143	2	5.714285714
30	0	0	4	11.42857143	2	5.714285714
36	0	0	4	11.42857143	3	8.571428571
42	0	0	4	11.42857143	3	8.571428571
48	0	0	6	17.14285714	3	8.571428571
54	0	0	6	17.14285714	4	11.42857143
60	0	0	7	20	4	11.42857143
66	0	0	7	20	4	11.42857143
72	0	0	9	25.71428571	6	17.14285714
78	0	0	11	31.42857143	6	17.14285714
84	0	0	13	37.14285714	8	22.85714286
90	0	0	13	37.14285714	9	25.71428571
96	0	0	13	37.14285714	9	25.71428571
102	0	0	14	40	10	28.57142857
108	0	0	16	45.71428571	11	31.42857143
114	0	0	18	51.42857143	11	31.42857143
120	0	0	18	51.42857143	11	31.42857143

Time (hr)	Volume of water separated for Span-80 1.5% (ml)	Percentage of water separated (%)	Volume of water separated for Triton X-100 1.5% (ml)	Percentage of water separated (%)	Volume of water separated for Cocamide DEA 1.5% (ml)	Percentage of water separated (%)
0	0	0	0	0	0	0
0.5	0	0	0	0	0	0
1	0	0	0	0	0	0
2	0	0	0	0	0	0
6	0	0	0	0	0	0
12	0	0	0	0	0	0
24	0	0	0	0	1	2.857142857
30	0	0	2	5.714285714	1	2.857142857
36	0	0	2	5.714285714	1	2.857142857
42	0	0	2	5.714285714	2	5.714285714
48	0	0	2	5.714285714	2	5.714285714
54	0	0	3	8.571428571	3	8.571428571
60	0	0	3	8.571428571	3	8.571428571
66	0	0	3	8.571428571	3	8.571428571
72	0	0	5	14.28571429	3	8.571428571
78	0	0	7	20	4	11.42857143
84	0	0	11	31.42857143	5	14.28571429
90	0	0	11	31.42857143	7	20
96	0	0	11	31.42857143	7	20
102	0	0	12	34.28571429	8	22.85714286
108	0	0	13	37.14285714	9	25.71428571
114	0	0	15	42.85714286	9	25.71428571
120	0	0	15	42.85714286	9	25.71428571

Time (hr)	Volume of water separated for Span-80 2.0% (ml)	Percentage of water separated (%)	Volume of water separated for Triton X-100 2.0% (ml)	Percentage of water separated (%)	Volume of water separated for Cocamide DEA 2.0% (ml)	Percentage of water separated (%)
0	0	0	0	0	0	0
0.5	0	0	0	0	0	0
1	0	0	0	0	0	0
2	0	0	0	0	0	0
6	0	0	0	0	0	0
12	0	0	0	0	0	0
24	0	0	0	0	1	2.857142857
30	0	0	2	5.714285714	1	2.857142857
36	0	0	2	5.714285714	1	2.857142857
42	0	0	2	5.714285714	2	5.714285714
48	0	0	2	5.714285714	2	5.714285714
54	0	0	3	8.571428571	3	8.571428571
60	0	0	3	8.571428571	3	8.571428571
66	0	0	3	8.571428571	3	8.571428571
72	0	0	5	14.28571429	3	8.571428571
78	0	0	7	20	4	11.42857143
84	0	0	11	31.42857143	5	14.28571429
90	0	0	11	31.42857143	7	20
96	0	0	11	31.42857143	7	20
102	0	0	12	34.28571429	8	22.85714286
108	0	0	13	37.14285714	9	25.71428571
114	0	0	15	42.85714286	9	25.71428571
120	0	0	15	42.85714286	9	25.71428571

EMULSIFICATION FOR RATIO OF O/W 80-20

Time (hr)	**Volume of water separated for Span-80 1.0% (ml)**	**Percentage of water separated (%)**	**Volume of water separated for Triton X-100 1.0% (ml)**	**Percentage of water separated (%)**	**Volume of water separated for Cocamide MEA 1.0% (ml)**	**Percentage of water separated (%)**
0	0	0	0	0	0	0
0.5	0	0	0	0	0	0
1	0	0	0	0	0	0
2	0	0	0	0	0	0
6	0	0	0	0	0	0
12	0	0	0	0	0	0
24	0	0	0	0	0	0
30	0	0	0	0	0	0
36	0	0	0	0	0	0
42	0	0	0	0	0	0
48	0	0	0	0	0	0
54	0	0	0	0	0	0
60	0	0	0	0	0	0
66	0	0	0	0	0	0
72	0	0	0	0	0	0
78	0	0	0	0	0	0
84	0	0	0	0	0	0
90	0	0	0	0	0	0
96	0	0	0	0	0	0
102	0	0	0	0	0	0
108	0	0	0	0	0	0
114	0	0	0	0	0	0
120	0	0	0	0	0	0

Time (hr)	Volume of water separated for Span-80 1.5% (ml)	Percentage of water separated (%)	Volume of water separated for Triton X-100 1.5% (ml)	Percentage of water separated (%)	Volume of water separated for Cocamide DEA 1.5% (ml)	Percentage of water separated (%)
0	0	0	0	0	0	0
0.5	0	0	0	0	0	0
1	0	0	0	0	0	0
2	0	0	0	0	0	0
6	0	0	0	0	0	0
12	0	0	0	0	0	0
24	0	0	0	0	0	0
30	0	0	0	0	0	0
36	0	0	0	0	0	0
42	0	0	0	0	0	0
48	0	0	0	0	0	0
54	0	0	0	0	0	0
60	0	0	0	0	0	0
66	0	0	0	0	0	0
72	0	0	0	0	0	0
78	0	0	0	0	0	0
84	0	0	0	0	0	0
90	0	0	0	0	0	0
96	0	0	0	0	0	0
102	0	0	0	0	0	0
108	0	0	0	0	0	0
114	0	0	0	0	0	0
120	0	0	0	0	0	0

Time (hr)	Volume of water separated for Span-80 2.0% (ml)	Percentage of water separated (%)	Volume of water separated for Triton X-100 2.0% (ml)	Percentage of water separated (%)	Volume of water separated for Cocamide DEA 2.0% (ml)	Percentage of water separated (%)
0	0	0	0	0	0	0
0.5	0	0	0	0	0	0
1	0	0	0	0	0	0
2	0	0	0	0	0	0
6	0	0	0	0	0	0
12	0	0	0	0	0	0
24	0	0	0	0	0	0
30	0	0	0	0	0	0
36	0	0	0	0	0	0
42	0	0	0	0	0	0
48	0	0	0	0	0	0
54	0	0	0	0	0	0
60	0	0	0	0	0	0
66	0	0	0	0	0	0
72	0	0	0	0	0	0
78	0	0	0	0	0	0
84	0	0	0	0	0	0
90	0	0	0	0	0	0
96	0	0	0	0	0	0
102	0	0	0	0	0	0
108	0	0	0	0	0	0
114	0	0	0	0	0	0
120	0	0	0	0	0	0

BROOKFIELD

RPM	Viscosity	Sheer Stress	Sheer Rate	Torque
100	347	5	34	49.6
150	291	3	51	33.3
200	248	3	68	32.6
250	193	3	85	30.1

Span-80 1.0% 65-35 O/W

RPM	Viscosity	Sheer Stress	Sheer Rate	Torque
100	430	6	18	56.6
150	389	5	27	43.7
200	321	5	43	32.1
250	280	3	57	29.4

Span-80 1.0% 80-20 O/W

RPM	Viscosity	Sheer Stress	Sheer Rate	Torque
100	-	-	-	-
150	-	-	-	-
200	-	-	-	-
250	-	-	-	-

Hexylamine 1.0% Span-80 50-50

RPM	Viscosity	Sheer Stress	Sheer Rate	Torque
100	-	-	-	-
150	-	-	-	-
200	-	-	-	-
250	-	-	-	-