SEPARATION OF-CRUDE OIL EMULSION VIA ULTRASONIC TECHNOLOGY

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SEPARATION OF CRUDE OIL EMULSION VIA ULTRASONIC TECHNOLOGY

SITI ZALEHA BINTI ABDULLAH

Thesis submitted to the Faculty of Chemical and Natural Resources Engineering in
Partial Fulfillment of the Requirement for the
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Faculty of Chemical & Natural Resources Engineering
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APRIL, 2009

I declare that this thesis entitled "*Separation of Crude Oil Emulsion Via Ultrasonic Technology*" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Special Dedication of This Grateful Feeling to My…

Beloved father and mother;
Mr.Abdullah Hj Saleh and Mrs. Mariah Ismail

Loving brothers and sisters;
Adenan and Siti Asmah

Supportive friends;
Norsuzieana and all my friends

For Their Love, Support and Best Wishes.

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ABSTRACT

Emulsions have long been of great practical interest due to their widespread occurrence in everyday life. They may be found in important areas such as food, cosmetic, pharmaceutical and agricultural industry. Emulsions are also found in the petroleum industry. Water separated from water in oil emulsion by various method such as ultrasonic, chemical or microwave demulsification. Emulsifier are surfactant used to develop high surface pressure at emulsion interface. In this research the ultrasonic technology used to break the water in oil emulsion. For stability part, about three type of crude oil used in the stability part which are include heavy and light crude oil. The emulsion prepared by mix the crude oil with the emulsifier such as Span 80.Tween 80 and SDDS and the propeller will used to mix the mixture vigorously for 5 minute. The next step pour some water slowly into the crude oil and wait until 10 minutes to ensure the mixture is completely mixing.The speed for propeller is about 1250rpm.the sample will check water in oil emulsion by filter paper or test tube test.Record the data and observed what happen occur during experiment. For the demulsification part the Masila crude oil will used to compare the ultrasonic with chemical demulsification method. The hexylamine is the chemical used to break the emulsion.The data and observation will be record and graph will be plotted to show which one give best performance to break the emulsion.In conclusion the ultrasonic is not effienct method to break the emulsion compared to the chemical method.

ABSTRAK

Emulsi sudah lama tersebar luas yang berlaku dalam kehidupan seharian. Ia berkemungkinan dijumpai dalam bidang penting seperti makanan,kosmetik,farmasi dan industri pertanian. Emulsi juga dijumpai dalam industri petroleum. Permisahan air dari emulsi dengan pelbagai cara seperti ultrasonic,kimia atau gelombang micro. Pengelmusi ialah *surfactant* yang digunakan untuk membantu menaikkan tekanan di permukaan emulsi. Dlama kajian ini teknologi ultrasonic adlah cara yang digunakan untuk memisahkan emulsi .Untuk bahagian kestabilan emulsi tiga jenis minyak petroleum digunakan termasuk minyak petroleum yg mempunyai struktur molekul yang komplek dan ringkas. Persediaan emulsi adalah dengan mencampurkan minyak dengan pengelmusi seperti *Span 80*,*Tween 80* dan juga *SDDS* dan pengadun akan digunakan untuk mengadun campuran selama 5 minit. Peringkat seterusnya air dimasukkan perlahan-lahan ke dalam campuran minyak dengan pengelmusi selama 10 minit untuk memastikan bahawa campuran emulsi tadi betul betul bercampur. Kelajuan pengadun di setkan sebanyak 1250 rpm dan sampel diuji dengan kertas turas atau ujian tabung uji untuk memastikan jenis emulsi mengikut yang dikehendaki. Data dan pemerhatian direkodkan sepanjang eksperiment dilakukan. Bagi bahagian untuk pemisahan emulsi pula,minyak Masila digunakan untuk membandingkan cara pemisahan menggunakan ultrasonic dengan cara pemisahan secara kimia. Cecair kimia Hexylamine digunakan untuk memisahkan emulsi.Data dan pemerhatian direkodkan kemudian plot grraf untuk menunjukkan cara mana yang terbaik untuk memisahkan emulsi yang berlaku. Kesimpulannya, cara ultrasonic adalh tidak effisen untuk memisahkan emulsi jika dibandingkan dengan cara pemisahan secara kimia.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The petroleum industry usually involved with process of exploration, extraction, marketing the petroleum product and so on. As it known that the petroleum is the main raw material to produce a lot of chemical product such as plastic, pesticides, pharmaceutical and many more. The petroleum consists of hydrocarbon chains in their chemical structure at different lengths. Hydrogen and carbon are two main atomic involved in hydrocarbon chain which are come in straight branching chain to rings. There are varies types of process to separate the petroleum to be used in variety of purpose. The most common of petroleum separation is distillation. From this separation there are a lot of product will produce such are gasoline, kerosene, fuel and so on at different temperature depend on their boiling point. The crude oil usually comes out from underground of the reservoir. The characteristic of the crude oil are smelly and yellow to black liquid.

Water is normally present in crude oil reservoir or is injected as steam to stimulate oil production (Abdurahman et-al 2007). The mixture of this substance cause the phenomenon called emulsion. Emulsions are found in a variety of industries, from food and pharmaceuticals to petroleum production and refining. An emulsion is a system consisting of a liquid dispersed in an immiscible liquid. Immiscible means not compatible or not be able to mix together to make a solution. Oil and water are great examples of two immiscible liquids (Anne et-al, 2008).). The separation of water from oil is a bottleneck in the offshore oil production. When oil and water is processed from the well-head to the manifold, pressure drops occurring over chokes and valves crush water droplets in the oil phase to stable water-in-oil (w/o) emulsion. Because of a large area to volume ratio, factors which affect the interfacial properties are of crucial importance in defining the level of stability encountered in crude oil emulsions from different wells or with different treatment strategies. There are three types of emulsion which are flocculation, creaming and coalescence. The flocculation occur when the particles form clumps meanwhile the creaming occur when the particle concentrate towards the surface depend on the density of the two phases of mixture while separate and breaking. In addition the emulsion also suffers from coalescence. Coalescence occur during the particle coalesce and form a layer of liquid.

Water-in-crude oil emulsions stabilized by various surface-active components are one of the major problems in relation to petroleum production. The surfactants are usually present in the oil phase. The mechanism for emulsion stabilization in petroleum and petroleum-derived fluids is not completely understood. Many attribute emulsion stability to the viscoelastic interfacial film mentioned previously. This skin is formed through the interactions of the surface-active molecules in the crude, which fall into two main categories, asphaltenes and resins.Formation of these emulsions during oil production is a costly problem both in terms of chemicals used and due to production losses (Abdurahman et-al 2007).

1.2 Problem Statement

Emulsions in refinery processes lead to sludge generation, high costs for recovering slop oils, and other problems. One of the largest problems in oil production is the formation of emulsions stabilised by heavy crude oil components like asphaltenes, resins and waxes. Such problems may in some cases be solved by means of injections of chemicals or introduction of mechanical separation facilities. However, the costs of these solutions are normally high and the search for new and efficient separation tools is important. Besides, the equipment also tend to damage because of emulsion. Usually all the equipment used in industry is huge and expensive, so it needed more cost to repair the maintenances of the equipment. This tow major problem that the industry to face it nowadays.

1.3 Objectives

I. To study the intensive demulsification of highly stable water-in-crude oil and understand the mechanism of demulsification using ultrasonic and chemicals.
II. Comparison between ultrasonic of chemical demulsificatio

1.4 Scope Of Research

Based on the objective above, several scopes have been outlines which are:

1) The potential of ultrasonic in demulsification of water in crude oil emulsions
2) Varying the power range via ultrasonic technology
3) Overall study of water in crude oil emulsion
4) The comparison between chemical and chemical method

CHAPTER 2

LITERATURE REVIEW

2.1 Separation

In the chemical and other physical processing industries the separation process have certain fundamental and basic principles in common. Separation processes can essentially be termed as mass transfer processes. However the term of unit operations has largely been superseded by the modern term separation process. These separation processes are common to all types of diverse process industries. A separation process is used to transform a mixture of substances into two or more distinct products. The desire products that form after separation process could differ in two characterizations such as chemical properties and physical properties. It can be characterize depend on it size, shape, color, crystal modification and so on. The classification of the separation based on mechanical or chemical which is chemical separation possible due the high cost of the operation rather than mechanical separation (Christie et al, 2003). Chemical separation is remaining solution if the system cannot separate purely by mechanical separation. There are many classification of separation process such as list in the table below:

Table 2.1: Type of Separation

Separation process	Meaning
1. Evaporation	This refer to the evaporation of a volatile solvent such as water from a nonvolatile solute as salt or any other material in solution
2. Drying	In this operation volatile liquids usually water are removed from solid materials
3. Distillation	This is an operation whereby components of a liquid mixture are separated by boiling because of their differences in vapor pressure
4. Absorption	In this process a component is removed from a gas stream by treatment with a liquid
5. Membrane separation	This process involves the separation of a solute from a fluid by diffusion of this solute from a liquid or gas through a semi permeable membrane barrier to another liquid
6. Liquid-liquid extraction	In this case a solute in a liquid solution is removed by contacting with another liquid solvent that is relatively immiscible with the solution
7. Adsorption	In this process a component of a gas or liquid stream is removed and adsorbed by a solid adsorbent
8. Ion exchange	Certain ions in solution are removed from a liquid by an ion-exchanged solid
9. liquid-solid leaching	This involves treating a finely divided solid with a liquid that dissolved out and removes a solute contained in the solid
10. Crystallization	This concerns the removal of a solute such as a salt from a solution by precipitating the solute from the solution

The most important thing about the separation process is it can separate in various types of separation or can be combined in various sequences in a process depends on it raw mixture. Separation applications in the field of chemical engineering are very important. A good example is that of crude oil. Crude oil is a mixture of various hydrocarbons and is valuable in this natural form

2.2 Crude Oil

The oil we find underground called crude oil. Crude oil is a naturally occurring substance found in certain rock formations in the earth. These were produced when tiny plants and animals decayed under layers of sand and mud millions of years ago. As these plants and animals die, they sink to the bottom of the sea where they mix with mud, sand, and clay. Year-after-year more mud and sediments are deposited on the sea floor. Over millions of years the layer of organic mud becomes buried thousands of feet deep in the earth. The temperature of the earth becomes hotter as you go deeper into the earth and the weight of all the mud and rocks above increase the pressure.

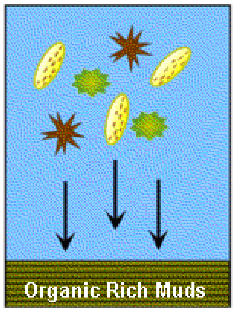


Figure 2.1: Process crude oil occur

The combination of increased temperature and pressure will change the organic material to crude oil. As the temperature increases the crude oil can be changed into natural gas.

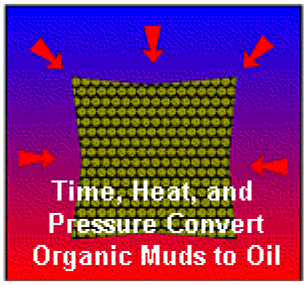


Figure 2.2: Process convert mud to oil

Crude oil does not look the way depend on where it comes from. It is a dark, sticky liquid which and classified as a hydrocarbon. These substances are mainly compounds of only two element which are carbon (C) and hydrogen (H). Refining crude oil involves two kinds of processes to produce the products so essential to modern society. First stage, there are physical processes which simply refine the crude oil into useful products such as lubricating oil or fuel oil. Second part, there are chemical or other processes which alter the molecular structure and produce a wide range of products, some of them known by the general term petrochemicals. As we know that the crude oil is highly flammable and can be burned to create energy.

2.3 Hydrocarbon

Hydrocarbon is the simplest organic compound consists of carbon and hydrogen. It can be straight chain, branched chain or cyclic molecules. Carbon tends to form four bonds in a tetrahedral geometry. Most of the hydrocarbons found naturally occur in crude oil. Hydrocarbons exist in liquid, gaseous or solid at normal pressure and temperature depending on the number and the arrangement of carbon atom in the molecules. Crude oil in liquid phase but maybe contain gaseous or solid compound in solution. The more carbon contain in the molecules it has tendency to being a solid especially the heavy crude oil. The simplest hydrocarbon is methane which is contain one carbon and bounded with four hydrogen atoms. The picture below show the molecule structure of methane

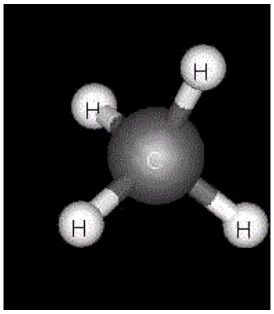


Figure 2.3: Methane (CH4) molecule structure.

A carbon atom has four bonds that can be connected with either one or more the carbon atom or another atoms element meanwhile the hydrogen atom only can unite with one atom only. The larger hydrocarbon has more carbon atoms joined to one another as well as to hydrogen atoms for example the propane (C3H8) which is exist in straight chain molecule and a branched chain structure like isobutene (C4H10) as shown below.

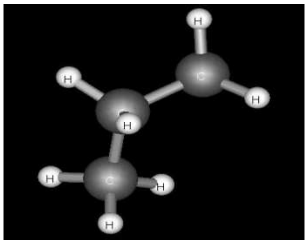


Figure 2.4: Propane (C3H8) molecule structure.

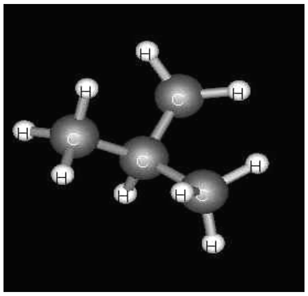


Figure 2.5: Isobutane (C4H10) molecule structure

The hydrocarbon can becomes complex. It is more complex when more hydrogen atoms replaced by hydrocarbon group or stacking of one or more ring. The naphthalene is the simple example shows the complex structure of hydrocarbon. At this point we can see the molecules structure found in the crude oil.

2.3.1 Types Of Crude Oil

Crude oil varies widely in appearance which range in color and properties they contain. Most of crude oil essentially hydrocarbon with difference in properties because the variations in the molecule structure. The variation may influence its suitability and quality of the product. Crude roughly divided in three groups depends on the nature hydrocarbon they contain.

1. **Paraffin Base Crude Oils**

These contain higher molecular weight paraffin which are solid at room temperature but it contain little or no asphaltic matter. They can produce high-grade lubricating oils.

2. Asphaltic Base Crude Oils

It consist large proportions of asphaltic matter and little or no paraffin. Some are predominantly naphtenes so yield lubricating oil is more sensitive to temperature changes than the paraffin base crudes.

3. Mixed Base crude Oils

Both paraffins and naphtenes are present as wellas aromatic hydrocarbons. Most crude fit this category.

2.3.2 Crude Oil Quality

The physical characteristics of crude oils differ. Crude oils are classified depends on their density and sulfur content in it. Crude generally have a higher share of light hydrocarbons classified as less dense which can be recovered with simple distillation and higher value products. Meanwhile, the denser or heavier crude oils produce a greater share of lower-valued products with simple distillation too. It is requires additional processing to produce the desired range of products. Some crude oils have a higher sulfur content with respect to both processing and product quality. For pricing purposes the crude oils with similar quality are often compared to a single representative crude oil. The quality of the crude oil dictates the level of processing and re-processing necessary to achieve the optimal mix of product output. Hence, price and price differentials between crude oils also reflect the relative ease of refining. In addition the type of hydrocarbon molecules and other natural characteristics may affect the cost of processing or restrict a crude oil's suitability for specific uses. The presence of heavy metals causes contaminants to the processing and to the finished product. The molecular structure of a crude oil also dictates whether a crude stream can be used for the manufacture of specialty products, such as lubricating oils or of petrochemical feed stocks. Refiners put some effort to run the optimal mix of crude through the refineries depends on their equipment, the desired output and the relative price of available crude

2.3.3 Crude Oil Composition

Crude oil is a complex mixture of hydrocarbons which consists of sulfur, oxygen, nitrogen, as well as various metallic constituent like nickel, copper, iron and so on. The element contain in crude oil are carbon (83.9-86.8%), hydrogen (11-14%), sulfur (0.06-8.00%), nitrogen (0.02-1.70), oxygen (0.08-1.82) and metal (0.00-0.14). Even though crude oil continuum with thousands different hydrocarbon molecule but the proportions of the elements in crude oil vary over fairly narrow limit. The SARA method is one example of separate the crude oil into four major fraction or chemical classed based on difference solubility and polarity. The four fraction are the saturates (S), aromatics (A), resins (R) and last but not least is the asphaltenes (A). The schematic of SARA method shown as below (Inge et al, 2002).

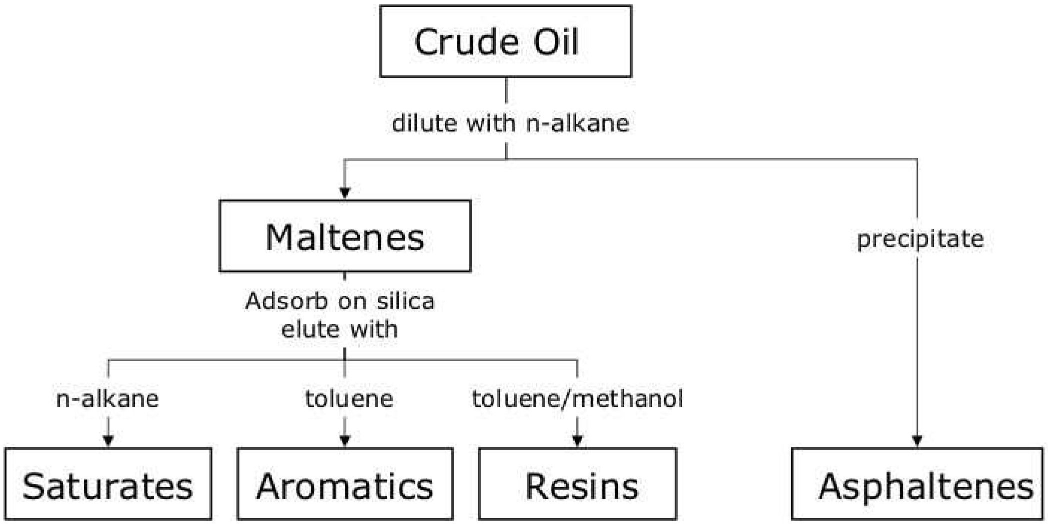


Figure 2.6: SARA separation scheme (Narve et a,l 2002

2.3.4 Saturates

The saturates (aliphatics) are non-polar hydrocarbons, without double bonds but including straight-chain and branched alkanes, as well as cycloalkanes (naphtenes). Cycloalkanes contain one or more rings, which may have several alkyl side chains. The proportion of saturates in a crude oil normally decreases with increasing molecular weight fractions, thus the saturates generally are the lightest fraction of the crude oil. Wax is a sub-class of the saturates, consisting primarily of straight-chain alkanes, mainly ranging from C20 to C30. Wax precipitates as a particulate solid at low temperatures, and is known to effect emulsion stability properties of crude oil systems (Musser et al , 1998;Zaki et al,2000;Lee et al,1999).

2.3.5 Aromatics

Group of hydrocarbons which benzene is the parent. They are called aromatics because many of their derivatives have sweet or aromatic odors. The term aromatics refer to benzene and its structural derivates. Aromatics are common to all petroleum which the majority of the aromatics contain alkyl chains, cycloalkane rings and along with additional aromatic rings. Aromatics are often classified as mono-, di-, and tri-aromatics depending on the number of aromatic rings present in the molecule. Polar, higher molecular weight aromatics may fall in the resin or asphaltene fraction

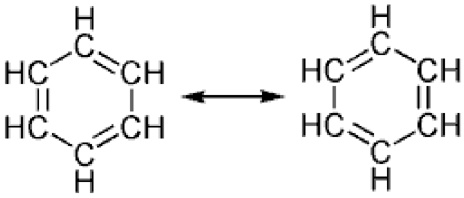


Figure 2.7: Benzene resonance

2.3.6 Resins

Resin is synthetic or natural compound. It begins with highly viscous state and hardens with treatment. Resin not soluble in the water but can soluble in alcohol. Resin can classified difference classes depending on their potential uses and exact chemical composition. Natural resin comes from the plants. Plant resins can dark brown in color. Some plant resin extremely volatile because it contain unstable compound. The resin fraction is operationally defined, and one common definition of resins is as the fraction soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane (Narve et al, 2000; Andersen et al, 2001; Speight et al, 1999; Sheu et al,1995). This fraction is comprised of polar molecules often containing heteroatoms such as nitrogen, oxygen or sulphur. Since the resins are defined as a solubility class, overlap both to the aromatic and the asphaltene fraction is expected. Despite the fact that the resin fraction is very important to crude oil properties, little work has been reported on the characteristics of the resins, compared to for instance the asphaltenes. However, some general characteristics may be identified. Resins have a higher hydrogen and carbon ratio than asphaltenes, 1.2-1.7 compared to 0.9-1.2 for the asphaltenes (Andersen et al, 2001). Resins structure is similar to asphaltenes but smaller in molecular weight which is below than 1000 g/mole. Naphthenic acids are commonly regarded as a part of the resin fraction.

2.3.7 Asphaltenes

The asphaltene fraction is defined as a solubility class namely the fraction of the crude oil precipitating in light alkanes like pentane, hexane or heptane. This precipitate is soluble in aromatic solvents like toluene and benzene. The asphaltene fraction contains the largest percentage of heteroatoms (O, S, N) and organometallic constituents (Ni, V, Fe) in the crude oil. The structure of the asphaltenes consists of polycyclic aromatic clusters, substituted with varying alkyl side chains (Sheu et al,1999). Figure 2-2 shows a hypothetical asphaltene monomer molecule. The molecular weight of asphaltene molecules has been difficult to measure due to the asphaltenes tendency to selfaggregate but molecular weights in the range 500-2000 g/mole are believed to be reasonable (Narve et al, 2002; Sheu et al, 2002, Buenrostro et al, 2001; Kilpatrick et al, 2001; Wang et al,2000). Asphaltene monomer molecular size is in the range 12-24 Å (Groenzin et al 2000; Speight et al, 1999). Asphaltene micelles are considered analogous to a surfactant micelle, where the association of molecules is driven by hydrophobic-hydrophilic interactions.

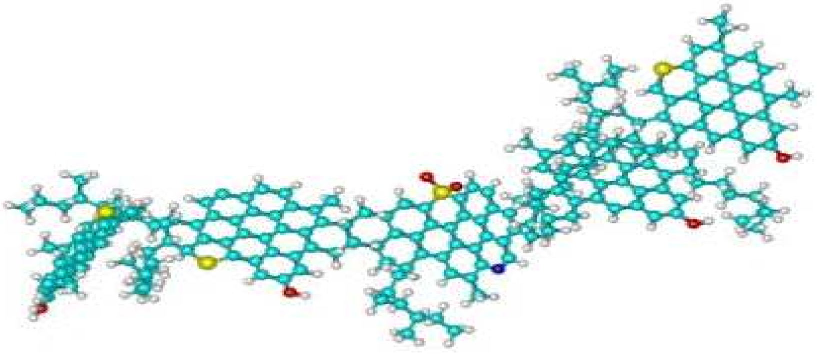


Figure 2.8: Hypothetical asphaltene molecule (Audral et al, 1998).

It is important to keep in mind that knowledge about the chemical composition of crude oils, gained from for instance a SARA-analysis, cannot fully explain the crude oil behaviour with regard to emulsion stability. Equally important is information of the structure of the crude oil, which is a result of interactions between the continuums of chemical constituents in the oil. The interactions between the heavy end molecules, the asphaltenes and resins, play the most significant role in this sense (Narve et al, 2002)

2.4 Emulsion

Emulsions have long been of great practical interest due to their widespread occurrence in everyday life. They may be found in important areas such as food, cosmetic, pharmaceutical and agricultural industry. Emulsions are also found in the petroleum industry. For the petroleum industry the usual emulsions encountered are water droplets dispersed in the oil phase (w/o) meanwhile if the oil is the dispersed phase, the emulsion is termed oil-in-water (o/w) emulsion, where they are typically undesirable and can result in high pumping costs, reduced throughput and special handling equipment. An emulsion is usually defined as a system consisting of a liquid dispersed in another immiscible liquid and the droplet of colloidal size between (0.1-10 μm). The emulsion formation is a result of the co-production of water from the oil reservoir. During processing, pressure gradients over chokes and valves introduce sufficiently high mechanical energy input (shear forces) to disperse water as droplets in the oil phase (Narve et al, 2002;Sjöblom et al 2000).

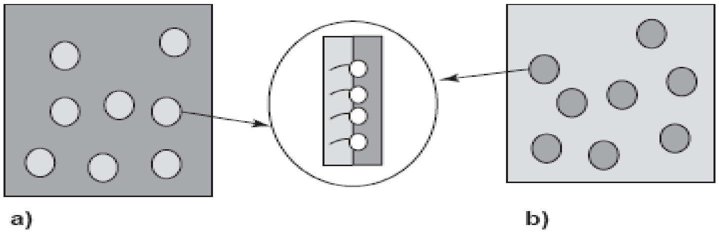


Figure2.9: Schematic representation of emulsion structure which a) O/W emulsion while b) W/O emulsion

2.4.1 Emulsion Stability

In the emulsified state, the interfacial area between the dispersed droplets and the bulk phase represents an increase in the systems free energy. All emulsions, perhaps with the exception of micro emulsions are thermodynamically unstable so that for an emulsion to separate the droplets must merge with each other (Narve et al, 2002). However, the destabilization may take time. Basically the water in crude oil emulsion involves three steps such are flocculation, sedimentation or creaming and coalescence. Flocculation is the aggregation of two or several droplets, touching only at certain points and with virtually no change in total surface area. Meanwhile the sedimentation or creaming process create a droplet concentration gradient due to a density difference between the two liquid phases, which result in a close packing of the droplets. Aggregation of droplets may be said to occur when they stay very close to one another for a far longer time than if there were no attractive forces acting between them (Inge et al, 2002). Besides, coalescence is the process of droplets fusing together and forming larger droplets until the oil and water is separated into two discrete phases.

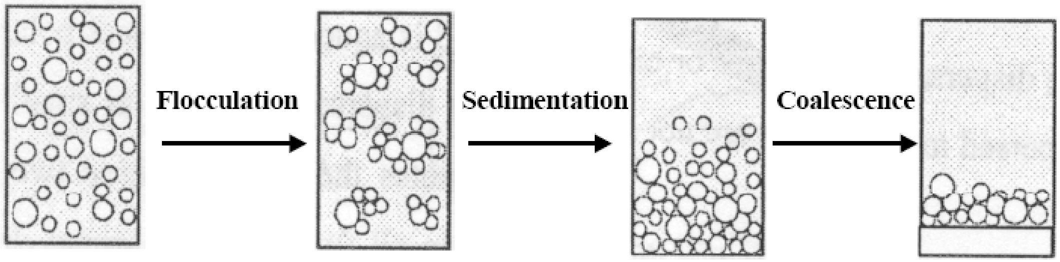


Figure 2.10: Emulsion separation by flocculation, sedimentation, and coalescence.

In crude oil emulsions emulsifying agents are present at the oil-water interfaces which hinder this coalescence process (Narve et al,2002). The mechanism of coalescence consists of film drainage where there must be a flow of fluid in the film while the film rupture occur when the difference pressure in the capillary causes the droplets to rapidly fuse into one droplets (Inge et al,2002). Steric stabilization by surfactants may avoid the droplet to contact each other. The surfactant can create mechanically strong interfacial films which act as a barrier between the aggregation and coalescence. Particles which are oil-wet, tend to stabilise w/o emulsions while those are water-wet tend to stabilise o/w emulsions. In order to stabilise the emulsions the particles should be least one order of magnitude smaller in size than the emulsion droplets and in sufficiently high concentration .The lighter resin acts as individual monomers which similar to traditional surfactant. It has a tendency than more active interfacially than aspaltenes (Narve et al, 2002).Other factors that usually favour emulsion stability are low interfacial tension, high viscosity of the bulk phase and relatively small volumes of dispersed phase.

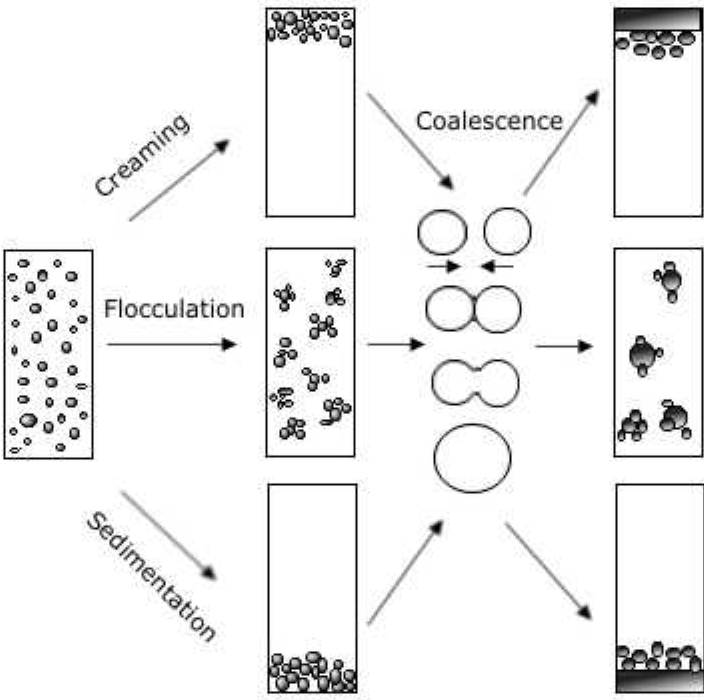


Figure 2.11: Processes taking place in an emulsion leading to emulsion breakdown and separation

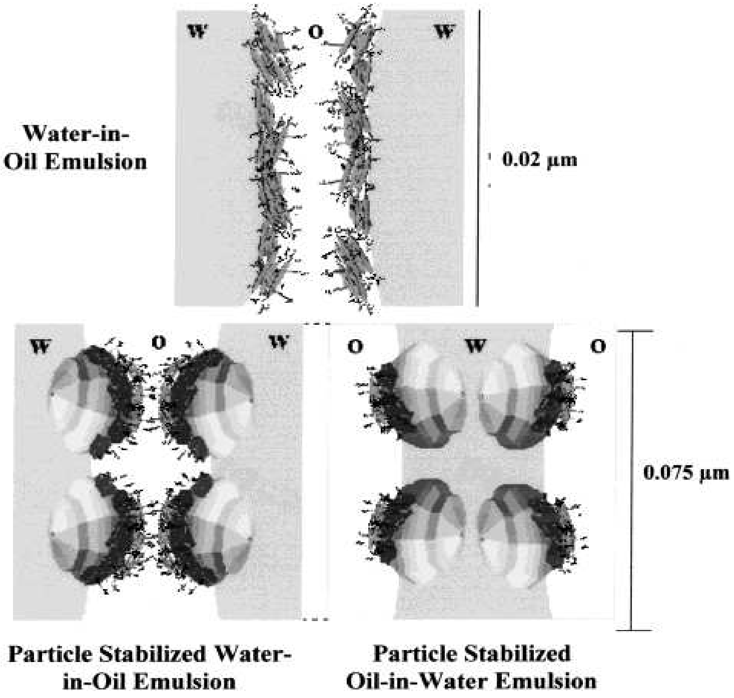


Figure 2.12

(a) In the absence of particles, water-in-oil emulsions are stabilized by resin/asphaltene films.

(b) Inorganic particles sit at the interface, stabilizing water-in-oil emulsions if a sufficient amount of asphaltene aggregates adsorb.

(c) The same particles with a lesser extent of asphaltene adsorption will stabilize oil-in water emulsions

2.4.2 Crude Oil Characterization

Crude oils from different sources exhibit a wide range of physical and chemical properties. To predict the behaviour of any crude oil depend on the knowledge about the properties such characterising the parameter includes the viscosity, interfacial tension, density and molecular weight too (Narve et al, 2002). Predicting emulsion stability behaviour from characterising data is a difficult task. The emulsion stability is the result of a complex interplay between the different crude oil constituents. Furthermore, the amount of the interfacially active fractions, resins and asphaltenes, is known to be important for emulsion stability.

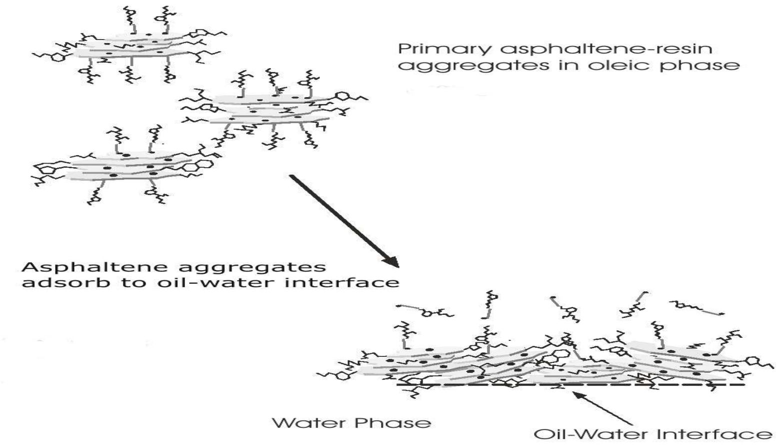


Figure 2.13: Proposed stabilising mechanisms for asphaltenes in petroleum by resin molecules.

2.5 Surfactant

A surfactant is a compound which lowers the surface tension of a liquid but increasing the contact between the liquid and other substance. There are variety of surfactant which works with oil, water and any other liquid. Many companies manufacture a range of surfactant for various purposes. The surfactants also called as wetting agents. The term of surfactant blend of surface acting agent referring to the fact that a surfactant interact with the surface of the liquid to change its properties. Surfactants are usually consists of organic compound that are amphipathic which contain hydrophilic and hydrophobic groups. They are typically soluble in both organic solvents and water. The term surfactant was coined by Antara Products in 1950. The surfactant operates by adsorbing air- water interface to reduce the surface tension of water. In addition, surfactants also reduce the interfacial between the oil and water by adsorbing the liquid-liquid interface. Among of the surfactant can assemble in the bulk solution into aggregates that are known as micelle. A micelle is monolayer sphere and can only reach a certain size whereas bilayers can be considerably larger

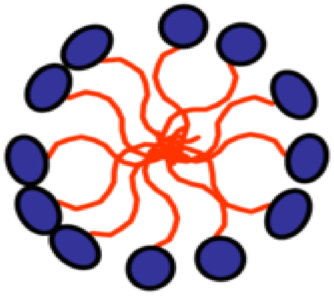


Figure2.14: A micelle - the lipophilic ends of the surfactant molecules dissolve in the oil while the hydrophilic charged ends remain outside shielding the rest of the hydrophobic micelle.

When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their polar heads form an outer shell maintains favorable contact with water. Meanwhile when the surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactants are classified into four primary groups such are anionic, cationic, non-ionic, and dual charge or zwitterionic Generally, surfactants with lighter molecular weight (short hydrophobic tail) will diffuse more rapidly to the interface than that with higher molecular weight. The lighter molecule mass surfactants will affect a higher equilibrium surface tension depression compared to lower molecule mass surfactants (Lixin Cheng et al., 2007). Actually, most of the surfactants at higher concentrations can cause a change of the physical properties of the surfactant solutions and also cause strong surface films between adjacent molecules. Basically, when increasing surfactant solution concentration, the surface tension will decrease, and the dynamic surface tension is usually higher than equilibrium surface tension at a fixed concentration. Higher solution temperature results in lower surface tension in both equilibrium and dynamics conditions. Additionally for all surfactants, surface tension decreases asymptotically with increasing concentration. The asymptotic limit is commonly referred to as the critical micelle concentration (cmc) of the surfactants. Critical micelle concentration (cmc) is characterized by micelle formation, or micellization, which is the property of surface-active solutes that lends to the formation of colloid-sized clusters, i.e. at a particular concentration, additives form aggregates in the bulk phase or a surfactant cluster in solution that are termed micelles. Different shapes and sizes of micelles such as globular or spherical, rod-shaped or cylindrical, and lamellar or plate-like exist depending upon the surfactant type and its concentration, solution temperature, presence of other ions and water-soluble organic compounds in the solutions (Lixin Cheng et al., 2007).

2.5.1 Classification of Surfactant

A surfactant can be classified by the presence of formally charged groups in its head. A non-ionic surfactant has no charge groups in its head. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic.

Table 2.2: Classification of Surfactant

Anionic	Cationic
• Sodium dodecyl sulfate (SDS), ammonium lauryl sulfate, and other alkyl sulfate salts • Sodium laureth sulfate, also known as sodium lauryl ether sulfate (SLES) • Alkyl benzene sulfonate • Soaps, or fatty acid salts	• Cetyl trimethylammonium bromide • Cetylpyridinium chloride (CPC) • Polyethoxylated tallow amine (POEA) • Benzalkonium chloride (BAC) • Benzethonium chloride (BZT)
Non-ionic	Zwitterionic

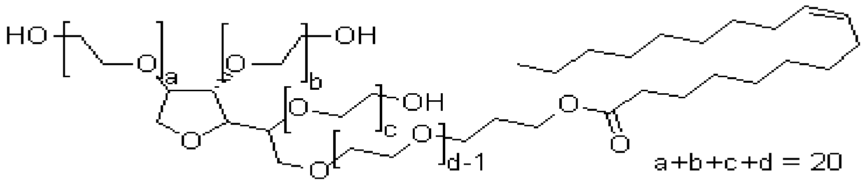
• Alkyl poly(ethylene oxide)
• Copolymers of poly(ethylene oxide) and poly(propylene oxide) (commercially called Poloxamers or Poloxamines)
• Alkyl polyglucosides, including:
  • Octyl glucoside
  • Decyl maltoside
	• Dodecyl betaine
	• Dodecyl dimethylamine oxide
	• Cocamidopropyl betaine
	• Coco ampho glycinate

2.5.2 Tween 80

2.5.2.1 Product Description

Polysorbate 80 commercially also known as **Tween 80.Tween 80** is a nonionic surfactant and emulsifier derived from polyethoxylated sorbitan and oleic acid, and is often used in foods. Polysorbate 80 is a viscous, water-soluble yellow liquid. The hydrophilic groups in this compound are polyethers also known as polyoxyethylene groups which are polymers of ethylene oxide. In the nomenclature of polysorbates, the numeric designation following polysorbate refers to the lipophilic group, in this case the oleic acid

2.5.2.2 Molecule Structure



2.5.2.3 Physical Properties

Table 2.3: Physical properties of Tween 80

pH	7
Physical state	Liquid
Color	Clear Amber. Yellow.
Melting point	-20.556℃ (-5℉)

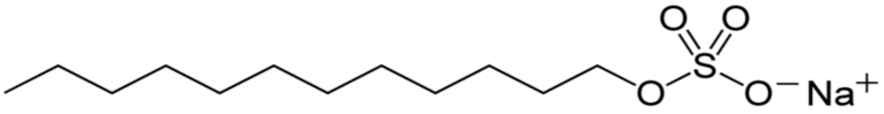
2.5.3 Sodium Dedocyl Sulphate (SDDS)

The outer part of the GC is a very specialized oven. The column is heated to move the molecules through the column. Typical oven temperatures range from 40°C to 320°C.

2.5.3.1 Product Description

Sodium lauryl sulfate (SLS) or sodium dodecyl sulfate (SDS or NaDS) ($C_{12}H_{25}SO_4Na$) is an anionic surfactant that is used in industrial products including engine degreasers, floor cleaners, and car wash soaps; as well as in household products such as toothpastes, shampoos, shaving foams, some dissolvable aspirins, fiber therapy caplets, and bubble baths for its thickening effect and its ability to create a lather. The molecule has a tail of 12 carbon atoms, attached to a sulfate group, giving the molecule the amphiphilic properties required of a detergent.

2.5.3.2 Molecule Structure



2.5.3.3 Physical Properties

Table 2.4: Physical properties of SDS

Molecular formula	$NaC_{12}H_{25}SO_4$
Molar mass	288.38 g mol^{-1}
Density	1.01 g/cm^3
Melting point	206 °C

2.5.3.4 Applications

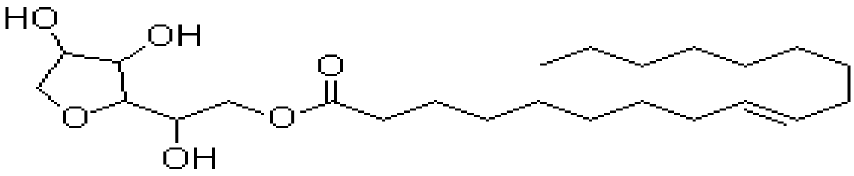
Sodium lauryl sulfate is probably the most researched anionic surfactant compound. Like all detergent surfactants (including soaps), sodium lauryl sulfate removes oils from the skin, and can cause skin and eye irritation. The critical micelle concentration (CMC) in pure water at 25°C is 0.0082 M, and the aggregation number at this concentration is usually considered to be about 50. The micelle ionization fraction (α) is around 0.3 (or 30%).It has recently found application as a surfactant in gas hydrate or methane hydrate formation reactions, increasing the rate of formation as much as 700 times.

2.5.4 Span 80

2.5.4.1 Product Description

This product is light yellow color and water in oil type emulsifier.it is also soluble inorganic solvents

2.5.4.2 Molecule Structure



2.5.4.3 Physical Properties

Table 2.5:Physical properties of Span80

Molecular formula	$C_{24}H_{44}O_6$
Molar mass	428.61
Density	0.986
Color	Amber. Yellow.

2.6 Ultrasonic

The ultrasonic measurement technique has been widely used for characterizing heterogeneous mixture in industrial processes (Guangtian et al, 2005).Ultrasonic detection and measurement can often be carried out relatively simply. Ultrasonic waves are of such a high frequency that they are generally unable to be detected by the human ear. Sound waves with a frequency higher than 20 kHz are referred to as ultrasonic waves. Ultrasonic waves are widely applied in the medical field, industry, food processing fields and even in household electronic appliances The basic set up in control situations consists of a hand-held unit with meter, sensitivity adjustment and one of a number of nozzles. Technically ultrasonic technology provides the most precise solution in countless application such are tightness, electrical discharge and mechanical movement. The ultrasound can be very précised measured. The high frequency sounds and more directional than lower frequency makes it easier to pinpoint the source even presence of other background noise. On a laboratory scale, ultrasound has been proved suitable for emulsification and has long been applied (O. Behrend et al, 1999).Ultrasound emulsification is an efficient method to obtain finally dispersed emulsions in a continuously operating mode.

2.7 Separation Crude Oil Emulsion via Microwave Radiation

In the petroleum industry, most of the crude oil produced is co-mingled with water and gas. It is therefore necessary to provide a means of sufficiently and economically separating the oil/water and gas for separate discharge. Usually the separated water is returned to a subterranean formation containing oil and the separated oil is conducted to a pipeline for ultimate transportation to a refinery and end use. Normally, the separated gas is vented if in small quantities or if in commercial quantities collected for distribution and sale. With the rising value of petroleum products it becomes increasingly important that separator equipment utilized by the petroleum industry extract the maximum possible recovered petroleum products from water and oil emulsions and dispersions. To this end improved separating vessels have been made from time to time over the years. Initially, the separators were merely open vessels providing a quiet zone with the intention that the water settle out and be withdrawn from the bottom of the vessel and that the petroleum float on the water be withdrawn from the top of the vessel. While this system is satisfactory to a degree, it nevertheless results in some oil remaining in the form of an emulsion with the withdrawn water and in like manner water being entrapped with the oil withdrawn from the top of the vessel. Further, such gravitational settling procedures are slow and require vessels of such volume that to allow separation by gravitation alone becomes exceedingly expensive and the reduced rate of flow results in general overall inefficiency. In general, there is a dramatic reduction in viscosity of emulsion subjected to microwave radiation. This reduction increases as time of exposure increases. Emulsions are much more easily broken as viscosity decreases. The microwave effect appears much greater than for externall supplied heat only

2.7.1 Experimental

An experiment was carried out to determine the effect of microwaves on breaking emulsions prepared using both non-ionic and cationic surfactants. Two water-in-oil emulsions were prepared with tap water and crude oil in a ratio of 3:7 and one weight percent surfactant. In the first case, TETRONIC (trademark of and sold by BASF Corp.) nonionic surfactant was used, in the second case a quaternary amine cationic surfactant was used. The emulsions were mixed in a blender prior to testing. One hundred milliliters of each emulsion was poured into each of three glass bottles. One bottle was placed in a 60° C. (140° F.) bath as a blank. The remaining bottles were submitted to two 20 and two 30-second exposures in the microwave, which raised the samples to a temperature of 46° C. and 58° C. respectively; then placed in the bath along with the control to raise and maintain their temperature. The amount of oil, emulsion, and water present in each bottle was recorded after one hour. The results for each emulsion are shown in Table 2.6

Table 2.6:

	2-20-Second Exposures	2-30-Second Exposures	Blank
Nonionic Surfactant			
Oil	40%	60%	70%
Emulsion	60%	35%	15%
Free Water		5%	15%
Cationic Surfactant			
Oil	--	--	--

Emulsion 100% 93% 90%

Free Water7% 10%

It is evident that the microwave did not have the same quantitative results, but it did improve breakout in all cases. This example clearly shows that microwaves benefited breakout time with a mechanism distinct from heating alone

2.8 Demulsification of Water in Oil Emulsion Using Porous Glass Membran

Demulsification is one of the critical processes of emulsion liquid membrane technique. The purpose is the separation of two immiscible liquids of internal aqueous phase containing concentrated solutes and oil phase containing surfactant and carrier that can be reused.Emulsion liquid membranes are thermodynamically unstable systems. The instability of emulsion is greatly affected by the nature of the surfactant film that is strongly dependent on surfactant adsorption and interfacial properties such as interfacial tension and viscosity. The instability of emulsion liquid membrane represents deformation, split phase, disturbance and rupture. Each form of them is a process of emulsion coalescence.

Generally, demulsification of water-in-oil emulsion consists of two processes: one is coagulation, i.e. disperse phase in emulsion gets together and reduces total interfacial area, but droplets in the emulsion do not combine to form a single unit of greater volume, this is a reversible process. Second step is coalescence, i.e. the coagulated droplets combine and become bigger droplets, this is an irreversible process and the emulsions are disrupted as a result. In general, demulsification of water-in-oil emulsions is mainly influenced by three physical characteristics of internal droplet size, surfactant concentration and oil viscosity. Demulsification rate is affected by both the emulsion preparation and demulsification condition. To demulsify completely and quickly, some additional forces are neede

In this paper, a hydrophilic porous glass membrane was used for demulsification of water-in-oil emulsions and demulsification efficiency can reach more than 96.2%. Effects of pore size of the membrane, transmembrane pressure and volumetric ratio of oil phase to internal aqueous phase in the emulsion on demulsification were investigated. It was found that pore size of membrane and transmembrane pressure can significantly affect demulsification efficiency. The smaller the pore size of the membrane, the better the demulsification efficiency. However, smaller pore size of the membrane has to be exerted a greater transmembrane pressure in order to make internal aqueous phase enter the membrane pore. Correspondingly, effect of transmembrane pressure on permeation flux of the droplets was also studied. In addition, recovered-oil phase by the demulsification were reused five times to extract cadmium from simulated aqueous waste. The results indicated that the extracting efficiency could arrive at 96.5%.

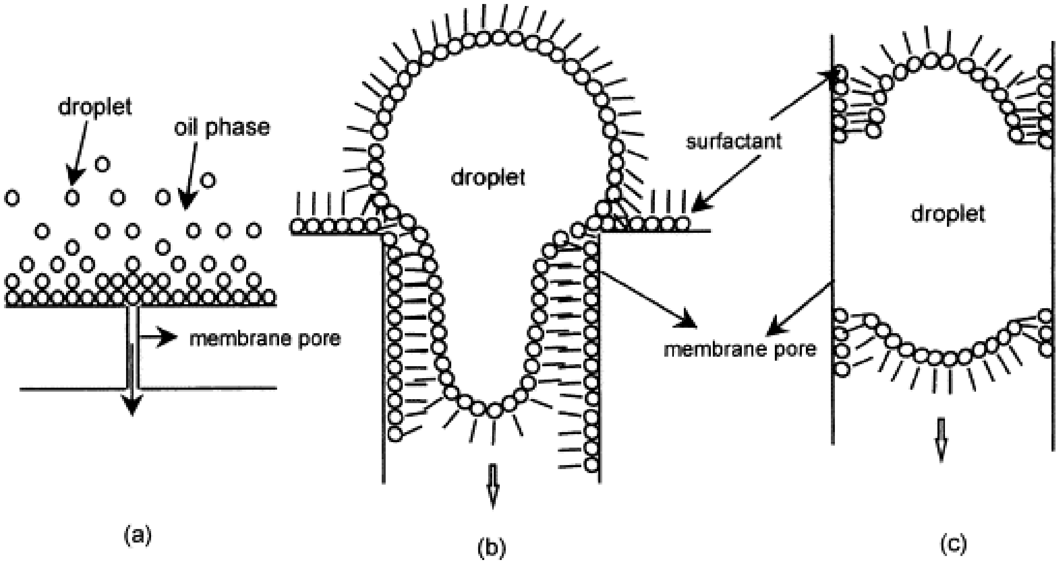


Figure2.15: Schematic diagram of demulsification by porous glass membrane

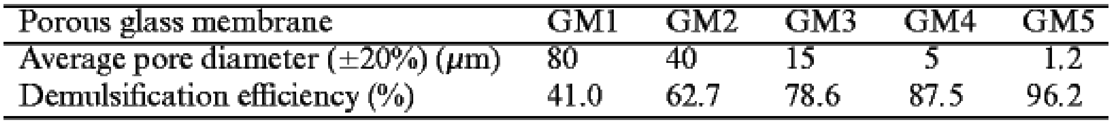
Figure (a): The droplets in emulsion are adsorbed on the surface of the porous glass membrane. If the pore diameter of membrane is so large that droplets can easily pass through, the emulsion cannot be demulsified. If the pore diameter of the membrane is smaller than the size of droplets, the droplets must deform to enter the membrane pore.

Figure (b): The droplets entering into smaller pore must deform.The results in the change of well-distributed surfactant film, and the droplets would easily rupture. In the membrane pore, deformed droplets are squeezed, collided and broken as a result.

Figure (c): The droplets in the pore are broken and adsorbed on the pore wall. So that internal aqueous phase is released out and contacts with the pore wall

2.8.1 Experimental

Uniform size glass particles to be controlled very precisely, were sintered to become tailor-made porous glass membrane whose thickness can be controlled according to the demand. Furthermore, pore wall surface of the porous glass membrane was modified in order to get the hydrophilic feature. The porous glass membrane were characterized by scanning electron microscope and Coulter Promometer which is a machine to provide a full pore size distribution of the membrane material, as shown in table below



Porous glass membrane	GM1	GM2	GM3	GM4	GM5
Average pore diameter (±20%) (μm)	80	40	15	5	1.2
Demulsification efficiency (%)	41.0	62.7	78.6	87.5	96.2

Table 2.7: Pore size of porous glass membrane and demulsification efficiencies

2.8.2 Effect of Pore Size of Porous Glass Membrane on Demulsiation

It can be seen from table 1 that the pore size of membrane has a great effect on demulsification, namely, demulsification efficiencies increase obviously as the decrease of pore diameter.

2.8.3 Demulsification Procedure

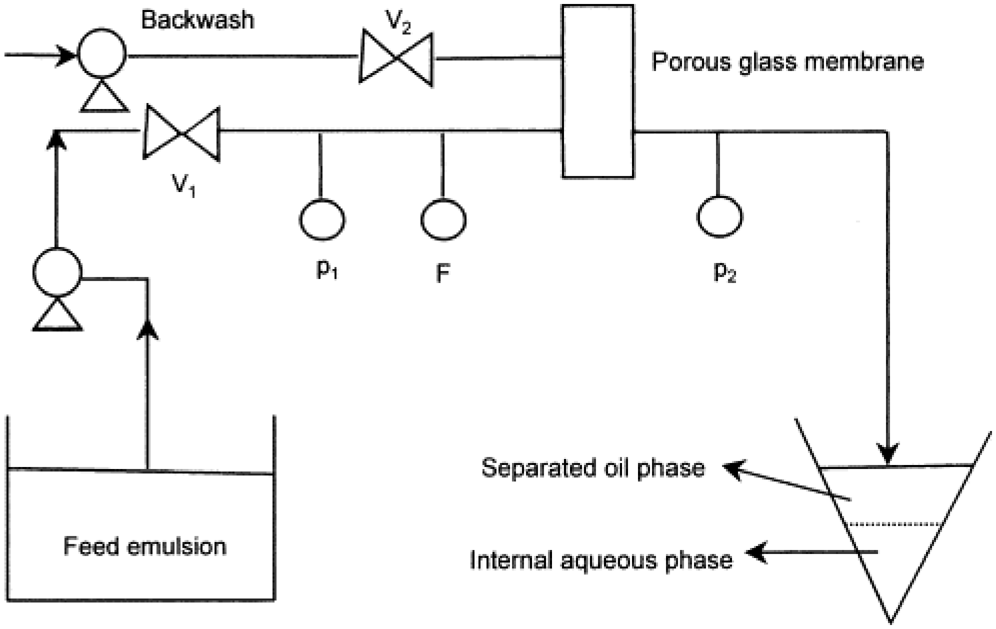


Figure 2.16: Schematic diagram

The porous glass membrane module is shown in figure, where P_1 and P_2 are pressure gauges for monitoring the transmembrane pressure. F is a meter for measuring the permeation flux. Demulsification tests were carried out at room temperature in a laboratory scale. The feed emulsions were pumped by means of a centrifugal pump into the module, and transmembrane pressure was adjusted by valve 1. The membrane pore was periodically washed by compressed-air and hot-water sequentially during demulsification.

CHAPTER 3

METHODOLOGY

3.1 Introduction

There are several equipment can separate the crude oil emulsion. It is like microwave, ultrasonic, chemical or other method. There is several processes that need to be done in separating crude oil emulsion. Different range of temperature level and also different range power is being use to determine the stability for emulsion. The best available technique in separating crude oil emulsion is by using ultrasonic technology because in this method we can manipulated the temperature level and power range so that it can be identified which level is the best way to separate completely between crude oil and water.

3.2 Emulsion Preparation

The emulsion preparation process begins with water in crude oil emulsions were prepared by adding the water slowly to the beaker. Emulsions were agitated vigorously using the mixer which is standard three blade propeller at speed 1250 rpm at different temperature for 18 min. In order to prepare the water in oil emulsions, the emulsifying agent dissolved in continuous phase and water gradually added to the mixture.

3.3 Checking Emulsion Process

The prepared emulsions were used to check for water in oil or oil in water emulsions. All emulsions investigated were in water in oil emulsions type using filter paper by dropping the mixture above it and it shows weather the emulsion preparation water in oil or oil in water. If the droplet spread very hardly on the filter paper it is sure the emulsion appear is water in oil emulsion.

3.4 Materials

The material used in this study is three crude oils. The crude oil comes from Dubai oil field, Khafi crude oil and Miri crude oil. The Dubai and Khafi crude oil categorized as heavy crude oil while Miri crude oil classification as light crude oil.

3.5 Stability Process

The stability process occurred after we leave it the emulsion preparation for 5 hours to observe the volume separated from crude oil emulsion depends on their ability for different volume ratio. In this study two volume ration used to investigate the stability process such as 50-50 %(v/v) and 20-80%(v/v). The total volume of emulsions is 400 mL for each beaker. The stability were investigated by record the volume separation occur every 30 min for 5 hours continuously

3.6 Ultrasonic Process

The different temperature and power range are used for the emulsification part. From this way we can predict which temperature and power give the best way to break the emulsion. This only used for the stabile crude oil emulsion. The power used for 200 and 400W while the temperatures used are 30^0C and 50^0C

CHAPTER 4

RESULT & DISCUSSION

4.1 Introduction

In the present investigation the various factors affecting the stability. Three crude oil will be used to investigate the stability which are heavy crude oil and light crude oil. The heavy crude oil are Dubai and Khafi crude oil while the light one is Miri crude oil. The demulsification method used Masila crude oil to compare the demulsification between ultrasonic and chemical demulsification.

4.2 The Stability Water in Crude Oil Emulsion

4.2.1 Effect of Emulsifier Concentration

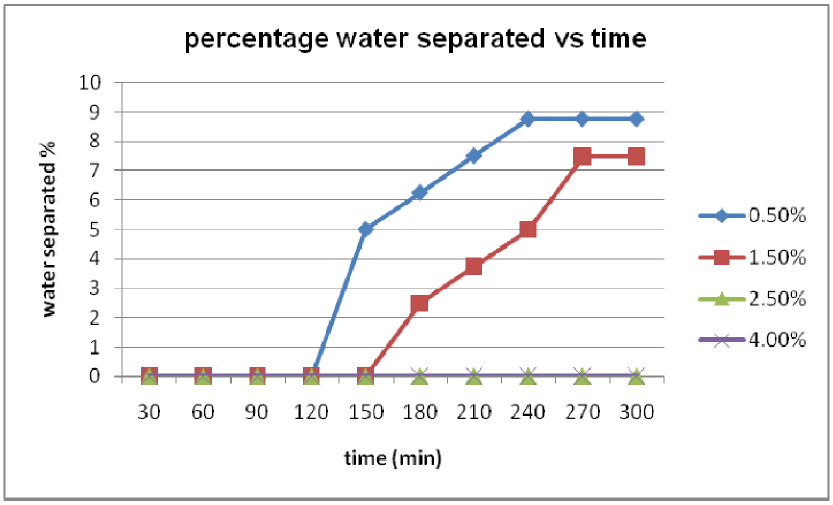


Figure 4.1: Effect Concentration of Span 80

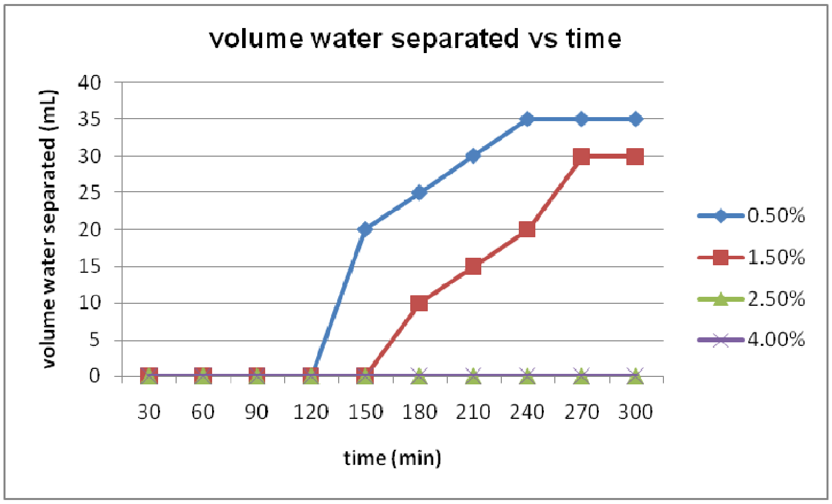


Figure 4.2: Amount Water Separation in Different Concentration

Data were collected for 5 hours to check the best emulsifier for water in crude oil emulsion type. The total volume ration for this type emulsion is 20-80% (v/v) by volume. From the experiment result the percentage water separate lower if the higher percentage of concentration of emulsifier used for water in crude oil emulsion. 2 hour earlier there is no separation occurred until the emulsion start to separate after 2 hour. For 0.5% concentration of emulsifier its start separate about 20 mL which is higher than

1.5% concentration which is about 10 mL only. The separation continuously separate and the volume increase time by time until 5 hours end. The emulsion stop separate after 4 and half hour because it already in stabile phase. For the rest concentration it is not separate from the start because the emulsion is already in stabile phase. The Span 80 is the best emulsifier to stabilize the water in crude oil emulsions. Higher concentration of emulsifier used in water in crude oil emulsion. resulting the emulsion more stabile It is because the Span 80 is most effective surfactant to interact two element which is immiscible liquid like water and oil. Span 80 also exist in liquid and more soluble in water in oil emulsion so it act as good emulsifier to separate the emulsion.

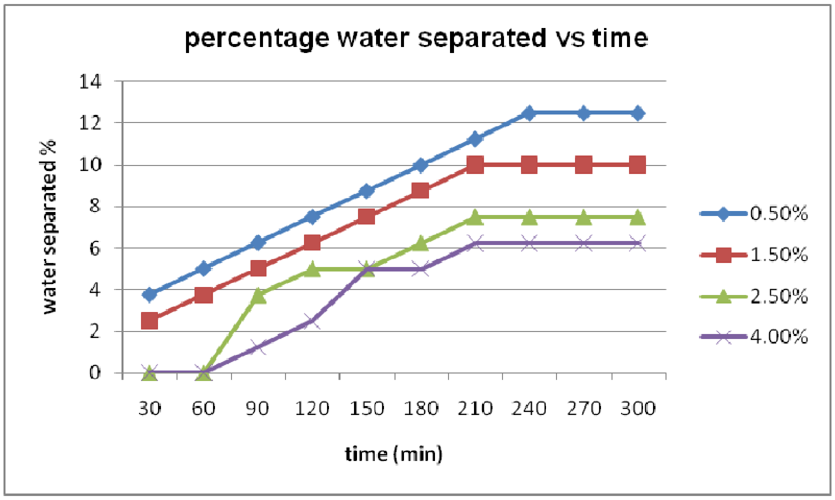


Figure 4.3: Effect Concentration of Tween 80

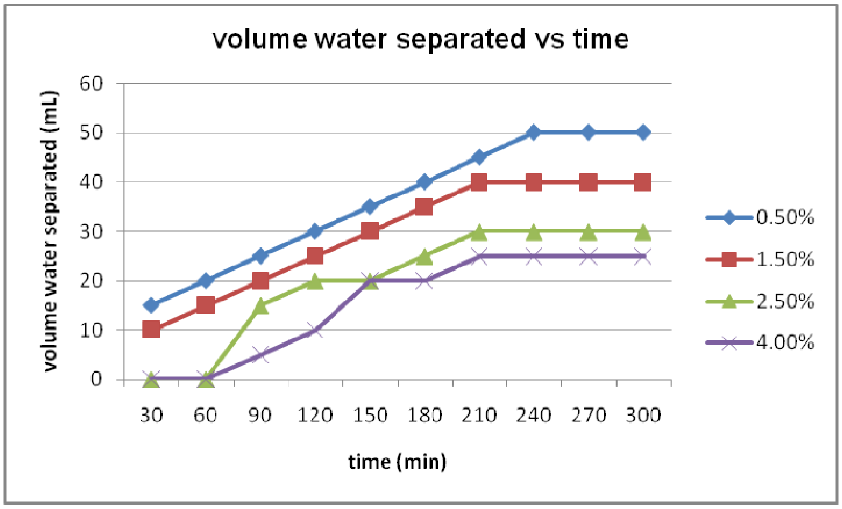


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Figure 4.4: Amount Water Separation in Different Concentration

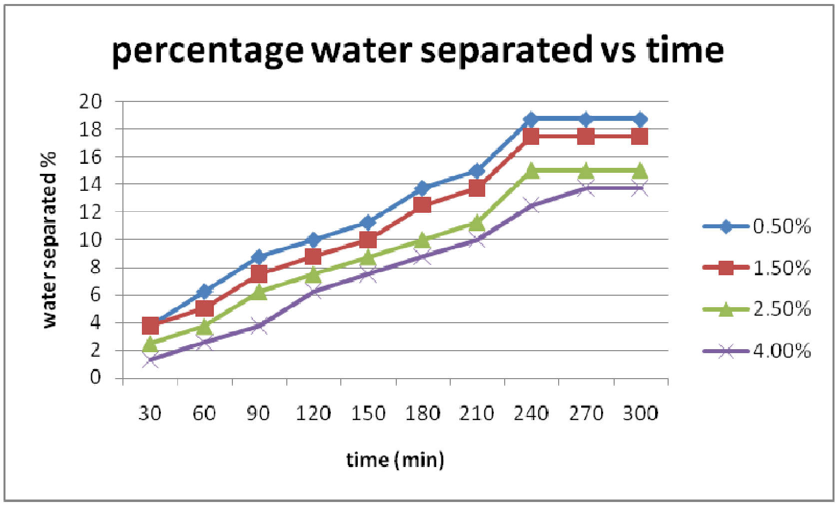


Figure 4.5: Effect Concentration of SDDS

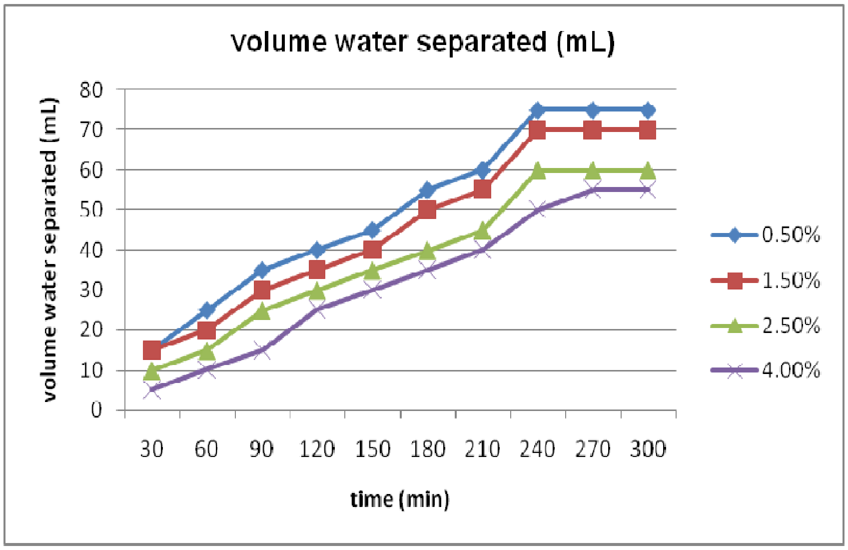


Figure 4.6: Amount Water Separation in Different Concentration

On the other hand, Tween 80 and SDDS are quite different from Span 80 performance in water in crude oil emulsion. It clearly shows in the graph plotted which is this two emulsifier in unstable position. For SDDS detect as the weakest emulsifier in this experiment because the separation occur after 30 minutes compared the rest emulsifier. For 4 percent concentration of emulsifier the SDDS separate about 1.25 percent rather than Tween 80 and Span 80 which are 0 percent for the first 30 minutes. SDDS is an anionic surfactant and in solid which is more difficult to act as good emulsifier. The SDDS more stable in oil in water emulsion rather than water in oil emulsion. As conclusion, the Span 80 is the best emulsifier followed by Tween 80 and last but not least the weakest emulsifier is SDDS.

4.2.2 **Type of Crude Oil**

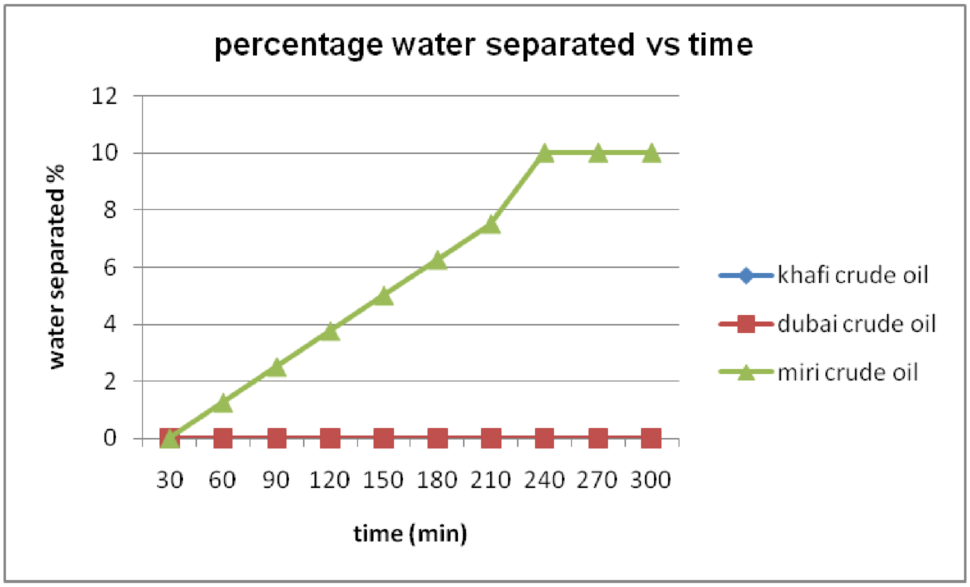


Figure 4.7: Water Separated with Different Crude Oil

From the figure above the stable crude oil is Dubai crude oil rather than Miri crude oil. it is because the molecule structure heavy crude oil is more stable than molecule structure light crude oil. The result shows that for early 30 minutes the water separation for Dubai crude oil 0mL. It continue maintain did not separate for the whole time meanwhile the Miri crude oil start to separate 1.25 percent water in oil emulsion and continue separate water in every 30 minutes. Khafi crude oil also shows the same character with Dubai crude oil. along the experiment the khafi did not separate any water even the higher concentration of emulsifier include in the emulsion. It is show the khafi crude oil is better than Dubai crude oil As the conclusion the better crude oil is Khafi crude oil followed by Dubai crude oil and the last one is Miri crude oil

4.3 Demulsification via Ultrasonic

Ultrasonic technology is one of the new technologies to break the emulsion. In this experiment the result for ultrasonic method will compare with chemical method to know which one method is better to break the emulsion and understand the mechanism of each method.

4.3.1 Effect of Temperature

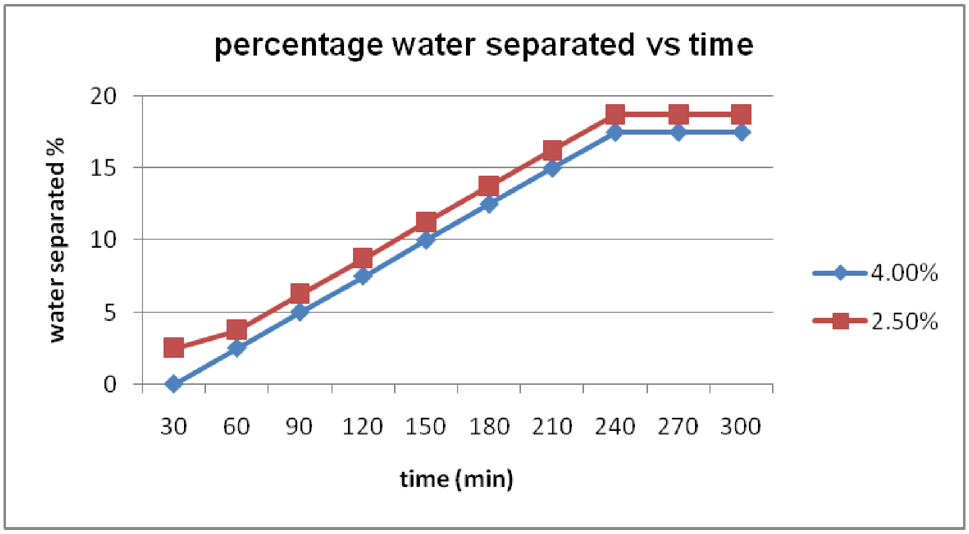


Figure 4.8: Water separated at 50^0C in Masila crude oil

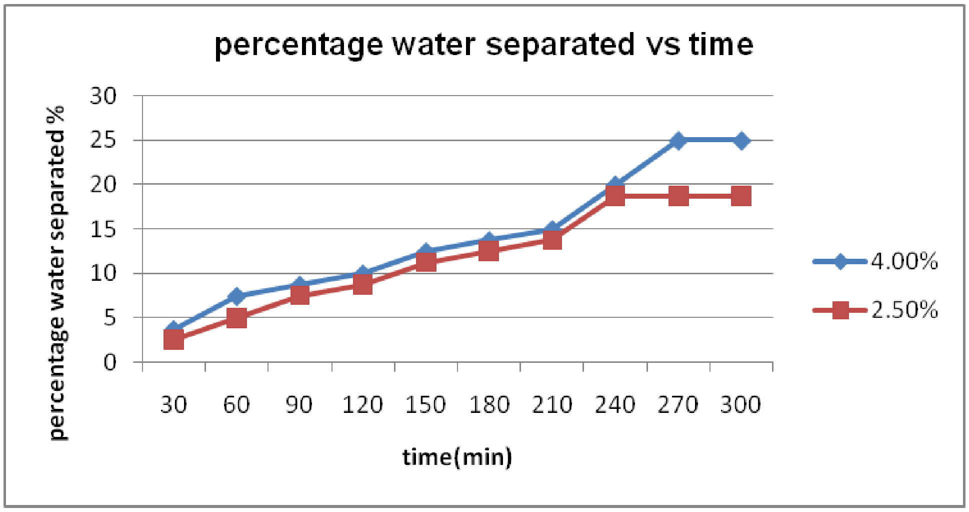


Figure 4.9: Water separated at 30^{0}C in Masila crude oil

The different temperature used to break the emulsion for Masila crude oil. From the observation the 500C is more better rather than 300C.The water separation increasing while we increase the temperature because the molecule interact along the interfaces. The time is still maintained for 5 hour to observe the separation occur using ultrasonic method. The water separation continuous separate from the beginning until next hour and start separate slowly at 240 minutes because the breaking emulsion did not occur again. The different temperature used to investigate the performance for the emulsion to break the emulsion in fast time. The best surfactant is used in this emulsion so that the better will get from this breaking emulsion part. In conclusion this result shows that the temperature also effect the breaking of the emulsion even we maintain the concentration.

4.3.2 Effect of Power

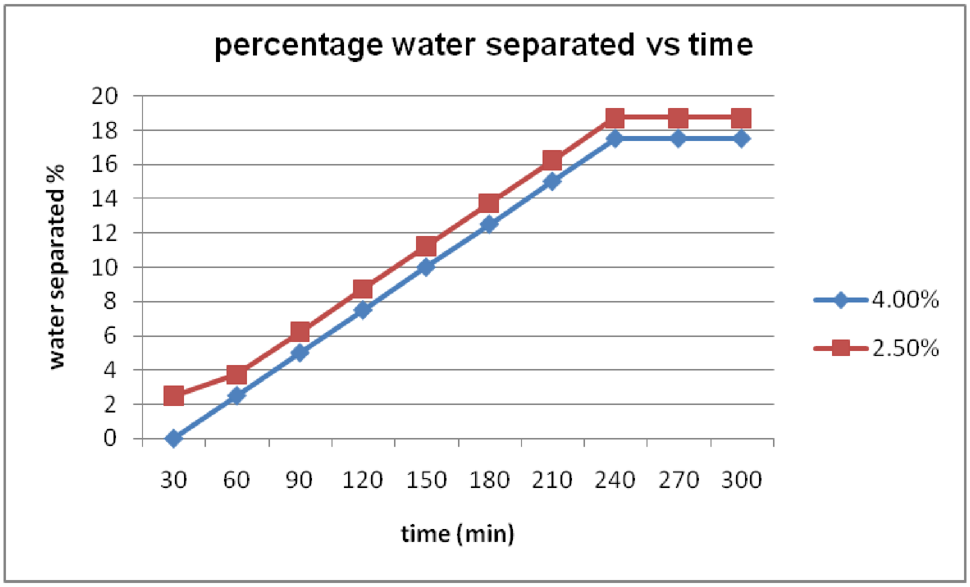


Figure 4.10: Water separated at 50^{0}C at 200 W

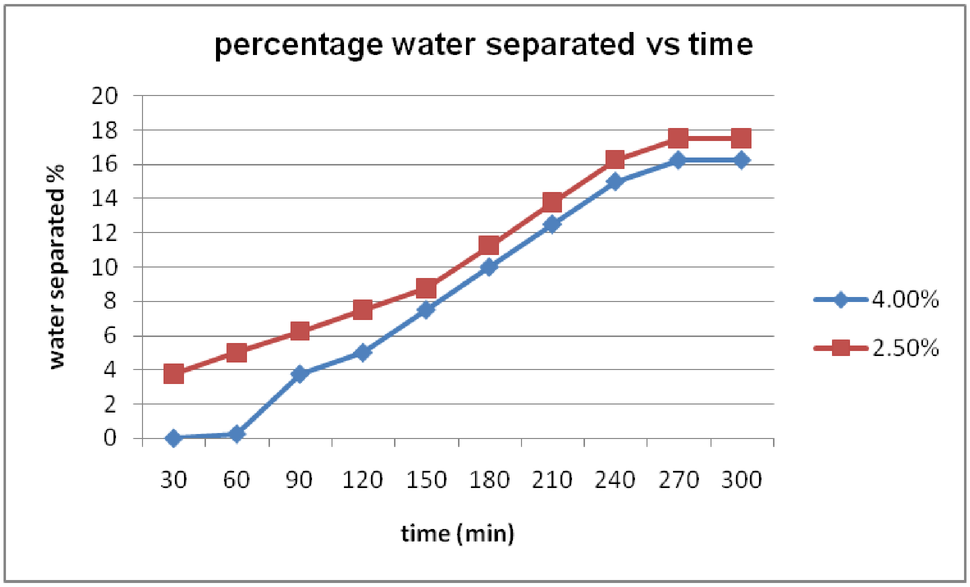


Figure 4.11: Water separated at 50^{0}C at 400 W

The figure above show the different parameter used to break the emulsion using ultrasonic technology. The temperature at 500C and the variable in this experiment is the rage of power used. The graph shows that the increase the power the breaking will slowly down. At first 60 minutes shows the different between two graph which the breaking in figure 4.11 did not separate meanwhile in figure 4.10 the emulsion start to break. Overall from this observation the break for two graph did not far away.until the final part shows that the power at 400W start to finish the breaking rather than the power at 200W. This results obviously that the power also can effect the breaking part in demulsification.

4.4 Comparison Ultrasonic and Chemical Demulsification

4.4.1 Comparison Equipment

The comparison method is needed to know which one the better method to use for demulsification for water in crude oil emulsion. As we know the chemical methos is more expensive rather than ultrasonic technology. There is advantage and disadvantage for both methods.

4.4.2 Comparison Graph

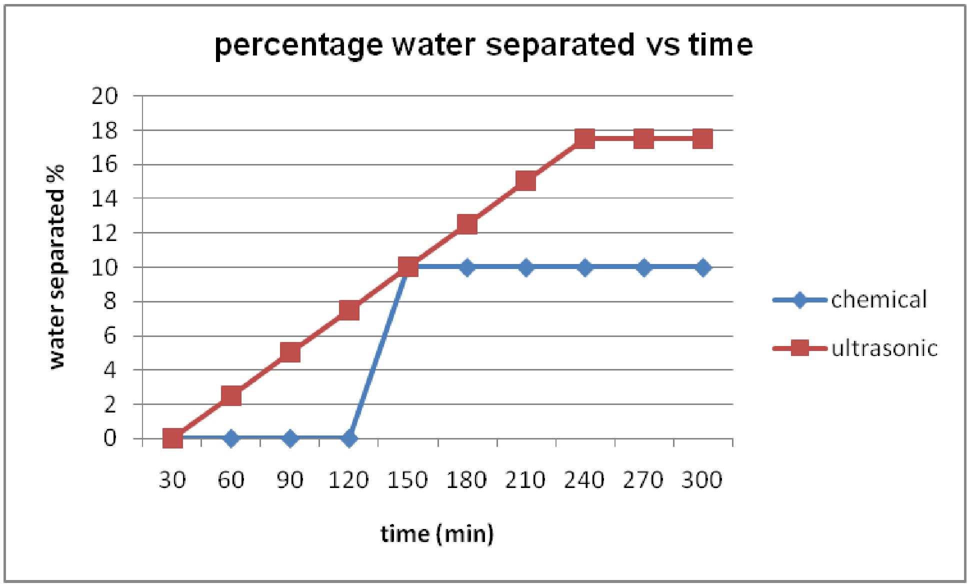


Figure 4.12: Breaking emulsion with chemical and ultrasonic

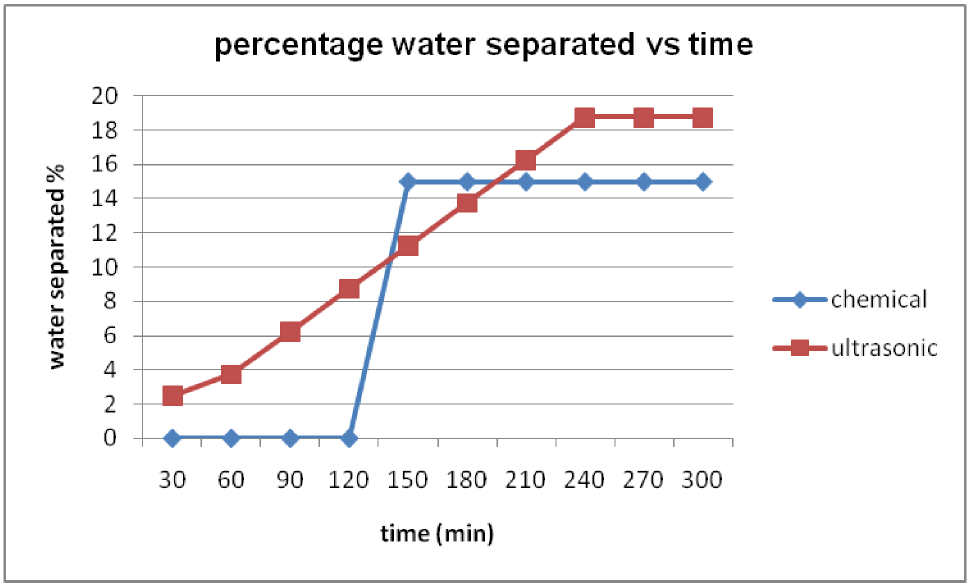


Figure 4.13: Breaking emulsion with chemical and ultrasonic

The comparison for both graph shows that the different method by using chemical and ultrasonic demulsification. Figure 4.12 shows that the 1% of hexylamine used while the figure 4.13 with 2% of hexylamine act to breaking the emulsion. From this observation the second graph is better than the breaking part in first graph. More concentration of chemical we used it will increase the water separation of emulsion. Ultrasonic method show better demulsification compared to chemical method. From figure 4.12 the ultrasonic is more efficient rather than chemical method because higher percentage can be achieved to break water in oil emulsion. It is not quite different for figure 4.13 which is sometimes chemical is better then ultrasonic. It is because the chemical have ability to interaction at interfaces between two liquid rather than ultrasonic. As a conclusion the ultrasonic is not efficient rather than chemical demulsification.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

Water-in-crude oil emulsions have great importance in the oil industry. From the expected result of this study tend to compare between ultrasonic of chemical demulsification. The conclusions are

I. Ultrasonic is also able to separation of water from emulsions

II. The water is the strong influence on emulsion stability

III. The ultrasonic not effective rather than chemical demulsification.

IV. The mechanism of ultrasonic technology sometimes more faster than chemical demulsification depends on the parameter

5.2 Recommendations

From this research, some recommendation can be made to improve the result of the analysis. The recommendations are:

I. Ensure the total volume for water and crude oil is totally accurate.
II. Follow the step by step every procedure so that the accurate emulsion is produce. Put the crude oil first in the beaker followed by the emulsifier and use the mixer at speed 1250 rpm to mix both of the mixture. After that pour the water slowly into the mixture so that it can totally mixing with crude oil. Continue stir the mixture until 18 minutes left.
III. Use the three blade propeller when mixing the mixture so that the emulsion produce is completely vigorous mixing.
IV. Check the emulsion weather it is oil in water or water in oil emulsions carefully.

REFERENCES

Abdurahman, H.N.; M.Y. Rosli.; and J. Zulkifly. 2006. *Study on demulsification of water crude oil emulsions via microwave heating technology*. *Journal of Applied Science*.,6:2060-2066

Abdurahman, H.N.; M.Y. Rosli.; A.Abu Hassan. Mohd, 2007. *Characterization and Demulsification of Water in crude Oil Emulsions*

Andersen, S.I.; Speight, J.G. *Petroleum Science and Technology 2001*, 19, 1-34

Aurdal, T.; Hjermstad, H. P.; Rønningsen, H. P.; Førdedal, H. Annual Report Saga Petroleum - Statoil. Research Co-operation on Asphaltenes , 1998, pp 100

Anne-Marie Faiola, 2008. *Using Emulsfying Wax. Teachsoap.com*

Buenrostro-Gonzales, E.; Groenzin, H.; Lira-Galeana; Mullins, O. C. *Energy & Fuels* 2001,*15*, 972-978.

Christie John Geankoplis, 2003.*Transport Process and Separation Process Principles (4th Edition)*,pg3-5

.

Dezhi Sun; Xiadong Duan; Wen Xu and Ding Zhou.*Demulsification of Water in Oil Emulsion by using Porous Glass Membrane*, 1999.

Groenzin, H.; Mullins, O. C. *Energy & Fuels* 2000, *14*, 677-684.

Inge Harald Auflem. *Influence of Asphaltene Aggregation and Pressure on Crude Oil Emulsion Stability*, 2002.

Kilpatrick, P. K.; Spiecker, P. M. In *Encyclopedic Handbook of Emulsion Technology*; Sjöblom, J., Ed.; Marcel Dekker: New York, 2001, pp 707-728

Lee, R. F. *Spill Science and Technology Bulletin* 1999, *5*, 117-126

Lixin Cheng a.c.; Dieter Mewes.; Andrea Luke.,2007.*Boiling Phenomena with Surfactants and Polymeric Additives. A state of the art review*. International Journal of Heat and Mass Transfer 50(2007)2744-2771

Musser, B. J.; Kilpatrick, P. K. *Energy & Fuels* 1998, *12*, 715-725

Narve Aske,2002. *Characterisation of Crude Oil Components, Asphaltene Aggregation and Emulsion Stability by means of Near Infrared Spectroscopy and Multivariate Analysis* pg:2-3

O. Behrend *, K. Ax, H. Schubert, 1999. *Influence of continuous phase viscosity on emulsification by ultrasound*.Ultrasonic Sonochemistry 7(2000) 77-85

Sheu, E. Y.; Mullins, O. C. *Asphaltenes : Fundamentals and Applications*; Plenum Press:
New York, 1995

Sheu, E. Y. *Energy & Fuels* 2002, *16*, 74-82

Sjöblom, J.; Johnsen, E. E.; Westvik, A.; Ese, M.-H.; Djuve, J.; Auflem, I. H.; Kallevik, H.In *Encyclopedic Handbook of Emulsion Technology*; Sjøblom, J., Ed.; Marcel Dekker Inc.:New York, 2000, pp 595-619

Speight, J. G. *The chemistry and technology of petroleum*; Marcel Dekker: New York, 1999

Wang, J. Ph. D. Thesis, New Mexico Institute of Mining and Technology, Socorro, 2000

APPENDICES

Figure A-1: Three blade propeller

Figure A-2: Ultrasonic technology

Figure A-3: Emulsifier

Figure A-4:Dubai Oil 20-80%-span 80

Figure A-5: Khafi Oil 20-80%-span 80

Figure A-6: Miri Oil20-80%-span 80

Stability

Result

Dubai oil

Volume ratio: 50-50

Surfactant: Span 80

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	5	1.25
120	10	2.5
150	15	3.75
180	25	6.25
210	30	7.5
240	45	11.25
270	50	12.5
300	50	12.5

Ratio: 1.5%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	0	0
120	5	1.25
150	15	3.75
180	20	5
210	25	6.25
240	40	10
270	45	11.25
300	45	11.25

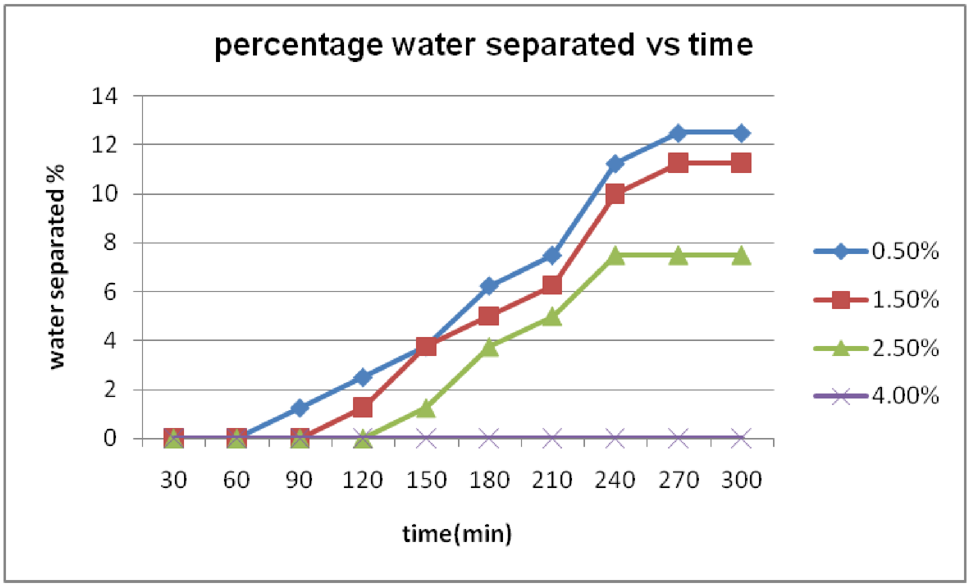
Ratio: 2.5%

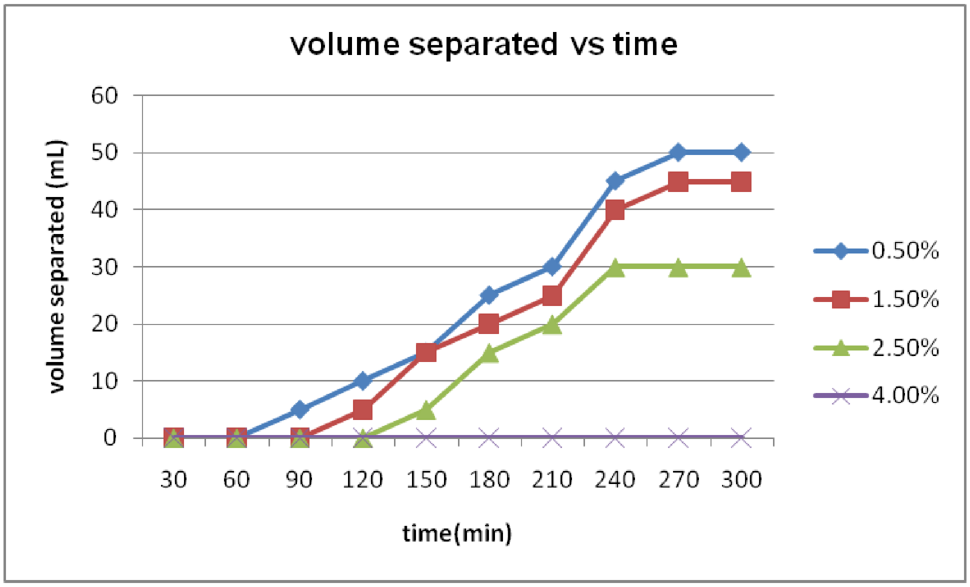
Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	0	0
120	0	0
150	5	1.25
180	15	3.75
210	20	5
240	30	7.5
270	30	7.5
300	30	7.5

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	0	0
120	0	0
150	0	0
180	0	0
210	0	0
240	0	0
270	0	0
300	0	0

Graph


percentage water separated vs time
water separated %
14
12
10
8
6
4
2
0
30
60
90
120
150
180
210
240
270
300
time(min)
0.50%
1.50%
2.50%
4.00%


volume separated vs time
volume separated (mL)
60
50
40
30
20
10
0
30
60
90
120
150
180
210
240
270
300
time(min)
0.50%
1.50%
2.50%
4.00%

Result

Dubai oil

Volume ratio: 20-80

Surfactant: Span 80

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	0	0
120	0	0
150	20	5
180	25	6.25
210	30	7.5
240	35	8.75
270	35	8.75
300	35	8.75

Ratio: 1.5%

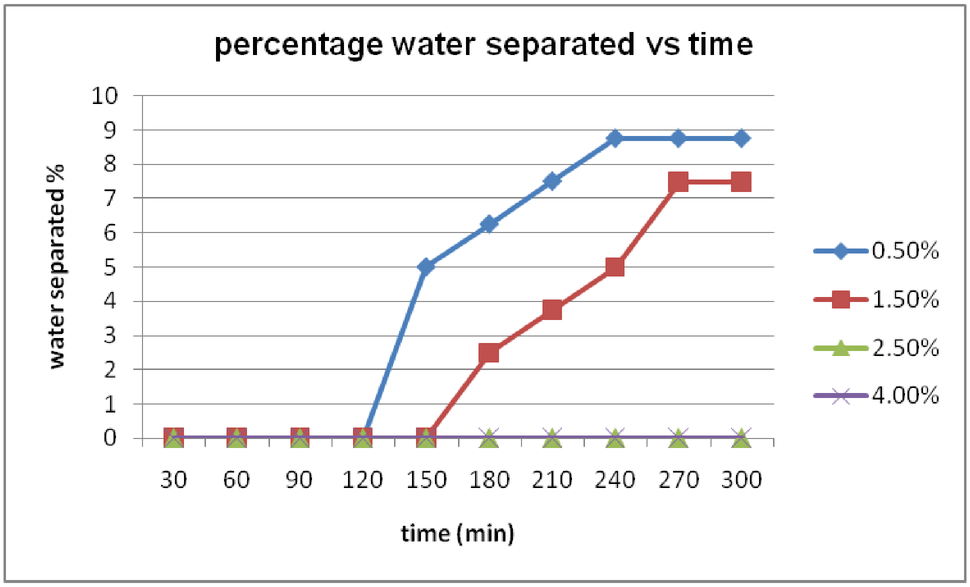
Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	0	0
120	0	0
150	0	0
180	10	2.5
210	15	3.75
240	20	5
270	30	7.5
300	30	7.5

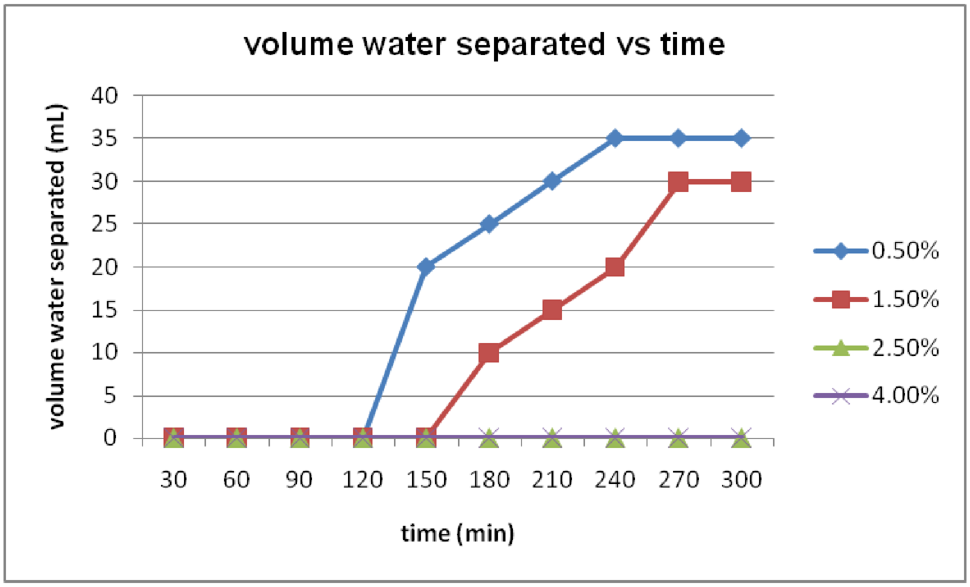
Ratio: 2.5%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	0	0
120	0	0
150	0	0
180	0	0
210	0	0
240	0	0
270	0	0
300	0	0

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	0	0
120	0	0
150	0	0
180	0	0
210	0	0
240	0	0
270	0	0
300	0	0


percentage water separated vs time
water separated %
10
9
8
7
6
5
4
3
2
1
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%


volume water separated vs time
volume water separated (mL)
40
35
30
25
20
15
10
5
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%

Result

Dubai oil

Volume ratio: 50-50

Surfactant: SDDS

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	10	2.5
60	30	7.5
90	50	12.5
120	65	16.25
150	80	20
180	100	25
210	130	32.5
240	145	36.25
270	150	37.5
300	150	37.5

Ratio: 1.5%

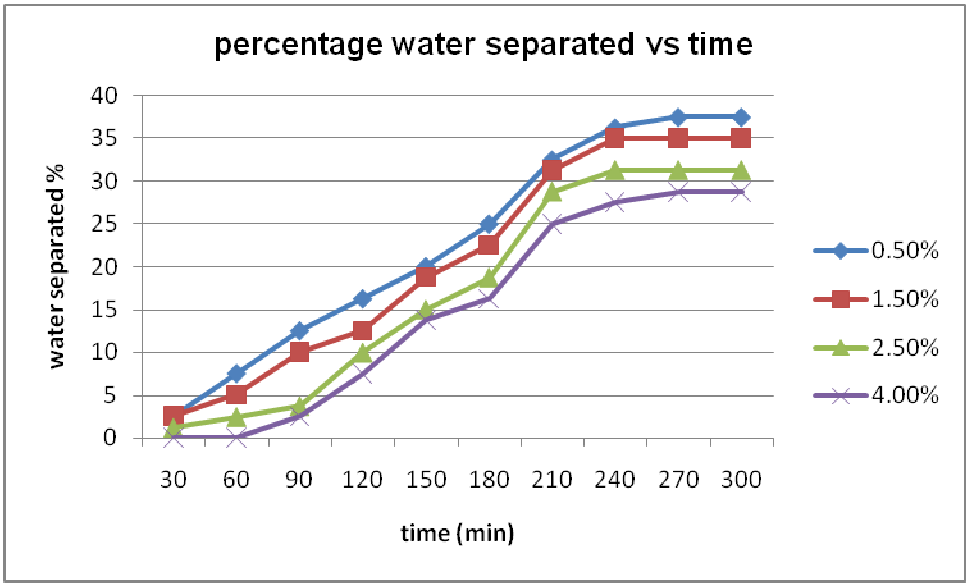
Time	water separated	
	Water (mL)	% water
30	10	2.5
60	20	5
90	40	10
120	50	12.5
150	75	18.75
180	90	22.5
210	125	31.25
240	140	35
270	140	35
300	140	35

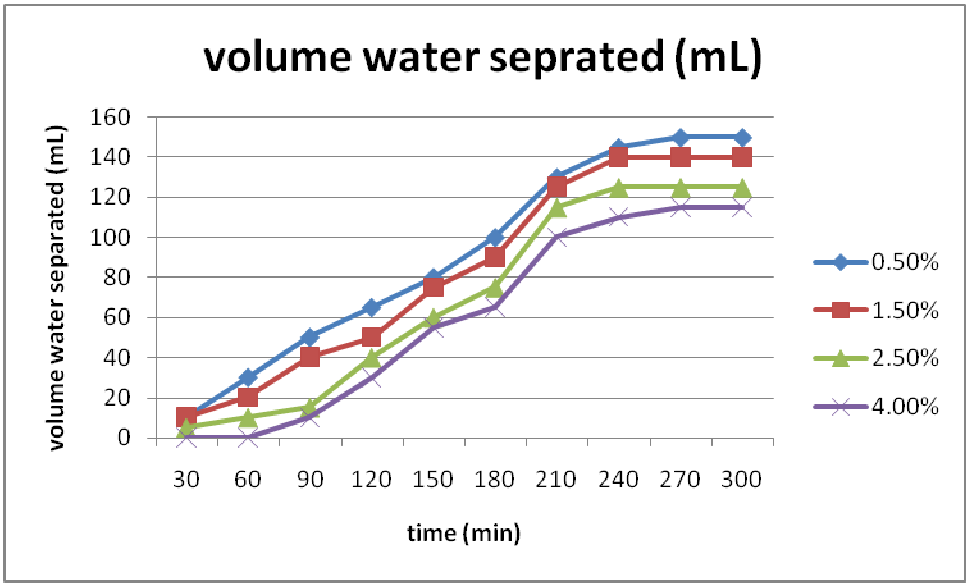
Ratio: 2.5%

Time	water separated	
	Water (mL)	% water
30	5	1.25
60	10	2.5
90	15	3.75
120	40	10
150	60	15
180	75	18.75
210	115	28.75
240	125	31.25
270	125	31.25
300	125	31.25

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	10	2.5
120	30	7.5
150	55	13.75
180	65	16.25
210	100	25
240	110	27.5
270	115	28.75
300	115	28.75


percentage water separated vs time
water separated %
40
35
30
25
20
15
10
5
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%


volume water seprated (mL)
volume water separated (mL)
160
140
120
100
80
60
40
20
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%

Result

Dubai oil

Volume ratio: 20-80

Surfactant: SDDS

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	15	3.75
60	25	6.25
90	35	8.75
120	40	10
150	45	11.25
180	55	13.75
210	60	15
240	75	18.75
270	75	18.75
300	75	18.75

Ratio: 1.5%

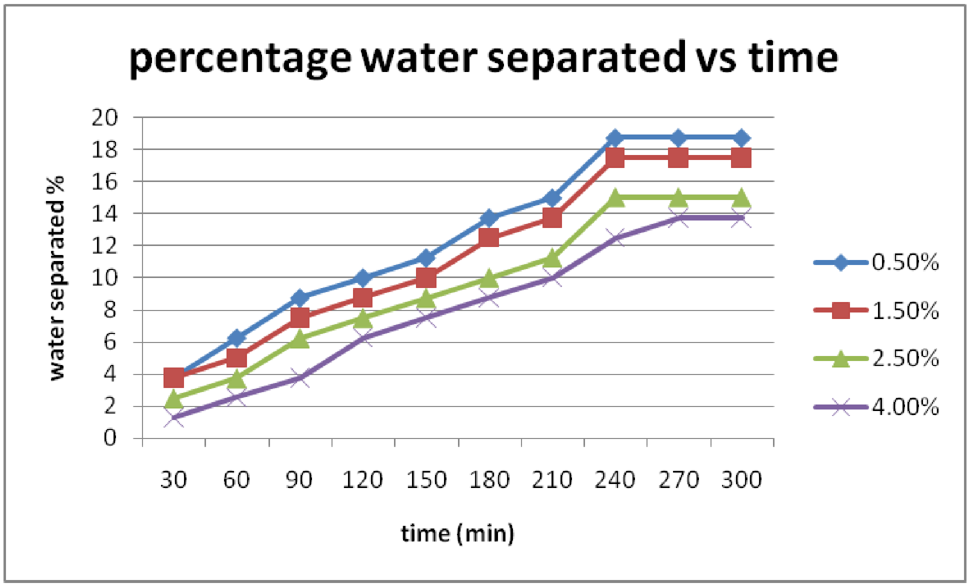
Time	water separated	
	Water (mL)	% water
30	15	3.75
60	20	5
90	30	7.5
120	35	8.75
150	40	10
180	50	12.5
210	55	13.75
240	70	17.5
270	70	17.5
300	70	17.5

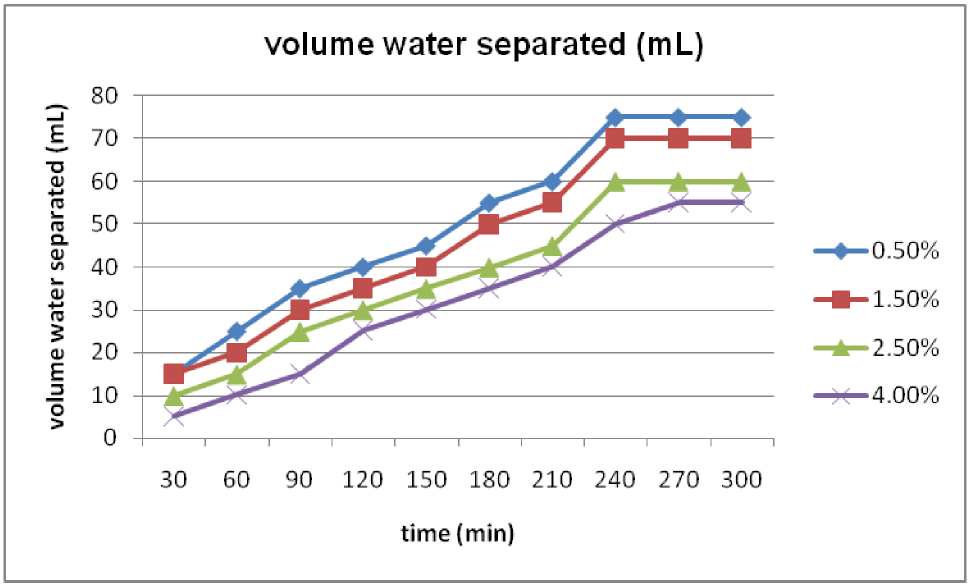
Ratio: 2.5%

Time	water separated	
	Water (mL)	% water
30	10	2.5
60	15	3.75
90	25	6.25
120	30	7.5
150	35	8.75
180	40	10
210	45	11.25
240	60	15
270	60	15
300	60	15

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	5	1.25
60	10	2.5
90	15	3.75
120	25	6.25
150	30	7.5
180	35	8.75
210	40	10
240	50	12.5
270	55	13.75
300	55	13.75


percentage water separated vs time
water separated %
20
18
16
14
12
10
8
6
4
2
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%


volume water separated (mL)
volume water separated (mL)
80
70
60
50
40
30
20
10
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%

Stability

Result

Dubai oil

Volume ratio: 50-50

Surfactant: Tween 80

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	0	0
60	5	0
90	10	2.5
120	20	5
150	25	6.25
180	30	7.5
210	35	8.75
240	40	10
270	45	11.25
300	45	11.25

Ratio: 1.5%

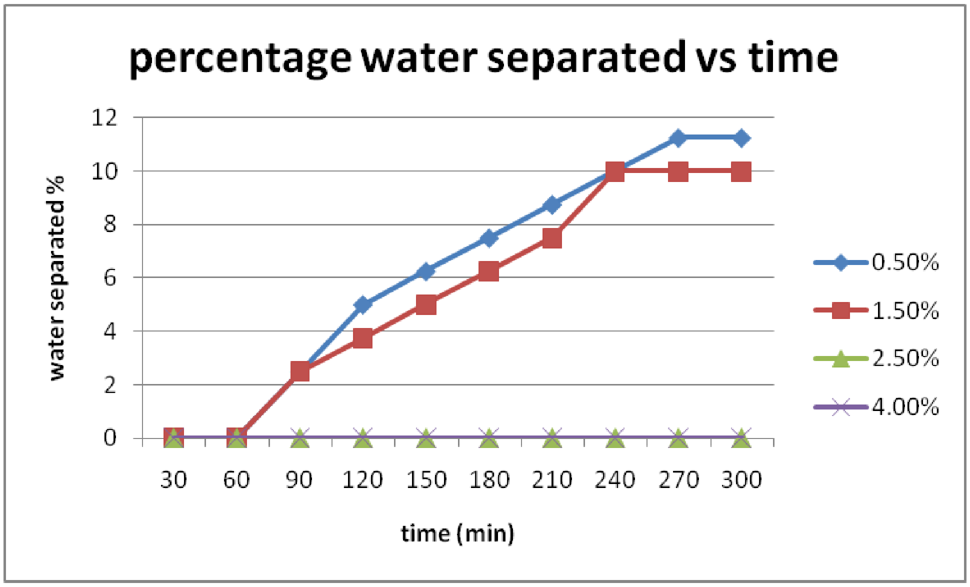
Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	10	2.5
120	15	3.75
150	20	5
180	25	6.25
210	30	7.5
240	40	10
270	40	10
300	40	10

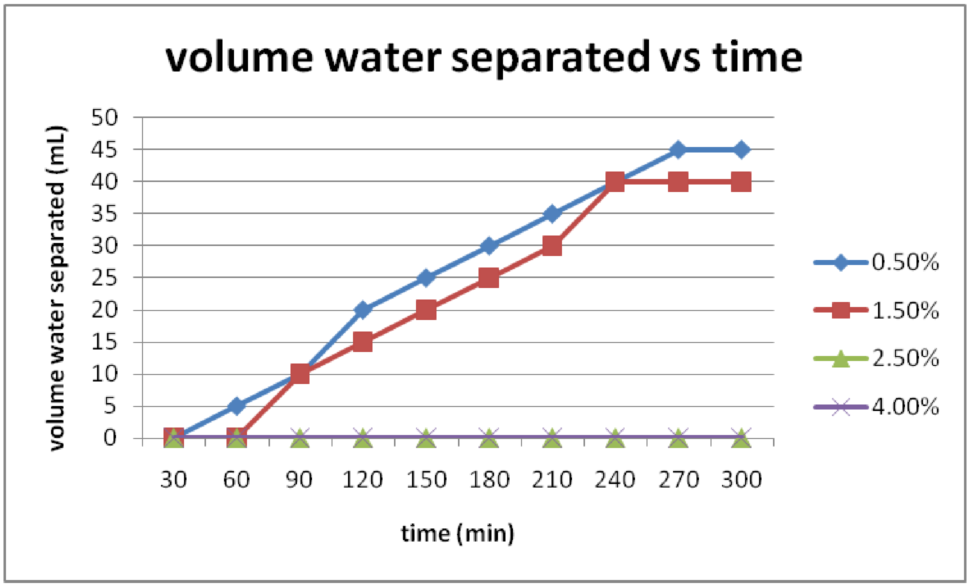
Ratio: 2.5%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	0	0
120	0	0
150	0	0
180	0	0
210	0	0
240	0	0
270	0	0
300	0	0

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	0	0
120	0	0
150	0	0
180	0	0
210	0	0
240	0	0
270	0	0
300	0	0


percentage water separated vs time
water separated %
12
10
8
6
4
2
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%


volume water separated vs time
volume water separated (mL)
50
45
40
35
30
25
20
15
10
5
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%

Result

Dubai oil

Volume ratio: 20-80

Surfactant: Tween 80

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	15	3.75
60	20	5
90	25	6.25
120	30	7.5
150	35	8.75
180	40	10
210	45	11.25
240	50	12.5
270	50	12.5
300	50	12.5

Ratio: 1.5%

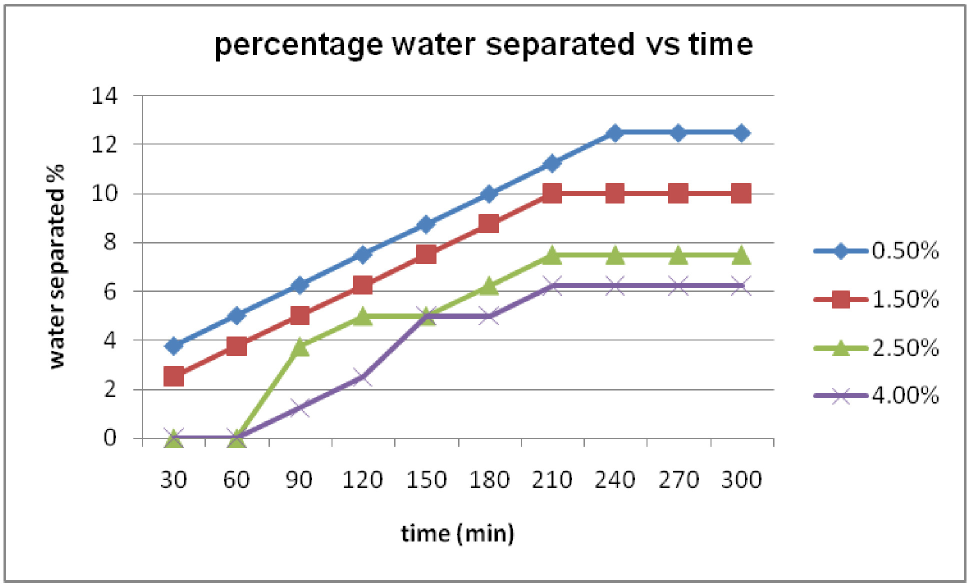
Time	water separated	
	Water (mL)	% water
30	10	2.5
60	15	3.75
90	20	5
120	25	6.25
150	30	7.5
180	35	8.75
210	40	10
240	40	10
270	40	10
300	40	10

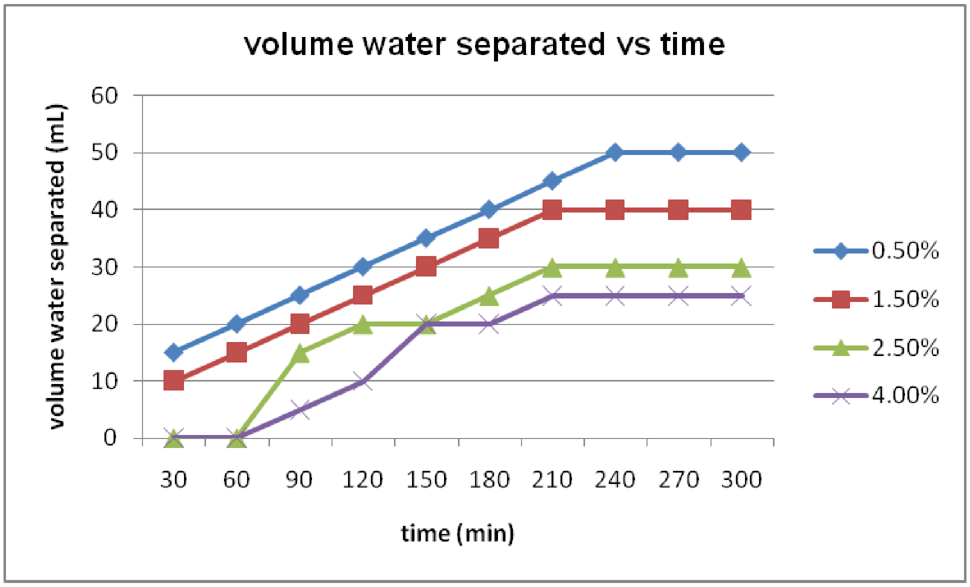
Ratio: 2.5%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	15	3.75
120	20	5
150	20	5
180	25	6.25
210	30	7.5
240	30	7.5
270	30	7.5
300	30	7.5

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	5	1.25
120	10	2.5
150	20	5.0
180	20	5.0
210	25	6.25
240	25	6.25
270	25	6.25
300	25	6.25


percentage water separated vs time
water separated %
14
12
10
8
6
4
2
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%


volume water separated vs time
volume water separated (mL)
60
50
40
30
20
10
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%

Result

Miri oil

Volume ratio : 50-50

Surfactant: Span 80

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	20	5
60	70	17.5
90	90	22.5
120	100	25
150	105	26.25
180	110	27.5
210	110	27.5
240	115	28.75
270	115	28.75
300	115	28.75

Ratio : 1.5%

Time	water separated	
	Water (mL)	% water
30	0	0
60	10	2.5
90	20	5
120	30	7.5
150	30	7.5
180	35	8.75
210	40	10
240	40	10
270	50	12.5
300	50	12.5

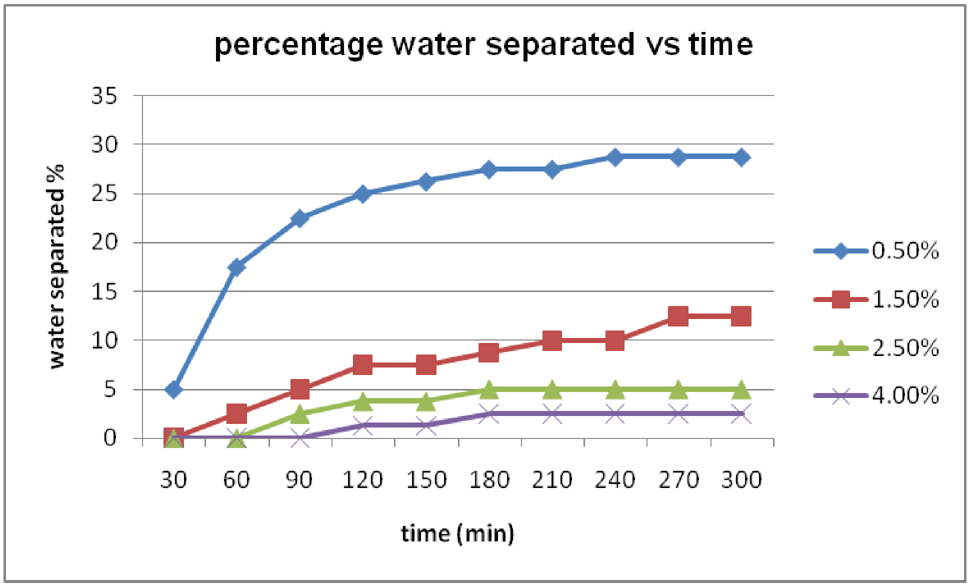
*when mixture crude oil with water,the mixture from black color turn to dark brown-yellow color

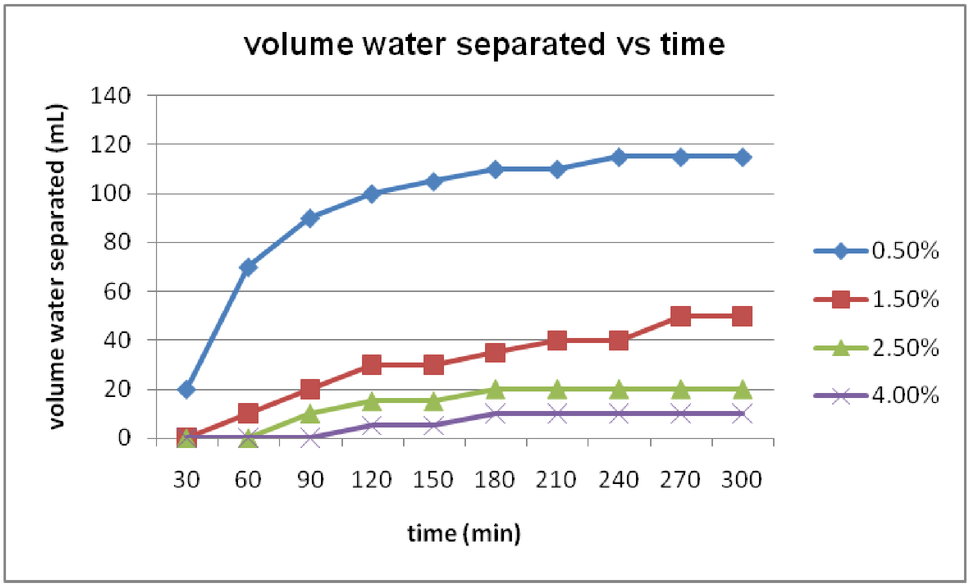
Ratio: 2.5%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	10	2.5
120	15	3.75
150	15	3.75
180	20	5
210	20	5
240	20	5
270	20	5
300	20	5

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	0	0
60	0	0
90	0	0
120	5	1.25
150	5	1.25
180	10	2.5
210	10	2.5
240	10	2.5
270	10	2.5
300	10	2.5


percentage water separated vs time
water separated %
35
30
25
20
15
10
5
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%


volume water separated vs time
volume water separated (mL)
140
120
100
80
60
40
20
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%

Result

Miri oil

Volume ratio: 20-80

Surfactant: Span 80

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	15	3.75
60	20	5
90	25	6.25
120	30	7.5
150	40	10
180	55	13.75
210	60	15
240	65	16.25
270	65	16.25
300	65	16.25

Ratio: 1.5%

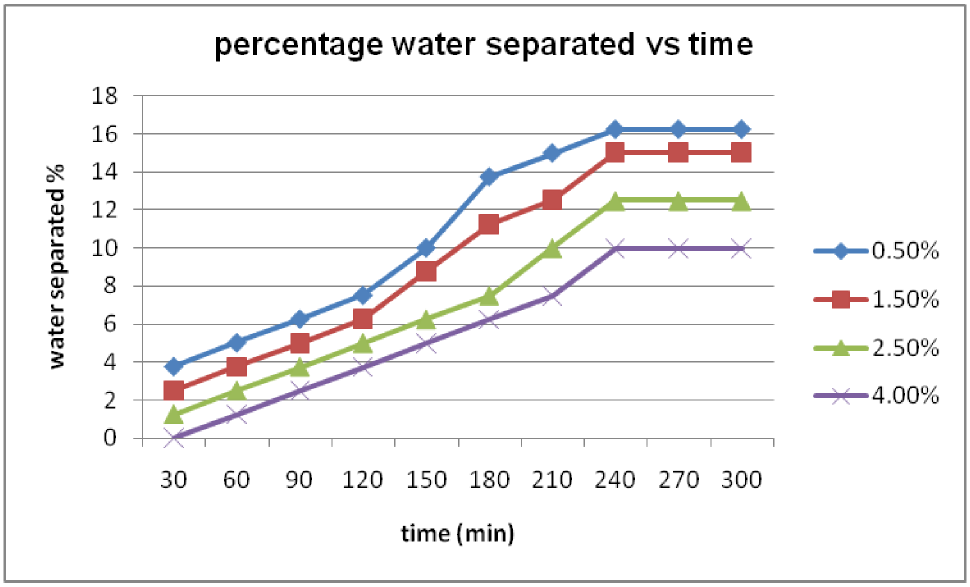
Time	water separated	
	Water (mL)	% water
30	10	2.5
60	15	3.75
90	20	5
120	25	6.25
150	35	8.75
180	45	11.25
210	50	12.5
240	60	15
270	60	15
300	60	15

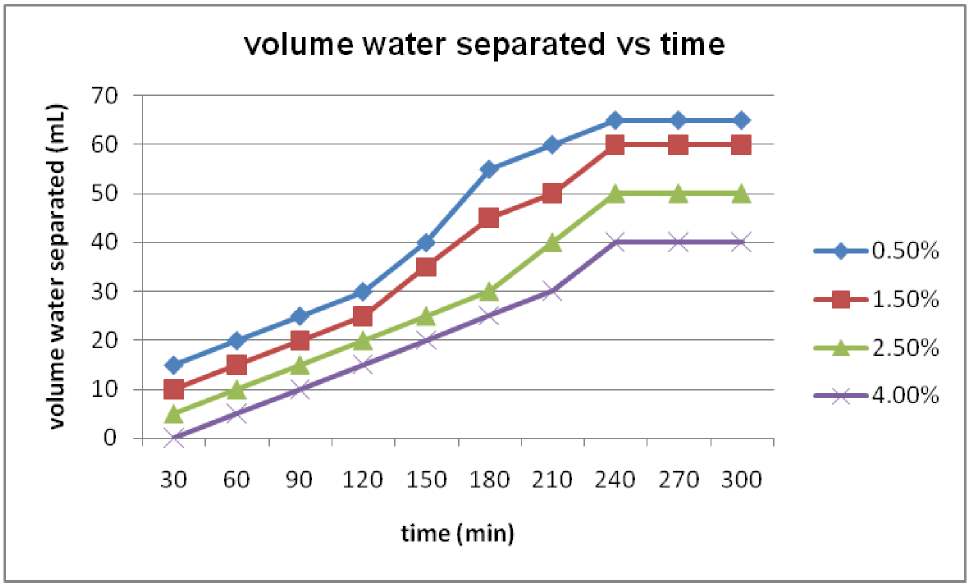
Ratio: 2.5%

Time	water separated	
	Water (mL)	% water
30	5	1.25
60	10	2.5
90	15	3.75
120	20	5
150	25	6.25
180	30	7.5
210	40	10
240	50	12.5
270	50	12.5
300	50	12.5

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	0	0
60	5	1.25
90	10	2.5
120	15	3.75
150	20	5
180	25	6.25
210	30	7.5
240	40	10
270	40	10
300	40	10


percentage water separated vs time
water separated %
18
16
14
12
10
8
6
4
2
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%


volume water separated vs time
volume water separated (mL)
70
60
50
40
30
20
10
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%

Result

Miri oil

Volume ratio: 50-50

Surfactant: Tween 80

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	30	7.5
60	80	20
90	100	25
120	110	27.5
150	115	28.75
180	120	30
210	120	30
240	130	32.5
270	130	32.5
300	130	32.5

Ratio : 1.5%

Time	water separated	
	Water (mL)	% water
30	20	5
60	30	7.5
90	40	10
120	45	11.25
150	50	12.5
180	55	13.75
210	70	17.5
240	70	17.5
270	100	25
300	100	25

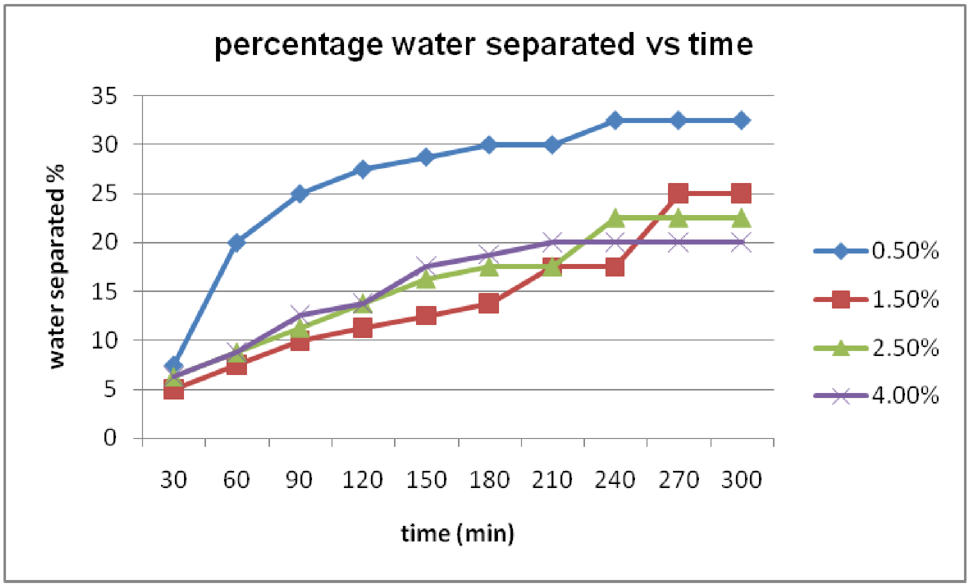
*when mixture crude oil with water,the mixture from black color turn to dark brown-yellow color

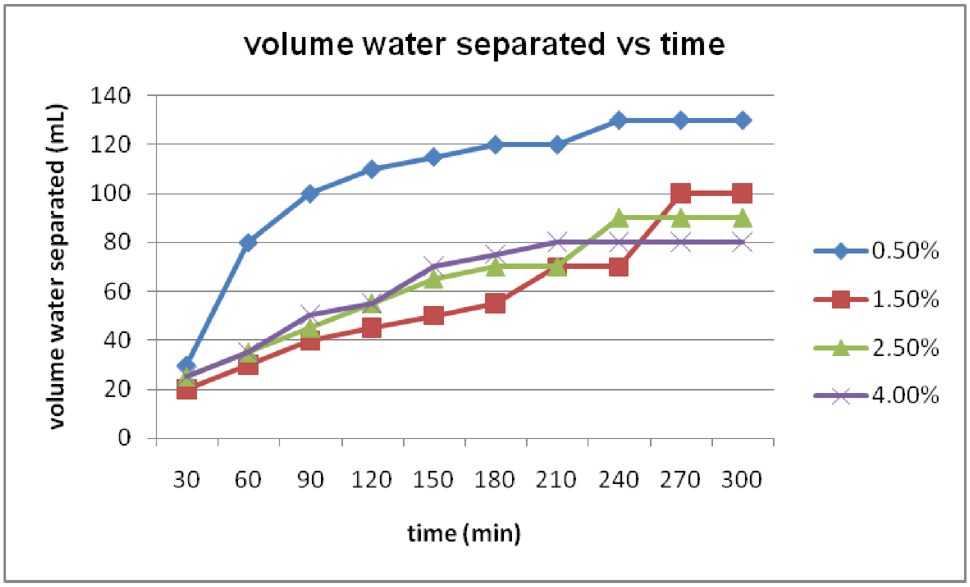
Ratio: 2.5%

Time	water separated	
	Water (mL)	% water
30	25	6.25
60	35	8.75
90	45	11.25
120	55	13.75
150	65	16.25
180	70	17.5
210	70	17.5
240	90	22.5
270	90	22.5
300	90	22.5

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	25	6.25
60	35	8.75
90	50	12.5
120	55	13.75
150	70	17.5
180	75	18.75
210	80	20
240	80	20
270	80	20
300	80	20


percentage water separated vs time
water separated %
35
30
25
20
15
10
5
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%


volume water separated vs time
volume water separated (mL)
140
120
100
80
60
40
20
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%

Result

Miri oil

Volume ratio: 20-80

Surfactant: Tween 80

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	35	8.75
60	40	10
90	45	11.25
120	55	13.75
150	60	15
180	65	16.25
210	70	17.5
240	75	18.75
270	75	18.75
300	75	18.75

Ratio: 1.5%

Time	water separated	
	Water (mL)	% water
30	30	7.5
60	35	8.75
90	40	10
120	45	11.25
150	50	12.5
180	55	13.75
210	60	15
240	70	17.5
270	70	17.5
300	70	17.5

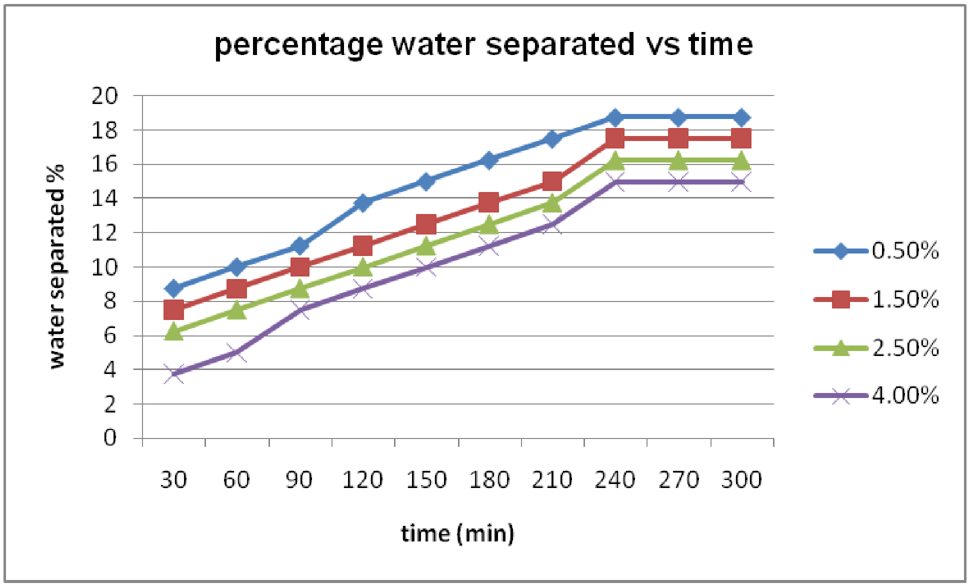
*when mixture crude oil with water,the mixture from black color turn to dark brown-yellow color

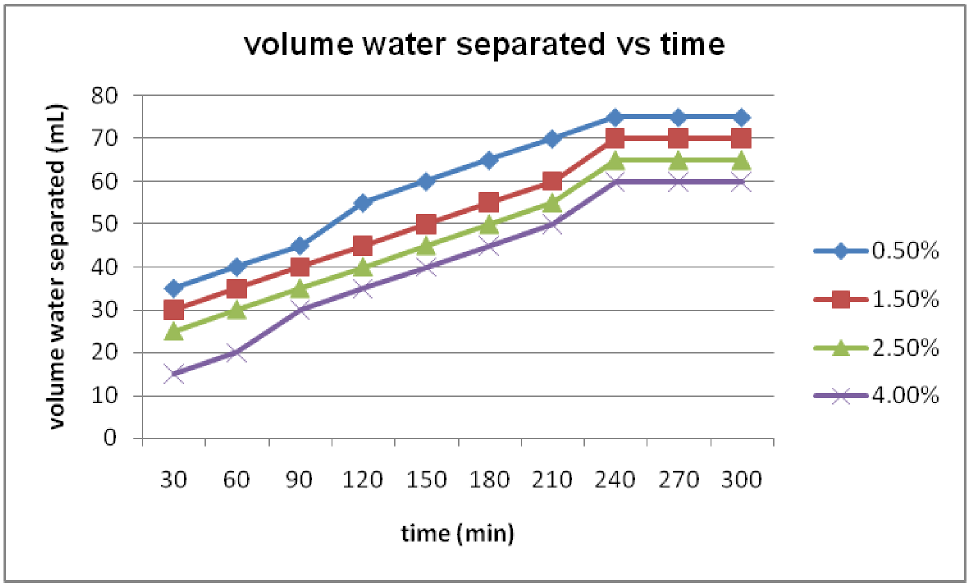
Ratio: 2.5%

Time	water separated	
	Water (mL)	% water
30	25	6.25
60	30	7.5
90	35	8.75
120	40	10
150	45	11.25
180	50	12.5
210	55	13.75
240	65	16.25
270	65	16.25
300	65	16.25

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	15	3.75
60	20	5
90	30	7.5
120	35	8.75
150	40	10
180	45	11.25
210	50	12.5
240	60	15
270	60	15
300	60	15


percentage water separated vs time
water separated %
20
18
16
14
12
10
8
6
4
2
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%


volume water separated vs time
volume water separated (mL)
80
70
60
50
40
30
20
10
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%

Result

Miri oil

Volume ratio: 50-50

Surfactant: SDDS

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	30	7.5
60	50	12.5
90	70	17.5
120	85	21.25
150	105	26.25
180	130	32.5
210	145	36.25
240	165	41.25
270	190	47.5
300	190	47.5

Ratio: 1.5%

Time	water separated	
	Water (mL)	% water
30	30	7.5
60	45	11.25
90	65	16.25
120	85	21.25
150	100	25
180	125	31.25
210	140	35
240	160	40
270	185	46.25
300	185	46.25

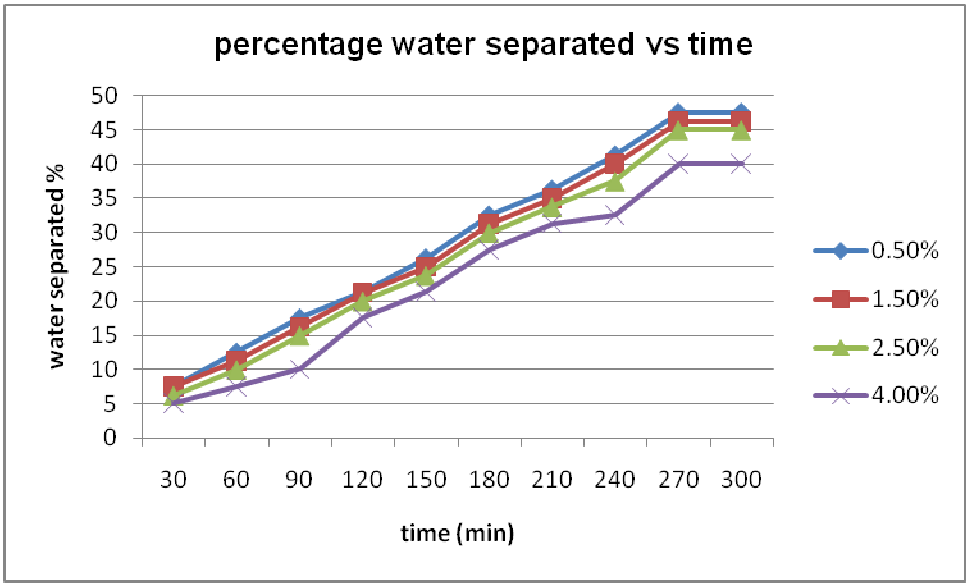
*when mixture crude oil with water,the mixture from black color turn to dark brown-yellow color

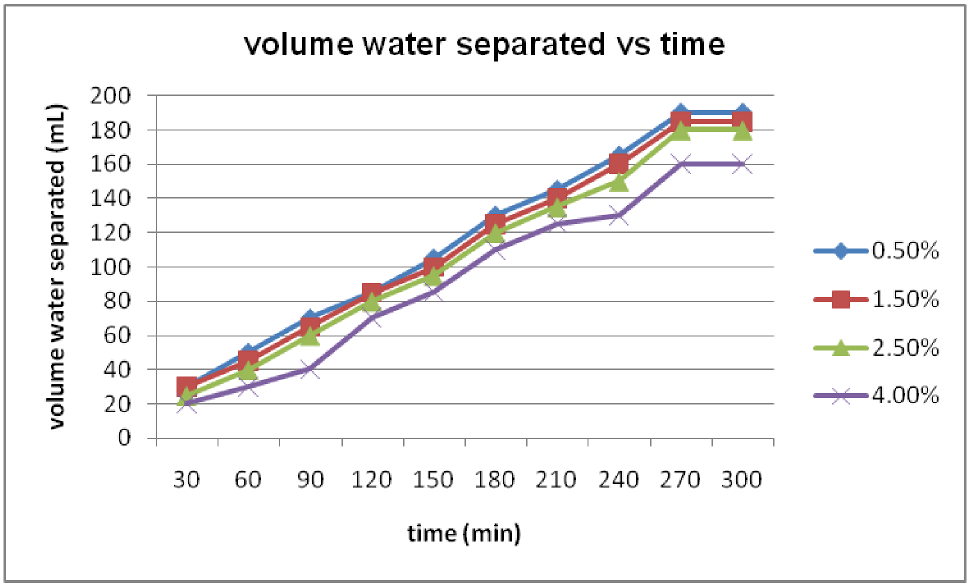
Ratio: 2.5%

Time	water separated	
	Water (mL)	% water
30	25	6.25
60	40	10
90	60	15
120	80	20
150	95	23.75
180	120	30
210	135	33.75
240	150	37.5
270	180	45
300	180	45

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	20	5
60	30	7.5
90	40	10
120	70	17.5
150	85	21.25
180	110	27.5
210	125	31.25
240	130	32.5
270	160	40
300	160	40


percentage water separated vs time
water separated %
0
5
10
15
20
25
30
35
40
45
50
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%


volume water separated vs time
volume water separated (mL)
0
20
40
60
80
100
120
140
160
180
200
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%

Result

Miri oil

Volume ratio: 20-80

Surfactant: SDDS

Ratio: 0.5%

Time	water separated	
	Water (mL)	% water
30	20	5
60	30	7.5
90	40	10
120	45	11.25
150	50	12.5
180	55	13.75
210	70	17.5
240	70	17.5
270	75	18.75
300	75	18.75

Ratio: 1.5%

Time	water separated	
	Water (mL)	% water
30	15	3.75
60	25	6.25
90	35	8.75
120	40	10
150	45	11.25
180	50	12.5
210	65	16.25
240	65	16.25
270	70	17.5
300	70	17.5

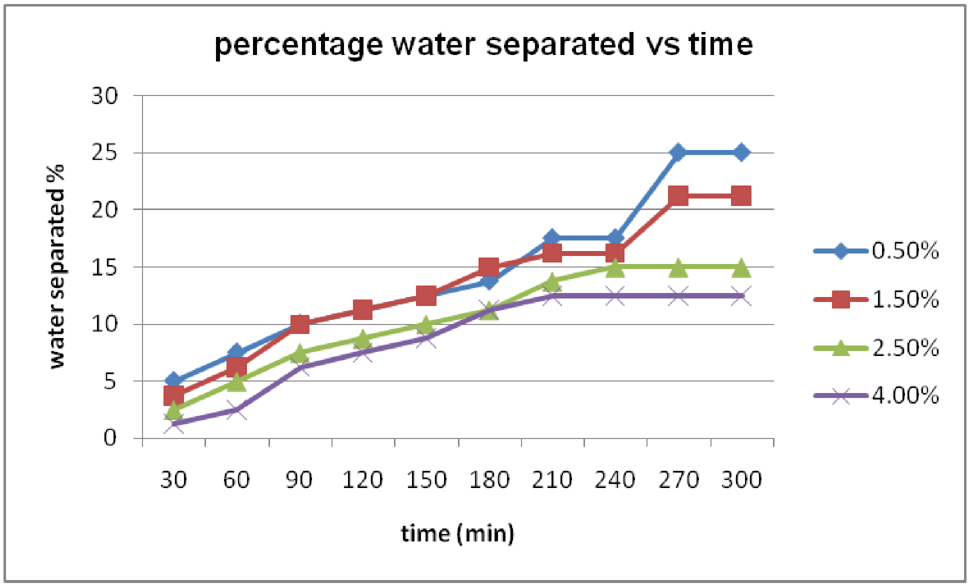
*when mixture crude oil with water,the mixture from black color turn to dark brown-yellow color

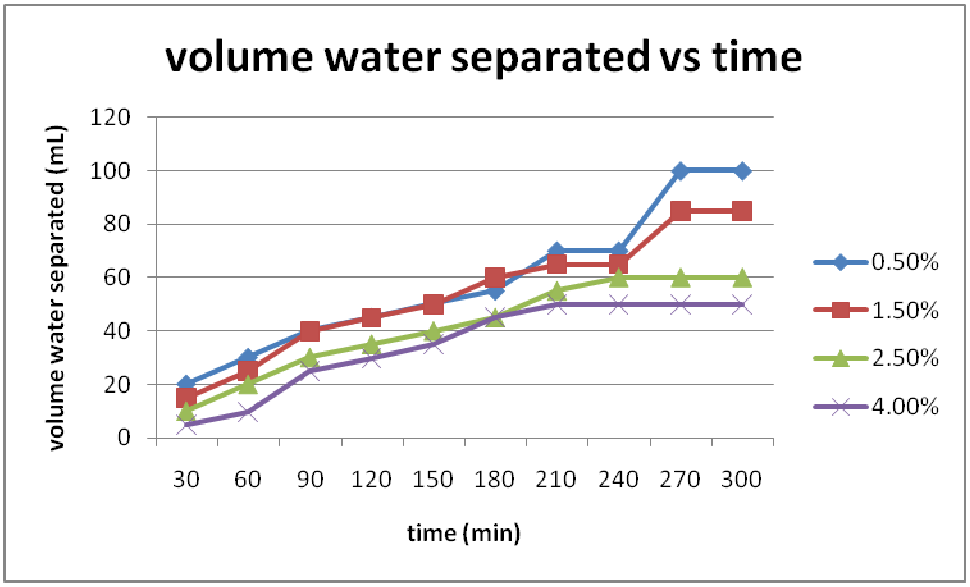
Ratio: 2.5%

Time	water separated	
	Water (mL)	% water
30	10	2.5
60	20	5
90	30	7.5
120	35	8.75
150	40	10
180	45	11.25
210	55	13.75
240	60	15
270	60	15
300	60	15

Ratio: 4%

Time	water separated	
	Water (mL)	% water
30	5	1.25
60	10	2.5
90	25	6.25
120	30	7.5
150	35	8.75
180	45	11.25
210	50	12.5
240	50	12.5
270	50	12.5
300	50	12.5


percentage water separated vs time
water separated %
30
25
20
15
10
5
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%


volume water separated vs time
volume water separated (mL)
120
100
80
60
40
20
0
30
60
90
120
150
180
210
240
270
300
time (min)
0.50%
1.50%
2.50%
4.00%

Demulsification part

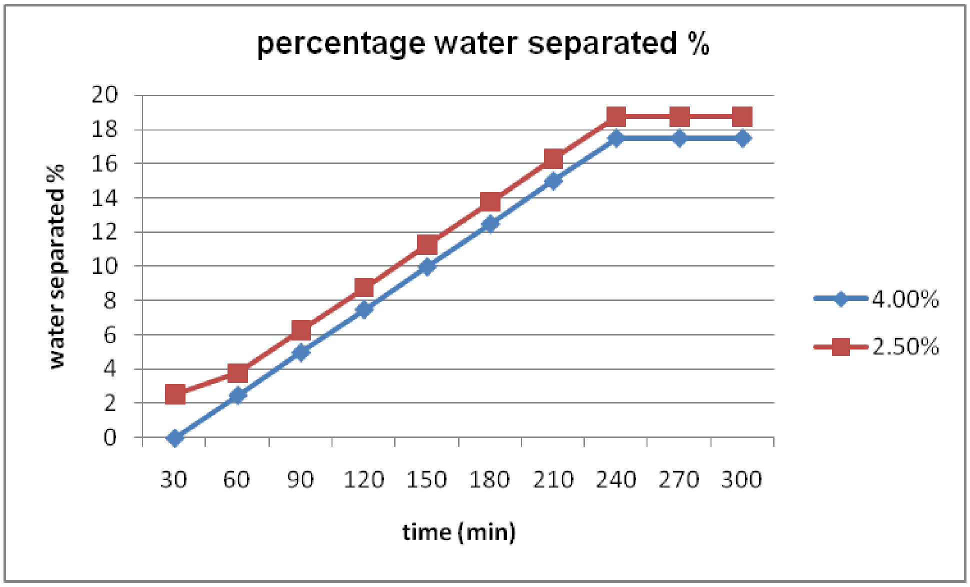
Effect of Temperature 50^0C

Time	water separated	
	Water (mL)	% water
30	10	2.5
60	15	3.75
90	25	6.25
120	35	8.75
150	45	11.25
180	55	13.75
210	65	16.25
240	75	18.75
270	75	18.75
300	75	18.75

Table B-1: concentration for 2.5% Span 80

Time	water separated	
	Water (mL)	% water
30	0	0
60	10	2.5
90	20	5
120	30	7.5
150	40	10
180	50	12.5
210	60	15
240	70	17.5
270	70	17.5
300	70	17.5

Table B-2: concentration for 4.0% Span 80



Effect of Temperature 30^{0}C

Time	water separated	
	Water (mL)	% water
30	15	3.75
60	30	7.5
90	35	8.75
120	40	10
150	50	12.5
180	55	13.75
210	60	15
240	80	20
270	100	25
300	100	25

Table B-3: concentration for 4.0% Span 80

Effect of Temperature 30^0C

Time	water separated	
	Water (mL)	% water
30	10	2.5
60	20	5
90	30	7.5
120	35	8.75
150	45	11.25
180	50	12.5
210	55	13.75
240	75	18.75
270	90	18.75
300	90	18.75

Table B-4: concentration for 2.5% Span 80