OPTIMIZATION AND CHEMICAL DEMULSIFICATION OF CRUDE OIL EMULSIONS

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OPTIMIZATION AND CHEMICAL DEMULSIFICATION OF CRUDE OIL EMULSIONS

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Thesis submitted in fulfilment of the requirements
for the award of the degree of
Master of Engineering in Chemical

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JUNE 2012

SUPERVISOR’S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Engineering in Chemical.

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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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Dedicated to my lovely husband, mother and to my late father

ACKNOWLEDGEMENTS

First and famous, I would like to devote my gratitude to our Creator for the compassion and for guiding me throughout my lifetime.

I am grateful and would like to express my sincere gratitude to my supervisor, Associate Professor Dr. Abdurahman Hamid Nour for his germinal ideas, individual guidance, continuous encouragement and constant support in making this research possible. He has always impressed me with his outstanding professional conduct, his strong conviction for science, and his belief that a Master program is only a start of a life-long learning experience. I appreciate his consistent support from the first day I applied to graduate program to these concluding moments.

I acknowledge my sincere indebtedness and gratitude to my mother and my late father for their love, dream and sacrifice throughout my life. Then, I also want to dedicate my appreciation to my beloved husband for his support, patience and understanding.

Special thanks should be given to Petronas Penapisan Melaka and Kerteh, Malaysia for providing the crude oil samples used in the project.

The financial support from the Ministry of Science, Technology and Innovation (MOSTI) through National Scholarship Financial (NSF) and research grant from Universiti Malaysia Pahang (UMP) are highly acknowledged.

ABSTRACT

In this thesis, the potentials of traditional and environmentally friendly chemicals in demulsification of water-in-crude oil emulsions were investigated. The work began with some characterization studies to provide understandings of fundamental issues such as formation, formulation and breaking of emulsions by both conventional and environmentally friendly chemicals approaches. ASTM column separation was utilized for SARA-fractionation technique to characterize crude oil into saturates, aromatics, resins and asphaltenes compounds. The aim was to obtain an optimized operating condition as well as fundamental understanding of water-in-crude oil stability upon which further developments on demulsification processes could be developed. The stability studies were carried out by analyzing operating conditions such as emulsion processing time, droplet size, types and concentration of surfactants, water-oil ratio and stirring intensity. In the demulsification part, this study also investigated the performances of four functional groups of chemical demulsifiers which were amine, polyhydric alcohol, alcohol and biodegradable functional groups. For chemical screening, One Factor at A Time (OFAT) method adopted. Three crude oils namely, crude oil A, B, and C were utilized. These crude oils were obtained from Petronas Penapisan Melaka, Malaysia. Among of these oils, crude oil C was found to be the heaviest and best for stability and followed by crude oil B and A respectively. For chemical demulsifiers, results show that octylamine was the best for water separation (99 % at day-one) and followed by palm based oleyl amine (PBOA) (99 % at day-three), hexylamine (98 % at day-five) and coca amine (97.5 % at day-five). For optimization part, the response surface methodology (RSM) was utilized and results showed that the optimum conditions for each crude oil. The results obtained in this study have exposed the capability of chemicals (conventional and environmentally friendly) method in breaking of water-in-crude oil emulsion. Further works are nevertheless required to provide deeper understanding the mechanisms involved to facilitate the development of an optimum system applicable to the industry.

ABSTRAK

Dalam tesis ini, potensi bahan kimia tradisional dan mesra alam untuk menyahemualsi air dalam emulsi minyak mentah telah disiasat. Kerja-kerja penyelidikan dimulakan dengan beberapa kajian pencirian untuk memberikan pemahaman mengenai isu-isu asas seperti pembentukan, formulasi dan pemecahan emulsi melalui pendekatan bahan kimia konvensional dan mesra alam. Teknik pemeringkatan *SARA* telah dijalankan dengan turus pemisahan *ASTM* untuk mencirikan minyak mentah kepada tepu, aromatik, resin dan kompaun asfaltena. Tujuannya adalah untuk mendapatkan keadaan operasi yang optimum di samping menambahkan pemahamam asas mengenai kestabilan air dalam minyak mentah. Kajian kestabilan telah dijalankan dengan menganalisis keadaan operasi seperti masa pemprosesan emulsi, saiz titisan, jenis dan kepekatan surfaktan, nisbah air-minyak dan keamatan kacauan. Dalam bahagian penyahemulsi, kajian ini menyiasat prestasi empat kumpulan berfungsi bahan kimia nyahemulsi iaitu amina, alkohol polihidrik, alkohol dan kumpulan berfungsi biodegradasi. Untuk mengenalpasti bahan kimia, kaedah *One Factor at A Time (OFAT)* telah diguna pakai. Tiga minyak mentah yang dinamakan sebagai A, B, dan C telah digunakan. Minyak mentah ini diperolehi dari Petronas Penapisan Melaka, Malaysia. Di antara ketiga-tiga minyak ini, minyak mentah C didapati paling berat dan terbaik untuk kestabilan dan diikuti oleh minyak mentah B dan A. Bagi penyahemulsi bahan kimia, keputusan menunjukkan bahawa oktil amina adalah yang terbaik untuk pemisahan air (99 % pada hari pertama) dan diikuti oleh oleil amina berasaskan kelapa sawit (PBOA) (99 % pada hari ketiga), heksil amina (98 % pada hari kelima) dan koka amina (97.5 % pada hari kelima). Untuk bahagian pengoptimuman, *Response Surface Methodology (RSM)* telah digunakan dan keputusan menunjukkan keadaan optimum bagi setiap minyak mentah. Keputusan yang diperolehi dalam kajian ini telah mendedahkan keupayaan kaedah bahan kimia (konvensional dan mesra alam) untuk memecahkan air dalam emulsi minyak mentah. Kajian selanjutnya diperlukan untuk memberi pemahaman yang lebih mendalam mengenai mekanisma yang terlibat untuk memudahkan pembangunan sistem optimum yang boleh diaplikasikan kepada industri.

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LIST OF SYMBOLS

°C	Degree Celsius
cP	Centipoise
ρ_w	Density of emulsified water
ρ_o	Density of oil
g	Gravitational constant
g/mole	Gram per mole
Ø	Interaction energy
Ø$_A$	Inter-particular attraction
Ø$_R$	Inter-particular repulsion
µm	micrometer
e	Phase separation
%	Percentage
v_m	Settling velocity of water
μ_o	Viscosity of continuous phase
v/v	Volume per volume
w/w	Weight per weight
Y_p	Yield predicted
Y_a	Yield actual

LIST OF ABBREVIATIONS

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
C	Carbon
D	Diameter of droplets
DCM	Dichloromethane
DOE	Design of experiment
H	Hydrogen
HLB	Hydrophilic-lipophilic balance
HPLC	High performance liquid chromatography
hr	Hour
LSWR	Low sulphur wax residue
Min	Minute
mL	Milliliter
MSDS	Material Safety Data Sheet
OFAT	One factor at a time
PAH	Polycyclic Aromatic Hydrocarbon
PEG	Poly ethylene Glycol
PBOA	Palm Oleyl Amine
R	Correlation coefficient, Radius
rpm	Rotation per minutes
RSM	Response surface methodology
SARA	Saturates, aromatics, resins and asphaltenes
SDDS	Sodium dodecyl sulfate

Span 80	Sodium monooleate
Span 83	Sorbitan sesquioleate
TLC	Thin layer chromatography
Triton X-100	Octyl phenol ethoxylate
Tween 80	Polyoxyethylene sorbitan monooleate

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Continuing advances in technology have increased the demand of crude oil. This is due to decrease of crude oil resources, so the oil industry demands more sophisticated methods for exploitation of natural resources. In addition, the use of oil field chemicals is becoming increasingly important.

Petroleum is one of the most versatile natural resources. In the past century and a half, petroleum has developed from a replacement for animal and vegetable oils in lighting and lubrication into one of the foundations of world economy. It provides not only raw materials for the ubiquitous plastics and other products, but also fuel for energy, industry, heating, and transportation (Silset, 2008). Petroleum is also known as fossil fuel because it was formed from the remains of tiny sea plants and animals that died million years ago. When the plants and animals died, they sank to the bottom of the oceans. They were buried by thousand of fee of sediment and sand that turned into rock. In addition to provide energy for transportation, petroleum is the source material for much of the chemical industry.

Crude oil or petroleum is basically unrefined oil that found in deep beneath the earth’s surface. It might come in range of colour from clear to black and can be found as liquid or solid form. Generally, the crude oil properties are depends on their chemical composition and structure. The crude oil is stored for future refinement after pumped from the underground of the reservoir. There have a number of steps during refinement process which involve the filtering, addition of additives and specialized separation techniques to create specific crude oils and crude oil products.

Petroleum and petroleum products are so important to the society that they warrant a little more attention than the occasional trip to the gasoline pump. It provides not only raw materials for the ubiquitous plastics and other products, but also fuel for energy, industry, heating, and transportation. Unfortunately, crude oil is not very useful in its raw form and must be processed extensively before it is marketable.

1.2 PROBLEM STATEMENT

Petroleum is seldom produced alone because it generally commingled with water. Water is normally present in crude oil reservoir or is injected as steam to stimulate oil production (Abdurahman et al., 2007b). As been stated by Abdurahman and Yunus (2006a), a significant portion of the world crude oil is produced as emulsion. Emulsion is almost occurred in all phases of oil production and processing included inside reservoirs, wellbores, wellheads, during transportation, storage and export also included petroleum processing (Mat et al., 2006). As well as during the lifting, transporting and processing of oil, emulsions and sludge's are created water (Abdurahman and Yunus, 2006a).

Abdurahman and Yunus (2006d) have mentioned that, crude oil is always produced with water and caused problems during oil production because of the formation of emulsions. From Wang (2010), it has two basic types of emulsion form in oilfield which is water-in-oil (W/O) and oil-in-water (O/W). It is about 95 % was in W/O form. Emulsions are undesirable because the volume of dispersed water occupies space in the processing equipment and pipelines, increased operating and capital costs. It is well known that the formation of water-in-crude oil emulsion is in the center of several economic and environmental problems.

Auflem (2002) has declared that oil industry has an interest in crude oil emulsion for two main reasons. First, water-in-crude oil emulsion can form in the processing of fluids from hydrocarbon reservoirs to the refinery or in production facilities during extraction and cleaning. The emulsified water adds significant volume to the crude oil causes corrosion in the pipelines and increases the cost of transportation and refining. Secondly, water-in-crude oil emulsions can form in oceanic spills. These emulsions are very stable and the oil phase is difficult to recover, leading to great environmental damage.

Emulsion problems in crude oil production and processing have gained serious consideration either from fundamental and practical aspects by oil companies as well as researchers for the last few decades (Mat et al., 2006). As been reported by Issaka (2007), the formation of emulsion during oil production is a costly problem, both in term of chemical used and production loss. Also these created emulsions can cause problems both upstream and downstream of petroleum industries. Almost eighty percent of the oilfield emulsion produced is the type of water-in-oil emulsion (Abdurahman and Yunus, 2006a).

Generally, these emulsions have to be broken to reach specified values of product quality, both for oil and produced water. Therefore, in terms of economic and operational purposes, they must to dewater and separate the water completely before transporting or refining them (Abdurahman and Yunus, 2006a; Abdurahman et al., 2007a). From Fan et al. (2009), demulsification is the process to break the emulsions to separate the water from oil which is also one of the essential industrial processes.

To date, there exist several techniques for enhancing the separation of water-in-oil emulsions, such as the addition of chemical demulsifier, pH adjustment, gravity or centrifugal settling, filtration, heat treatment and electrostatic demulsification (Alinezhad et al., 2010). Abdurahman and Yunus (2006a) have stressed out the chemical demulsification is the most widely applied method of treating water-in-oil emulsion. This method involves the use of chemical additives to speed up the breaking process. The usage of chemicals as demulsifier for treating crude oil are specially tailored to act at the oil/water interface and their high efficiency makes their use a very economic way and attractive to separate oil and water (Mat et al, 2006).

Although various researches were made since many years ago, there still no specific solution found to overcome this emulsion problems. In fact, there still a lot of things should be covered to find better understanding and the research was going on until today. This research potentially contributing to reduce the gap between the problems existed in the petroleum industry with the petroleum production.

This research was involved conventional and environmentally friendly chemical demulsifiers in order to enhance the separation efficiency. Conventional chemical demulsifiers was known as ordinary demulsifier which have been used previously and according to the accepted standards. For this research, amines, alcohol and polyhydric alcohol demulsifiers group was known as conventional or traditional demulsifying agent. While, environmentally friendly chemical demulsifiers was defined as the chemical that not harmful to the environment.

Generally, the uses of chemicals are often associated contribution towards environmental pollution. This problem can be reduced by minimizing the use of chemicals or consumes environmentally friendly chemical. Therefore, this study aims to investigate the problem by minimizing the usage of chemicals and tried to propose environmentally friendly demulsifier. The minimum demulsifier usage with high water removal is the good practice to the environment and also to the petroleum industry. Besides that, the two demulsifiers that introduced in this work namely as palm based oleyl amine and coco amine were previously used in cosmetic emulsion. Both demulsifiers are environmentally friendly and never been used yet in petroleum emulsion.

1.3 OBJECTIVES OF THE RESEARCH

The objective of this study is to investigate the stability of W/O emulsion by using different types of crude oil. The different properties of crude oil influencing the stability behavior of the crude oil. Secondly, this work was done to investigate the performance of conventional and environmentally friendly chemicals in demulsification of W/O emulsions. Thirdly, this research has to compare the results between the chemical and other conventional demulsification method. Lastly, to optimize the chemical demulsification results by using response surface methodology (RSM) in order to calculate the optimum condition of demulsification process. This method was utilized through Design-Expert software.

1.4 SCOPES OF THE RESEARCH WORK

To accomplish the objectives of this study, the scope of this work focuses on:

i. Characterization of emulsions in terms of physical and chemical properties.
ii. The effect of surface active molecules on emulsions. There were four types of emulsifier studied namely Span83, Triton X-100, Tween 80 and SDDS. The studied was included the effect of solubility factor for each emulsifiers.
iii. The effect of the oil compositions on emulsion formation and stability. This scope is involving the SARA separation in order to know the percentage of saturates aromatics, resins and asphaltenes in the crude oil.
iv. The effect of demulsifier's characteristics, in terms of chemical such as functional group, Hydrophile-Lipophile Balance (HLB), molecular weight and demulsifier solubility on demulsifier performance.
v. Other conventional demulsification method whereby, only the heating demulsification method is covered in this research.

1.5 LAYOUT OF THE THESIS

This research is focusing on emulsification, stabilization and chemical destabilization of water-in-crude oil emulsion. Overall, this thesis is separated into five main chapters which respectively consist of introduction, literature review, materials and methodology, results and discussion and lastly is conclusion and recommendations.

In chapter 1, it was briefly described about the surface of research background which related to emulsion in term of petroleum field. Besides, the objectives and scope of study that should be covered in this research is also mentioned.

For chapter 2, a general description on history and theory of emulsion has been details. The basic concept to understand regarding water-in-oil emulsions is elaborated in this chapter. It is included the emulsification, stabilization and destabilization of the emulsion.

Chapter 3 presents the experimental methods included the materials and equipments used in order to achieve all the objectives of this study. Basically, this chapter has divided into chapter introduction, materials, methodology and ending by chapter summary. Details on methodology steps were included in this chapter.

In chapter 4, shows the results and discussions of the experimental works. Details explanation on emulsion stability and demulsification of the emulsion is included in this chapter.

Lastly, in chapter 5, describes the conclusion that can derive from this work and followed by some recommendation for the future study.

CHAPTER 2

LITERATURE REVIEW

2.0 INTRODUCTION

In this chapter, a review about crude oil emulsion has been described in detail based on the previous studies. The characteristics of crude oil emulsion are important to understand in terms of physical and chemical. Hence, it is necessary to clear the fundamental concept that involved in formation of crude oil emulsion. First, this chapter starts with the description on crude oil and its characteristics. Then, there were followed by emulsion which goes details on type of emulsions, the mechanism of emulsification process, the emulsion properties and also stability part of emulsion. Besides, the next section is enlightened about the basic principle of surfactant and demulsification process.

2.1 CRUDE OIL

2.1.1 Chemical Composition of Crude Petroleum

Crude petroleum is a complex mixture of hydrocarbon which occurs in nature. It could be either solid, liquid or gas form depends on the composition and also the pressure and temperature at which it is confined. From the previous study, they found that the liquid phase of crude petroleum exists naturally in underground reservoirs land remains liquid at atmospheric pressure after passing through surface separation facilities. Besides, it may have some compounds that diminish the purities of the crude oil such as carbon dioxide, hydrogen sulfide and other complex compounds of nitrogen, sulfur and oxygen.

According to Chen (2006), it is impossible define the structure and composition of each individual molecule since there have thousands of chemical compound exist in the crude oil. Therefore, they need to divide crude oils into different fraction with respect to their polarity and solubility through SARA separation method. Sjöblom et al. (2003) said that SARA-separation is an analysis which separating the crude oils into four main chemical classes based on differences in solubility and polarity. Therefore, the four groups which consist of saturates, aromatics, resins and asphaltenes will be isolated from the crude oil system. Figure 2.1 display the SARA-separation scheme. The details of saturates, aromatics, resins and asphaltenes component have been described in the next paragraph.

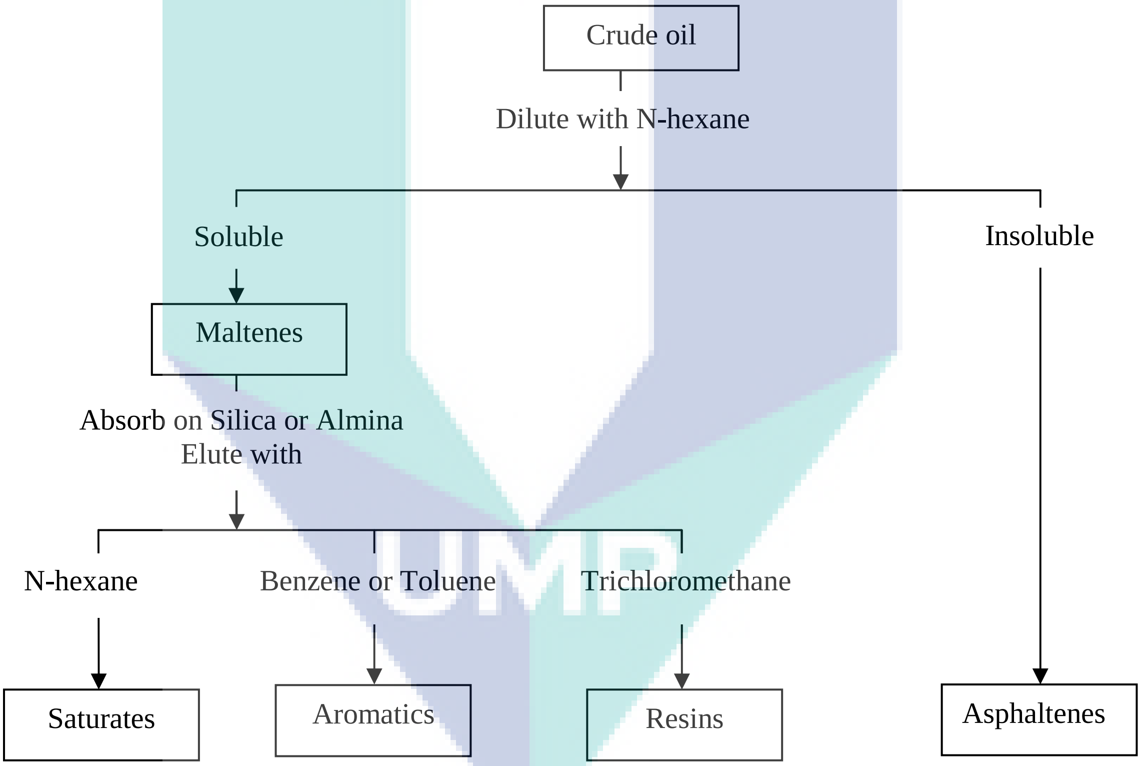

Figure 2.1: Schematic of SARA-separation

Source: Wattana (2004) and Silset (2008)

Basically, asphaltenes are removed through precipitation in parafinic solvent such as n-pentane, n-hexane or n-heptane. While, chromatic fractionation method is used to separate the deasphaltened oil into saturates, aromatic and resins (Mat et al., 2006). 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 behavior regarding emulsion stability, asphaltene deposition etc. Equally important is information of the structure of the crude oil, which is resulted 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. Brief explanations on SARA components are mentioned as follows:

Saturates

As been described by Aske (2002), saturates (aliphatics) are non-polar hydrocarbons, straight-chain and branched alkanes, without double bonds, as well as cycloalkanes (naphtenes). For cycloalkanes, it has one or more rings, which may have several alkyl side chains. The amount of saturates in a crude oil usually inversely proportional towards molecular weight, where it reduces with increasing molecular weight fractions, thus saturates generally are the lightest fraction of the crude oil.

Wax is a sub-class of saturates, consisting primarily of straight-chain alkanes. The wax presents in petroleum crudes primarily consists of paraffin hydrocarbons (C_{18} - C_{36}) known as paraffin wax and naphthenic hydrocarbons (C_{30} - C_{60}). Hydrocarbon components of wax can exist in various states of matter (gas, liquid or solid) depending on their temperature and pressure (Silset, 2008).

Wax precipitates as a particulate solid at low temperatures, and is known to effect emulsion stability properties of crude oil systems (Aske, 2002). Mat et al. (2006) have mentioned in their study that most of the wax that existed in the crude oil is monoxidized alkanes form as a result of the anaerobic condition under which biodegradation of organic matter to form crude oils. Saturates are sometimes called as “white oils” due to their pearly colour. Besides, Wang (2010) has mentioned that the viscosity of waxy crude oils is speculated to be sensitive to temperature change, and larger decrease of emulsion stability for waxy crude oils may be observed when temperature increase.

Aromatics

Aromatic is composed of structures containing aromatic ring. The aromatics component refers to benzene and its structural derivates include toluene and xylenes and polycyclic aromatic hydrocarbon (PAHs) such as naphthalene, anthracene and phenathrene. These components are common to all petroleum, and most of the aromatics contain alkyl chains and cycloalkane rings, along with additional aromatic rings. They 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 (Aske, 2002 and Silset 2008). PAHs are particular environmental concern consequent from their properties as potential carcinogen or may be transformed into carcinogens by microbial metabolism (Saravanabhavan, 2007).

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Resins

This fraction is comprised of polar molecules often containing heteroatoms for example nitrogen, oxygen or sulphur. The resin portions were 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. Resins are commonly extracted from crude oil by adsorption onto a polar such as hydrophilic silica particles (Zulkania, 2004).

The resins are semiliquid and sometimes solid materials of dark red color at room temperature (Oyekunle, 2006). Since the resins are a solubility class, overlap both to the aromatic and the asphaltene fraction is expected. Despite the fact that the resin fraction is very important with regard to crude oil properties, little work has been reported on the characteristics of the resins, compared to the asphaltenes. However, some general characteristics may be identified. Resins have a higher H/C ratio than asphaltenes, 1.2 - 1.7 compared to 0.9 - 1.2 for the asphaltenes. Resins are structural similar to asphaltenes, but smaller in molecular weight (< 1000 g/mole).

Asphaltenes

The asphaltenes fraction, like the resins, is a solubility class, namely the fraction of the crude oil insoluble in light alkanes like pentane, hexane or heptane. Asphaltene is soluble in aromatic solvents like toluene and benzene. Asphaltenes are dark brown to black amorphous powders, have a specific gravity just above unity, and molar masses of 1000 to 10,000 g/mole (Gafonova, 2004). The asphaltene fraction contains the largest percentage of heteroatoms such as oxygen, sulphur and nitrogen. Besides, it also contains organometallic constituent likes nickel, vanadium and ferum in the crude oil. The structure of the asphaltenes has been the subject of several investigations, but is now believed to consist of polycyclic aromatic clusters, substituted with varying alkyl side chains. The chemical characteristics of asphaltenes cause them to be amphiphilic and therefore exhibit surface activity (Sztukowski, 2005).

2.1.2 Properties of Crude Oil

Zulkania (2004) has mentioned in her study that it is important to class the crude oil so that the petroleum geologies can compare the crude oils from different depths, horizons, ages, and assist them in answer the problems of generation and migration. Crude petroleum could be characterized base on physical and chemical properties.

Penassa (2008) has expressed chemical properties of crude oil by referring the relative quantity of sulfur in the crude oil. Crude oil with sulfur level < 0.5 % was referred as sweet crude oil. Petroleum is known as sour if it contains > 0.5 % sulfur. Usually, sour crude oil is considered to be of lower quality. The crude oil samples used in this work were consisted with both sweet and sour crude oil. The sweet crude oil was referred to Tapis oil and sour crude oil was referred to the heavy crude oil.

There have several physical properties that effect the behavior of the crude oil for instance color, specific gravity, density, pour point, viscosity, volatility and ext. The physical properties are described as follows:

Specific Gravity and Density

Frequently, the term of specific gravity or relative density are broadly used in the oil industry (Zulkania, 2004). According to the American Petroleum Institute (°API), gravity is actually a measure of oil's density, and is related to specific gravity. Mehta (2005) has defined density as mass per unit volume of oil and expressed as specific gravity. Normally, specific gravity for oil is less than 1.00 g/ml with exception of some heavy crude oils.

The API gravity have been developed which expresses the ratio of weight of equal volume of oil and pure water at a temperature 16 °C and one atmosphere pressure. Usually, the dense oil is more viscous, less volatile and has high specific gravity and lower API gravity. Light oils have API gravity greater than 20, whereas extra heavy oils and bitumen have API gravity less than 10 (Hannisdal, 2005). From Crude oil can be grouped according to their API gravity as listed in Table 2.1 below:

Table 2.1: Class of crude oil

Type of crude oil	API gravity, °API
Light	> 31.1
Medium	22.3-33.2
Heavy	10-22.3
Extra heavy/ bitumen	<10

Source: Penassa (2008)

Viscosity

Issaka (2007) has defined viscosity as a measurement of flow of properties of oil/material. Commonly, viscosity and specific gravity of petroleum relate directly to each other and vary with the composition of the oil. The oil with high average molecule weight will also have high specific gravity and viscosity.

Previous works have revealed that viscosity is depended on temperature changes. The viscosity of petroleum is inversely proportional towards temperature.

When the temperature is high, the viscosity of crude oil is low and vice versa. The viscosity values of petroleum can range from few centipoises (cP) to as large as 1 200, 000 cP (Zulkania, 2004).

Pour Point

Pour point can be defined as a temperature limit for the oil stops flowing and turns into semi-solid or plastic. The pour point temperature is directly proportional to the wax or asphaltenes content in the crude oil. In addition, the lighter oils with low viscosity and density have lower pour point (Issaka, 2007). Besides, pour point has direct correlation towards the indication of oil property of at low temperatures. Besides, it was indirectly correlated in estimation of either presence or absence of paraffin wax. However, if there were no paraffin wax in the oil, the viscosity of the crude oil will be considered instead of paraffin wax (Zulkania, 2004).

Volatility

According to Cormack (1999), this property has been explained as the lost of the crude oil components to the atmosphere due to evaporation. Normally, it is represented as the percentage of total oil evaporated at different temperature ranges. Besides, the rate and extent of loss of volatile depends on surface to volume ratio and thus, the loss of volatile increase for thin layers of oil as compared to the situation with oil in bulk.

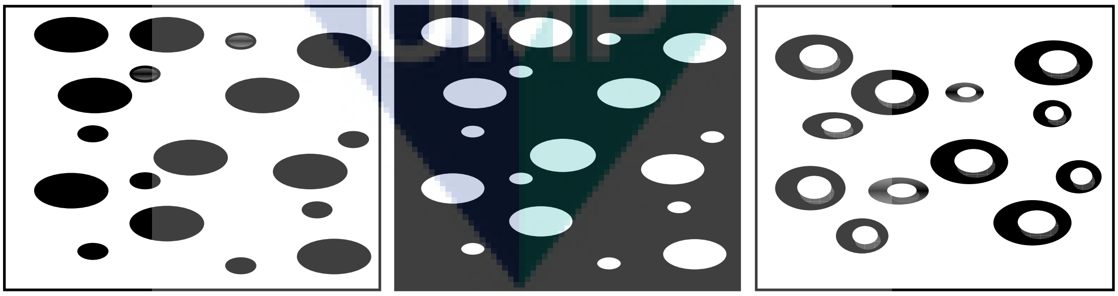
2.2 CRUDE OIL EMULSIONS

2.2.1 Basic Definition of Emulsions

Referring to Salomon (2006), emulsion can be defined as dispersion of small droplets of one liquid in another liquid. Other than that, Peña (2003) has stated that emulsion is a relatively stable dispersion of a liquid within another liquid with which it exhibits limited miscibility. Emulsions can be formed by any two immiscible liquids. However, most of the emulsions were consisted with water phase. An oil-in-water emulsion is that in which the continuous phase is water and disperse (droplet) phase is an "oily" liquid. A water-in-oil "inverted" emulsion is those in which the continuous phase is oil and the disperse phase is water. Schramm and Stasiuk (2005) had been writing that the dispersed phased is sometimes referred to as the internal dispersed phased and the continuous phase as the external phase.

As been pointed out by Mehta (2005), water in oil emulsions may be extremely stable because the water droplets (1-10 μm diameter range) are held in a rigid structure by the components like asphaltenes, waxes, and resins. On the other hand, oil in water emulsion is less stable because the inner droplet distance is comparatively very large and the oil droplets are relatively free to migrate.

Schramm (2005) had mentioned that, there was not only O/W and W/O emulsions exists in real life. This is because, in practical situations are not always so simple and one may encounter double emulsions such as oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W). For example, O/W/O denotes a double emulsion, containing oil droplets dispersed in aqueous droplets that are in turn dispersed in a continuous oil phase. Salomon (2006) also revealed that, emulsion can have more complex structures. In multiple emulsions, the disperse phase contains another phase which may not have the same composition as the continuous phase. Figure 2.2 below shows the types of emulsions.



O/W emulsion W/O emulsion multiple W/O/W

Figure 2.2: The types of emulsion

Source: Salomon (2006)

Emulsions are classified according to the sign of the charge on the droplets and according to their reactivity. Commonly, emulsions have a polar and a non-polar liquid phase. The former usually water or solution of electrolytes, polymer or other chemicals in water (Peña, 2003). Cationic emulsions have droplets which carry a positive charge. Anionic emulsions have negatively charged droplets (Salomon, 2006).

Generally, W/O emulsions contains ≤ 50 % of water, whereas for oil in water emulsions contain ≥ 80 %. In certain condition, the oil O/W emulsions may exist with ≥ 20 % water. These have been determined by factors listed below:

i) Relative specific gravities of oil and water: The difference in specific gravity would play important role on the stability of emulsions

ii) Dielectric constants of the internal phase: Similar charges on the dispersed bulk phase aid in emulsion stability because of repulsion of the bulk

iii) The pH of water: many emulsifiers are designed for various pH ranges. If pH falls outside these ranges, changes in surface tension and viscosity of the emulsifier may occur.

iv) Type of emulsifying agent: Many emulsifiers which affect the stability of emulsions are to various factors such as temperature and salinity.

2.2.2 The Formation of Crude Oil Emulsions

Naturally, crude oil is found in reservoirs along with water or brine and during oil removal, water is often coproduced. According to Mat et al. (2006), there have three main criteria that are essential for formation of crude oil emulsion. The formation of emulsion will happened when two immiscible liquids must be brought in contact. Besides, the emulsifying agent should be present and follow by providing sufficient mixing or agitating effect in order to disperse one liquid into another as droplets.

In Spiecker (2001) study also revealed that the emulsions are generally formed when two immiscible liquid are mixed due to the presence of a stirrer, a pump or flow in a pipeline. Mixing immiscible liquids such as oil and water with a surface active agent will often yield an emulsion of oil droplets in water (O/W) or water droplets in oil

(W/O) according to Bancroft’s rule. Bancroft’s rule states that the liquid in which the surfactant is soluble becomes the continuous phase. Other factors such as oil-water volume fractions, surfactant concentration and hydrophile-lypophile balance will influence the type of emulsion formed. After droplets are completely dispersed within the continuous phase, surfactants migrate to the oil-water interface and can inhibit droplet rupture by steric, Marangoni-Gibbs, or rigid-film forming interactions.

Alwadani (2009) had state in his study that the process through which an emulsion is formed is called emulsification. Emulsification could be induced by the action of devices such as a turbine blender, an ultrasonicator, or by the flow of the two phases through a membrane, static mixer or porous media. Emulsification could also take place spontaneously when the phases are contacted. Here, selective mass transfer of some of the components present in one phase into the other provides the energy needed to create the dispersion. Spontaneous emulsification could also occur, for example, by chemical reactions or by the nucleation of one phase in another due to a reduction in temperature. The steps occurred during emulsification process was allocated in Figure 2.3 below.

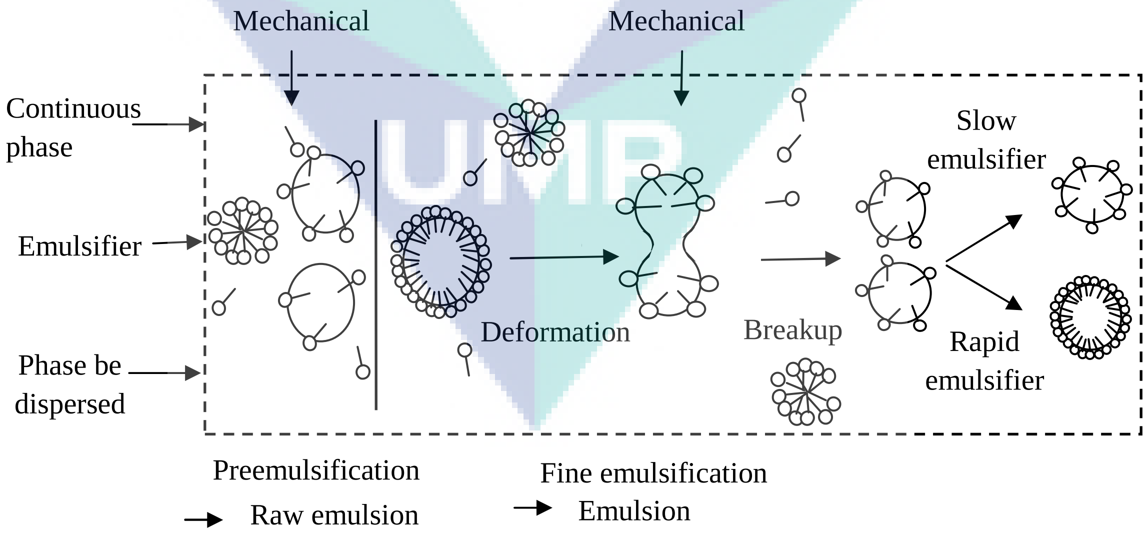


Figure 2.3: A general step occurs during emulsification process.

Source: Mat et al. (2004)

2.2.3 Test for Emulsion Type

The test is important and very helpful for the researcher to determine and find the solution for the problems occurred by the emulsion. Previous researchers have introduced many ways to identify the type of emulsion formed. As been expressed by Issaka (2007), there have three methods that are commonly used to determine the emulsion whether is W/O or O/W type. The tests were consisted with dilution, staining the continuous phase and electrical conductivity methods. The details of these methods have been explained as follows:

Dilution Method

This method is carried out by add a drop of emulsion into a test tube containing water. The emulsion will spread into the water if it is oil-in-water type and will disperse in water with gentle shaking. Otherwise, there is no dispersion occurred and the droplet retains with separate identity if the emulsion is water-in-oil type. However, this method work for dilute emulsion and may be experienced difficulty for very concentrated emulsions. This method has been practiced in this work since it was easy and the emulsion prepared was not too concentrated.

Staining the Continuous Phase

Generally, this test work based on solubility properties of dye towards emulsion tested. A droplet of emulsion is placed on a microscope slide adjacent to a few crystals of water soluble colored dye. Then, the slide is titled slightly in order to allow the drop runs over the dye. The emulsion is referred as O/W if the continuous phase is observed has taken up the color. Nevertheless, the test is repeated with an oil soluble dye if the continuous phase does not stain consequently to confirm the emulsion is W/O type. Staining the continuous method can also be made on a bulk of emulsion in a test tube. A few crystals of water soluble dye are added and gently shaking the test tube. If the color is spread throughout the test tube, the emulsion is referred as O/W.

Electrical Conductivity

This test has been proposed to recognize O/W and W/O emulsion since many years ago. The electrical conductivity is measured with a conductivity bridge using platinum electrodes fused into glass tube. O/W would be expected to show higher conductivity compare to w/o emulsion. This technique performed by placed two electrodes in the emulsion where a neon lamp is attached to the circuit. If the neon lamp is lighting up, means the emulsion is O/W type. Meanwhile, the W/O emulsion will shows vice versa. Oil continuous phases have a low conductivity since it was stabilized with non-ionic emulsifiers. Whereas, the conductivity for water continuous phase will progressively increasing with increasing of continuous phase concentration.

2.2.4 The Stabilization Factors of Crude Oil Emulsions

As been reported by Redford (1993), the first factors that influence the stability is the presence of solid particles in the emulsion. They were, tends to accumulate and adsorb onto the surface of the droplets. The layer formed physically diminishes the droplet's ability to approach other droplet by reason of the droplet must force its way through that layer so that the droplets can contact each other.

Long-chain polymers give good influenced on the effectiveness of the physical barrier to the droplets contacts. These polymers have providing a large physical barrier to the droplet approach and contact among them. As presented in Figure 2.4 below, the polymer is only adsorbed onto the droplets surface at a few points on the chain, leaving the remainder of the chain extended into the continuous phase. Redford (1993) also mentioned that the long-chain polymers exert significant osmotic pressure effects which further hamper droplets approach and contact. This osmotic repulsion occurs when two polymer layers enhancing the energy barrier between the droplets.

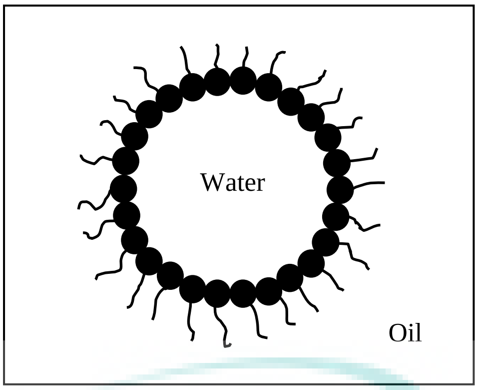


Figure 2.4: A water droplet stabilized by surfactant in the continuous oil phase

Source: Gao (2010)

Gonzalez (2009) has stated the summary of factors that involved in emulsion stability as follows:

i) Low interfacial tension makes it easier to form and maintain large interfacial areas
ii) Electric double layer repulsion reduces the rates of aggregation and coalescence
iii) Surface viscosity retards coalescence
iv) Steric repulsion reduces the rates of aggregation and coalescence
v) Small volume of dispersed phase reduces the rate of aggregation
vi) Bulk viscosity reduces the rate of creaming and aggregation
vii) Small density difference between phases reduces the rate of creaming and aggregation
viii) Dispersion force attraction increases the rates of aggregation and coalescence

2.2.5 Crude Oil Emulsions Stability

From a purely thermodynamic point of view, an emulsion is an unstable system because there is a natural tendency for a liquid/liquid system to separate and decrease its interfacial area and, hence, its interfacial energy. However, most emulsions display kinetic stability (i.e., they are stable over a period of time). Produces oilfield emulsions are classified on the basis of their degree of kinetic stability. Loose emulsions separate in a few minutes, and the separated water is free water. Medium emulsions break up in tens of minutes. Tight emulsions separate (sometimes only partially) in hours or even days (Kokal, 2006).

From Mat et al. (2006), stability is broadly referred to the persistence of an emulsion in the environment, and has been identified as a significant characteristic of water in oil emulsions. An emulsifying agent must be present to form stable water in crude oil emulsions. Such agents include clay particles, added chemicals or the crude oil components like asphaltenes, waxes, resins and naphthenic acid (Mehta, 2005). These emulsifiers assist the formation of rigid layer around the dispersed droplets that will prevent coalescence from happen.

Spiecker (2001) has elaborated the formation of rigid film in emulsion system. The most probable mechanism of petroleum emulsion stabilization comes from an adsorbed layer of materials with high rigidity and elasticity. When the asphaltenes aggregates in the oleic phase, it will adsorb to the oil-water interface and form a consolidate film that resists droplets coalescence. Stable emulsions influenced by high viscosity of continuous phase, small dispersed phase volume and droplet size and low interfacial tension.

As mentioned in Mat et al. (2006) studies, emulsions can be classified into three main group namely stable, unstable and mesostable emulsion. These groups were categorized according to stability and operational definitions as below:

Stable

Stable emulsion will persist doe days, weeks and longer. They showed the viscoelastic properties are at least three orders of magnitude greater than that of the starting oil. Furthermore, stable emulsion will increase with viscosity overtime. It has been postulated that the stability is derived from the strong viscoelastic that were caused by asphaltenes and perhaps along with resins. Increasing alignment of asphaltenes at the oil-water interface may cause the increasing of viscosity.

Unstable

Unstable emulsions normally persist for only a few hours after mixing stops. These emulsions are ready to break into oil and water due to insufficient water particle interactions. Though, the oil may retain small amount of water, especially if the oil is viscous.

Mesostable

Mesostable emulsions are probably the most common emulsion that was formed in the fields. These emulsions can be red or black in appearance. This emulsion has the properties between stable and unstable emulsions. It is suspected that these emulsions contained either insufficient asphaltenes to render them completely stable or contained too many destabilizing materials such as smaller aromatics. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Mesostable emulsions may also degrade to form layers of oil and stable emulsions.

2.2.6 Interaction Energies between Emulsion Droplets

Sullivan (2000) and André (2009) and Tadros (2009) have highlighted several mechanisms that can be clearly determined for emulsion stabilization. These mechanisms are outlined as electrostatic forces, the Marangoni- Gibbs effect, DLVO theory, electrical double layer repulsion, steric repulsion and rigid-film-forming interaction. The details of these mechanisms have been explained as follow.

Electrostatic forces

Sullivan (2000) has stated that, the approach of emulsion droplets to another may be resisted by electrostatic forces. This force consists of coulombic repulsion between two like charged objects and attractive van der Waals forces. The electrostatic repulsive force occurred when the electrical double layers of two particles overlap (Gonzalez, 2009). For water-in-crude oil emulsions, electrostatic forces are weak enough to neglect it because the continuous oil phase has a low dielectric constant and thus a low ion concentration (Yarranton et al., 2007).

Marangoni-Gibbs Effect

The Marangoni-Gibbs effect can stabilize emulsions by preventing the drainage of continuous phase from between two opposing droplets. As droplets approach, their surface eventually become parallel and the film layer attempt to drain. This outward convection draws surfactants towards the droplets edges leaving a region of low surfactant concentration in the middle. This process sets up an unfavorable interfacial tension gradient along the interface. The interfacial tension gradient causes flow of the surfactant along the surface of a droplet away from each other. Surfactant diffusion this proceeds in the direction opposing convection to eliminate the interfacial tension gradient. Stable emulsions can result from the balance of surface diffusion and film convection. This mechanism is dependent on the film thickness and drain velocity of the continuous phase between the droplets (Spiecker, 2001 and Gonzalez, 2009). The mechanism of Marangoni-Gibbs effect has been shown in Figure 2.5.

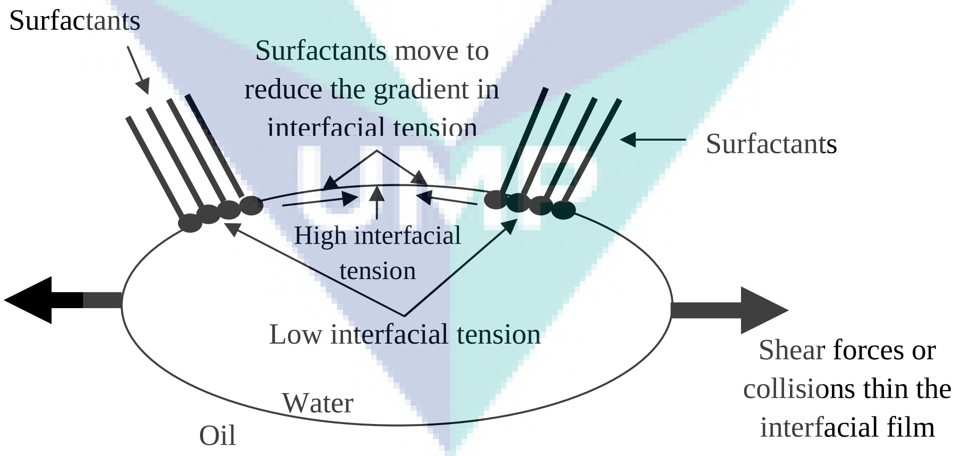


Figure 2.5: Marangoni-Gibbs effect

Source: Silset (2008)

DLVO theory

This theory was introduced by Derjaguin, Landau, Verwey and Overbeek which successfully explains the colloidal stability systems. The attraction between the particles is dominated by the van der Waals forces and also double-layer repulsion by considering the particles interaction energy:

$$\emptyset = \emptyset_R + \emptyset_A \qquad 2.1$$

Where $\emptyset_A$ and $\emptyset_R$ represent inter-particular attraction and repulsion, respectively. The attraction forces will always be present and are accounted for by the long-range van der Waals forces, which have their origin in dipole induces dipole interaction.

Electric Double Layer Repulsion

This force is important in oil-in-water emulsion. When the charge surface is present in the aqueous solution, the ionic strength influenced the particle charges in the solution. Counter ions will be distributed strongly enough to overcome thermal agitation. In the diffuse layer the counter ions are more loosely bound and can be affected by electrical forces and random thermal effects as shown in Figure 2.6.

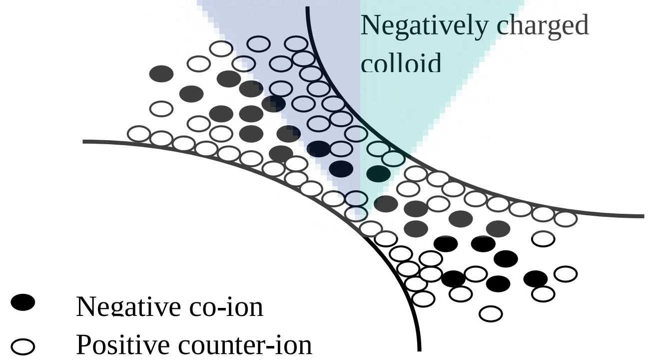


Figure 2.6: Schematic illustration of the electric double layer

Source: Mat et al. (2004)

Steric Repulsion

Steric stabilization or a steric barrier refers to adsorb material around the dispersed droplets in the emulsion and will form a physical barrier around the dispersed droplets (Gonzalez, 2009). The mechanism of steric repulsion has been explained by Sullivan (2000) where it is a result of strong interaction between solvent and material adsorbed at the droplet interface. Due to this strong interaction, there are both enthalpic and enthropic penalties brought about by the approach of the droplets to another. McClements (2004) has elaborated that when two droplets approach each other sufficiently closely, then the emulsifier layers starts to overlap and interact with each other. At close droplets separation steric interaction are strongly repulsive and may therefore prevent the emulsion droplets from aggregating.

Surfactant containing a hydrophilic polar head group and hydrophobic tail group will typically orient themselves at oil-water interfaces. The head group has natural affinity for water while the tail group has natural affinity in the oleic phase. Dispersed water droplets will thus be coated by surfactant materials with hydrophobic tails protruding into the oil phase. When droplets approach each other, their adsorbed surfactant tails prevent droplet contact and coalescence (Ekott and Akpabio, 2010). The image of this interaction has been shows in Figure 2.7.

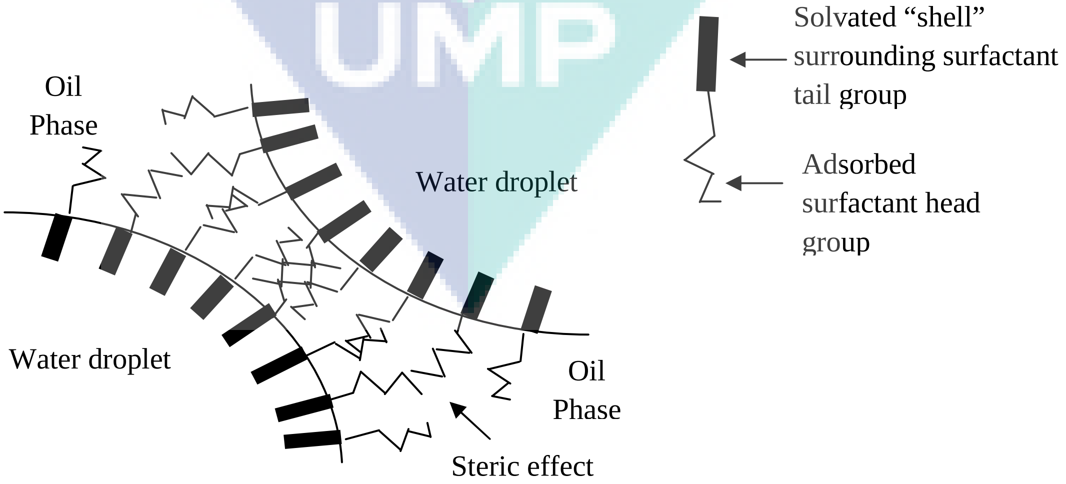


Figure 2.7: Steric repulsion

Source: André (2009)

Rigid-Film-Forming Interaction

The presences of asphaltenes and resins in the emulsion have influenced the stability of the emulsion (Sullivan, 2000). The mechanism of asphaltenes stabilization of water-in-crude oil emulsion is through the formation of viscous, cross-linked three dimensional networks with high mechanical rigidity.

The film is composed of asphaltenes aggregates that interact through donor-acceptor interaction and are solvated by resins. When the resins on one side of the asphaltenes aggregate are removed, it can adsorb to the water/oil interface. Once there, the aggregates can crosslink through hydrogen bond or electron donor-acceptor interactions. Consequently, a rigid network can be formed and stabilized the emulsion strongly (Zulkania, 2004). The crosslinked network is illustrated in Figure 2. 8.

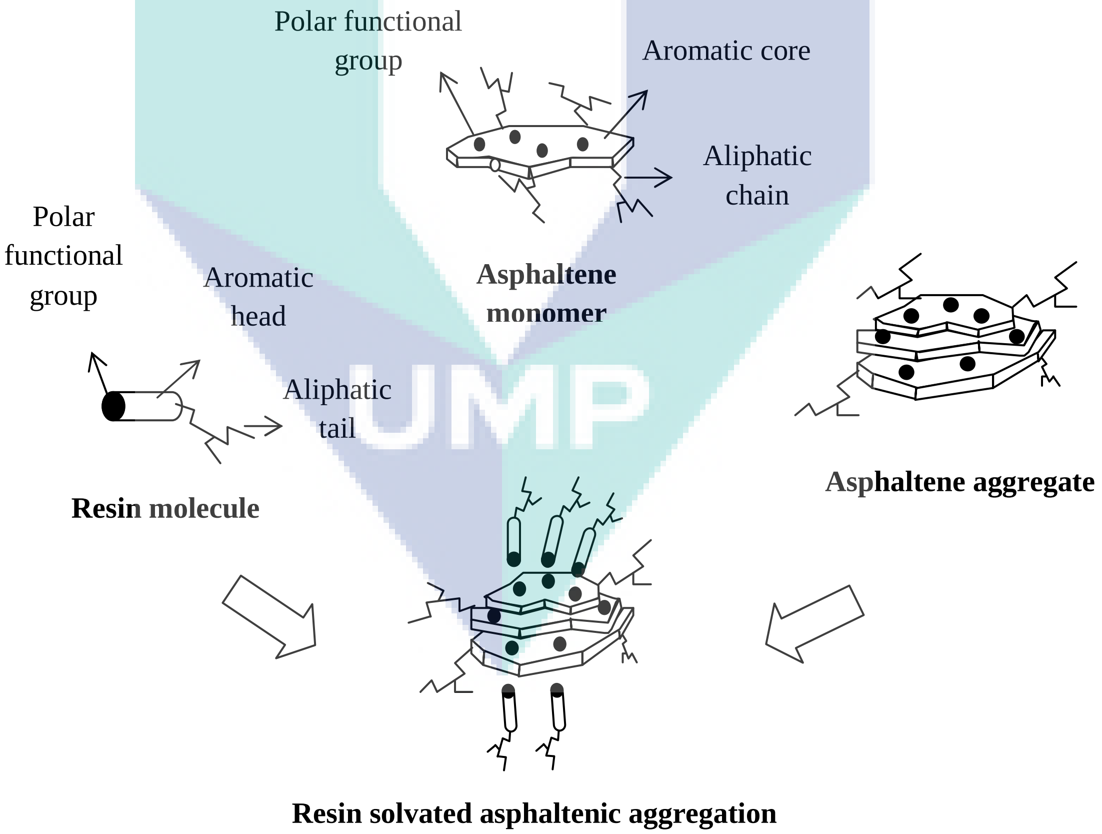


Figure 2.8: Schematic of salvation of asphaltenes by resins

Source: André (2009)

2.2.7 Rheology of emulsions

According to Barnes et al. 1993, the term of rheology was defined as the study of the deformation and flow of matter. Alwadani (2009) has defined rheology as the deformation and flow of materials under influence of an applied shear stress. Rheology properties are obviously important physical attributes.

Becker (2005) has mentioned that there have six factors which may affect the rheological properties of emulsion namely as follow:

i) Viscosity of external phase.
ii) Volume concentration of the dispersed phase.
iii) Viscosity of the internal phase
iv) Nature of the emulsifying agent and the interfacial film formed at the interface
v) Droplet Size distribution in the continuous phase
vi) Shear rate

Alwadani (2009) has stated that, the rheology behavior of an emulsion can be either Newtonian or non-Newtonian depending upon its composition. Generally, emulsion may exhibit Newtonian behavior at low to moderate values of dispersed concentration. For high concentration of dispersed phase, emulsions may behave as shear-thinning fluids. The viscosity increases with the dispersed phase content due to interaction among droplets.

2.3 DEMULSIFICATION OF CRUDE OIL EMULSIONS

As been mentioned by Yanru et al. (2009), demulsification can be defined as a process of breaking emulsions in order to separate the water from oil which is also one of the first steps in processing crude oil. The emulsion has to be separated into their original phase with the intention of achieving the oil specification for production facilities.

Sjöblom (2006) informed that demulsifiers have been used to break down the emulsified water and its development initiated in the early of twentieth century. It is necessary in many practical applications such as in petroleum industry, coating, painting and waste water treatment technology (Mat et al., 2006).

2.3.1 Demulsification Mechanism

The practices of chemical demulsification of emulsion system involve the acceleration of the coalescence as well as the film rupture process. During the demulsification process, the emulsions have to go through several steps before separated into water and oil phase. The mechanism that involved in this process was consisted of creaming/sedimentation, flocculation, Oswald Ripening then coalescence and followed with partial stage which has been detailed in the next subtopic. Figure 2.9 have shown the schematic of destabilizing mechanism.

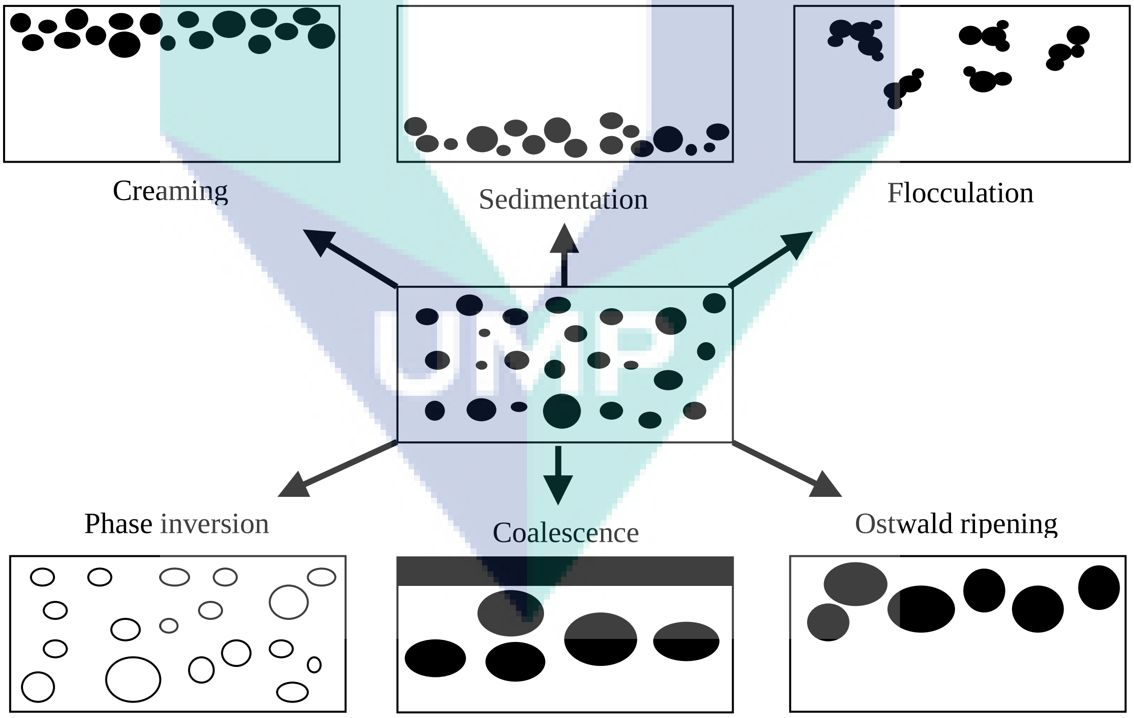


Figure 2.9: Scheme of destabilizing mechanisms of emulsions

Source: Tadros (2009)

Creaming/Sedimentation

Creaming is defined as the rising up of the oil phase, leaving an oil-in-water emulsion at the bottom. Meanwhile, sedimentation is the opposite movement of water droplets to the bottom, leaving water-in-oil emulsion above (Wang, 2010). Tadros (2009) has mentioned in his book that this stage is resulted from external forces, usually gravitational or centrifugal. When such forces go over the thermal motion of the droplets, the concentration gradient in the system will builds up where the larger droplets move speedily either to the top or to the bottom of the container. The movement is depended on their density. If their density is less than that of the medium, they will go up and vice versa. As been mention by Langevin et al. (2004), the emulsion with small drops (R<1µm) are insensitive to sedimentation or creaming due to Brownian motion dominates over gravitational forces. When the size of drops is larger than a few microns, the drops were sediment or cream. According to Stoke's law, if oil is the continuous phase, the creaming or sedimentation rate is given by equation 2.2 (Abdurahman et al., 2006c, 2006e, 2007a).

$$v_s = \frac{gD^2(\rho_w - \rho_o)}{18\mu_o} \tag{2.2}$$

Where, g is representing the gravity constant and D is diameter of the droplets. While, ρ_w and ρ_o stand for density of water and oil, respectively. Whilst, μ_o be a symbol of viscosity of oil phase.

Flocculation/ aggregation

This phase is referred to the aggregation of the droplets into a larger unit without ruptured of the stabilizing layer of the interface (Tadros, 2009 and Hannisdal, 2005). During aggregation, two or more droplets clumps together and contact each other at certain point. Means, the aggregation was occurred when the droplet stayed too close to each other for a long time (Mat et al., 2006). The approach that is most often referred to emulsion literature to explain emulsion interaction is DLVO theory, based on the long range London-van der Waals attractive and repulsive electrostatic forces between two close spheres (Alwadani, 2009). As mentioned in Hannisdal (2005) ‘s study, the flocculation process occurred when the van de Waals attractive energy exceeds the repulsive energy and can be weak or strong, depending on the strength of the inter-drop forces.

Ostwald ripening

As been mentioned by Fernando et al. (2007), Ostwald ripening is the phase consists of a diffusive transfer of the dispersed phase from smaller to larger droplets as been shown in Figure 2.10. Ostwald ripening plays an important role in oil-in-water emulsion stability (Wang, 2010). As been explained by Gonzalez (2009), the surface concentration of the dispersed phase material is higher at the surface of small droplets due to high Laplace pressure. Consequently, materials that contained in small droplets diffuse through the continuous phase to form the larger drops. From the previous study found that in the presence of ionic micelles in the continuous phase have gave small effect on the ripening rate. This phenomenon causes a general increase in the size of the emulsion droplets (Bink, 1998).

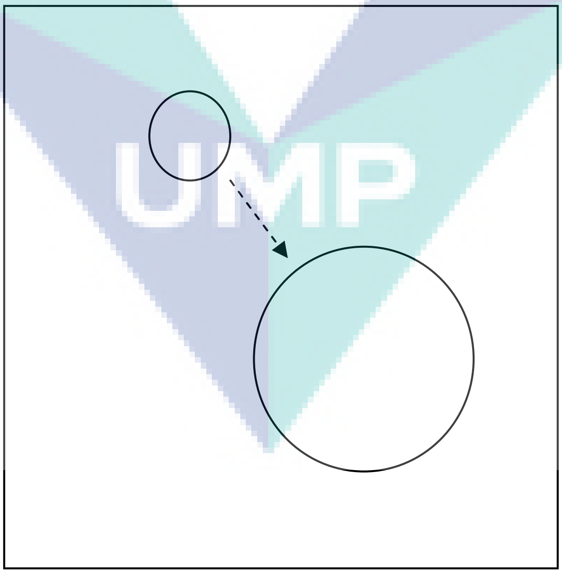


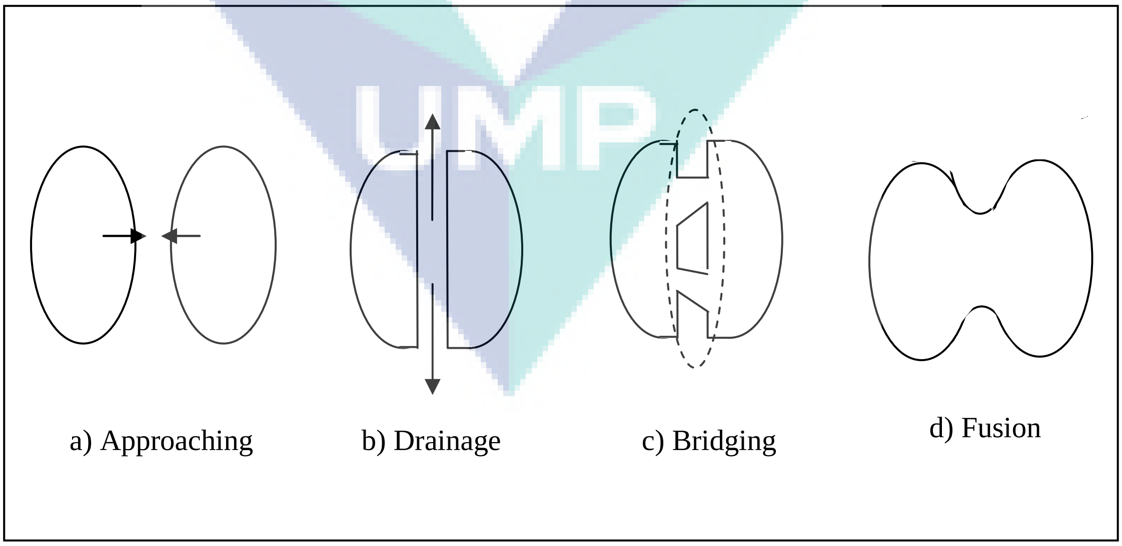
Figure 2.10: Mechanism of Ostwald ripening

Source: Gonzalez (2009)

Coalescence

At this phase, a single larger unit has been formed by fusing together two or more droplets. In coalescence, two or more droplets fuse together to form a single larger unit with a reduced total surface area. The mechanism of coalescence occurs in two stages; film drainage and film rupture. The must be a flow of fluid in the film and present of pressure gradient in order to have film drainage. However, when the interfacial film between the droplets has thinned to some critical thickness, it ruptures, and the capillary pressure difference causes the droplets to fuse rapidly into one droplet. Hence, the properties of the thin film are of uttermost importance for the separation. If the droplets deform, the area of the interface increases and consequently the drainage path in the film also increases, resulting in lower drainage rates (Silset, 2008).

Sams and Zaouk (1999) has reported that during coalescence, the dispersed phase will increase the droplet diameter, spacing between droplets and also the attractive forces among the droplets. Meanwhile, the droplets population, total interfacial area and droplet mobility will be reduced. Figure 2.11 shows the steps involved in coalescence stage.


a) Approaching

b) Drainage

c) Bridging

d) Fusion

Figure 2.11: Steps in coalescence

Source: Gonzalez (2009)

Phase inversion

This phenomenon is referring to conversion between internal phase and external phase of emulsions. For example, an O/W emulsion may with time or change of condition invert to a W/O emulsion. Usually, phase inversion passes through a transition state whereby multiple emulsions are produced (Tadros, 2009).

2.3.2 Demulsification Methods

Emulsion breaking technique is designated to reduce effectiveness of the emulsion stability factor. The previous researchers have approached various methods to separate the emulsion. Currently, the available method for demulsification can be generally classified into three namely chemical, electrical, thermal and mechanical (Al-Jaziri, 1995, Peña, 2003 and Mat et al., 2006). Filtration, pH adjustment and membrane separation is such of techniques use to demulsify the emulsion (Gafanova, 2000).

Jiang (2009) and Auflem (2002) have briefly explained that mechanical method is focused on breaking the physical barrier and/or on the difference in density between the aqueous and oil phases to achieve separation. There are various types of mechanical separation tools that utilized in destabilization of crude oil emulsion such as cyclones, gravity settling tanks, centrifugal separator and so on. Whereas, demulsification via electrical is based on the application of an electric field to deform the droplets and produce a force of attraction between drops, thus leading to coalescence. The electric field promoted disturbs the surface tension of each droplet, possibly, by causing polar molecules to orient themselves.

Thermal method is implemented by supplying heat to the emulsion like hotplate (Abdurahman and Yunus, 2006a). Heating reduces the bulk emulsion viscosity, which facilitates drainage of the continuous phase from between droplets and may also reduce the rigidity of the interface. Nevertheless, this method may lead to loss of light end hydrocarbon (Sztukowski, 2005).

Besides, chemical destabilization refers to use chemicals to promote flocculation and/or modify the properties of the interfacial films to cause coalescence. Chemical destabilization method is the most broadly applied to treat water-in-oil and oil-in-water emulsion where chemical additives used to accelerate the breaking process (Abdurahman et al., 2007c).

2.3.3 Demulsification Factors

This section is more focus on factors that influences the efficiency of chemical destabilization. The purpose of demulsification is to destroy the interfacial film and make most water droplets to coalesce. Basically, chemical demulsifiers are surfactant which consisted of hydrophilic and hydrophobic group. Kokal (2006) has listed several factors that affected of surface-active materials and also chemical demulsifiers efficiency namely as temperature, agitation/ shear, retention time, solid removal and control of emulsifying agent.

Jiang (2009) has expressed the requirement that allowed the demulsification to occur by chemical demulsifiers. First, the demulsifiers should be having strong attraction to the oil/water interface with the ability to destabilize the protective film around the droplet and/ or to change the wet ability of solids. Besides, the ability to flocculate the droplets and also to promote coalescence by opening pathways for water's natural attraction to water will influenced the process. Then, demulsifiers should able to promote the film drainage and thinning by inducing the changes of the interfacial rheology such as decreased interfacial tension and increased compressibility of the interfacial film.

In addition, there have other factors that influenced demulsifiers to promote the aggregation and coalescence of droplets in order to break down the emulsion system. Usually, the destabilization performance is affected by oil type, viscosity of oil, presence and wettability of solids, size distribution of water phase (Mikula and Munoz, 2000).

As been mentioned by Jia (2010), when the demulsifiers added to an emulsion, they migrate to the oil-water interface. Generally, demulsifiers have stronger interfacial activity than natural surfactant in the crude oil. So, they will adsorb at the oil-water interface to partly displace natural emulsifiers adsorbed at the interface, forming a compound film with lower film strength.

Mahmood (2009) has listed four elements should be fulfilled in order to achieve successfulness in chemical demulsification. There were listed as below:

i) An adequate quantity of properly selected chemical must add into the emulsion
ii) Through mixing of chemical in the emulsion must occur
iii) Sufficient heat may be required to facilitate or fully resolve an emulsion
iv) Sufficient residence time must exist in treating vessel to permit settling of demulsified water droplets.

2.4 SURFACTANT

Surfactant is also known as surface active agent. They adsorb at the oil-water interface and prevent drop growth and phase separation into the original oil and water phases. After adsorption, the surfaces become viscoelastic and the surface layers provide stability to the emulsion (Langevin et al., 2004).

2.4.1 Properties of Surfactant

Surfactant Structure

Chemically, the surfactant molecule can be divided into two diverse characteristics. Salomon (2006) has mentioned that surfactant was consisted of polar hydrophilic (water-loving) and nonpolar lipophilic (oil-loving) part. Both parts were important to make the surfactant role as amphipathic molecule.

As been detailed by Myers (2006), the chemical structures of surfactant having solubility properties for surfactant activity vary with the solvent system to be employed and the condition of use. There have two parts of the surfactant which consisted with "head" and "tail". "Head" was referred to the solubilizing group which can be either lypophilic or hydrophilic while tail was referred to the hydrophobic or lipophobic group in water. Figure 2.12 shows the schematic illustration of a surfactant.

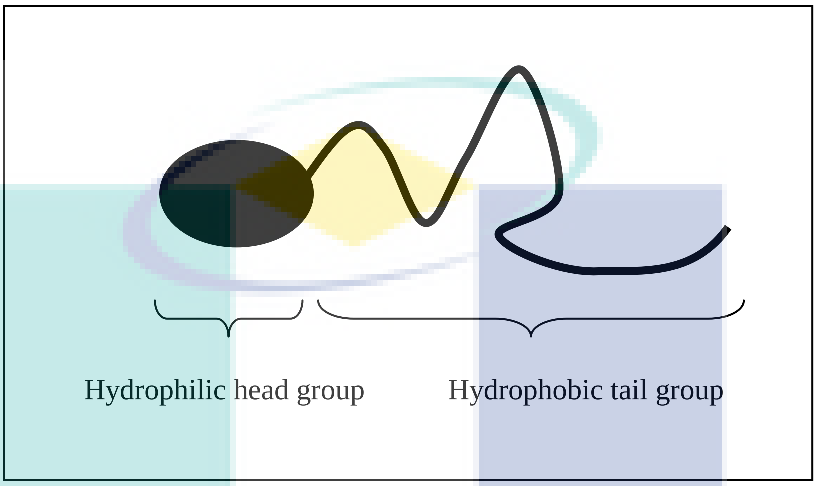


Figure 2.12: Schematic illustration of a surfactant

Source: Issaka (2007)

Hydrophilic-lipophilic balance (HLB)

The HLB system has been used since last five decades (Ahmed, 2001). This concept was developed by Griffin in 1949. Gonzalez (2009) has described this system as an empirical quantity to define the polarity or solubility of surfactant. Hydrophilic-Lipophilic Balance means the balance of the size and strength of the hydrophilic (water-loving polar) and the lipophilic (oil-loving) groups of the emulsifier and demulsifier. The system utilizes certain empirical formulas to calculate the HLB number.

Generally, HLB number calculated within range 0-20 on some arbitrary scale (Myers, 2006) has been shown in Table 2.2 below. This system certainly changes with temperature, the oil types, the types and amount of additives in water an in oil and so on (Shinoda et al., 1926). Low HLB number means low solubility in water whereas high solubility represented high solubility in water (Gonzalez, 2009).

Table 2.2: HLB ranges and their general areas of application

HLB Range	Use
4-6	W/O emulsifiers
7-9	Wetting agent
8-15	O/W emulsifiers
13-15	Detergent
15-18	Solubilizer

Source: Gonzales (2009)

Critical Micelle Concentration

Critical micelle concentration (CMC) is defined as surfactant concentration at which an appreciable number of micelles are formed (Liu, 2006). This phenomenon occurs spontaneously and unique to each surfactant. Scott (2009) has mentioned that the structural features of the surfactant have influenced the CMC formation. Due to surfactant structure, a CMC will increase when the hydrophilic head group is increased or, when the hydrophobic tail is decreased. The CMC for pure surfactant is commonly observed by a sharp break in the interfacial tension versus concentration curve as shown in Figure 2.13. Besides, for mixtures of surfactants, the break in the curve may not be sharp.

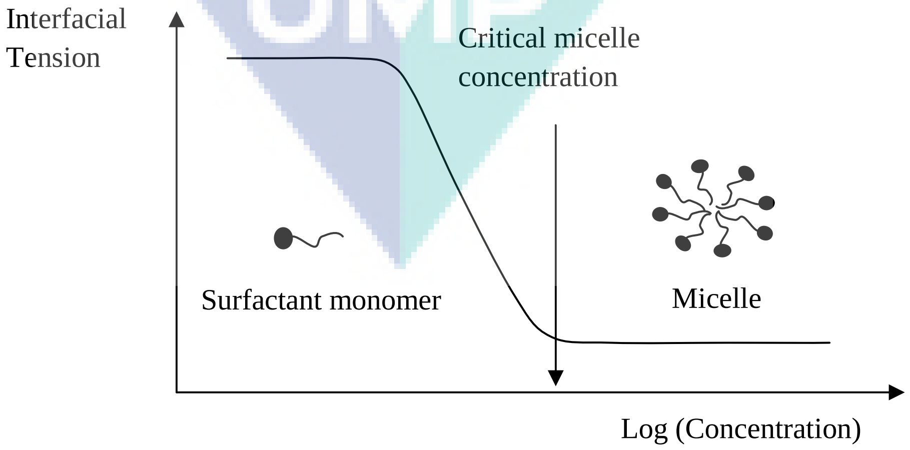


Figure 2.13: Micellization of pure surfactant molecules

Source: (Sztukowski, 2005)

When surfactant is present above the CMC, they can act as emulsifiers that will allow a compound that normally insoluble to dissolve. In fact, dilute concentration of surfactant in aqueous solution act much as normal electrolytes, but in a higher concentration of surfactant will result very different behavior. (Zulkania, 2004).

2.4.2 Basic Classification of Surfactant

Surface active agent can be categorized based on the nature of hydrophile, with subgroup based on the nature of the hydrophobe or tail. The four class of the surfactant have been mentioned in the Table 2.3.

Table 2.3: Type of surfactant

Surfactant Type	**Description**
Ionic	Surfactants that carry a negative charge on the surface active portion of the molecule.
Cationic	Surfactant that carrying a positive charge on the surface-active portion of the molecule.
Nonionic	Surfactants that carry no electrical charge, as their water solubility is derived from the presence of polar functionalities capable of significant hydrogen bonding interaction with water
Amphoteric	Surfactants that can be either cationic or anionic depending on the pH or other solution conditions, including those that are zwitterionic—possessing permanent charges of each type.

Source: Myers (2006)

Myers (2006) has defined emulsifier as a surfactant or materials that added into a blend of two immiscible liquids to assist the formation and stabilization of an emulsion. Meanwhile, Gonzalez (2009) has described demulsifier as a surfactant that responsible for flocculation, coalescence or wetting agent.

2.4.3 Emulsification Modes

As the concentration of the emulsifier increases, the particle size of the emulsion is reduced. Generally more emulsifier is required to provide good stability and the right performance properties to the emulsion than is necessary to fill the interface (Salomon, 2006). The addition of emulsifier during emulsification can be classified into four modes namely agent-in-oil, agent-in-water, nascent soap and alternate addition method that briefly explained as below:

Agent-in-Water Method

This method is introduced to form O/W emulsion by dissolved the emulsifying agent directly in the water followed by addition of oil with considerable agitation. However, W/O emulsion will form if the oil phase concentration continuously added until phase inversion takes place.

Agent-in-Oil Method

This procedure is performed by dissolved the emulsifier into the oil phase. Previous studies have concluded that there have two ways of emulsion formation. First, if the mixture is added straightly into the water phase, thus O/W emulsion forms spontaneously. Secondly, W/O emulsion occurred if water directly added into the mixture. Further addition of water will leads the emulsion to invert. This mode of emulsification have been practiced in this study according to the emulsion type required is W/O.

Nascent Soap Method

Nascent soap method may be used to prepare either O/W or W/O emulsion. This method is applicable by dissolves the emulsifier in the oil and the alkaline part in the water.

Alternate Addition Method

In this method, small portions of water and oil are added alternately to the emulsifying agent. This method is particularly suitable for the preparation of food emulsions.

2.5 Chapter Summary

Crude oil is a mixture that containing a least a range of hydrocarbon. The presence of saturates, aromatics, resins and asphaltenes in crude oil have been reported to influence the stability performance of the emulsion system. In general, there have correlation between chemical and physical characteristics of crude oil. Both were playing important role in stability and demulsification study.

Emulsions are often encountered in the petroleum industry where created by a reduction in the reservoir pressure, friction losses, and the presence of surfactants. They might exist in various types and most of the time they were produced in stable form. Stable emulsion is undesirable in petroleum industry since it raise problems in many stages, thus it is necessary to demulsified.

Previous studies have revealed numerous ways to deform emulsion which classified as mechanical, chemical, electrical and thermal. However, chemical demulsification method is broadly used in petroleum industry and this method is still applies as the operation cost is lower compared to others.

Surfactant has played an importance role in stabilization of emulsion system. Emulsifier is used to enhance the stability of emulsion by reduce the interfacial tension of the droplets. Meanwhile, demulsifier is utilized during demulsification process by penetrate the stabilizing film at the droplets interfaces and modify its compressibility and rheology properties by disrupting the tight conformation of adsorbed asphaltenes.

The parameters that affect the formation and stabilization of the emulsion have been investigated by many researchers since four decades ago. However, most of the studies required further enhancement to correlate of those factors towards the emulsion system.

CHAPTER 3

MATERIALS AND METHODS

3.0 INTRODUCTION

This chapter presents to describe the materials and equipments included the methods that used in this work. In order to fulfill the objectives and scope of this research, the study was carried out in four stages. Firstly, characterization of crude oil samples through SARA (Saturates, Aromatics, Resins and Asphaltenes) fractionation. Besides, the physical properties of crude oil samples also analyzed using appropriate equipments. Then, followed by emulsion stability analysis where emulsifier's performances have been investigated systematically. Next stage is studied the performance of demulsifiers in demulsification of W/O emulsion. Finally, the optimizations of demulsification for crude oil samples have been completed throughout the experimental design. The experimental workflow is illustrated in Figure 3.1. Details of the experimental works are discussed in the next sections. All experiments were carried out in University Malaysia Pahang, Malaysia.

3.1 MATERIALS

3.1.1 Crude Oil Samples

The sample of crude oils that used was contributed by PETRONAS Penapisan Sdn Bhd (Kertih Kemaman and Melaka, Malaysia). To accomplish this study, there were three crude oils were used namely Tapis, 50-50 and 30-70 (v/v) % blended Tapis-heavy crude oil. The purpose of blending the crude oil is to study the effect of different properties of crude oil on emulsion stability.

3.1.2 General Chemical

The chemicals required were obtained from various suppliers. In this research, the chemicals were utilized in each stage of experimental works. Firstly, there were several chemical materials were used for characterization of the crude oil stage. There were comprised of n-hexane, toluene, dichloromethane (DCM) and Silica gel 60 for chromatography, with a 70-230 mesh filter was provided by Merck.

3.1.3 Chemical Demulsifiers

There are wide ranges of demulsifiers that can be used as breaking agent. This research has selected four groups of demulsifier purposely to break down the emulsion into water and oil phase. They were consisted with polyhydric alcohol, alcohol, amine and natural group. Their derivatives were listed in the Table 3.1 below:

Table 3.1: List of demulsifiers used to break the emulsions.

Group	Demulsifier	Supplier
Polyhydric alcohol	Polyethylene glycol 300	Merck
	Polyethylene glycol 400	Merck
	Polyethylene glycol 600	Merck
	Polyethylene Glycol 1000 for Synthesis	Merck
Alcohol	Methanol GR for Analysis ACS, ISO, Reag. PH EUR	Merck
	Ethanol Absolute AR 99.4%	Fisher Scientific
	Butan-1-Ol AR	Fisher Scientific
	1-Hepthanol for Synthesis	Merck
Amine	n-Decylamine 99%	Fisher Scientific
	Octylamine for synthesis	Merck
	N-methyldioctylamine for synthesis	Merck
	Hexylamine 99%	Sigma-Aldrich
	n-Pentylamine for synthesis	Merck
Biodegradable	Coco Amine	Merck
	Palm Based Oleyl Amine	Merck

3.1.4 Emulsifiers

Additionally, there were four types of chemical that used as an emulsifier included sorbitan sesquioleate (Span 83), polyoxyethylene sorbitan monooleate (Tween 80) and Triton X-100 as well as dodeyl sulfate sodium salt biochemistry (SDDS). All emulsifiers were consumed as supplied without further dilution. The emulsifiers used in this study are supplied from Sigma Aldrich, Fisher Scientific and Merck.

3.2 EXPERIMENTAL PROCEDURES

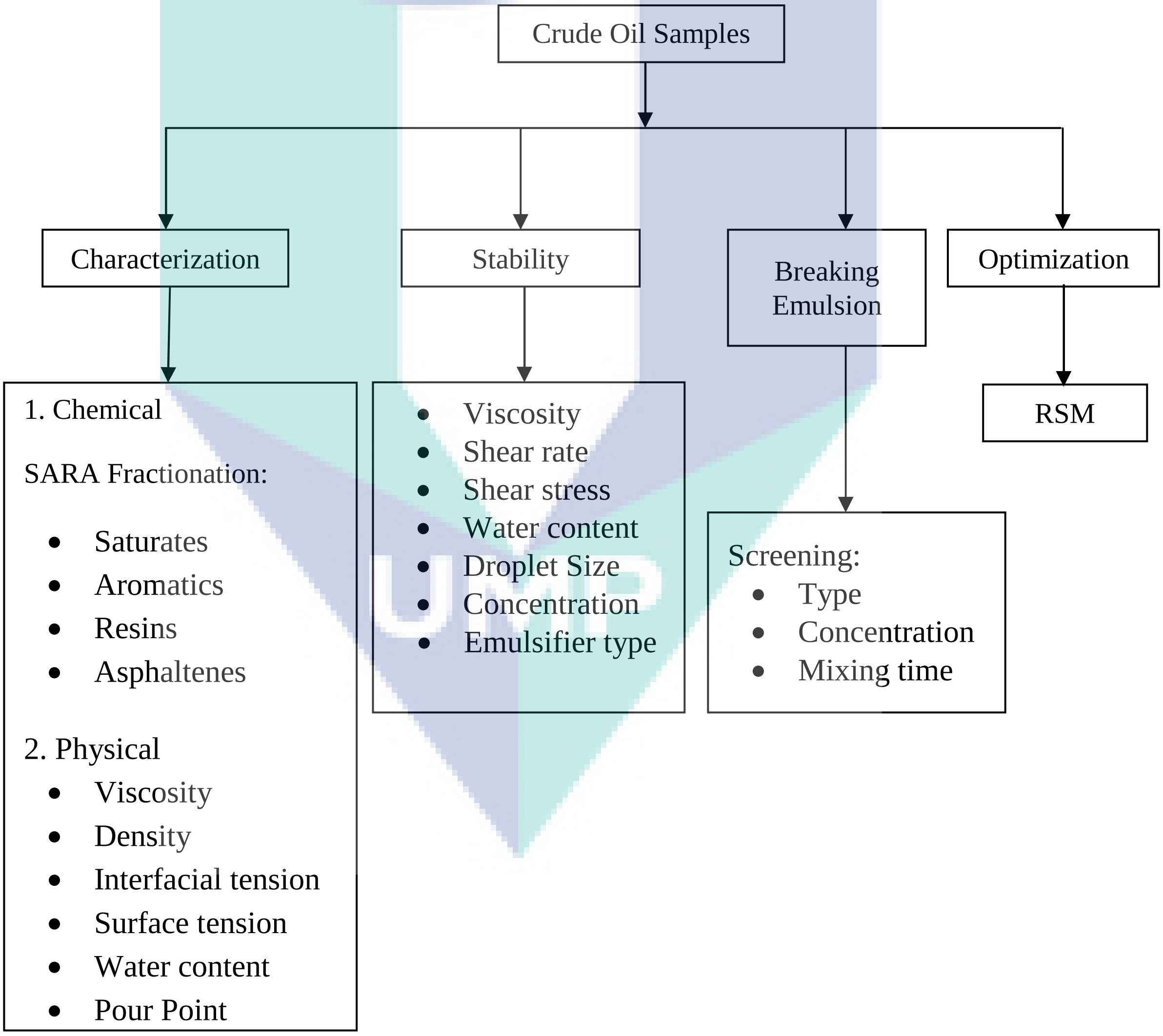


Figure 3.1: Experimental Flow

3.2.1 Emulsions Preparation

As been mentioned earlier, there have various types of emulsion can be gotten. However, only water-in-oil emulsion is needed to finish this research. Therefore, the agent-in-oil method was followed where the emulsifying agent dissolved in the continuous phase (oil) and dispersed phase (water) were added gradually to the mixture (oil + emulsifying agent). During prepared the emulsions, different parameter has been control in order to find the most stable emulsion.

According to Abdurahman (2006a,b), the water in oil emulsions was prepared by dissolved the emulsifier into the external phase in a glass beaker (100 mL). Then, internal phases were slowly added into the mixing phase. In this case, the external phase was referring to oil while the internal phase is water. Emulsions were agitated vigorously using a standard three blade propeller at speed ranges between 500 and 2000 RPM at ambient temperature for 5 to 12 minutes.

The prepared emulsions were used to check for W/O or O/W emulsions. In order to indentify the emulsion type, dilution method was carried out where the emulsions prepared to be dropped into a test tube containing dispersed phase (water). Then the test tubes were shaking vigorously till the oil dispersed in the water. After that, the test tubes were leaved. If the emulsions prepared to be W/O type, the oil layer will appear on the top of the test tube otherwise; the emulsion prepared to be O/W type.

3.2.2 Conventional Heating Demulsification

This work also studied the demulsification through thermal besides the chemical method. A conventional heating demulsification method was done by using a hotplate. The parameters that examine in this technique were heating time and temperature. The calculation of heating rate was done in order examine the thermal breaking performance.

3.2.3 Emulsions Stability Performance

Stability performance studied was done for emulsification and demulsification stages. The determination of stability performance for lab scale is the simple bottle test (Mahmood, 2009). In order to form a stable emulsion, there have sixth parameters have been examined, which consisted with effect of water content, mixing time, mixing speed, type of emulsifier and emulsifiers concentration. The best parameters that can produce the most stable emulsion were accepted for the next experiment. The percentage of phase separated was calculated using equation 3.1 (Abdurahman and Yunus, 2006a).

$$\%\, phase\ separation, e = \frac{Volume\ of\ phase\ seperated, mL}{Initial\ volume\ of\ phase\ separated, mL} \times 100\% \qquad 3.1$$

Selection of mixing speed

The previous researchers have mixed the emulsion component by using various types of mechanical devices at different speed of agitation. Table 3.2 shows some of the mixing speed that has been used by past researchers. The equipment used in this study has limited speed which ranges between 0 to 2000 rpm. Thus, the selection of the mixing speed study for this study was consisted with 500, 1000, 1500 and 2000 rpm.

Table 3.2: Selection of mixing speed range

No.	Author	Mixing speed
1	Issaka (2007)	1800 rpm
2	Follotec et al. (2010)	10 000 rpm
3	Chen and Tao (2005)	500-2500 rpm
4	Fingas and Fieldhouse (2003)	55 rpm
5	Peralta -Martínez et al. (2004)	800-2500 rpm
6	Shigemoto et al. (2007)	4000 rpm
7	Ashrafizadeh and Kamran (2010)	1000-15 000 rpm
8	Jia (2010)	1500 rpm
9	Sajjadi (2006)	500 rpm
10	Souleyman (2010)	500-2000 rpm

Selection of processing time

The period of mixing during preparing emulsion was considered important and there has a lot of processing time have been investigated by previous work as can be seen in Table 3.3. The time consumed was depends on the efficiency of the equipment used to form stable emulsion. The processing time that used to in this study was 5, 7, 9 and 12 minutes as the volume of sample in this studied was as little as 50 mL each.

Table 3.3: Selection of processing time

No.	Author	Processing time
1	Follotec et al. (2010)	7 min
2	Chen and Tao (2005)	3-15 min
3	Fingas and Fieldhouse (2003)	12 hr
4	Abdurahman et al. (2006a)	5 min
5	Ashrafizadeh and Kamran (2010)	5-40 min
6	Jia (2010)	5 min
7	Souleyman (2010)	7 min
8	Zulkania (2004)	30 min
9	Shigemoto et al. 2007	3 min

Selection of volume phase ratio

Volume phase ratio for this study was referred to ratio of volume water phase to volume oil phase as the emulsion is W/O type. The range of the ratio used in this research was referring to previous studies as illustrated in Table 3.4 below. The ratio of 20/80, 30/70, 40/60, 50/50 v/v % have been chosen to complete this study.

Table 3.4: Selection of volume phase ratio

No.	Author	Volume phase ratio, v/v
1	Follotec et al. (2010)	30/70
2	Chen and Tao (2005)	50/50
3	Souleyman (2010)	50/50
4	Abdurahman et al. (2006e)	20/80
5	Dicharry et al. (2006)	30/70
6	Yarranton et al. (2007)	40/60
7	Farah et al. (2005)	60/40
8	Goldszal and Bourrel (2000)	10/90

Selection of emulsifier type

There was a lot of emulsifiers have been introduced to stabilized the petroleum emulsions. Table 3.5 below has mentioned some of the emulsifiers that have been used by earlier researchers. Based on Table 3.5, the research has found that Span 80, SDDS, Triton X-100 and Tween 80 have performed well in stabilization of W/O emulsions. Thus, those emulsifier have been chosen to be tested their performance towards the crude oil emulsion used in this study.

Table 3.5: Selection of emulsifier type

No.	Author	Emulsifier
1	Malkin et al. (2004)	Poly(isobutylene) succinic anhydride
2	Abdurahman (2007b)	Span 83
3	Issaka (2007)	Triton X-100
4	Arriola-Medellin et al. (2008)	Carboximethylcellulose
5	Souleyman (2010)	Span 80
6	Sajjadi (2007)	Igepal
7	Aruna (2009)	Span 20, Tween 80
8	Chen and Tao (2005)	Span 83
9	Diana (2009)	Nonylphenol ethoxylate, Sodium naphthanate
10	Abdurahman et al. (2006c)	SDDS, LSWR

3.2.4 Screening of Single Demulsifiers

The screening process is purposely to test the effectiveness of each demulsifier to break down the W/O emulsion. This experiment was completed throughout a bottle test where an amount of potential demulsifiers was added into the emulsion samples to be broken. After some specific time, the extent of phase separation and appearance of the interface separating the phase are noted (Mahmood, 2009).

Screening One Factor at A Time (OFAT) method was utilized to accomplish the screening works. The selection process was done by manipulated the type and concentration of demulsifiers used. The performance of demulsification for each sample was carried out through gravity separation in the presence of chemical demulsifiers. Demulsifier was mixed together with the emulsion, and they were left at room temperature. The demulsifiers were used as received from the supplier without any dilution. This experiment took seven-day observations. The amount of water separations was read from the scale at the measurement cylinder. The greatest demulsifiers with high-water separation was being selected to continue for optimization.

3.2.5 Optimization by Using Response Surface Methodology

RSM are very helpful in analyzing problems influence a dependent variables and independent variables or response (Mat et al., 2006). The intention of using RSM is to optimize the response according to the type of response surface formed from the two levels full factorial design test. Data that collected from preliminary studied were utilized in RSM method as requirement for optimization calculation through Design-Expert 6.0.8 software. This software has provided numerous designs which depend on the number of design factor. From the list given, Central Composite Design (CCD) has been chosen to fulfill the optimization analysis. This design widely used for estimating second order response surface (Park et al., undated).

For the experimental set-up stage, the experimental factor and factor level were chosen. Table 3.6 illustrated the independent variables of CCD design. The effect of two independent variables (A and B) on one response variable (water separation) has been evaluated using RSM. The specific test samples were determined by the experimental design stage and tested. Data from the experiment perform were analyzed using the statistical software and then interpreted.

Table 3.6: Independent variables of CCD design

Name	Units	Low Level	High Level
A : Concentration Octylamine	w/w %	0.5	2
B : Processing time	minute	1	3

3.3 ANALYTICAL PROCEDURES

3.3.1 Physical Characterization

Pour Point

This analysis was tested by using Cloud and Pour Point Bath, Bench Model 230V produced by Koehler. Standard test method for pour point of crude oil, which is coded as D5853 was referred for this work. The samples were poured into the test jar to the level mark. Then, the crude oil samples were cooled at the specific rate. The lowest temperature at which the oil will just flow was recorded as the pour point. All data produced were averages of triplicate measurement.

Droplet Size

As mentioned by Jiang (2009), there were several experimental methods have been used to determine droplets size in emulsion, including microscopy, photomicrography, video microscopy, light scattering, sedimentation, Coulter counting, turbid meter, nuclear magnetic resonance (NMR) and acoustics among others. For this research, droplet's size was measured through a Carl Zeiss Axiostar Plus inverted microscope equipped with camera and image analysis software (Yarannton et al., 2007). All the droplet's images were captured at constant magnification in order to obtain standard image size. Measurements of average sizes were checked by processing images obtained from emulsions by a camera connected to an optical microscope and computer (Sajjadi, 2006).

Dynamic Viscosity, Shear Rate and Shear Stress

Brookfield Rotational Digital Viscometer Model LV/DV-III with UL adapter and spindle type 31 was used to determine the apparent dynamic viscosity of the freshly prepared emulsions (Abdurahaman et al., 2007a). The samples were transferred into the stainless steel cylinder with jacket that connected to a thermostat circulating water bath

(Zaki, 1996). Before taking the measurement, the calibration of the viscometer was checked with laboratory standard viscosity oil (Mahmood, 2009).

Water content

This study has utilized METHROM Karl Fisher Analyzer Model 787 KF Titrino to analyze water content that presence in the crude oil samples. The crude oil samples were dropped into the analyzer using a disposable syringe. These steps have to be done cautiously by punctured the septum and disposed the samples without dipping into the solvent. Before that, the syringe was weighed by applying back-weighing technique. The syringe with sample was weighed just before the titration and tares it on a balance with an appropriate precision. After disposed the sample, the syringe was weighed again to evaluate the weight difference. The transfer balance data have been used for analysis. All data resulted were averages of triplicate analysis.

Density (°API)

There have two densities that often used, which are related to properties of oils. They were known as specific gravity and American Petroleum Institute (API) gravity. The density of crude oils was determined by using gas pycnometer Model Micromeritis AccuPyc II 1340.

°API density was calculated via equation 3.2 and 3.3 below:

$$Specific\ gravity = \frac{Density\ of\ crude\ oil}{Density\ \ of\ water} \qquad 3.2$$

$$°API = \frac{141.5}{Specific\ gravity(15℃)} - 131.5 \qquad 3.3$$

Surface Tension and Interfacial Tension

Butt et al. (2006) have noted that the important techniques to measure the surface tension of liquids are the sessile drop method, the pendant or sessile bubble method; the Du-Noüy ring tensiometer, and the Wilhelmy-plate method. Du-Noüy ring tensiometer is a common way of measuring surface tension (Rayaji, 2010) and this method has been chosen to finish up this study. This method has been applied by Abdurahman et al. (2008). A digital tensiometer, Surface Tension Meter DST 30 series was used to measure the surface and interfacial tension.

For surface tension measurement, the sample was places on the sample platform. Then the sample platform was raised up by manipulating the screw until the ring was submerged. The, the platform was lowered at the same time applying torsion to the ring by the dial-adjusting screw. These simultaneous adjustments were carried out cautiously proportioned, while the ring systems remained constant at its zero position. As the breaking point was approached, the adjustment was made more cautiously. The dial reading was recorded when the ring detached from the surface. The experiment was repeated three measurements for accuracy.

Meanwhile, the interfacial tension of sample was followed the same procedure as surface tension but with some modifications. Generally, the density of water is over the density of oil. Thus, the water phase was first placed in the sample vessel, and the ring was immersed therein. Oil phase was then poured on the top of water phase to form the two-layer system. At this time, contact between the oil and the ring was avoided. After allowing sufficient time for the interfacial tension to come to its equilibrium condition, measurements were made in the same procedure as used to determine surface tension (Issaka, 2007). All data resulted were averaged of triplicate analysis.

3.3.2 Chemical Characterization

Commonly, chemical fractionation method was used to separate those components from crude oil. This chemical method was based on separation by solvent and chromatography. It was known as SARA analysis method where non-volatile oils such as heavy oils were screened into four chemical classes namely saturates, aromatics, resins and asphaltenes. The fractionation was based on solubility and polarity. In general, this method is done in two stages. The first, precipitation asphaltenes and the second is separation of maltenes through chromatography column. Details of these methods have been described in the next paragraph.

Separation of Asphaltenes

The first steps of SARA fractionation is separation of asphaltenes form bitumen. The precipitation of asphaltenes from crude oils was achieved by adding n-hexane in the ratio 1g oil: 40 mL n- hexane (Fan and Buckley, 2002). The mixture was sonicated for an hour and allowed to settle overnight. Next day, the mixture is filtrated using a Whatman's No. 1 filter paper (Klein et al., 2006). The filter cake was mixed with 4 volumes of n-hexane, sonicated for an hour and left overnight. The mixture is again filtered (Agrawala, 2001). The dark brown/black powder remaining in the filter paper comprises the asphaltenes. The asphaltenes were washed with n-hexane several times until colorless (Wang and Buckley, 2003). Finally, the asphaltenes was dried in a vacuum oven at 60 °C for 24 hours (Castro and Vazquez, 2009).

Fractionation of Maltenes

Previous researchers have introduced various methods to analysis maltenes fractions. For example, open column chromatographic, low-pressure liquid chromatographic, thin-layer chromatographic (TLC), high-performance liquid chromatography (HPLC) and, etc. This study was utilized an open column chromatographic in order to screen saturates, aromatics and resins fraction. The procedure for this experiment was adapted from studies done by Flores et al. (2004) and Zulkania (2004).

The silica gel was activated overnight at 120 °C under vacuum. 1 g of sample of deasphaltenes oil was weighed and dissolved in 40 mL of DCM. The solution was then placed in 500 mL round-bottom flask with the activated silica gel. The consumption of activated silica gel for this step was followed 1:4 mass ratio of sample: activated silica gel.

The solution was placed in a 500 mL round-bottom flask with the activated silica gel. Then, the slurry was placed in a rotary evaporator to remove the DCM and to adsorb the sample onto the silica in the homogenous way. A 5 g sample of clean activated silica placed in glass column. The slurry was then placed in a rotary evaporator to remove the DCM and to adsorb the sample onto the silica homogeneously. A 5 g clean activated silica gel was weighed and placed in a glass column. The silica gel that adsorbed with the maltenes was then placed above the clean silica in the column. After that, 1 g of clean activated silica was putted on the top of the two layers silica that already in the column. The third silica gel that added was functioned as a buffer for the solvent flow. The three silica layers were cautiously prepared to have horizontal ends at the top and at the bottom. Approximately, 300 mL of n-hexane was gently filled gradually on the top of the glass column. The n-hexane was passed through the column by gravity force until colorless effluent from the column observed and the n-hexane mobile fractions were collected. Hexane was passed until the top clean silica was dry at the top, and then the top of the column was gently filled with toluene. The heptane mobile fractions were collected until the toluene front reached the bottom of the column. The collection flask was then changed, and the toluene mobile fractions were collected. Approximately, 300 mL of toluene was passed through the column until no color was observed in the effluent. The same procedure was followed for a DCM. A 300 mL DCM of the mixture was passed through the column.

3.4 Chapter Summary

There was numerous of experiments required to complete this research included stability performance determination, analysis of crude oil component, screening of demulsifiers and optimization. This work has introduces two demulsifiers which not yet used in petroleum crude emulsion. All the experimental procedures were referred to work done by previous researchers. The optimization part was the most critical part since there is no specific techniques or method to find the best demulsifier. Thus, this method was considered as trial and error. The results from these tests were mentioned in the next chapter with detail's discussion.

CHAPTER 4

RESULTS AND DISCUSSION

4.0 INTRODUCTION

Previous chapters have reviewed the fundamental literature and research methodologies which helpful for this work. Furthermore, this chapter is presented to report and discuss the experimental outcomes. This chapter was divided into five main elements which comprised the characterization of crude oils, stabilization and demulsification of emulsions, DOE and optimization. Comparison of demulsification method between chemical and thermal heating was also discovered in this section. Those investigations were focused on water-in-crude oil emulsion type. The data for all assessments were shown in appendixes as been mentioned in the discussions. There were three types of crude oil samples used in order to accomplish this study. The crude oils used were listed as Pure Tapis, 50/500 and 30/70 (v/v) % blended heavy-Tapis and called as crude oil A, B and C, respectively. Various aspects have been covered in order to understand the stability properties of water-in-oil emulsions utilized in this research. The details of discussion were explained in the next subchapter.

4.1 CHARACTERIZATION

Crude petroleum exhibited a broadly range of physicochemical properties since it origin from different sources. The characterizations of crude oil samples are necessary in pursuance of gained better understanding about the characteristics of the crude oil. This knowledge is highly importance in order to predict the behavior of any crude oil with regard to for instance emulsion stability (Aske, 2002).

4.1.1 Physical Characterization

The physical properties of crude oil are of a considerable importance in the field of both applied and theoretical science and especially in the solution of petroleum reservoir engineering problems. There were several physical properties of crude oil have been investigated included density, water content, pour point, surface and interfacial tension. The findings from those tests were tabulated in Table 4.1.

According to the Table 4.1, found that the density for crude oil A, B and C shows almost nearly same. The results revealed that the crude oil A was 0.8214, B was 0.8598 and crude oil C was 0.8725 g/cm^3. A comparison study of density the samples show that, crude oil C was the heaviest while sample A shows the lightest crude oil. The API density of crude oil A had shown the highest value of 40.749 followed by B and C with 22.073 and 30.515, respectively. These values have been associated with the sulfur content in the crude oil which is high in sulfur content shows the higher API value. Besides, the viscosities of crude oil A, B and C have shown as 3.803, 6.259 and 16.254 cP, respectively. From the results obtained, it found that the viscosities of samples were directly proportional to density of samples. However, the API density values were inversely proportional to samples' viscosities. The pour point of each samples was also determined where crude oil A has achieved to -14 °C meanwhile sample B gained -13 °C and -12 °C for crude oil C. As been noted by Mehta (2005), lighter crude oil with low viscosity and density has lower pour point.

Water content in crude oil also tested using a Karl Fisher titration, where it has shown the percentage of water content in crude oil A, B and C as 0.02, 0.05 and 0.07, respectively. The surface and interfacial tension of samples were determined through tensiometer. Crude oil B was indicated as the highest reading for surface tension test with 33.6967 mmN/m followed by A (27.8715) and C (27.786). According to interfacial tension test, it found that crude oil A exhibited the highest value and pursued by B and C with 38.955 and 25.8707 mmN/m, respectively. As the interfacial tension decreased, the emulsion stability increased. This was due to the formation of a rigid surfactant layer (Zulkania, 2004). Based on the experimental results, found that crude oil C more stable compared to crude oil B and A. There were a correlation between the physical and chemical properties of crude oil, and they were discussed later.

Table 4.1: Physical properties of crude oil

Physical Properties	Units	Type of Crude Oils		
		A	**B**	**C**
Density	g/cm^3	0.821	0.86	0.873
$^{\circ}$API density	-	40.75	33.073	30.515
Viscosity	cP	3.803	6.259	16.254
Water content	%	0.02	0.05	0.07
Pour point	^{o}C	-14	-13	-12
Surface tension	mmN/m	27.872	33.697	27.786
Interfacial tension	mmN/m	29.721	38.955	25.871

4.1.2 Chemical Characterization

Table 4.2 represented the chemical properties of crude oils used. The total amount of asphaltenes precipitated in n-hexane were determined. The compositions of asphaltenes were measured by weighed the dried asphaltenes precipitated. As been reported in the Table 4.2, the highest percentage of asphaltenes was exhibited by crude oil C with 4.73 %. By the meantime, crude oil B and A were gone after with 3.43 and 0.58 % of asphaltene content, respectively. The existences of resin in the crude oil samples were also been studied. The highest amounts of resin were obtained by crude oil A with 20.2 %. Crude oil C was become as the second highest of resins content where it shows 16.3 % and followed by crude oil B with 18.3 %. The presence of asphaltenes and resins in crude oil can stabilize the emulsion. Both are known as the natural surfactant where acts as emulsifying agent who reduced the interfacial tension and to induce the repulsive forces between the droplets (Abdurahman et al., 2008). Ratio of resins to asphaltenes (R/A) is an important parameter in order to predict the emulsion stability. In this regards, the R/A ratio for crude oil A, B and C were found as 34.83, 5.336 and 3.44, respectively. The resins play an important role in the stability of asphaltenes. They believed to disperse the asphaltenes and preventing them from separation as a separate phase (Oyekunle, 2006). However, Based on the experimental results, it found that crude oil A which have higher R/A ratio easily to separate compared to low R/A ratio. This behavior explained that when the R/A ratio increase, the emulsion becomes looser and easier to break down (Abdurahman et al, 2008). High R/A ratio means high resin content. High concentration of resins keeps more of the asphaltenes dissolved in the oil phase.

Table 4.2: Chemical properties of crude oil A, B and C

Chemcial Properties		**Crude Oils**		
Components	**Units**	**A**	**B**	**C**
Saturates	wt%	51.7	53.03	55.23
Aromatics	wt%	27.67	25.3	23.8
Resins	wt%	20.2	18.3	16.3
Asphaltenes	wt%	0.58	3.43	4.73
R/A	-	34.83	5.33	3.44

* Note: R/A is ratio of resins and asphaltenes

Figure 4.1 depicted the correlation between asphaltenes' content with °API density for all crude oil samples used. The figure revealed that the higher asphaltenes' content tended to cause lower °API. This means high asphaltenes contributes to high density. The saturates content, and viscosity have correlation as illustrated in Figure 4.2. According to the results, found that low saturates content exhibited high viscosity properties. The saturate content and °API density have shows inversely proportional as plotted in Figure 4.2. The graph has explained that at low saturates concentration exhibited high value °API density of crude oil. As discussed previously, °API density was correlated to viscosity properties of the crude oils. At low saturates concentration, the crude oil viscosity was also low.

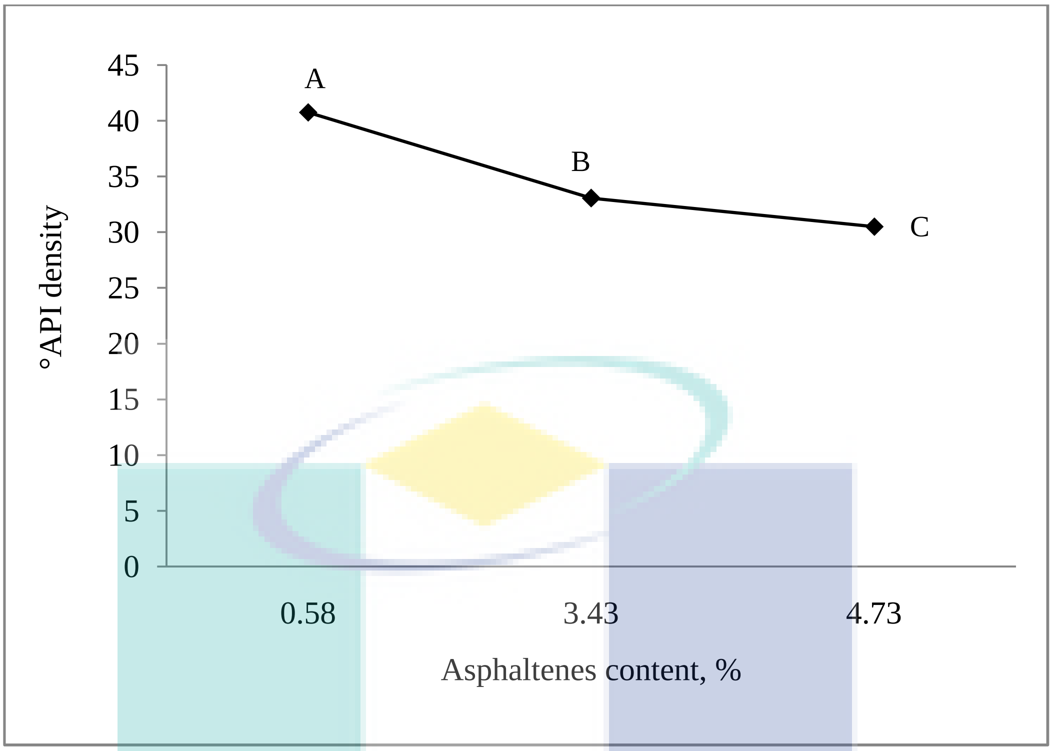


Figure 4.1: Correlation between asphaltenes content and °API density of crude oils

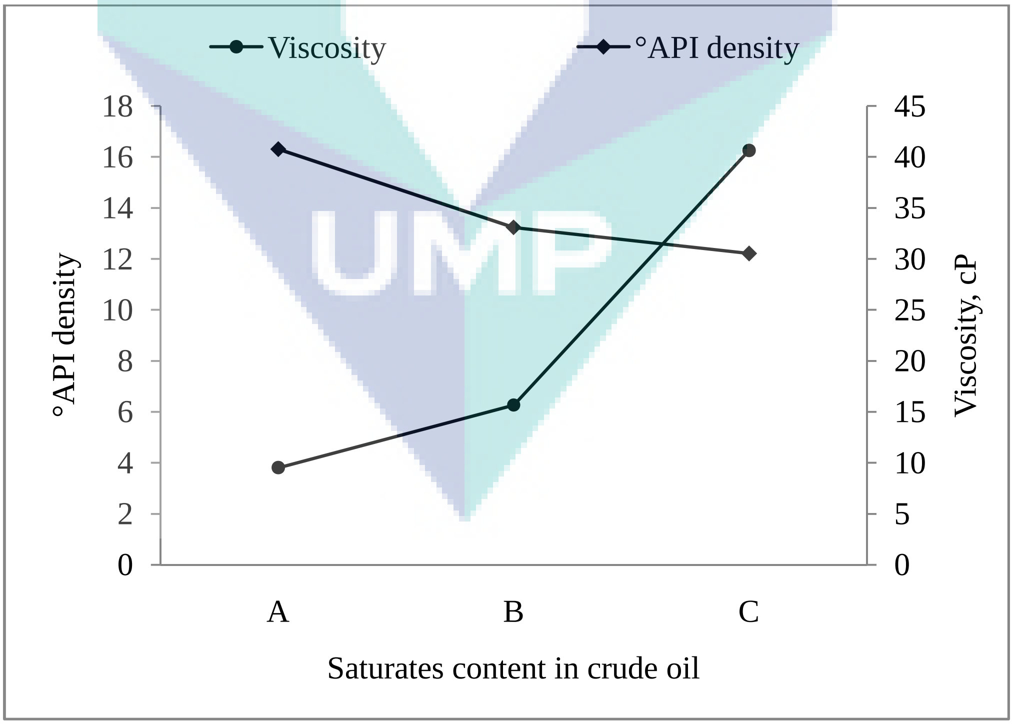


Figure 4.2: Correlation between saturates content agains °API density and viscosity of crude oils

4.2 STABILITY

Generally, the basic principle for stable emulsion is the presence of only single phase. Chen and Tao (2005) have defined the W/O emulsion stability as the resistance by the dispersed water droplets against coalescence. The emulsion is considered as unstable if more than one phase was found. The stability of WO emulsion that formed was depended upon numbers of factors, including operating condition. The operating parameters whose influences were examined in this study included the mixing speed, processing time, volume phase ratio, emulsifier type and also emulsifier concentration. The details of the discussion were reported as well in next subchapter.

4.2.1 Effect of Mixing Speed

Already existed various ways to form an emulsion since long time ago and one of the most commonly used is the mechanical method. The mechanical mixing process offered great benefits for the emulsification process since the interface between the dispersed and continuous phases is deformed to form droplets (Ghannam, 2005). As been explained previously, this energy is capable to break the larger liquid droplet into small droplets.

To investigate the influences of mixing speed, the behavior of W/O emulsions were studied at different speeds of 500, 1000, 1500 and 2000 rpm. The other operating conditions were: room temperature, mixing duration of 7 minutes, and 1.0 w/w % of Span 83. These mixing speed were select based on the capability of the equipment used as the lower speed can performed is 500 rpm and 2000 rpm for the highest speed. The results were plotted in Figures 4.3 to 4.5.

Figure 4.3 was represents the effect of mixing speed on emulsion for crude oil A. According to Figure 4.3, it found that after 300 minutes observations, the percentage of oil separated was 23.2 % mixing speed of 2000 rpm. However, the separation percentage increased with lowering mixing speed. As been seen in Figure 4.3, the amount of oil separated was 24 % for agitation speed of 1500 rpm and followed by 32 and 46.4 % for 1000 and 500 rpm, respectively.

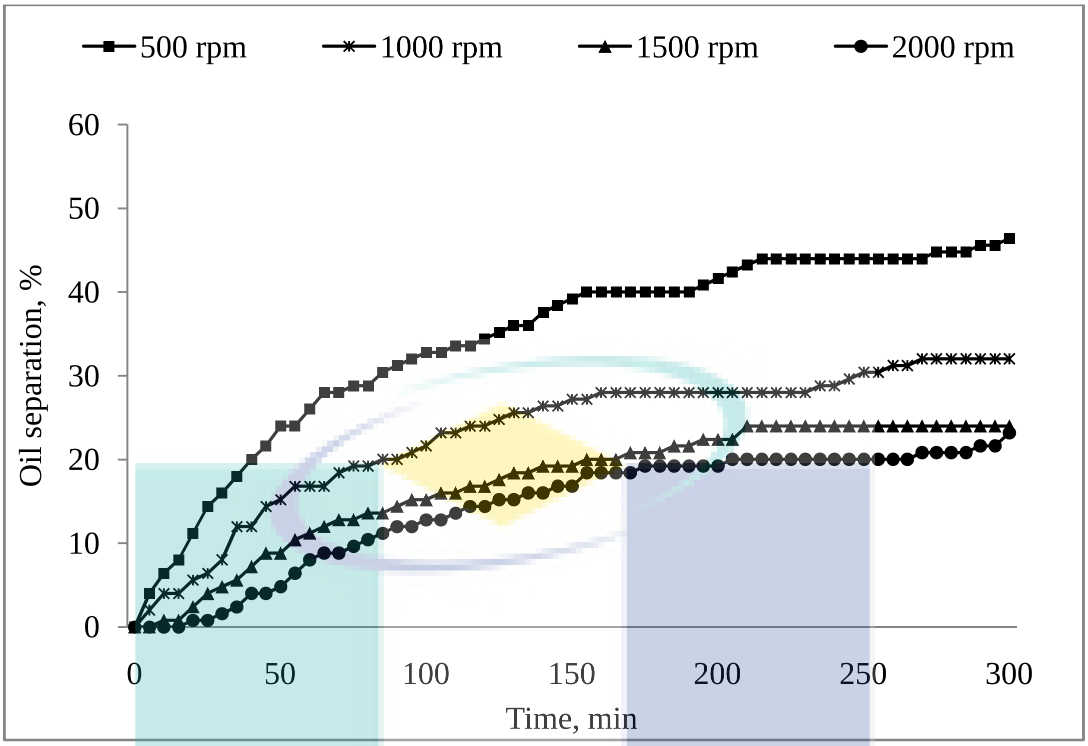


Figure 4.3: Effect of mixing speed on emulsion stability (crude oil A)

Figure 4.4 indicated the findings for crude oil B where the results obtained for 2000 rpm is 2 % followed by 1500 rpm (3.2 %), 1000 rpm (4.8%) and 500 rpm with 24.8% oil separated from the emulsion. The graph line for mixing speed at 500 rpm has shows very rapid separation has occurred compared to other speed. The low speed of mixing has made it unable to spread the emulsifier homogenously into the emulsion. In addition, the low speed has made it harder to break down the droplet into small size. Due to this condition, the stability of the emulsion was less stable and the large droplet formed can coalescence easily.

For the crude oil C, the percentage of oil separated is represented in Figure 4.5 where the highest percentage was performed at 500 rpm (23.2 %). Rapid separation occurred after 25 hours observation at this speed. This situation was happened due to the droplets coalescence. As been explained previously, at this speed the emulsifier was not too homogenous so the rigid films of the droplets not completely stabilized by the surfactant and lead to film rupture. The lowest oil separated was obtained at 2000 rpm (3.2 %). The emulsion formed was more stable at this high speed of mixing.

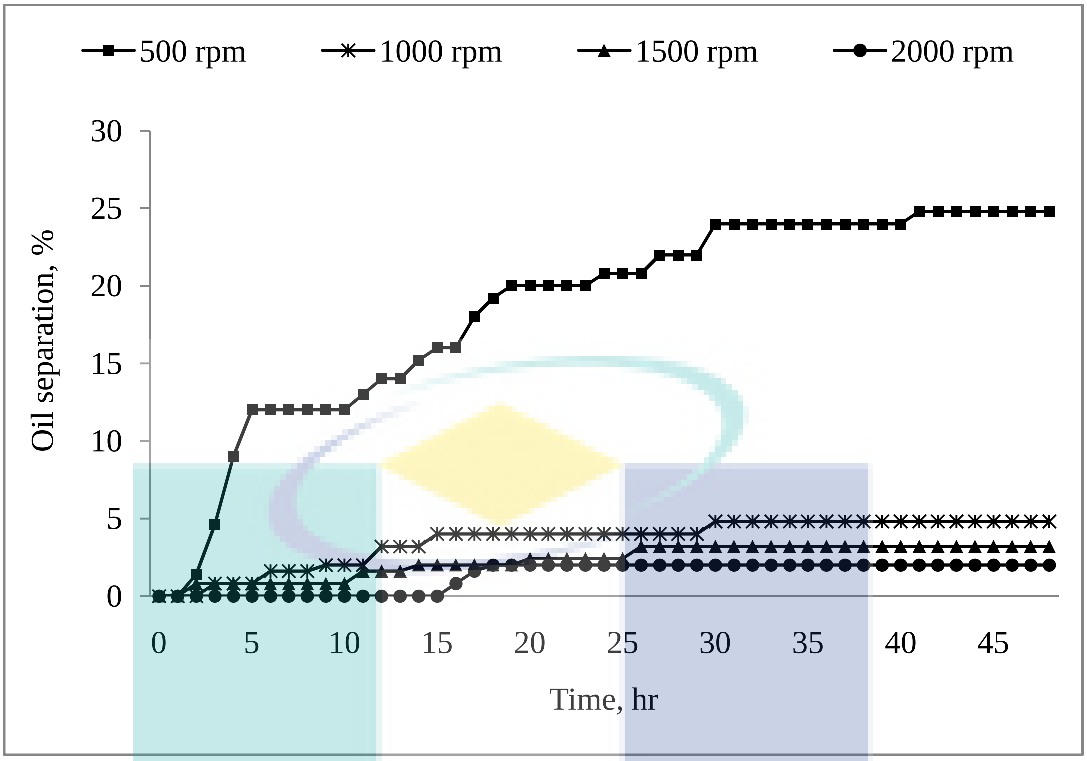


Figure 4.4: Effect of mixing speed on emulsion stability (crude oil B)

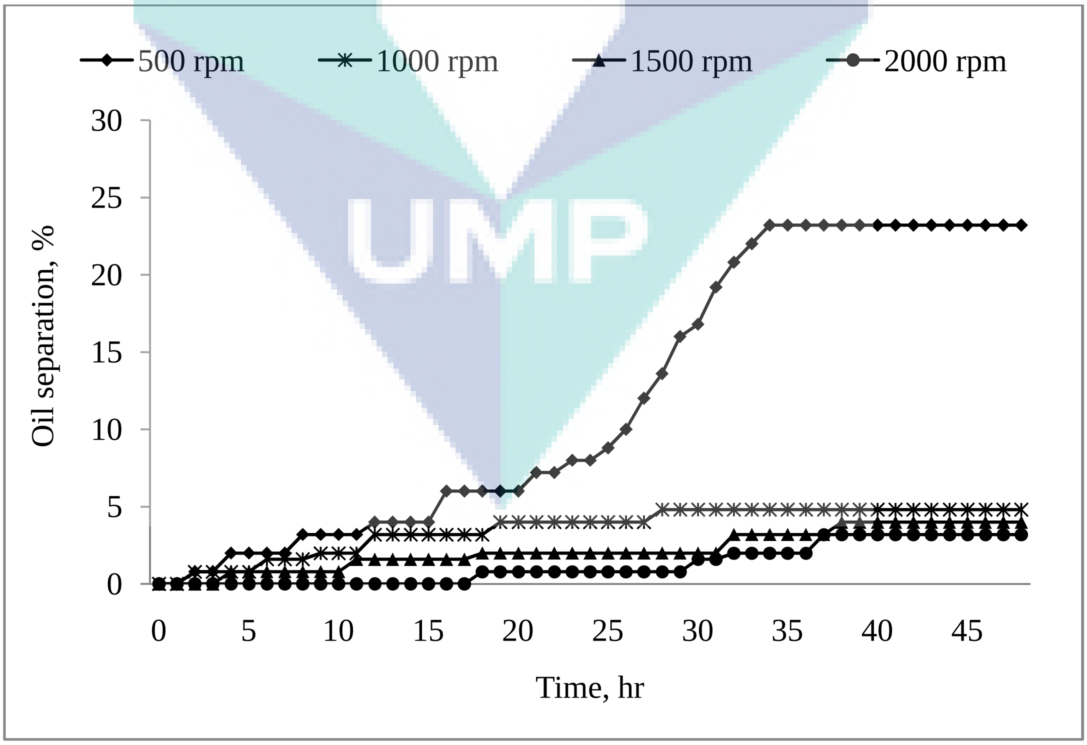


Figure 4.5: Effect of mixing speed on emulsion stability (crude oil C)

Generally, emulsions were more stable when high speed of mixing supplied during preparing the emulsions. This effect has a correlation to droplets sizes formed. As been explained by Ghannam (2005), the droplets' sizes are mostly too large at the beginning of the emulsification process. Consequences from the mixing process, these large droplets are broken down into smaller ones due to the disruption process of the big droplets. Thus, the more rpm supplied; the more stability achieved.

A study regarding droplets size was performed by using a microscope that equipped with camera and image analysis software. The droplets were directly viewed through the microscope. The microscope images of droplets formed at the different speeds of agitation during preparing the W/O emulsions can be referred in Appendix A. Referring to Figures A.1, A.2 and A.3, the comparison of droplets sizes are indeed promising. The pictures were clearly shown the changes of droplets as a function of mixing speed. The mean droplet' diameter for all samples was measured and been transferred into a graph as depicted in Figure 4.6.

Figure 4.6 displays the water droplets' distribution within different stirring speed for crude oil A, B and C. From that figure, the mean droplets' size was gradually decreased as a function of operating speed. The highest mean droplets' size represented at 500 rpm for each sample. While, the lowest of means droplets size was exhibited at 2000 rpm. As plotted by crude oil A, the mean diameter was achieved to 0.59, 0.126, 0.134 and 0.346 µm at 2000, 1500, 1000 and 500 rpm, respectively. As well as crude oil B, the mean size of water droplets indicated as 0.059, 0.126, 0.134 and 0.346 µm when the mixing speed is 2000, 1500, 1000 and 500 rpm, respectively. Meanwhile, crude oil C is reported as 0.034, 0.080, 0.123 and 0.496 µm with respect to 2000, 1500, 1000 and 500 rpm.

Increases in stirring energy generally tend to produce a decrease in droplets size. As been mentioned earlier, this is due to the disruption process of the large droplets. As been reported in studies done by Ghannam (2005), the decrease of diameter size was significantly and consequently, enhances the emulsion stability. As revealed by Fournier at al. (2009), the high energy of agitation may promote a more efficient particle anchoring at the water-oil interface with considering that agitation intensity can modify the adsorption parameters. According to this phenomenon, the surface area of the droplets' interface became higher. This will affect the emulsion viscosity to increase as droplet size decreased when high mixing speed supplied (Souleyman et al., 2010). From Song et al. (2011), the increases of emulsion viscosity contribute to the breakup of large drops and again giving fine emulsion. Furthermore, Langevin et al. (2004) has mentioned in their study where the emulsion with small drops (R<1 µm) are insensitive to sedimentation or creaming because Brownian motion dominating the effect of gravity. However, when the droplets size is larger than a few microns, they may sediment or creaming.

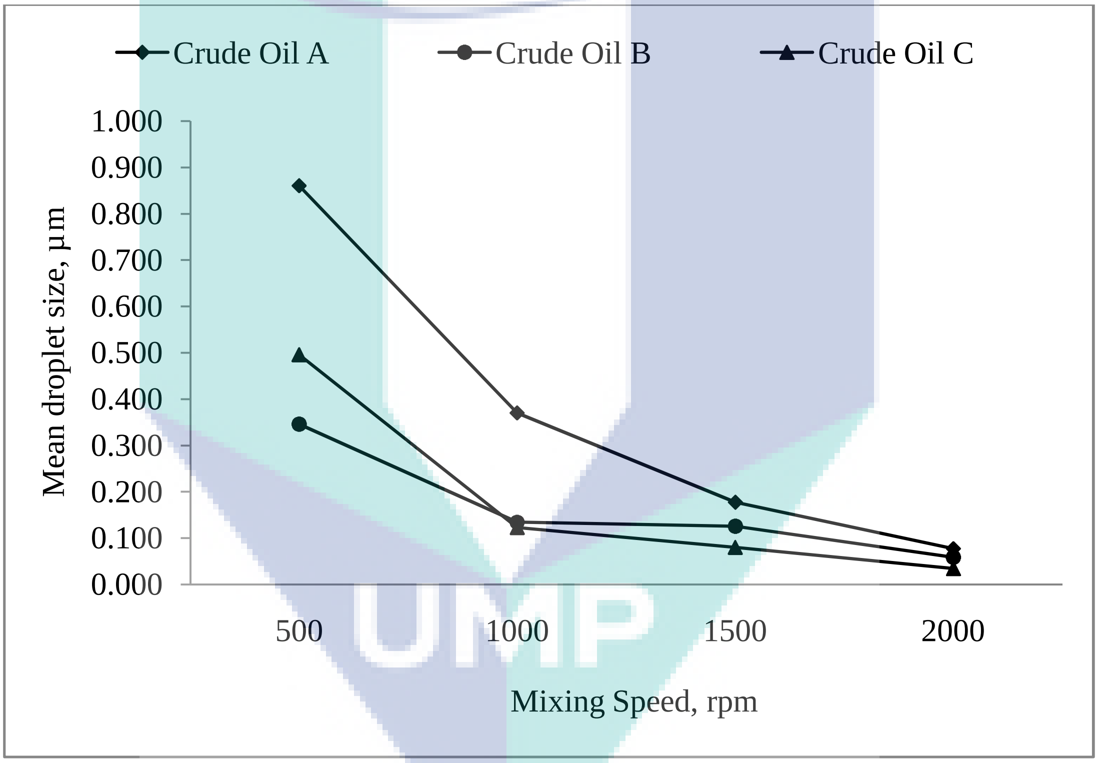


Figure 4.6: Effect of mixing speed on droplet size for crude oil A, B and C

The effect of stirring intensity towards emulsion viscosity at 50 °C had been represented in Figure 4.7. It was obviously shown the correlation between the emulsion viscosities as a function of mixing speed during the emulsification process. The viscosity of W/O emulsion for crude oil A was 44.6 cP at 2000 rpm. However, the viscosity lowered to 3.96 cP when 500 rpm supplied during the emulsification. Crude oil B has been obtained as 88.8, 72.2, 62.4 and 47.8 cP at 2000, 1500, 1000 and 500 rpm, respectively. And crude oil C has shown the result as 62.6 cP at 500 rpm followed by 89.4 (1500 rpm), 102.8 (1000 rpm) and 139.2 cP when the mixing speed is 2000 rpm.

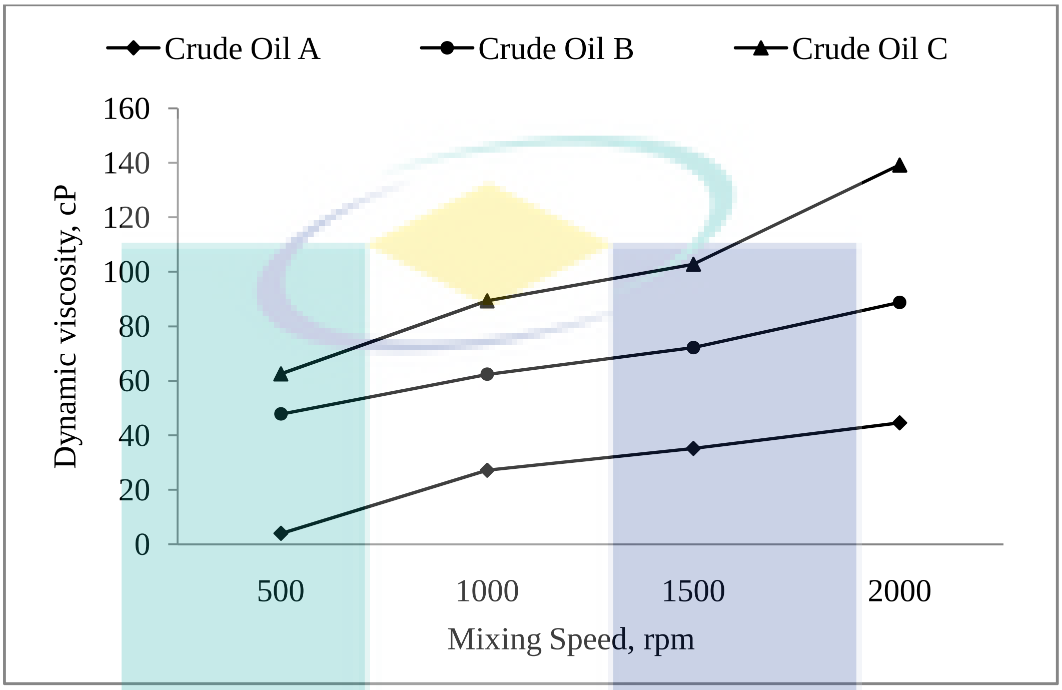


Figure 4.7: Effect of mixing speed on viscosity for crude oil A, B and C

4.2.2 Effect of Processing Time

The emulsion stability for crude oils A, B and C were examined as a function of processing time. The evaluation was carried out with agitation speed 2000 rpm, 1.0 w/w % of Span 83, at phase volume fraction of 50/50 v/v %. The W/O emulsions behavior were studied at different mixing time for 5, 7, 9 and 12 minutes. Results of these experiments were shown in Figures 4.8, 4.9 and 4.10.

The oil separation performance as a function of processing time for crude oil A was depicted in Figure 4.8. It's interesting to observe that, low stability was obtained at low processing time. As can be seen, the highest separation was occurred up to 40 % for 5 minutes of mixing time. The separation occurred was very fast and only stable less than 5 minutes. While, the lowest oil separation was obtained at 12 minutes of processing time with 16 % separation. Moreover, this emulsion was maintained stable till 50 minutes. For 7 and 9 minutes condition, they have take place between 5 and 12 minutes from the standpoint of oil separation performance with 32.8 and 24 %, respectively.

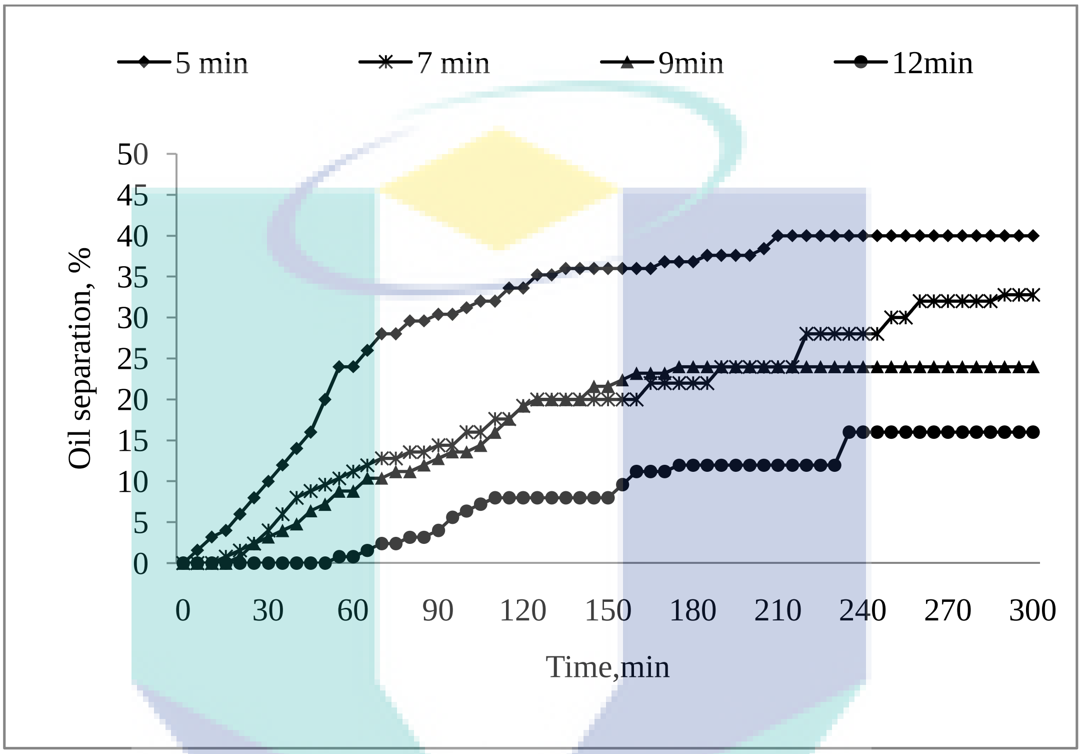


Figure 4.8: Effect of processing time on emulsion stability for crude oil A

As it can be seen in Figure 4.9, the stability performance for crude oil B was plotted and the observation was took 14 days since the emulsions are more stable compared to crude oil A. The emulsion with 5 minutes of processing time just only lasted less than a day then it separated up to 8.8 %. When the processing time increased to 12 minutes, the emulsion was still homogenized and stable until day three then it started to separate till 7.2 %. These results were almost similar to crude oil C as illustrated in Figure 4.10. From the graph, it found that the oil separation was the highest when the mixing time was the lowest. For this case, the separation for 5 minutes of stirring intensity is about 8.8 % then followed by 7, 9 and 12 minutes with 4, 6 and 7.2 % of separation, respectively. Sample for 12 minutes took three days to start separate, while sample for 9 minutes took a day to separate.

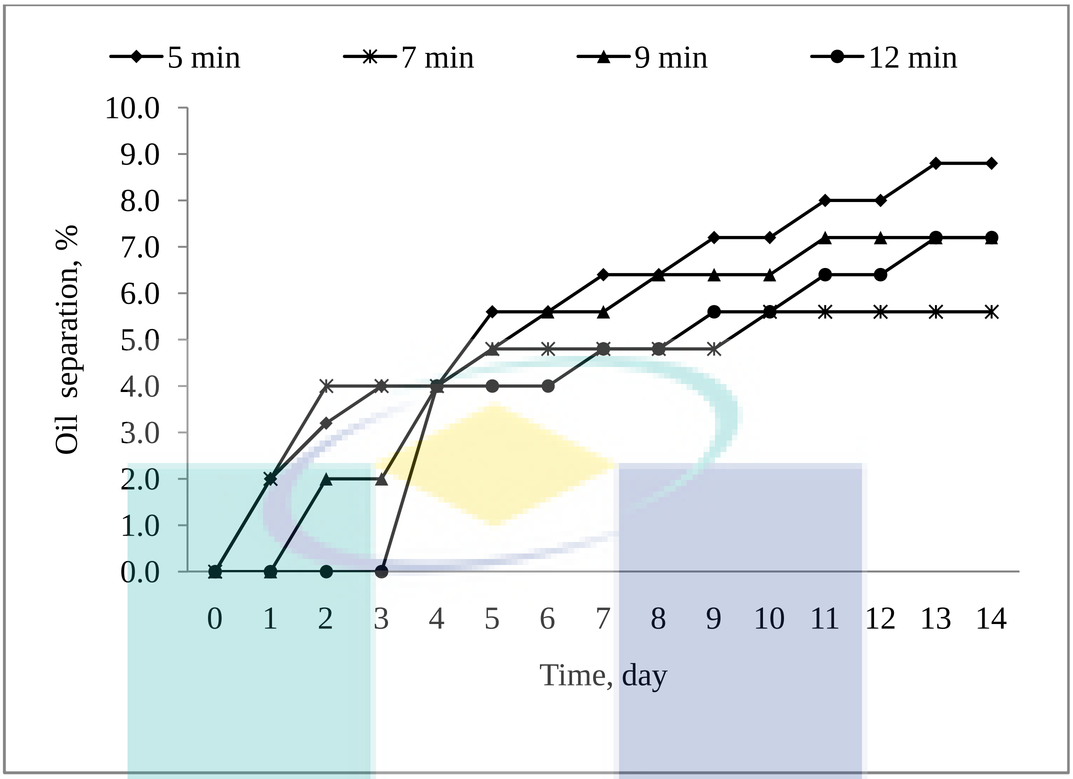


Figure 4.9: Effect of processing time on emulsion stability for crude oil B

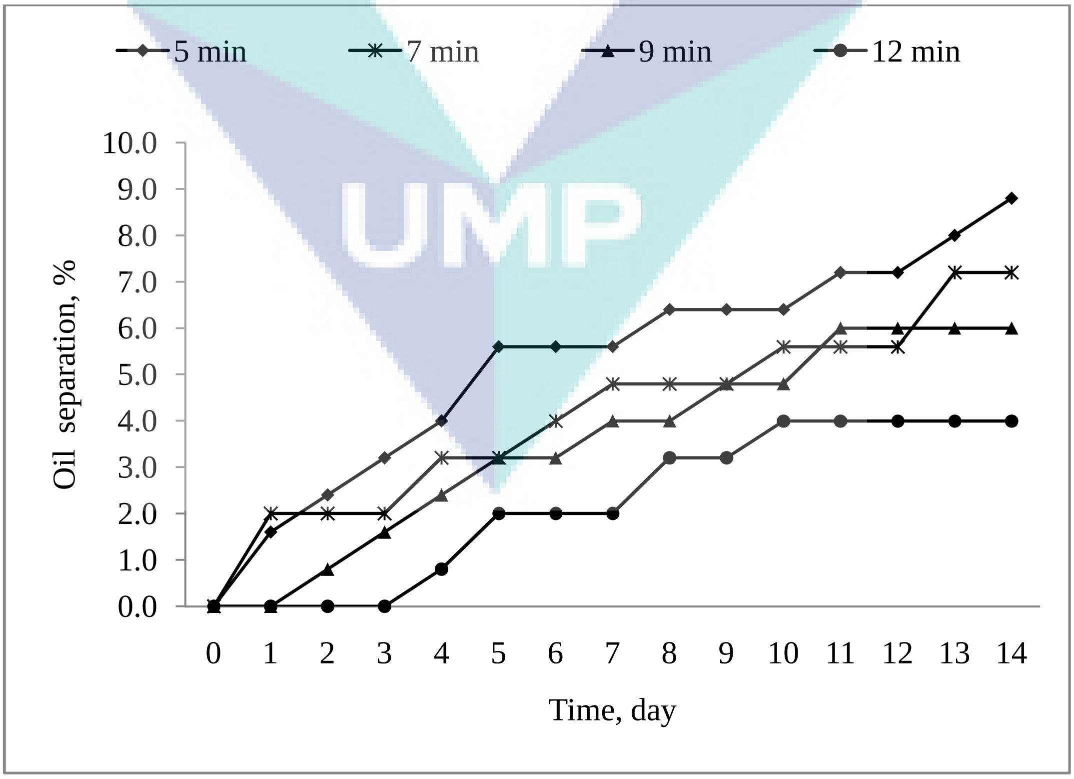


Figure 4.10: Effect of processing time on emulsion stability for crude oil C

Overall, it was observed that the increasing of the agitation time, the consistency of the emulsion also increases. Insufficient processing time resulted in non-homogeneous droplet in the continuous phase (Aruna, 2009). In order to confirm the effect of processing time on emulsion stability, the droplets size was determined and the mean of the size were illustrated in Figure 4.11. As can be seen, when the processing time reduced, the radii of the droplets were increased. Crude oil A has shown the gradual fall from 0.103 µm at 5 minutes to 0.049 µm at 12 minutes. As well as crude oil B where the highest reading was exhibited at 5 minutes with 0.091 µm and followed by 0.086, 0.059 and 0.044 µm at 7, 9 and 12 minutes, respectively. The crude oil C also clearly shows the slump in droplet size as the processing time raised. As can be seen, the droplet size is about 0.089 µm when the mixing time was 5 minutes. However the size was reduced to 0.037 µm when the time was 12 minutes.

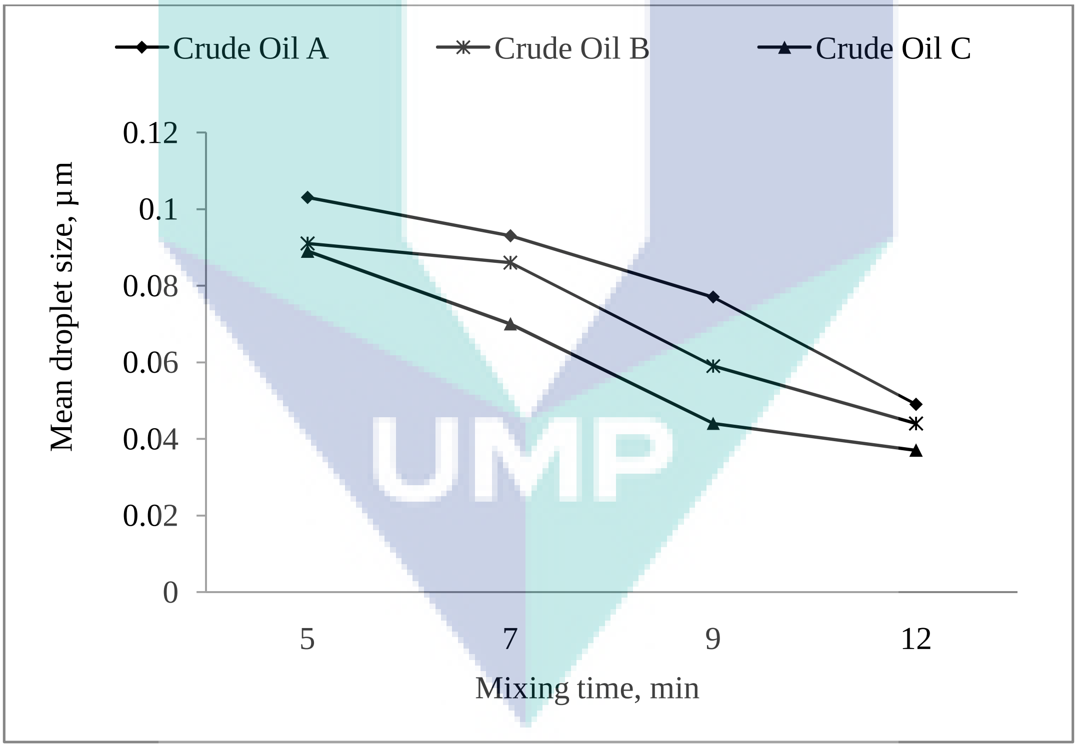


Figure 4.11: Effect of processing time on droplets size distribution for each crude oil

The rheological properties of W/O emulsion at various processing time were also been determined in this study. The correlation between processing time and dynamic viscosity for three types of crude oil were depicted in Figure 4.12. As can be seen, the viscosities were gradually declined as the processing time inclined. The changes of mixing duration have influenced the viscosity of the emulsion. From Aruna (2009), this result was due to the formation of homogenous droplets.

As been explained by Omole and Falode (2005), the reduction of water droplets size is result of prolonged agitation which also permits surface active particles to reach the vicinity of the interfaces stabilize them. This allowed the surfactant to adsorb into the droplets interfaces efficiently. This was justified by Ghen and Tao (2005), the emulsifiers have enough time to accumulate at the droplets interface as the time of mixing increased. Due to this condition, the interfacial film of the droplets formed is rigid and elastic thus avoid coalescence. Fournier at al. (2009), have the same opinion where the processing time play an important role in creating solid stabilized emulsion since the particle need time to achieve its stability contact angle.

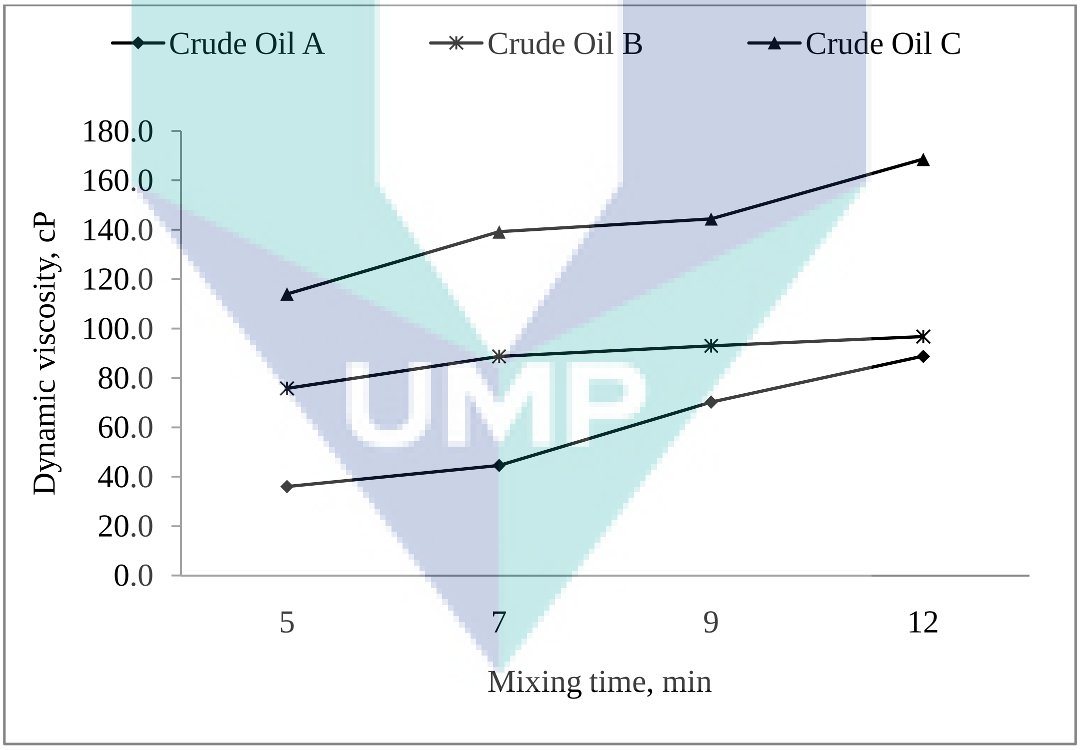


Figure 4.12: Effect of processing time on viscosity for crude oil A, B and C

4.2.3 Effect of Volume Phase Ratio

The emulsion stability for crude oil A, B and C were examined as a function of water-oil phase ratio. Wide range of volume water to oil ratio has been studied and the samples were namely as 20/80, 30/70, 40/60 and 50/50 v/v %. The stability investigation for all samples was illustrated in Figure 4.14, 4.15 and 4.16 where it shows the separation of oil from the emulsion which calculated after 300 minutes observation.

In Figure 4.13, the oil separation for 20/80 v/v % was 2.5 % and then followed by 30/70 v/v % (50.9 %), 40/60 v/v % (37.3 %) and 50/50 v/v % (26.4 %). Overall, the oil separation performance was inclined as the volume of dispersed phase increase except 20/80 v/v %. Based on that graph, this sample showed the lowest percentage in oil separation. But, if considered the observation of the sample during experimental work, it shows bubbles in the emulsion until end of the observation period. This can be explained due to incomplete of separation since the process occurred was till flocculation but no coalescence happened to the droplets. Thus, sample 20/80 v/v % was considered as unstable compared to 50/50 v/v %.

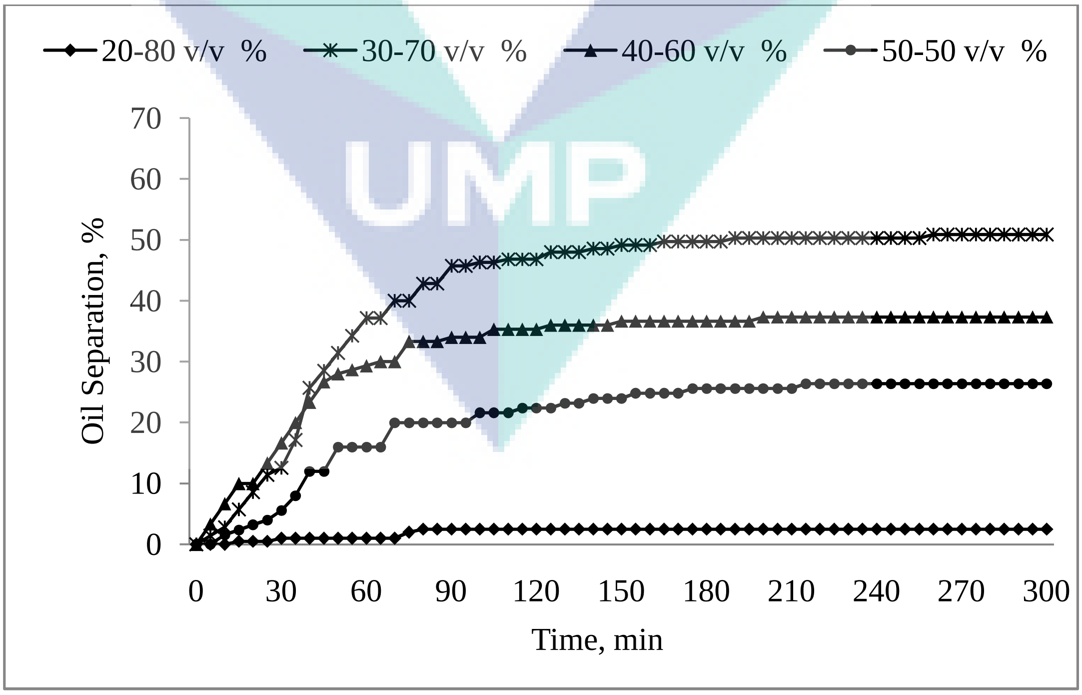


Figure 4.13: Effect of phase volume on emulsion stability for crude oil A

Figure 4.14 was represented the results for crude oil B. The graph was clearly shows the effect of volume phase ratio towards the emulsions stability. The graph shows dramatically increase in oil separation at 20/80 v/v % and 30/70, 40/60 and 50/50 v/v % were going after, respectively. There was no oil separated from the emulsion until after 300 minutes when the volume phase ratio is 50/50 v/v %. Meanwhile, 20/80 v/v % only can maintained stable till 30 minutes and after that the oil started to separate.

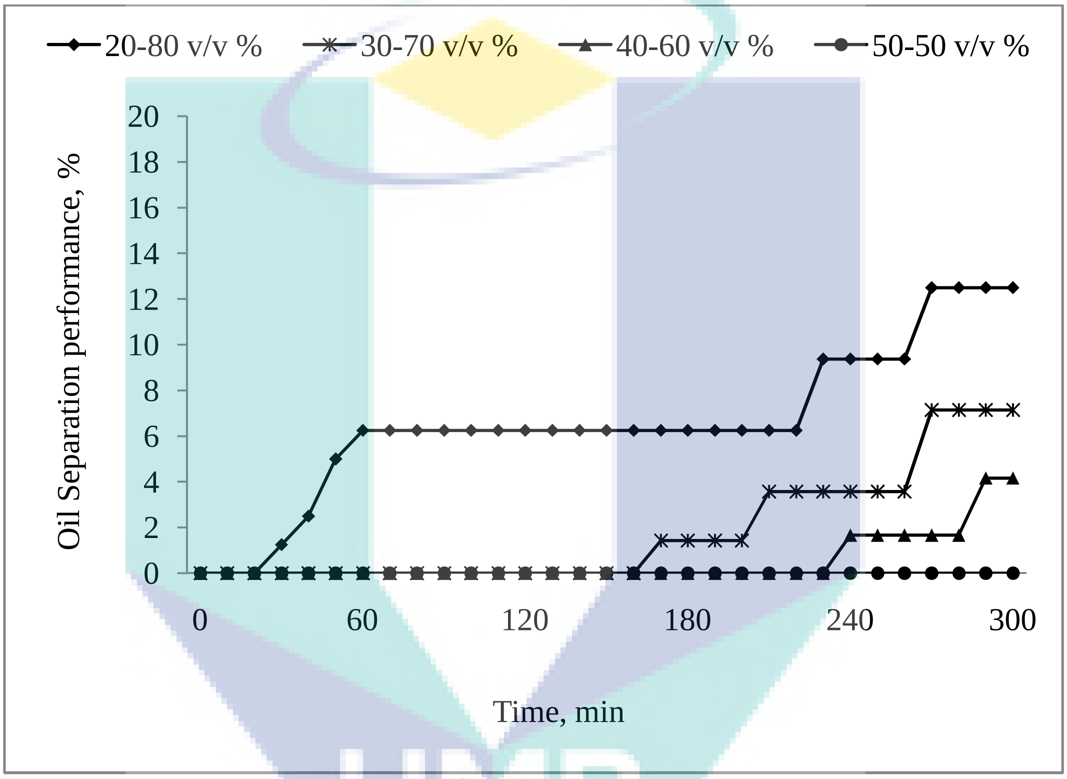


Figure 4.14: Effect of phase volume on emulsion stability for crude oil B

This trend was also observed by crude oil C as shown in Figure 4.15. The most unstable emulsion was acted by emulsion with the lowest water volume, 20/80 v/v %. The separation occurred was very fast compared to other ratio. Other three ratios were slightly increased with time of observation. The emulsion with 50/50 v/v % was the most stable emulsion among the samples since it can maintain in homogenous phase till 120 minutes.

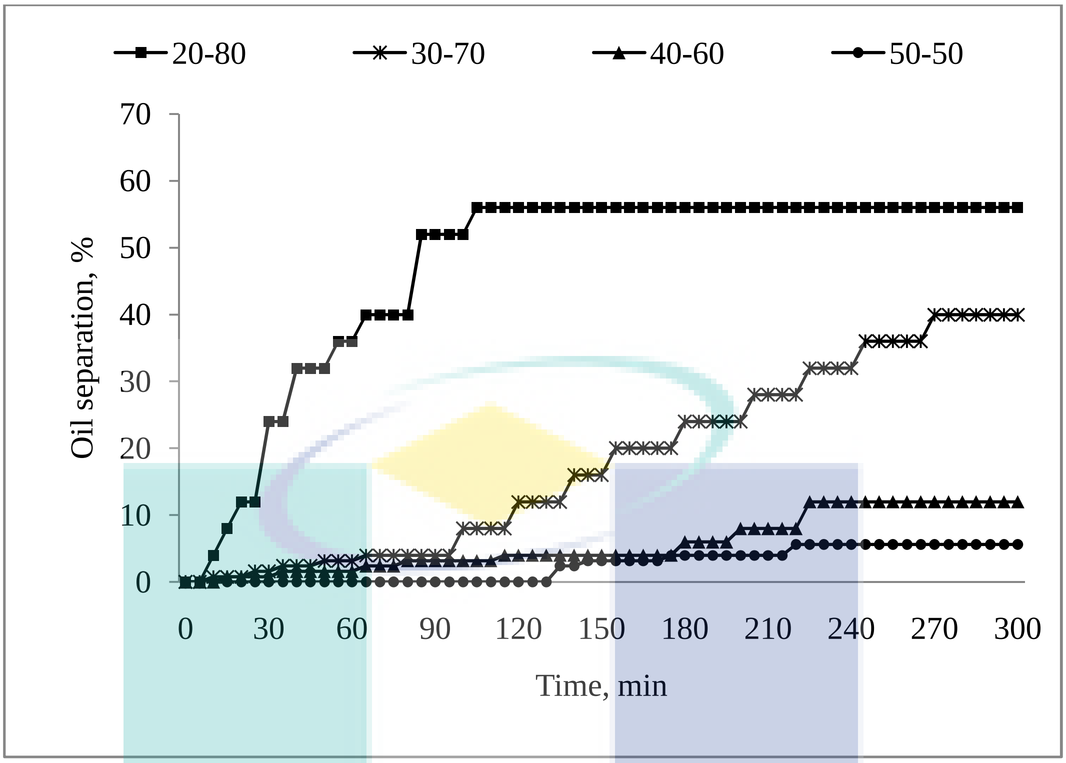


Figure 4.15: Effect of phase volume on emulsion stability for crude oil C

Theoretically, the stability of emulsion is declined as inclined of internal phase. In other words, the more stable W/O emulsion were obtained with the increase in oil volume. However, the results obtained shown the opposite where the emulsion more stable with increases of water phase content. As been explained by Kokal (2002), when the volume fraction of one phase was small compared to the other, then the phase which has smaller fraction is the dispersed phase and the other will form the continuous phase. When the volume phase ratio was close to 1, then the other factors will determined the type of the emulsion formed. This phenomenon is also correlated to the size of the droplets formed.

The effect of water-oil content changes on the droplets diameter of the emulsions also been investigated. Figure 4.16 has illustrated the correlation between them. The radii of the droplets were reduced as the volume of internal phase increased. From the graph, found that the larger size was obtained by 20/80 v/v % for crude oil A, B and C where the mean droplet diameter was 0.103, 0.091and 0.089 µm, respectively.

The effect of water-oil content changes on the droplets diameter of the The size was gradually decreased till 0.049, 0.044 and 0.037 µm for crude oil A, B and C, respectively when the volume phase ratio was 50/50 v/v %. Ashrafizadeh and Kamran (2010) have stated that decreases of droplet size lead to enhance the interfacial area and particle interaction which would finally increase the stability of the emulsion.

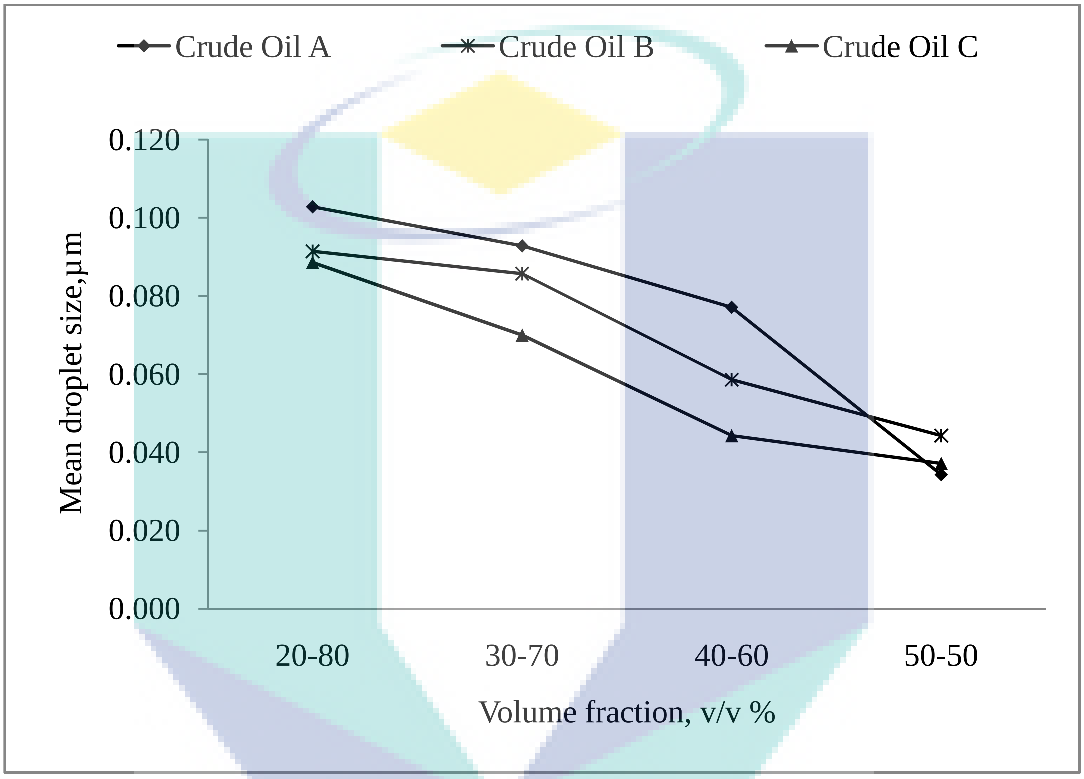


Figure 4.16: Effect of phase volume on droplet size for crude oil A, B and C

To further strengthen the involvement of volume phase ratio on emulsion stability, a study on viscosity has been done for crude oil A, B and C. All the samples have been determined their viscosity and as plotted in Figure 4.17. Here, it was found that the viscosity behavior of the emulsion was directly proportional to volume phase ratio. This trend was interrelated to the diameter size of droplet and emulsion viscosity as been stated in Stock's Law as mentioned in equation 4.1 below (Abdurahman et al., 2007b).

$$v_m = \frac{gD^2(\rho_w - \rho_o)}{18\mu_o} \qquad 4.1$$

According to the Stock’s law, settling velocity is inversely proportional to viscosity but directly proportional to diameter of droplets. If viscosity is lower, the density different of internal and external phases increases. Consequently, lead the higher velocity settling of the droplets. In this case, the settling velocity is less for volume phase ratio at 50/50 v/v %. The settling velocity for 40/60 v/v % was higher than 50/50 v/v % since its viscosity is bigger. This condition was followed by 30//70 and 20/80 v/v %, respectively. As a general rule of thumb, the smaller the average size of the dispersed water droplets, the longer the residence time required (Kokal, 2002). This can promote to the stability behavior of the emulsion.

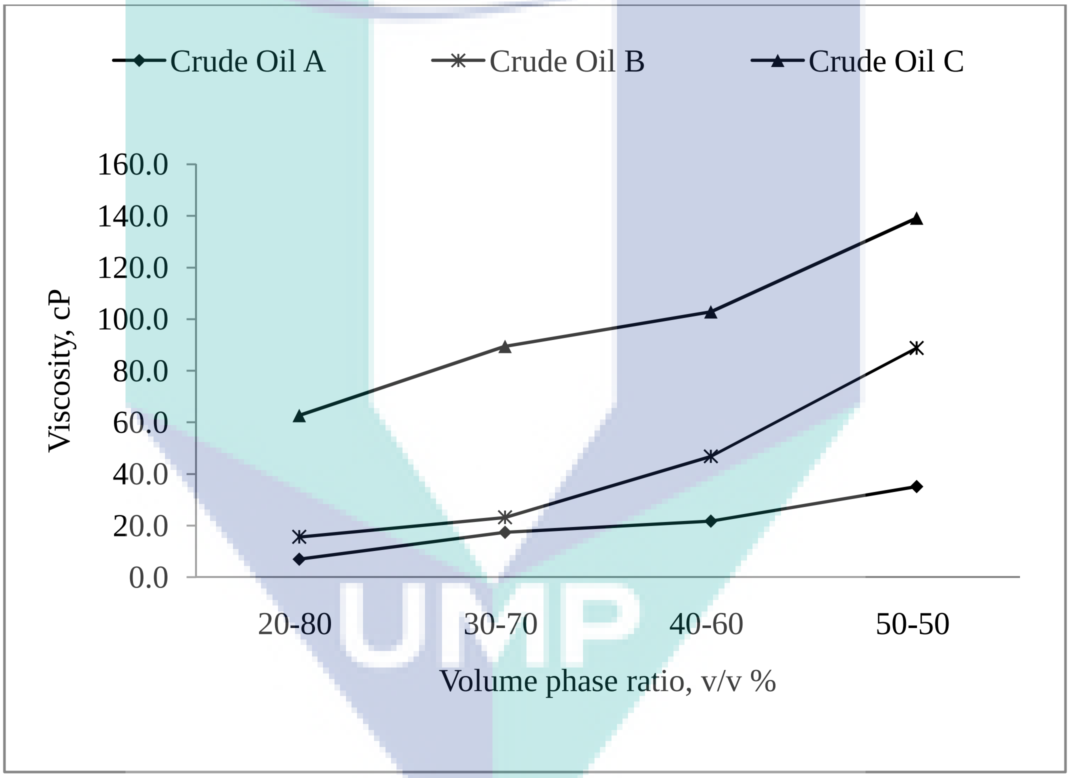


Figure 4.17: Effect of phase volume on viscosity of emulsion for crude oil A, B and C

4.2.4 Effect of Emulsifier Type

Emulsifier type plays a significant role in order to form stable emulsion. When oil and water are mixed together, a temporary emulsion may form. However, they might break up quickly because of high interfacial tension except emulsifier is used to stabilize the emulsion (Issaka, 2007). In the present investigation, influenced of Span

83, Tween 80, Triton X-100 and SDDS as emulsifying agent were thoroughly studied. The performance of oil separation against time was plotted in Figure 4.18, 4.19 and 4.20.

Figure 4.18 has indicated the emulsion stability for crude oil A. It is found that Span 83 revealed as the lowest separation with 19.2 % of oil separated. Then, it followed by Tween 80 and Triton X-100 with 92 %, 96 %, respectively. Triton X-100 and Tween 80 shows rapid separation and required short time to separate almost complete at the end of observation. However, there was no separation occurred for emulsion with SDDS but during the observation stage, it containing small bubbles in the emulsion. Thus it was considered as unstable since it failed to maintain in a single form. The coagulation and flocculation of water droplets has formed the small bubbles inside the emulsion. Perhaps, it was because of the high interfacial energy at the droplet film so the rupture of the film cannot happen efficiently. Consequently, the coalescence of the droplet retarded.

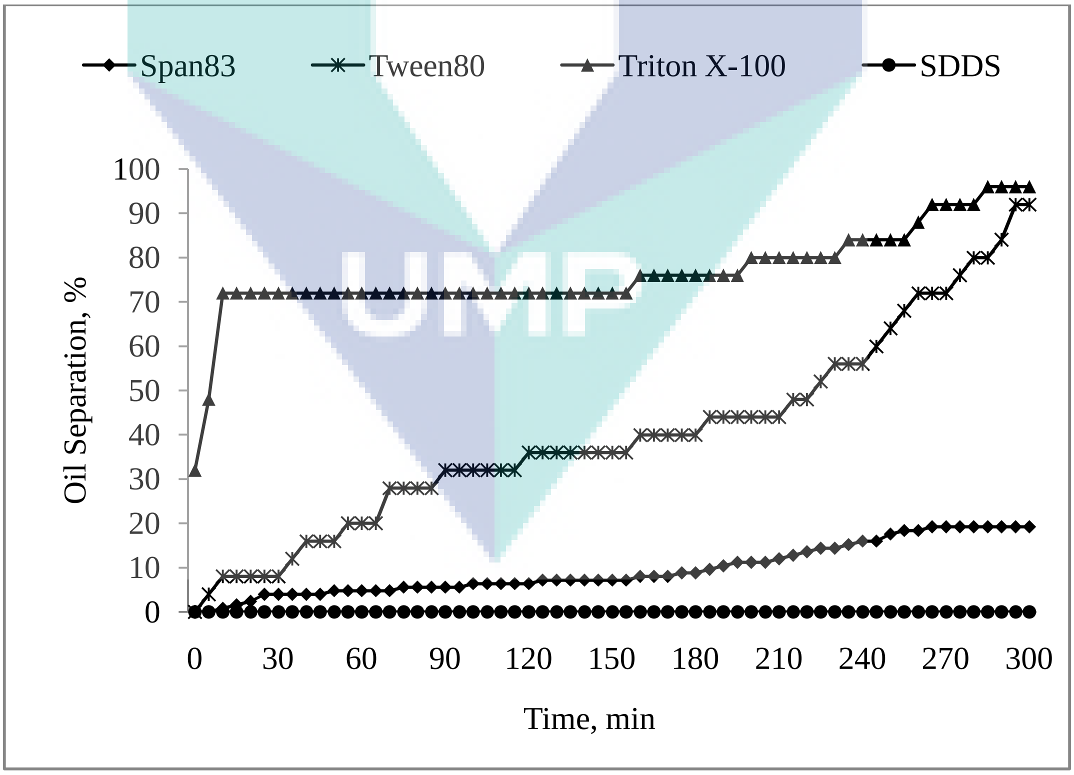


Figure 4.18: Effect of emulsifier type on oil separation performance for crude oil A

Then, the results of oil separation for crude oil B can be seen in Figure 4.19. From the Figure, it noticed that the Tween 80 also has showed rapid oil separation and achieved till 40 %. Meanwhile, Triton X-100 directly separated the emulsion after prepared the emulsion. The emulsion for Span 83 stabilized emulsions exhibited only slight coalescence over 30 minutes. The stability performance for crude oil C has represented as shown in Figure 4.20. Triton X-100 has shows 16 % of oil separation and became the highest percentage for crude oil C. Tween 80 and SDDS have revealed the same results but Tween 80 was separated a little bit early compared to SDDS. However, event there is no separation occurred until minutes 195, SDDS still classified as unstable because there has bubbles appeared in this emulsion. In contrast, the emulsion with Span 83 was maintained stable till end of the observation time.

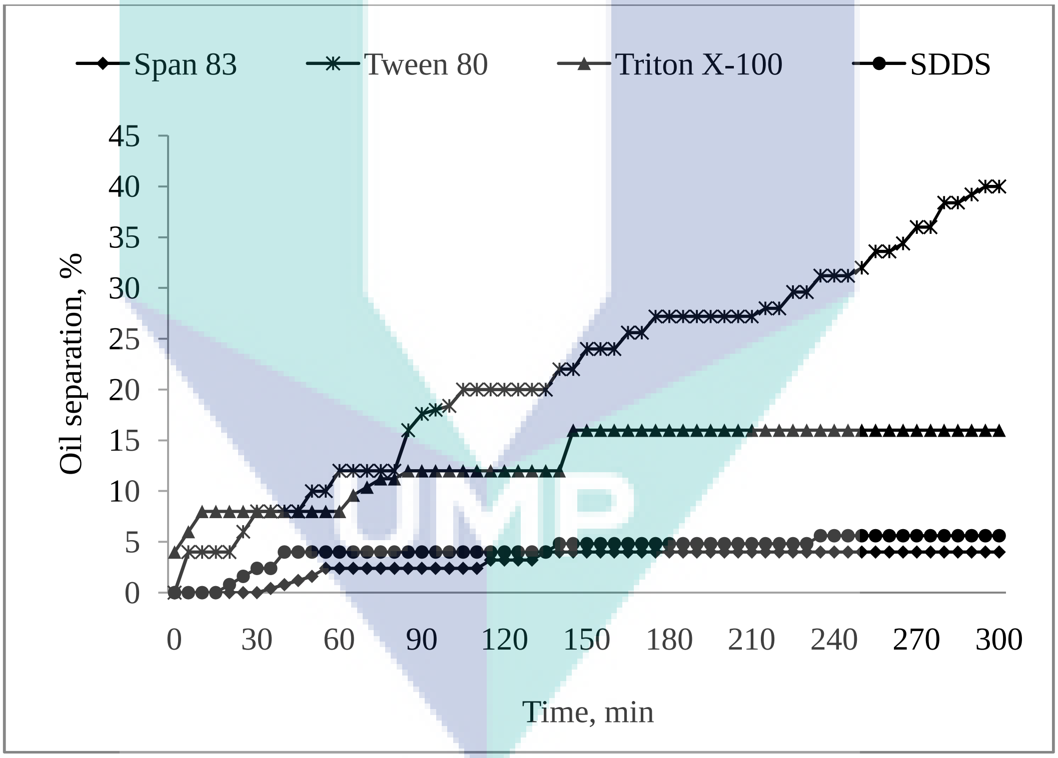


Figure 4.19: Effect of emulsifier type on oil separation performance for crude oil B

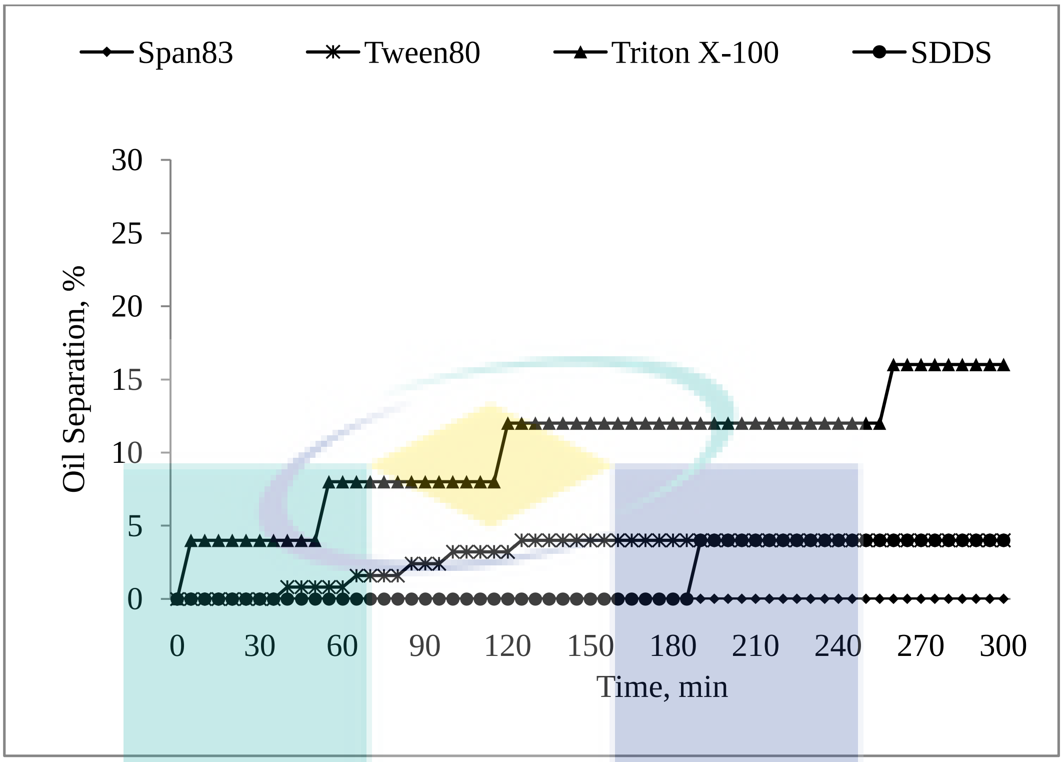


Figure 4.20: Effect of emulsifier type on oil separation performance for crude oil C

The efficiency of emulsifier to stabilize the emulsion can be explained according to water-oil solubility of the surfactant itself. Sajjadi (2006) reported that according to Bancroft's rule, the emulsifier is most soluble in the continuous phase. In this study case, the continuous phase was referring to oil phase since the emulsion formed is water-in-oil type. Moreover, solubility of the emulsifiers can be referred to Hydrophile-Lipophile Balance (HLB) system which is related to surfactant solubility behavior and can be used to select the suitable surfactant. Table 4.3 has allocated the characteristics of emulsifiers used for this study.

Table 4.3: HLB value for emulsifier used

Emulsifier	HLB Value	Solubility	Characteristic
Span 83	4.3	Oil soluble	Non-ionic
Tween 80	16	Water soluble	Non-ionic
Triton X-100	13.4	Water soluble	Non-ionic
SDDS	40	Water soluble	Anionic

The HLB value of the emulsifier used was referred to the earlier researcher and also from the Material Safety Data Sheet (MSDS). As been explained in previous chapter, HLB system was expressed in arbitrary scale, typically from 1 to 20 where, low HLB number means low solubility in water while high HLB number means high solubility in water (Diana, 2009). From Table 4.3, found that Span 83 was characterized as non-ionic oil soluble which has HLB number 4.3. Whereas, Tween 80 and Triton X-100 were classified as non-ionic water soluble and carried HLB number as 15 and 18, respectively. Meanwhile, SDDS has grouped as anionic water soluble. The HLB number of 40 for SDDS is outside of the range of 0 to 20 and simply means that SDDS is strongly soluble or hydrophilic.

Ekott and Akpabio (2010) have reported that the emulsifier's performance was influenced by steric stabilization. Broadly, surfactants containing a hydrophilic polar head group and hydrophobic tail group that typically orient themselves at oil-water interfaces. Dispersed water droplets will thus coated by surfactant with hydrophilic head protruding into the water phase. When droplets approach each other, their adsorbed surfactant tails prevent droplets contact and coalescence. Span 83 has gone through this mechanism to form stable emulsion as well. The oil solubility behavior of Span 83 has influenced its effectiveness since the external phase is consisted with oil phase.

Moreover, the oil soluble emulsifiers have good properties in order to stabilized the W/O emulsion such as lowering the interfacial tension between the two phases, can form a rigid interfacial film and also can rapidly adsorbed into the oil-water interface (Issaka, 2007).

4.2.5 Effect of Emulsifier Concentration

The surfactant concentration required for stabilizing the emulsion and forming an emulsion with acceptable viscosity should be determined. From the economic point of view, it would be more profitable to decrease as much as we can the surfactant concentration consumption to stabilize the crude oil emulsion. The concentration of emulsifier is one of the most significant factors that affect the emulsion stability. Besides, Zulkania (2004) also be of the same mind where surfactant concentration and type influenced the stability of thin liquid film and emulsion stability. For that, this study has discovered the effect of different concentration of emulsifier towards W/O emulsion stability. In order to accomplished this part, single emulsifier namely Span 83 have been chosen. The evaluation was carried out with agitation speed at 2000 rpm for 7 minutes at ambient temperature.

As demonstrated in Figures 4.21, 4.22 and 4.23, in most cases stability of emulsion increases with concentration of emulsifiers. The effect of Span 83 concentration on the stability performance for crude oil A was plotted in Figure 4.21. At 0.5 w/w % of Span 83, the oil separation was achieved till 40 %. However, when the concentration of surfactant increased to 1.0 w/w %, the separation occurred has shown less compared to 0.5 w/w %. As well as at 1.5 and 2.0 w/w %, the emulsion was much stable with 28 and 20 % of separation, respectively. However, when the concentration of Span 83 increased to 2.5 w/w %, the separation process was much higher than emulsion with 2.0 w/w % emulsifier.

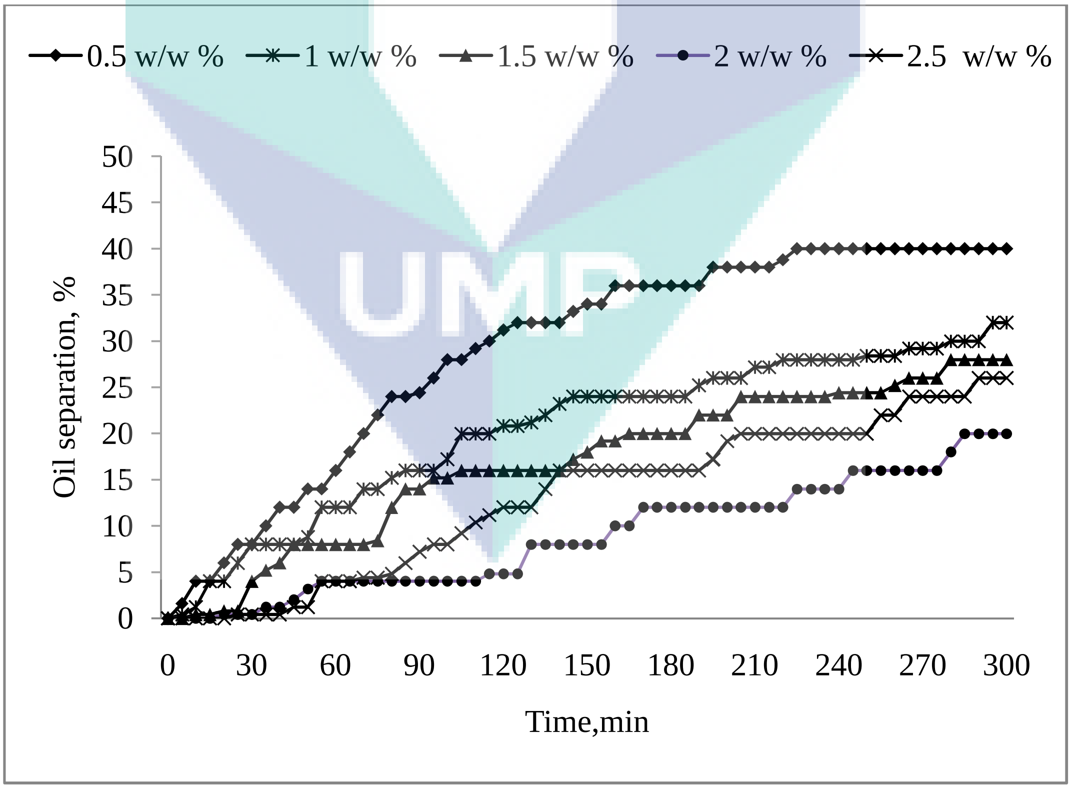


Figure 4.21: Effect of emulsifier concentration on emulsion stability for crude oil A

The results obtained from crude oil B was shown in Figure 4.22. The percentage of oil separated looked high when low concentration of Span 83 used. At 0.5 w/w % of emulsifier concentration, the oil separation occurred was 8 %. The emulsion with 1.0 w/w % has shows gradually increase in oil separation till 4.8 %. The stability performance for 2.0 w/w % was revealed as the lowest oil separation compared to other as low as 1.6 %. However, at 2.5 %, the emulsion has removed about 4 % of oil after 300 minutes observation. Meanwhile, Figure 4.23 has plotted the same effect as crude oil A and B where the more addition of Span 83, the better stability is reported. As can be seen in that figure, the highest oil removal was achieved at 0.5 w/w % with 7.2 % and followed by 2.5 (4.8 %), 1.0 (4 %), 1.5 (3.2 %) and 2.0 w/w % (2.4 %).

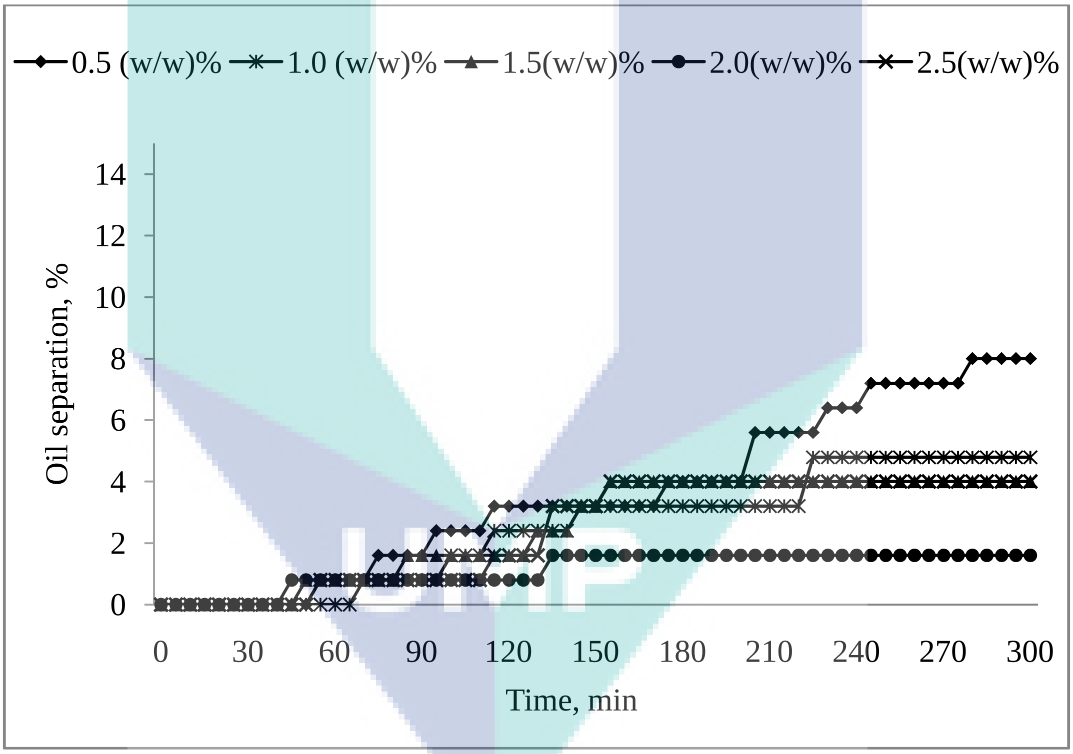


Figure 4.22: Effect of emulsifier concentration on emulsion stability for crude oil B

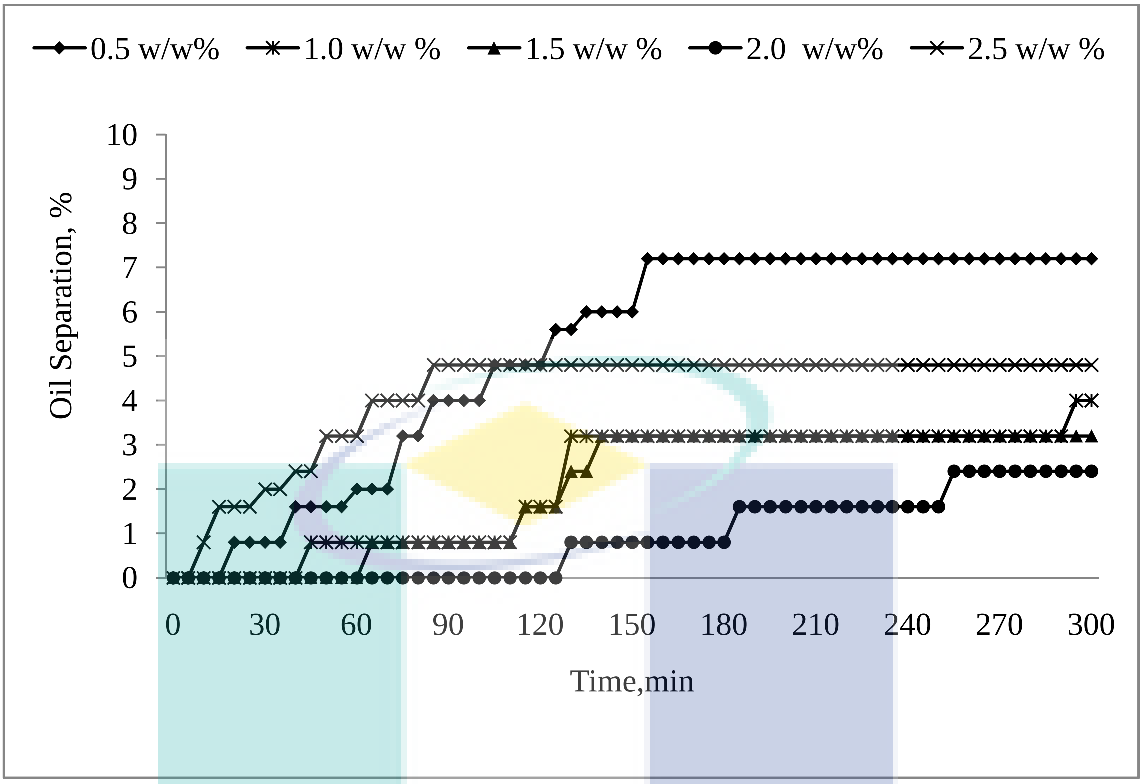


Figure 4.23: Effect of emulsifier concentration on emulsion stability for crude oil C

Generally, the emulsion stability enhanced with surfactant concentration. This has been explained by Ghen and Tao (2005) in their previous study where at low concentration of surfactant, the emulsion is unstable due to agglomeration of the droplets. Zulkania (2004) has explicated that the presence of emulsifier in the continuous phase is adsorbed onto the interface and form a film on the surface of the dispersed phase. Thus, when the concentration of emulsifier is increase, the amount of surfactant adsorbed on the layer is also increase and the stability also increases.

As been pointed out by Abdurahman et al. (2007b) and James (2007), the addition of surfactant may form stable emulsion due to the decreasing of the interfacial tension. In addition, the enhancement of the emulsifiers' concentration causes an increase in the amount of barrier between the two phases and provided a better distribution of dispersed droplets in the continuous phase (Ashrafizadeh and Kamran, 2011).

The surface concentration increased until reaches a maximum level where aggregation of dispersed droplets was occurred. This point was kwon as critical micelle concentration (CMC). In this study, as the concentration of emulsifier increased further up to 2.5 w/w % reduction of emulsion stability was observed. This phenomenon was due saturated concentration of adsorbed surfactant molecule at the droplets surfaces corresponding to the molecule size. James et al. (2001) have noted that if the concentration of surfactant is increasing gradually, the surface concentration also increase and reaches the maximum level at a specific bulk concentration.

4.3 DEMULSIFICATION

For economic and operational reasons, it is necessary to remove the water completely from the crude oils through demulsification process. Abdurahman et al. (2007b) have noted that the demulsification or emulsion breaking was evaluated based on two aspects. Firstly, the rate or speed at which separation takes place and the total volume of water left in the crude oil after separation. These criteria have been used as a guide for evaluation this section.

This experiment was carried out into two parts where the first part was deal with heating method and the second part was done through chemical demulsification method. These methods have used the same emulsions samples in order to study the effectiveness of method performance. The detailed discussions were elaborated in the next sub-chapter.

4.3.1 Thermal Demulsification

To accomplish this part, an emulsion sample was carried out with agitation speed at 2000 rpm for 12 minutes and under temperature of 28 °C using 2.0 w/w % of Span 83 for 50/50 % of volume phase ratio. Hot plate has been used to study the effect of heating on emulsion breaking. The test was used on crude oil A, B and C. The result obtained as illustrated in Figure 4.24. The heating temperature used was in range of 30 to 90 °C.

Based on the observation on this experimental work, only oil phase was removed from the emulsion between 0 to 360 minutes observation. The results of oil separation were illustrated in Figure 4.24. According to the graphs, it was found that crude oil A shows rapid separation and the amount of oil separated was 36 % after 360 minutes. Crude oil B was also exhibited gradually increases in oil separation with 25.6 % and followed by crude oil C with 22 %. The heating rate involved can be referred in Appendix F.

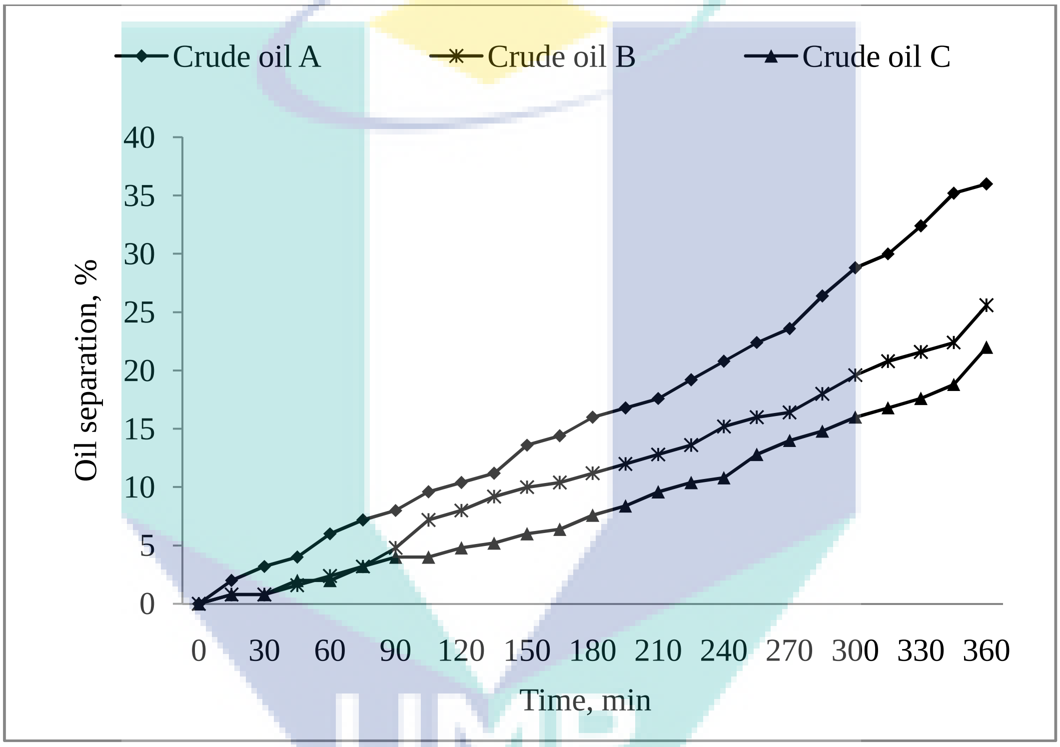


Figure 4.24: Effect of heating on emulsion stability

The demulsification of emulsion can be enhanced by heating process. Through this process, the viscosity of the emulsion might decrease and leads the water settling rates (Kokal, 2002). As been explicated by Kristiansen et al (1996), the mixing caused by the convection throughout the liquid was related to the viscosity where, it reduces as the temperature increases. From these results, crude oil A was found easier to break since its viscosity was only 3.803 cP compared to crude oil B and C with, 6.259 and 16.254 cP, respectively. However, there was no water phase separated from the emulsion event after 30 days of observation for settling gravity process. This can be explained due to evaporation process of water droplets during heating the emulsion.

Crude oil A has shown a rapid oil separation compared to crude oil B and C. This was due to the properties of the crude oil such as low asphaltenes contented, low viscosity and high R/A ratio were tended to form less stable emulsion compared to other crude oil samples.

4.3.2 Chemical demulsification

This method commonly used to treat the emulsions. The chemical that added into the emulsions was called as demulsifiers and they were designed to neutralize the emulsifying agents that stabilized the emulsions. Generally, the demulsifiers will migrate into the oil-water interface and rupture the rigid film then enhanced the coalescence of droplets (Kokal, 2002).

The action of demulsifiers was tested on stable W/O emulsions for crude oil A, B and C. There were four types of demulsifiers family have been investigated in this project. In order to execute this study, there were two criteria been kept for the determination of demulsifiers efficacy which is separation of water must achieve at least 80 % and the separated water should be clear. Wu et al. (2003) have mentioned the efficiency of a demulsifiers was determined by the characteristics of the demulsifiers. The present works also have discussed the competency of the demulsifiers used and the characteristics were illustrated in Table 4.4.

This study was accomplished by using stable emulsion from crude oil A, B and C. Those emulsions were prepared at 2000 rpm for 50/50 v/v % in 12 minutes by consumed 2 w/w % of Span 83 under temperature of 28 °C. The prepared emulsions were added 0.1 w/w % of demulsifiers and agitated vigorously for 1 minute at 1000 rpm. Then, they were leaved for gravity settling in order to evaluate the emulsion separation.

Table 4.4: Characteristic of demulsifiers used

Group	Demulsifier	Molecular weight, g/mole*	HLB number*
Amine	Dioctylamine	241.46	6.75
	Octylamine	129.25	6.88
	Hexylamine	101.19	6.98
	Penytlamine	87.16	6.87
Polyhydric alcohol	PEG 300	300	10.0
	PEG 400	400	12.0
	PEG 600	600	13.2
	PEG 1000	1000	16.0
Alcohol	Ethanol	46.07	7.9
	Buthanol	74.12	7.0
	Heptanol	116.23	5.6
Natural	Coco amide	204.00	6.0
	PBOA	267.49	5.5

* References: Provided in MSDS and bottle label.

4.3.2.1 OFAT screening of amine demulsifier group

Figures 4.25 and 4.26 represent the effect of amine group demulsifiers on stability of crude oil A. It found that amine group demulsifiers were capable to separate water and oil from the emulsions except for dioctylamine. The highest oil separated was performed by octylamine and followed by hexylamine, dioctylamine and pentylamine. After seven days observation, octylamine has almost completely removed the oil as well as water phase which is 97.5 and 99 %, respectively. Hexylamine was successfully removed 85 % of oil and 75 % of water from the emulsions. The dioctylamine was only achieved 55 % of oil separated and no water separation was occurred. Meanwhile, pentylamine has achieved 20 % and 5 % of oil and water separation, respectively.

The stability behavior for crude oil B was revealed as illustrated in Figure 4.27 and 4.28. As been seen, octylamine has removed the water and oil at 98 and 97.5 %, respectively within 24 hours left for gravity settling. The hexylamine also showed impressive results as the separation occurred were at 99 an 98 % in first day observation. Meanwhile, the other two demulsifiers which were dioctylamine and pentylamine were showed low separation where only 27 % for oil separated by dioctylamine and 36 % comes from pentylamine. Moreover, they were not efficient to separate water after seven days observation.

Figure 4.29 was depicted the results of oil separation performance for crude oil C. Referring to the graph, it was found that the performance of octylamine and hexylamine were very impressive towards oil and water phase separation. Octylamine has removed the oil and water phase at 99 % for both water and oil phase within 24 hours meanwhile hexylamine was performed after two days evaluation with 96 and 98 % oil and water separated. The separation process was very slow for emulsions with dioctylamine and pentylamine. As allocated in Figure 4.30, the emulsion was maintained stable for three days after added pentylamine in the emulsion. Then, it successfully removed only 12.5 % of oil and 1 % of water after one week observation. Dioctylamine has shows slightly separation of oil within 24 hours and the volume was constant for three days and it has removed the oil up to 25 % after seven days.

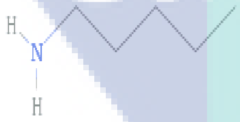
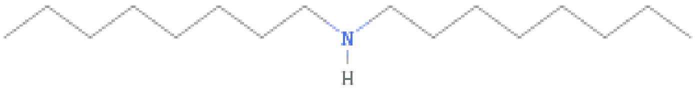
The solubility characteristics of the demulsifier has played significant role in demulsified W/O emulsion. Mat et al. (2006) has mentioned in their study that for W/O emulsion cases, the most effective demulsifiers are oil soluble or hydrophobic. This is because; oil is the continuous phase while water is the dispersed phase. Thus, the surfactants will absorb directly into the continuous phase without any resistance in optimum temperature. The results obtained show the pentylamine exhibited the lowest efficiency to separate the water and oil phases. This was due to its low solubility towards oil phase. As been explained by Lide (2005), the water solubility of simple amine is largely due to hydrogen bonding between protons in the water molecules. Lide (2005) also has mentioned that the water solubility behaviour of amine was decrease with the increased of carbon number.

Referring to Issaka (2007), an efficient oil soluble demulsifier usually decrease 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 octylamine, hexylamine, and dioctylamine, respectively. Regarding to this study, the solubility of amine group falls off as the hydrocarbon chains get longer which noticeably so after about six carbons. The small amines of all types are very soluble in water. The hydrocarbon chains have to force their way between water molecules, breaking hydrogen bonds between water molecules.

Abdurahman et al. (2007b), the descending sequence of amine demulsifier efficiency was consequent to high molecular weight factor which act as flocculants in adsorption and interaction activities. Dioctylamine and pentylamine are insoluble in water but soluble in less polar solvent like benzene, alcohol and ether. Nevertheless, octylamine and hexylamine are slightly soluble in water due to their hydrophobic chain which is shorter compared to dioctylamine and pentylamine. This factor influenced the octylamine and hexylamine demulsifiers to break the interfacial film of the droplets as well as coalescence rate increased.

The effect of molecular weight of demulsifiers on emulsion stability also studied by Wu et al. (2003) and it was found that the dewatering performance of demulsifiers increased as the molecular weight increased. Dioctylamine has the highest molecular weight compared to other four demulsifier in this group. However, its molecular weight was no longer effect on enhance the breaking process due to its high molecular weight. As been mentioned by Lochel and Watson (Undated), the smaller molecule exhibited the faster migration. The long molecular structure of dioctylamine has delayed the molecule to demulsified the emulsion. The details molecular structure of amines used were illustrated in Table 4.5.

Table 4.5: Molecular structure of amines demulsifier family used

Name	Molecular Structure
Pentylamine	
Hexylamine	
Octylamine	
Dioctylamine	

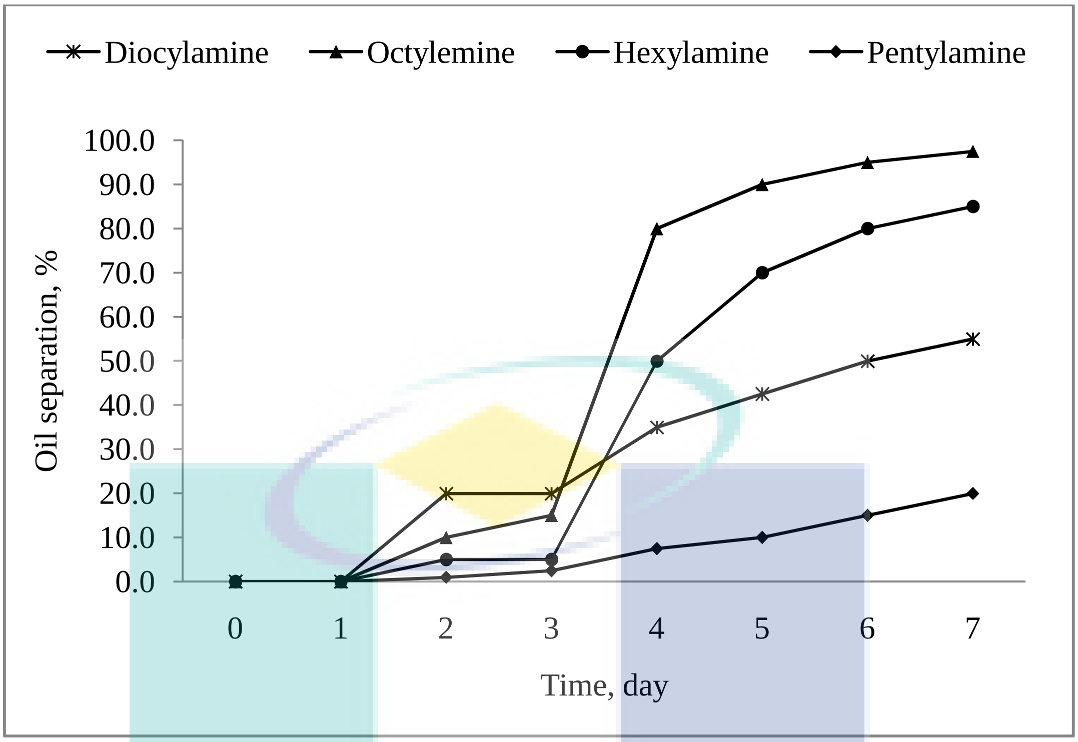


Figure 4.25: Effect of amine group demulsifiers on oil separation for crude oil A

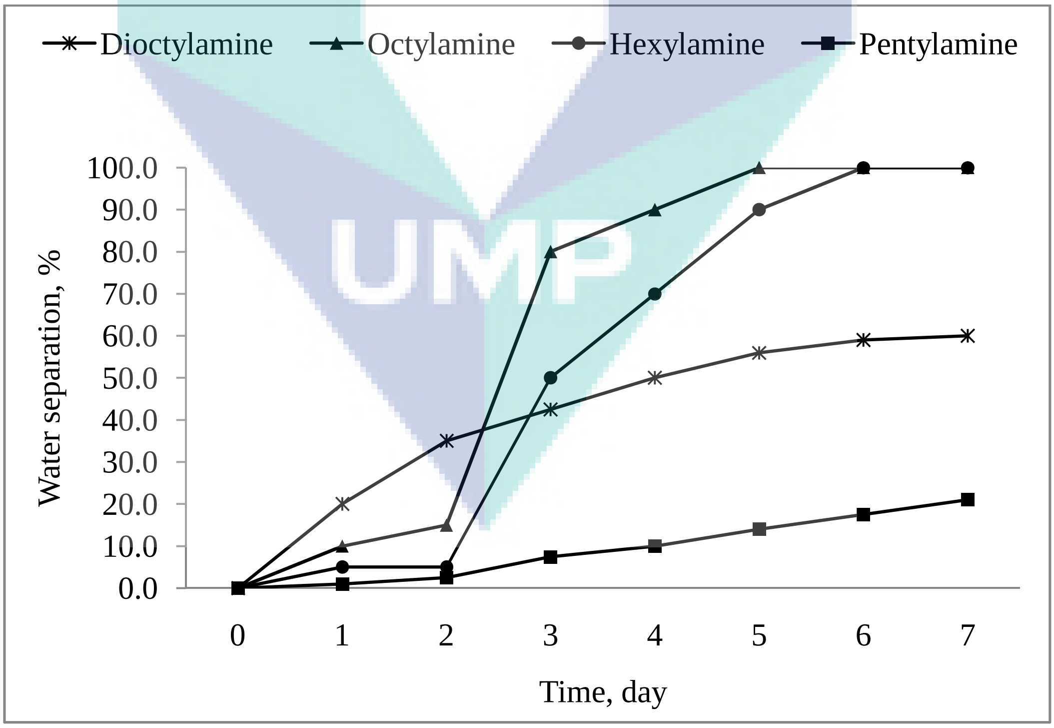


Figure 4.26: Effect of amine group demulsifiers on water separation for crude oil A

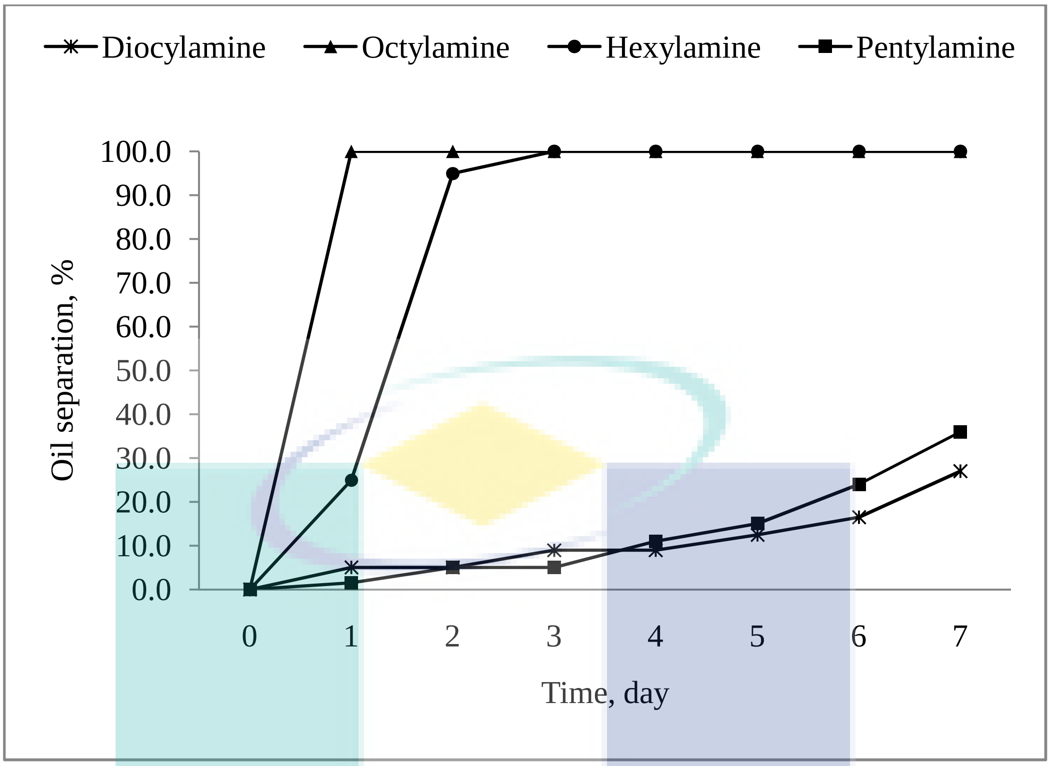


Figure 4.27: Effect of amine group demulsifiers on oil separation for crude oil B

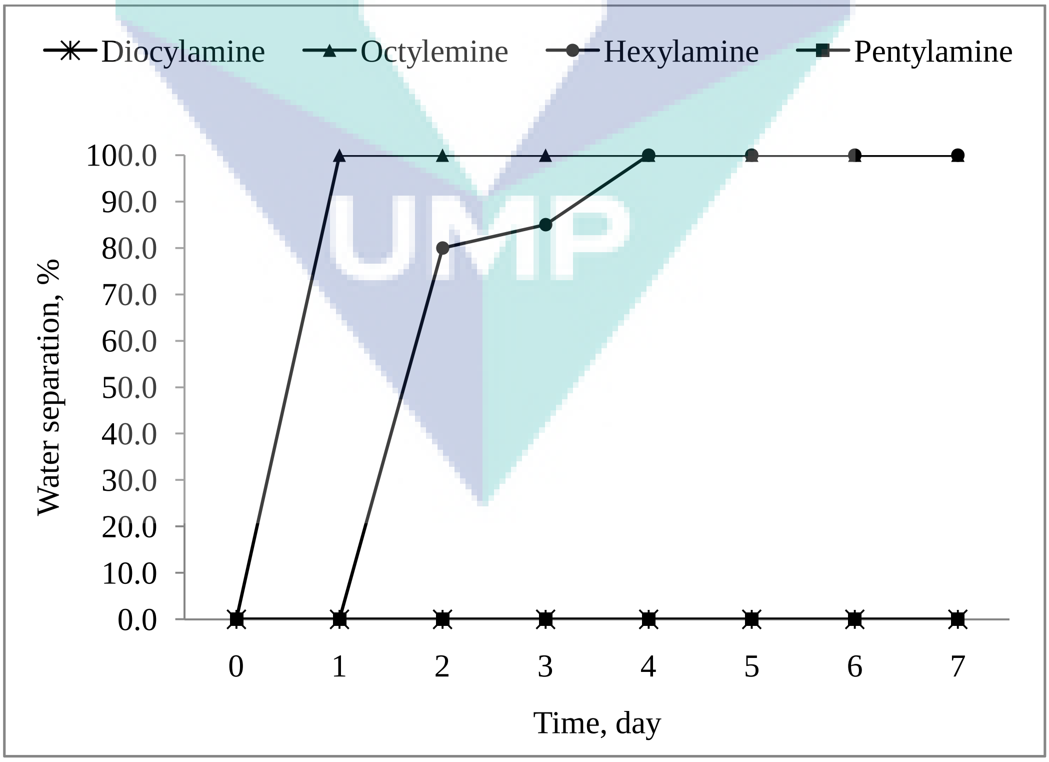


Figure 4.28: Effect of amine group demulsifiers on water separation for crude oil B

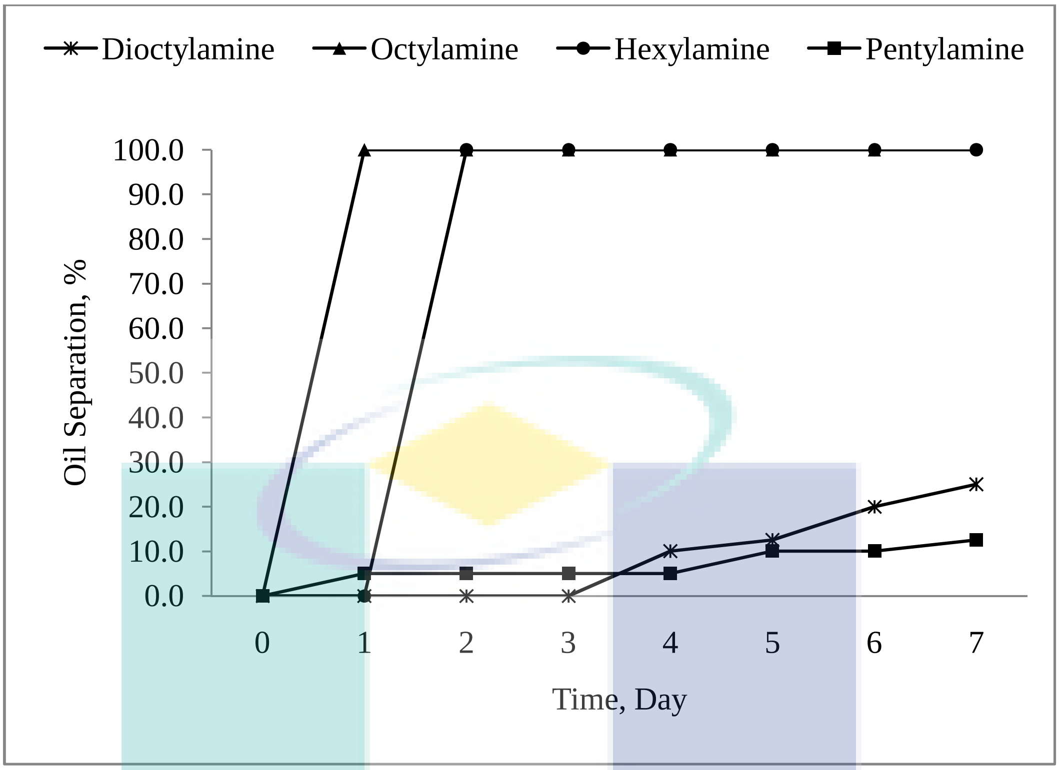


Figure 4.29: Effect of amine group demulsifiers on oil separation for crude oil C

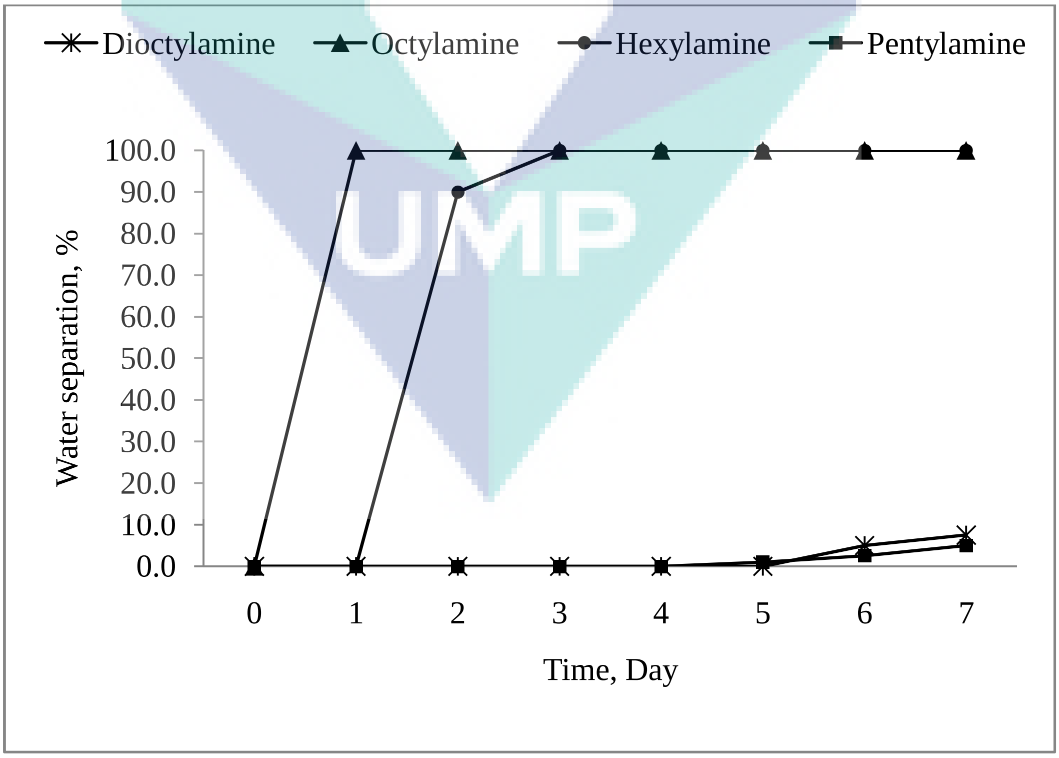


Figure 4.30: Effect of amine group demulsifiers on water separation for crude oil C

4.3.2.2 OFAT screening of polyhydric alcohol demulsifier group

The influenced of polyhydric alcohol demulsifier group also determined and the results were represented in Figures 4.32 to 4.34. There were four types of polyhydric alcohol derivatives have been used namely as PEG 300, PEG 400, PEG 600 and PEG 1000. Overall, only oil separations were observed since there is no water was removed by using this demulsifiers group.

Figure 4.32 was depicted the results obtained for crude oil A. As shown, the highest of oil volume that succeed removed was exhibited by PEG 1000 where it can separate about 30 %. Then, it was followed by PEG 600 with 25 %, PEG 400 with 20 and the less oil separated was shows by PEG 300 with 10 % resolution. Figure 4.35 has allocated the results for crude oil B. Crude oil B has gained the similar trends where PEG 1000 has became as the best demulsifier among polyhydric alcohol group which can achieved till 45 % of oil phase separation. Then, PEG has shows 20 % followed by PEG 400 and PEG 300 with 15 and 9 % of oil resolution. This effect was also performed by crude oil C as results plotted in Figure 4.36. PEG 1000 has dominated in oil separation performance where 12.5 % oil was removed from the emulsion. The emulsion was maintained stable for five days after added PEG 300. The breaking process occurred very slowly with PEG 300 and only 1 % of oil was successfully removed after a week evaluation.

The descending in percentage of oil separated could be explained based on its characteristic where this group acts as water soluble. The solubility property is related to HLB number for each demulsifier. PEG 1000 has HLB value as 16, meanwhile 13.2, 12 and 10 is belonging to PEG 600, PEG 400 and PEG 300, respectively. Since the value is over 9, they were carried more hydrophilic parts compared to lipophilic parts.

Figure 4.31 shows the basic molecular structure of polyethylene glycol and it was found that there have hydroxyl groups (OH) in the structure. Generally, polyhydric alcohol was contained hydroxyl group as a functional group of alcohol. This functional group was containing an oxygen atom connected by a covalent bond to a hydrogen atom. The hydroxyl group makes the alcohol molecule polar. This characteristic have been discussed by Abdurahman et al. (2007b) which have explained that the polar molecules are attracted to hydroxyl group by hydrogen bonding at hydrogen bonding that occurred between hydrogen of water molecule and the oxygen in the alcohol molecule. Thus, the addition of hydroxyl group to a compound makes it more soluble in water.

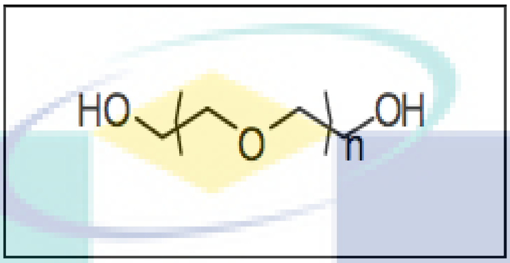


Figure 4.31: Polyethylene glycol molecular structure

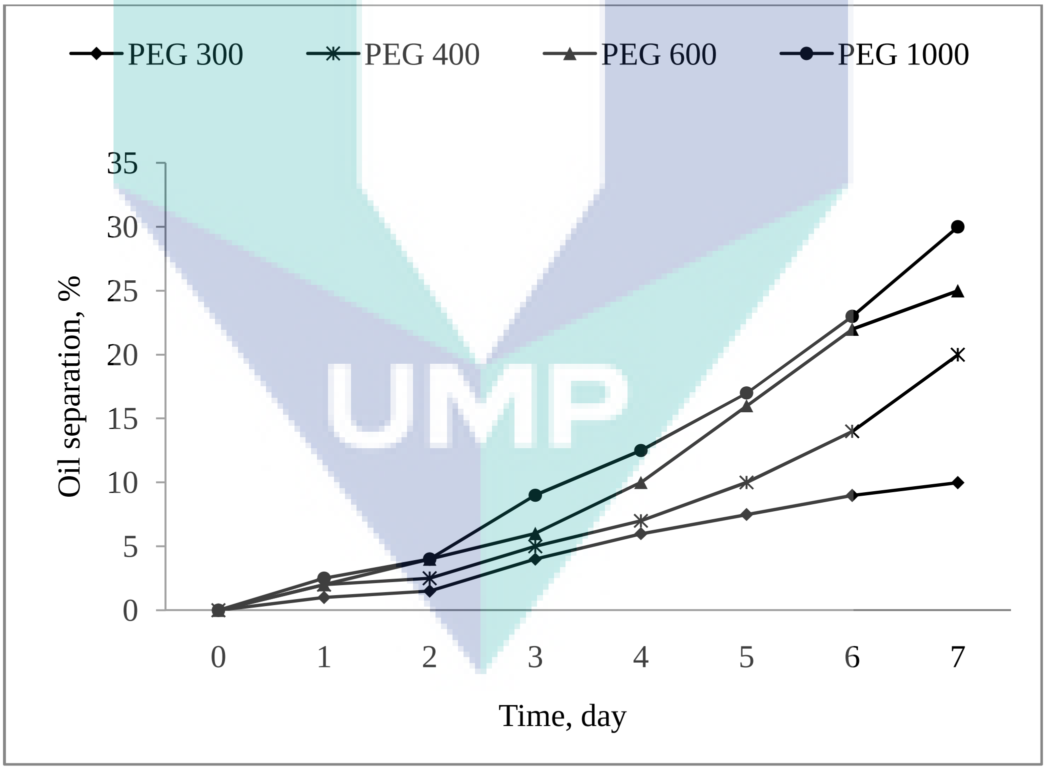


Figure 4.32: Effect of polyhydric alcohol group on oil separation for crude oil A

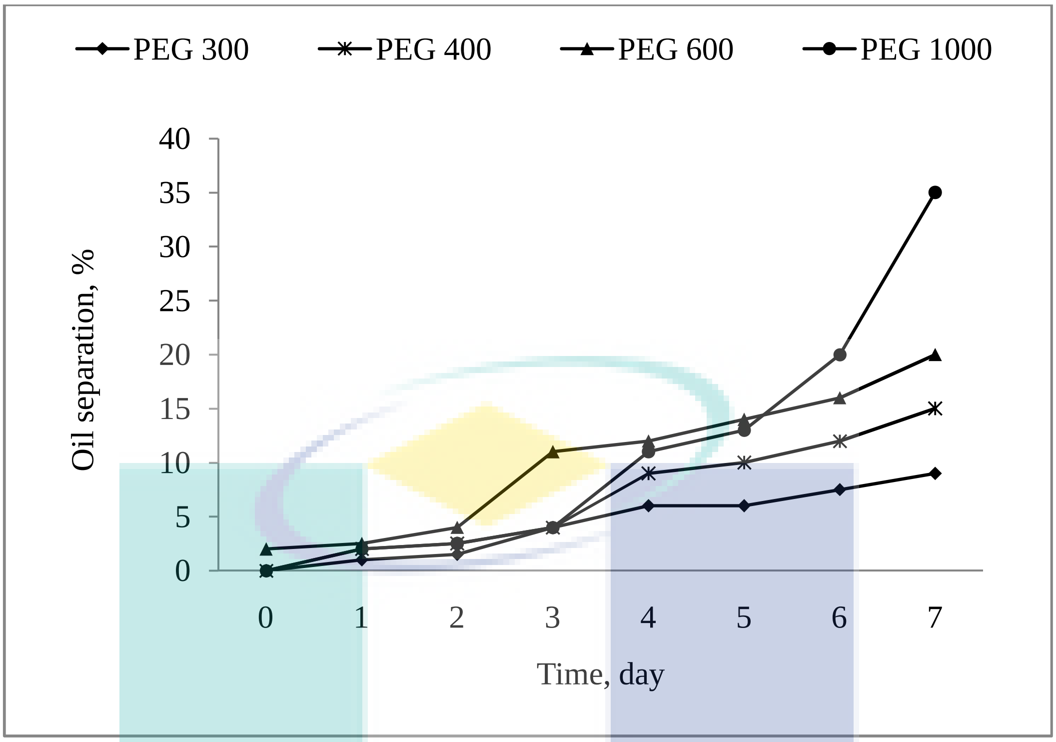


Figure 4.33: Effect of polyhydric alcohol group on oil separation for crude oil B

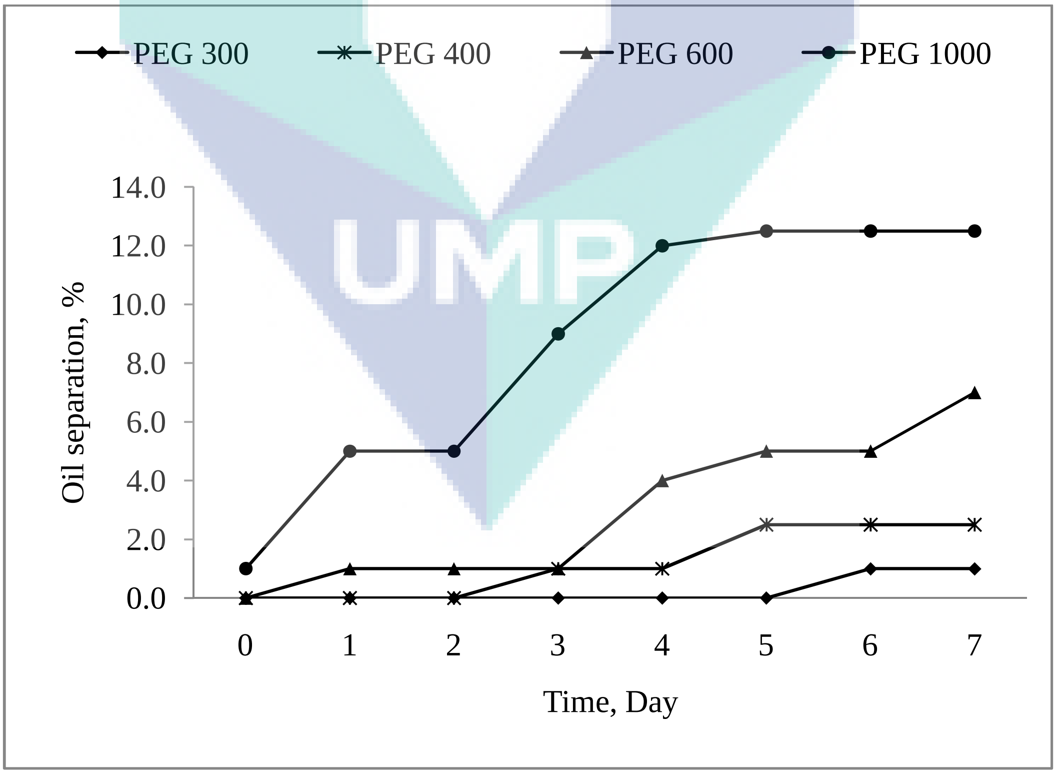


Figure 4.34: Effect of polyhydric alcohol group on oil separation for crude oil C

4.3.2.3 OFAT screening of natural demulsifier group

The effect of adding palm based oleyl amine (PBOA) and coco amine from natural demulsifier group was presented in Figure 4.35 to 4.40. This demulsifier group was observed very efficient in oil-water removal. From Figures 4.35 and 4.36, it was found that PBOA has lead the oil and water separation and almost completely break up the emulsion from crude oil A within four days. From the observation found that PBOA can remove 99 % of water and oil phase at the end of observation period. Meanwhile, coco amine has taken six days to form two layers with 98 and 95 % of oil and water removal, respectively. As can be seen in Figure 4.37, the emulsion from crude oil B was started to deform less than 24 hour and after two days, the emulsion was rapidly destabilized and almost fully broken at day-6 for both demulsifiers. The water separation performance for crude oil B was allocated in Figure 4.38. Based on the graph, the destabilization rate of water phase was drastically occurred within two days. PBOA was 99 % remove the water phase at day-4 meanwhile coco amine was 99 % separated at day-5. Impressive results also performed by crude oil C as plotted in Figure 4.39 and 4.40. PBOA has exhibited good performances in breaking emulsion where it has lead the water separation as early as day-3 compared to coco amine which was performed at day-5. From the experimental work, the emulsions were almost completely separated the water and oil phase with 99 and 97.5 % of oil and water separated. They were clearly deformed into two layers after seven days evaluation.

PBOA and coco amine have shows their capability to enhance the coalescence of the droplets. Both demulsifiers were behaved as oil soluble since the HLB value was below than 9. Thus, PBOA and coco amine can dissolve in continuous phase easily and adsorbed into the droplets film through the Brownian diffusion. As been explicated by Djuve et al. (2001), the adsorption of demulsifier onto the droplets film causes interfacial gradient set up and leads the film drainage. Consequent to this phenomenon, the film becomes thin and induces the film rupture.

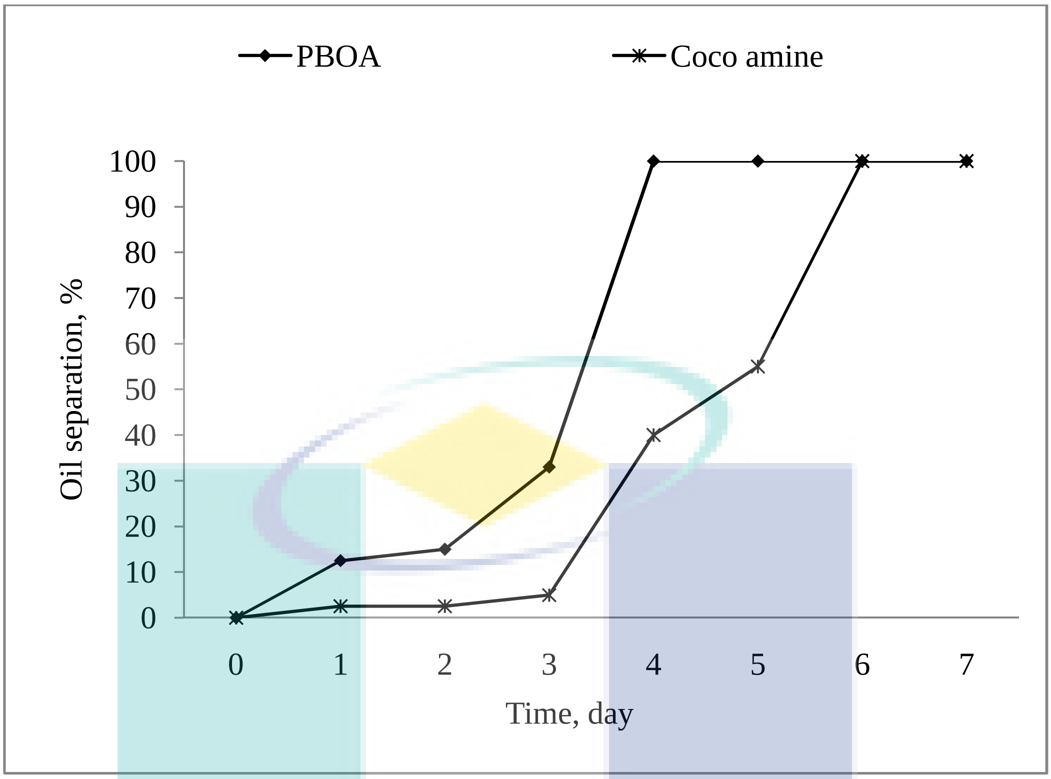


Figure 4.35: Effect of natural group demulsifiers on oil separation for crude oil A

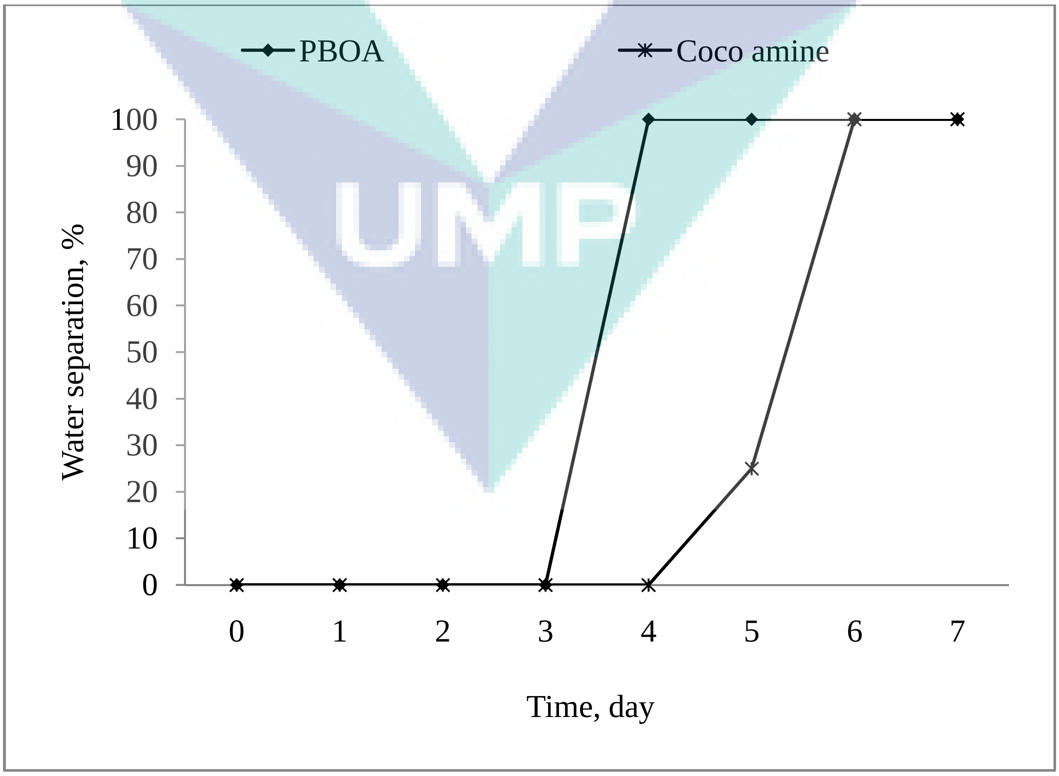


Figure 4.36: Effect of natural group demulsifiers on water separation for crude oil A

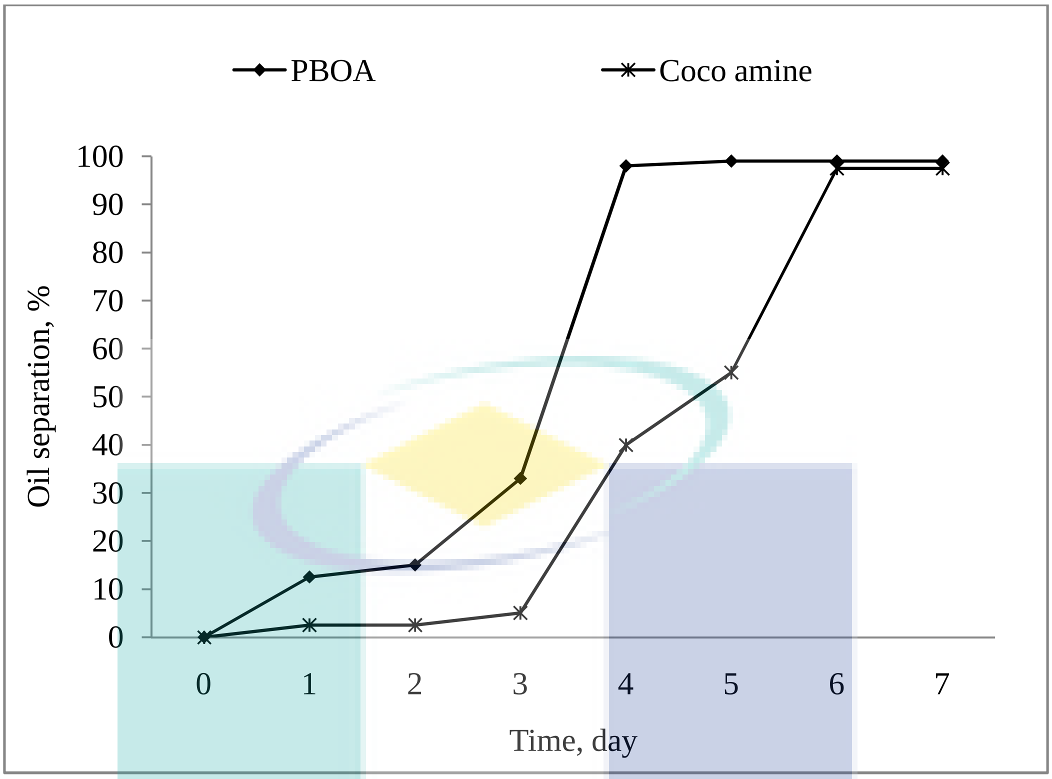


Figure 4.37: Effect of natural group demulsifiers on oil separation for crude oil B

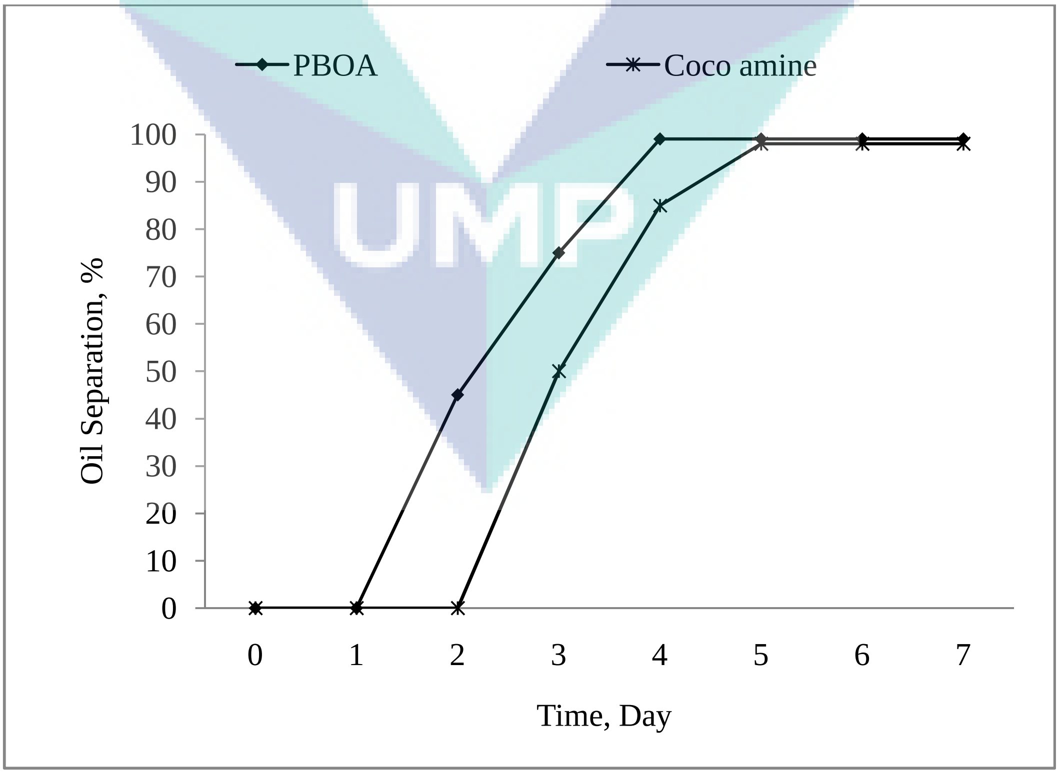


Figure 4.38: Effect of natural group demulsifiers on water separation for crude oil B

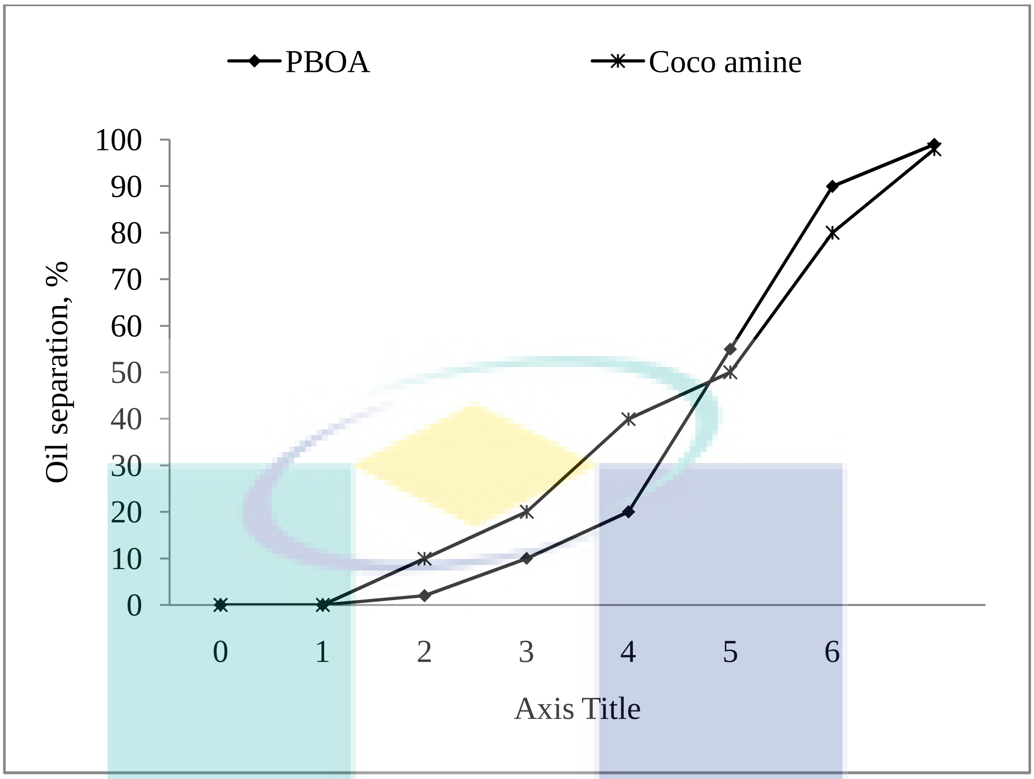


Figure 4.39: Effect of natural group demulsifiers on oil separation for crude oil C

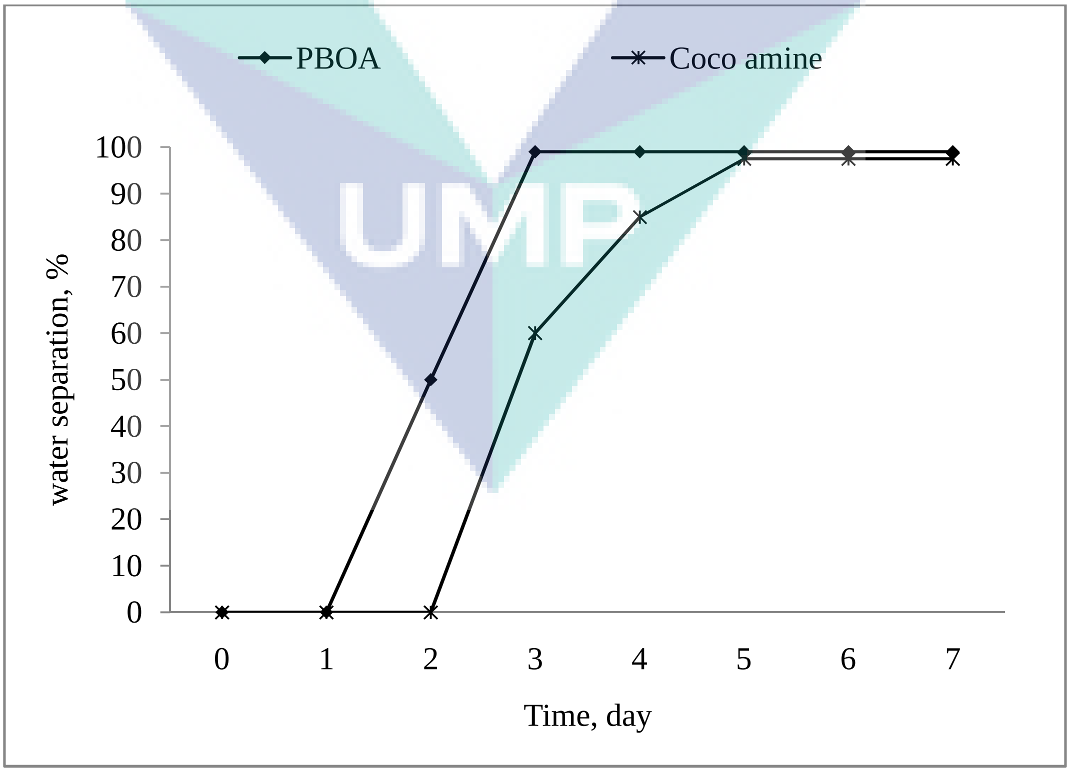


Figure 4.40: Effect of natural group demulsifiers on water separation for crude oil C

4.3.2.4 OFAT screening of alcohol demulsifier group

Destabilization of W/O emulsion using alcohol demulsifier group was studied by varied the alcohol derivatives. There were three derivatives have been used namely ethanol, butanol and heptanol.

Figure 4.41 has indicated the results obtained for crude oil A. The result shows that heptanol has removed 27 % of oil phase from the emulsion and meanwhile, butanol and ethanol have separated 20 and 16 %, respectively. As well as results for crude oil B where heptanol was again showed high separation compared to butanol and ethanol. As can be seen in Figure 4.42, the highest oil separated was shown by heptanol (25 %) followed by butanol and ethanol with 19 and 13.5 % oil separated, respectively. Crude oil C also has similar performance with other two crude oils. The results obtained has been plotted in Figure 4.43 where heptanol has leads the destabilization process and followed by butanol and ethanol with respect to 20, 17.5 and 10 % of oil separation, respectively.

The results obtained can be explained based on solubility properties, where the solubility of alcohols was related to the molecular weight. As been noted by Abdurahman et al. (2007c), alcohol with low molecular weight is more soluble towards water while, low water solubility was exhibited by alcohol with four carbons and higher. Mahmood (2009) also has stated that the short chain alcohols are very soluble in water and long chain alcohols are very soluble in oil phase. Cotton (undated) has noted that, alcohols with more than four carbons were usually less soluble due to the longer carbon chain is more nonpolar. Table 4.6 has illustrated the molecular structure of alcohol demulsifier family used. The length of the carbon chains were clearly observed from the molecular structure.

This can be explained by considering the way that water molecules can disperse solute molecules into a solution. The polar water molecules are attracted to the hydroxyl group (OH) by hydrogen bonding that occurs between the hydrogen of water molecules and oxygen in the alcohol molecules. As the hydrogen portions of the alcohol become more extensive, they would be in higher molecular weight.

Table 4.6: The molecular structure of alcohol demulsifier family used

Name	Molecular Structure
Ethanol	
Butanol	
Heptanol	

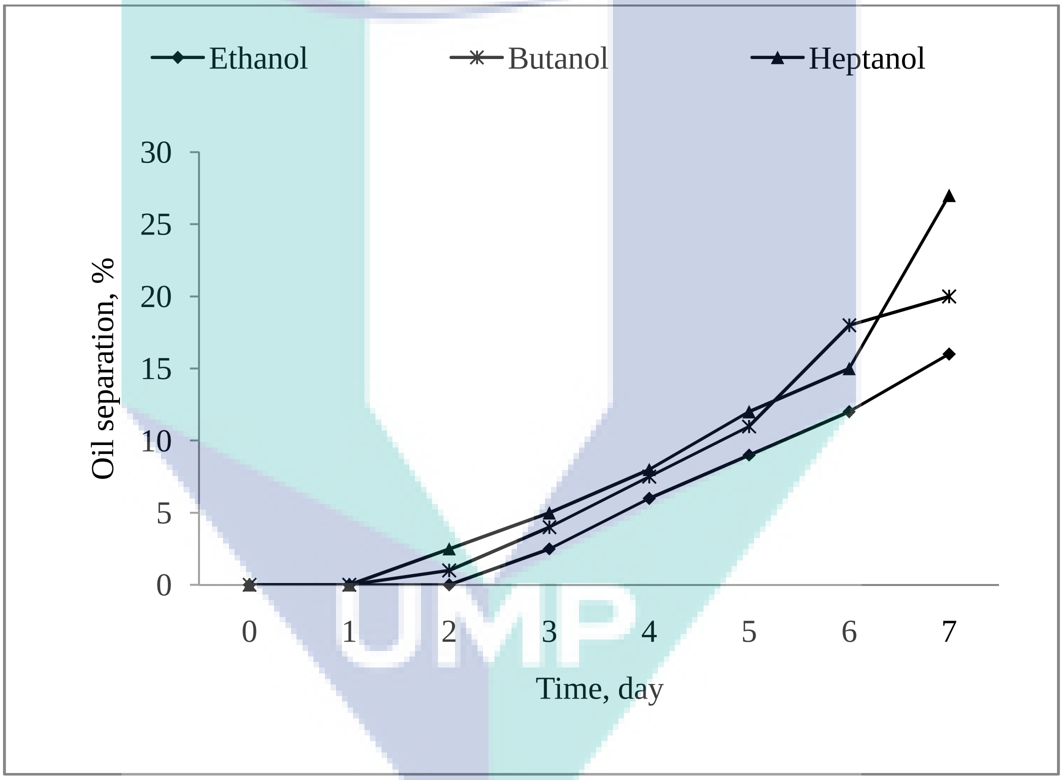


Figure 4.41: Effect of alcohol group demulsifiers on oil separation for crude oil A

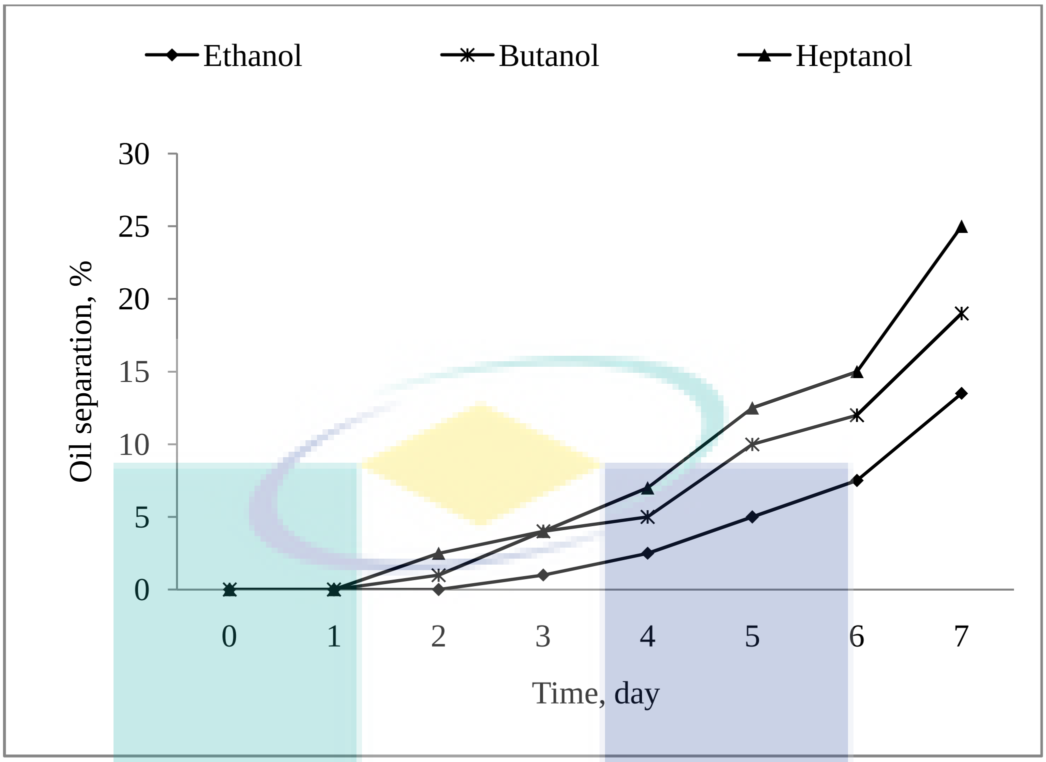


Figure 4.42: Effect of alcohol group demulsifiers on oil separation for crude oil B

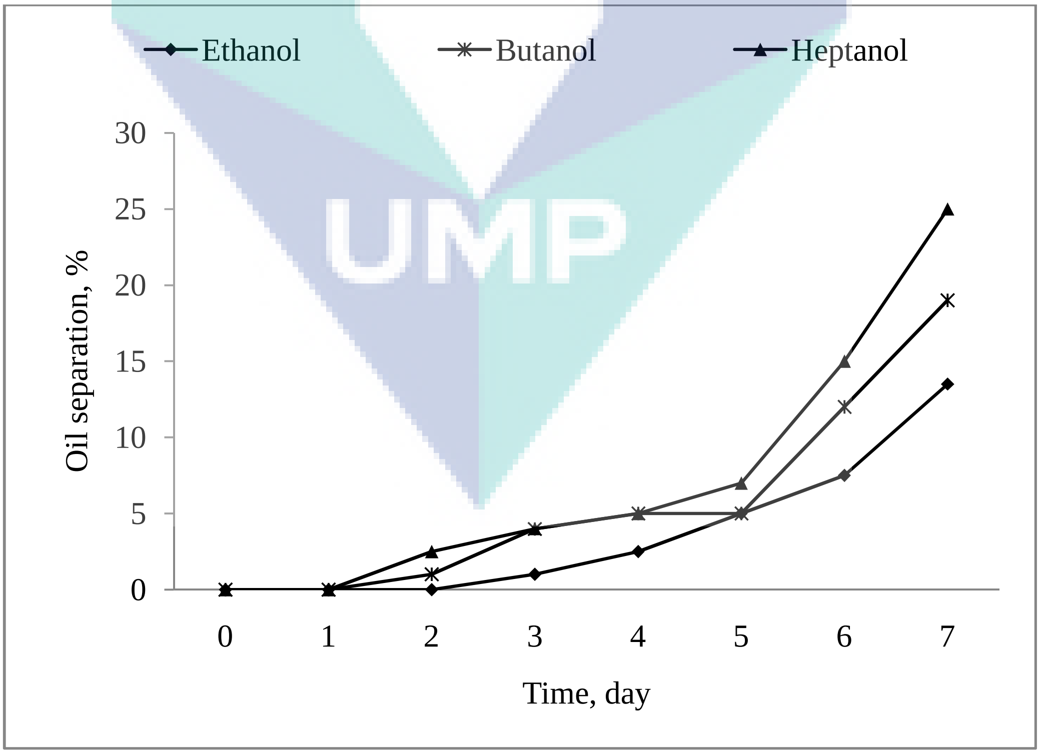


Figure 4.43: Effect of alcohol group demulsifiers on oil separation for crude oil C

4.3.2.5 Comparison between demulsifiers group

This part was to evaluate and select the best demulsifier among four demulsifier groups that have been discussed earlier. The comparison criteria were based on the performance of demulsifier to destabilize W/O emulsion into water and oil phase and the shorter time taken to achieve 80 % of separation in both phase. The best demulsifier for each group were selected to be compared in order to accomplish the optimization of chemical demulsifier. According to the OFAT studies on demulsifier group's performance, there were four demulsifiers selected namely as octylamine, PEG 1000, heptanol and PBOA.

Overall, octylamine and PBOA has shown separation in both phase for crude oil A, B and C. Besides, PEG 1000 and heptanol only can separate oil phase from the emulsion. Thus, based on the criteria needed octylamine and PBOA were considered to be carried for optimization stage whereas PEG 1000 and alcohol were eliminated.

Octylamine and PBOA were grouped as oil soluble demulsifier which is suitable for W/O destabilization. This behavior has influenced them to dissolve into continuous phase. Hence, octylamine and PBOA have performed well in destabilization of W/O emulsion by showing 100 % separation of oil and water. However, the duration times taken for each demulsifier to separate were differed. As can be seen in Figure 4.44 till 4.49, octylamine has taken shorter period to start coalescence compared to PBOA. This means octylamine has fulfill the criteria needed and be selected for optimization stage.

As been mentioned earlier, molecular weights of the demulsifiers have given a significant effect on breaking down the stable emulsion. The molecular weight of PBOA was 267.49 g/mole and octylamine was 129.25 g/mole. However, PBOA and octylamine have exhibited opposite behavior. The high molecular weight of PBOA was results the slower coalescence rate. This phenomenon might be because of slow migration rate of PBOA to the droplets interface compared to octylamine.

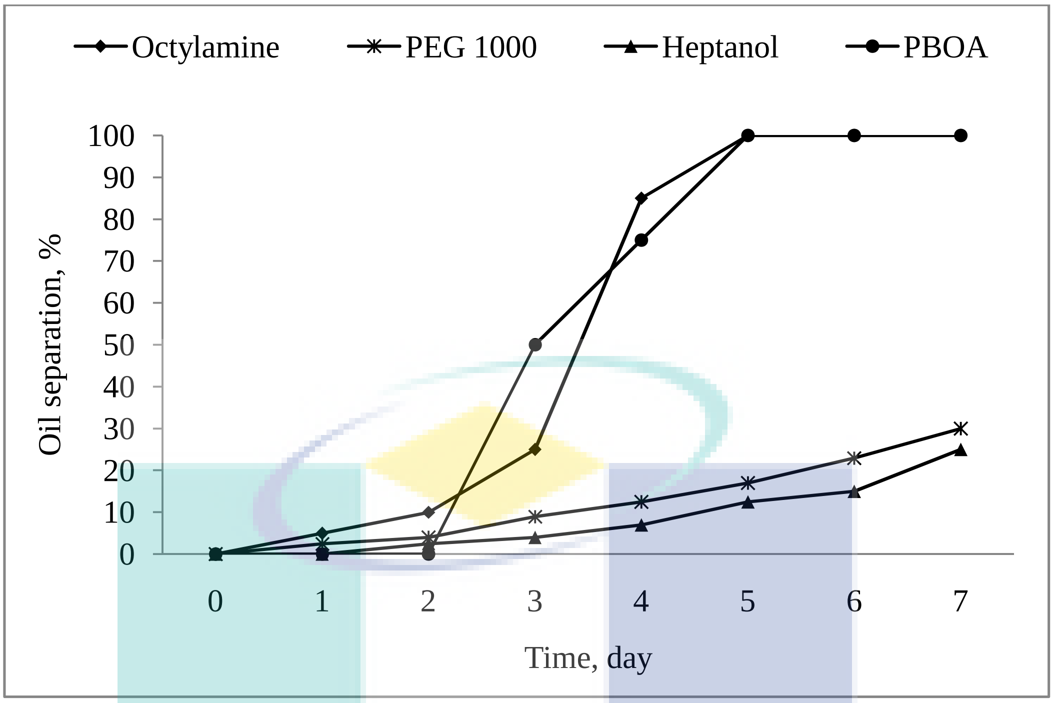


Figure 4.44: Comparison of oil separation performance between octylamine, PEG 100, heptanol and PBOA for crude oil A

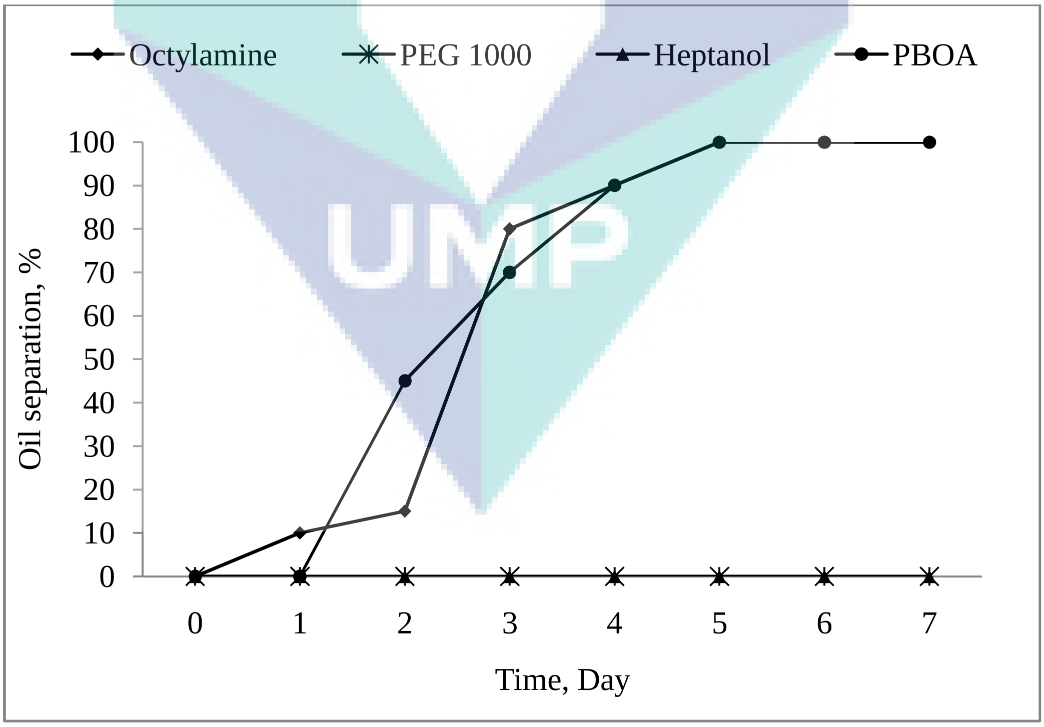


Figure 4.45: Comparison of water separation performance between octylamine, PEG 100, heptanol and PBOA for crude oil A

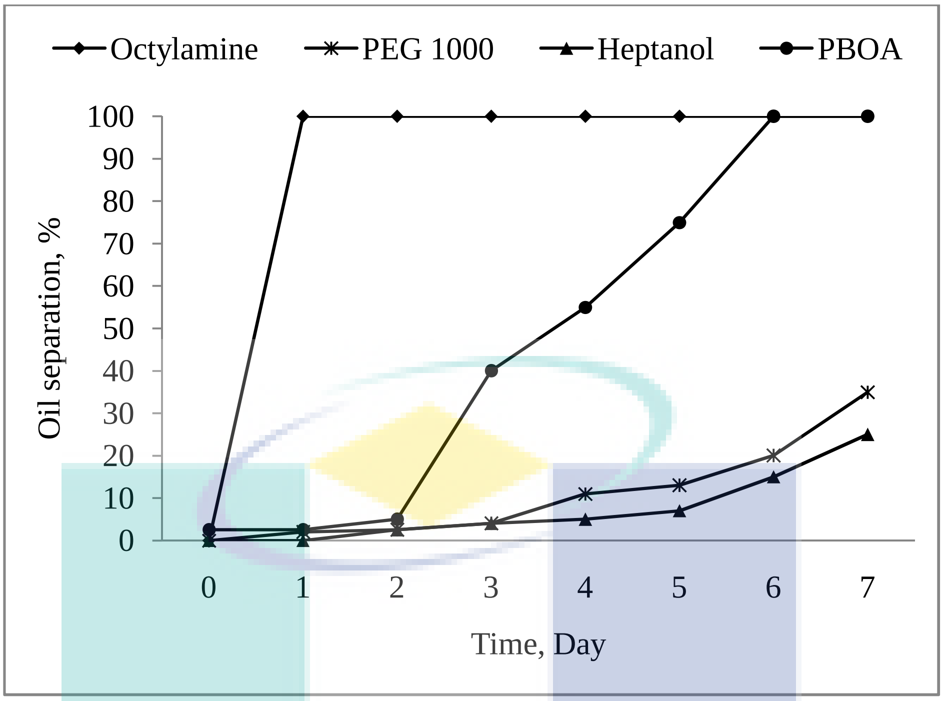


Figure 4.46: Comparison of oil separation performance between octylamine, PEG 100, heptanol and PBOA for crude oil B

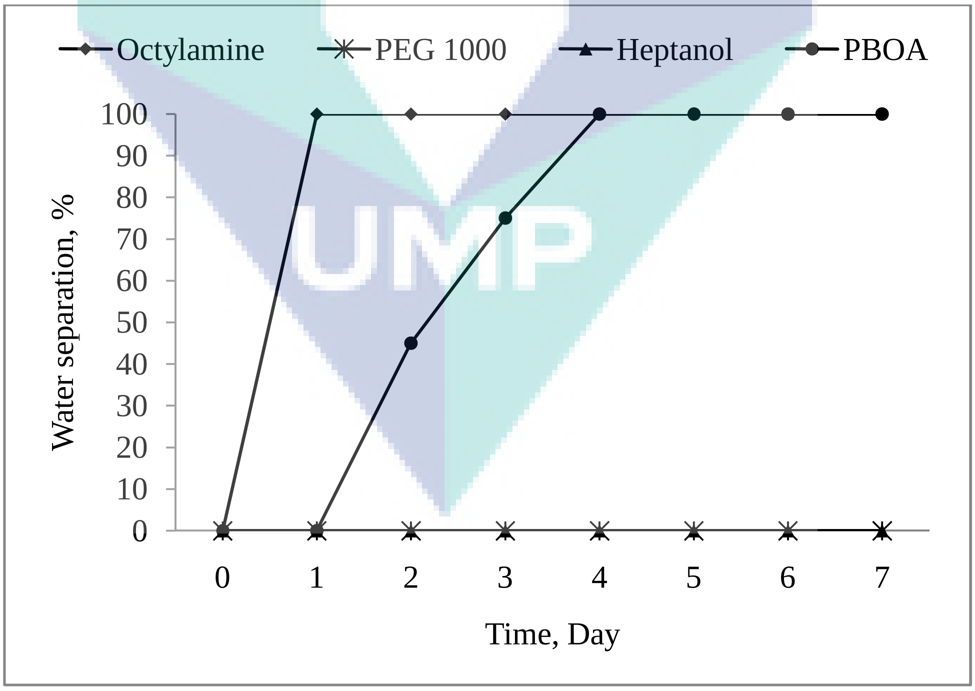


Figure 4.47: Comparison of water separation performance between octylamine, PEG 100, heptanol and PBOA for crude oil B

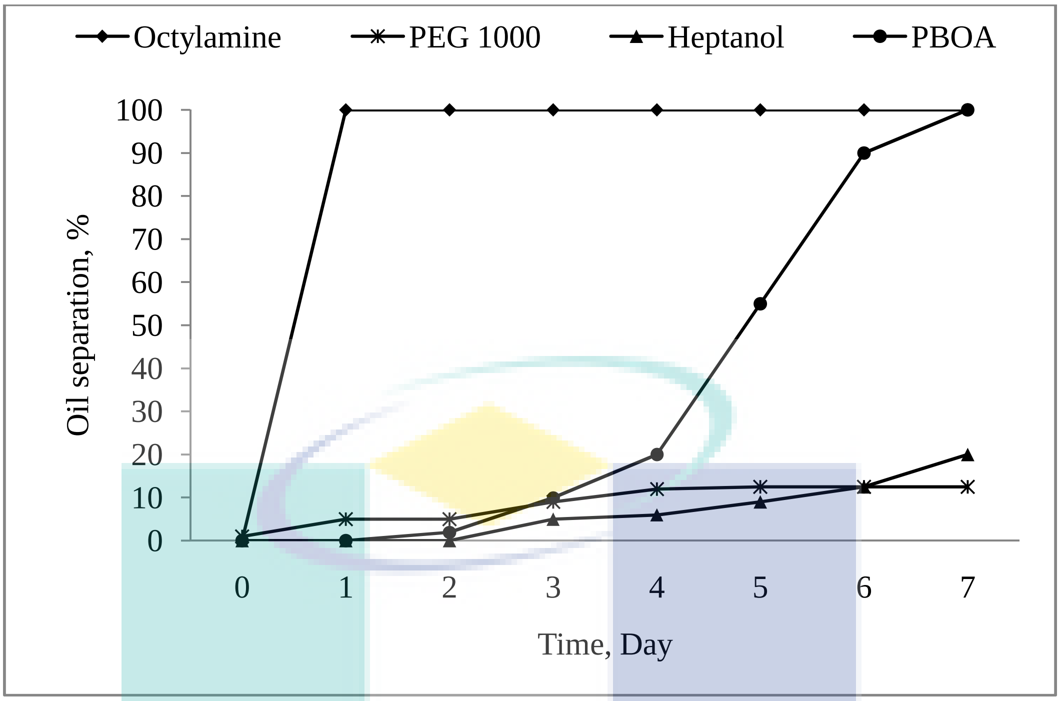


Figure 4.48: Comparison of oil separation performance between octylamine, PEG 100, heptanol and PBOA for crude oil C

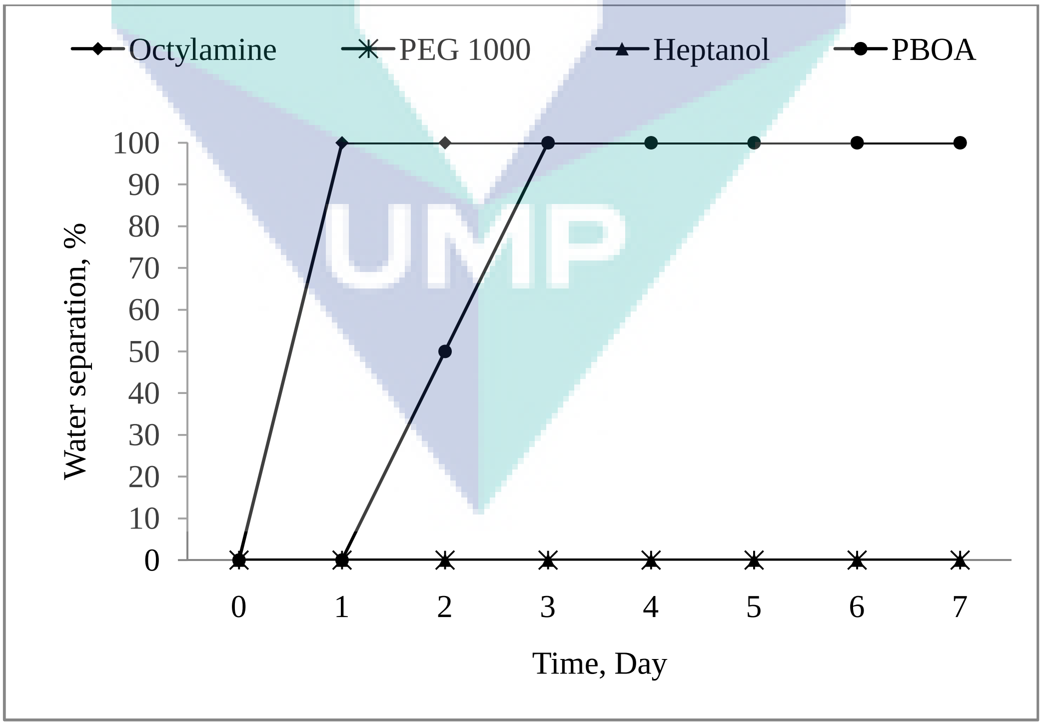


Figure 4.49: Comparison of water separation performance between octylamine, PEG 100, heptanol and PBOA for crude oil C

4.3.2.6 Effects of different concentrations of demulsifiers

The previous test has revealed the efficiency of each demulsifier on water-oil removable from W/O emulsion. From those tests, octylamine was found as the best demulsifier and it was carried out for used in concentration changes effect test. This test was conducted by varied the concentration as low as 0.5 w/w % to 3.0 w/w %. The demulsification was done by agitated the stable W/O emulsion at 2000 rpm within 3 minutes under ambient temperature.

Figures 4.50 and 4.51 illustrated the oil results of demulsification experiments conducted to test the influence and performance of octylamine at different concentration on the emulsion stability for crude oil A. The figures depicted the separation of oil and water from W/O emulsion as function of time, respectively. As can be seen, the concentration of demulsifier has influenced the emulsion breaking performance. The slowest demulsification rate was showed at concentration of 0.5 w/w % octylamine where only 3.2 % oil and 6 % of water separated. The breaking rates were increased as the concentration increase. The total amount of oil separated at 2.0 w/w % was almost 90.4 % meanwhile water removed was 92 %. The results were shown the highest separation for crude oil A. However, when the concentration was increased to 2.5 and 3.0 w/w %, the separation became slower and less separation occurred.

Figures 4.52 and 4.53 show the results obtained for crude oil B. According to the both graphs, it was found that the increases of concentration of octylamine, has exhibited high separation of water and oil phase. The amount of water separated was achieved till 90 % and 86 % of oil removal. The separation process became slower as the concentration over 2.0 w/w %. The figures have showed that at 2.5 w/w %, the separation occurred was 32.8 and 11.8 % for oil and water separation, respectively. The same trend was exhibited by emulsion added with 3.0 w/w % of octylamine.

The results for oil and water removal from the W/O emulsion for crude oil C was represented in Figures 4.54 and 4.55. This crude oil also showed the same behavior with other two crude oil samples, but it’s taken more time to start breaking. The results obtained have shown that the highest separation was performed by emulsion with 2.0

w/w % of octylamine. Both water and oil separation was achieved over 80 %. The emulsion breaking process looked slower when the concentration of octylamine below than 2.0 w/w %. Nevertheless, the destabilization of the emulsions was unsuccessful as the concentration is over this level. The water and oil separated at 2.5 and 3.0 w/w % were decreased as a function of time compared to 2.0 w/w % octylamine.

Kim et al. (2002) have explained the effect of various dosages of breaking agent on emulsion stability. In demulsification process, droplets were approached and flocculated each other and the thickness of the film between the droplets decreases. The drainage tends to increase the concentration of the natural surfactant molecule such as asphaltenes outside the film along the droplet surface and drive the surfactants molecules from the inside to the outside the film.

Too little of demulsifier will leave the emulsion unresolved. In contra, high concentration of demulsifier may be detrimental to the treatment process. Since the demulsifier are also surface active agent like the emulsifiers, an excess quantity of demulsifier may also produce very stable emulsion where the demulsifier simply replaces the natural emulsifier at the interface (Kokal, 2002).

Peña et al. (2005) have revealed that addition of demulsifiers beyond the optimum resulted in an increased of the stability of the emulsion, probably due to the formation of a new stabilizing film in which the excess of demulsifier would play the significant role. According to the experimental works, it was found that 2.0 w/w % of octylamine has performed high resolution. At the concentration above that point, low resolution occurred. Thus, 2.0 w/w % of octylamine was determinate as optimum concentration for this works.

As can be seen in the results obtained, all emulsions showed slower in emulsion breaking rate below 2.0 w/w % of octylamine. This phenomenon was expected correlated to CMC. The relation between CMC and emulsion stability has also been found by Fan et al. (2009) in their demulsification studies. They have mentioned that these concentrations may correspond to the onset formation of demulsifiers micelles in the continuous phase.

Al-Otaibi et al. (2003) have stated that, the demulsifier acts to neutralize the effect of the emulsifying agent, freeing more water drops from the surrounding interfacial. The excessive use of demulsifier can decrease the surface tension of water droplets and actually create more stable emulsion, which difficult to treat.

According to the experimental work, it was found that the concentration was indicative of the efficiency of the demulsifiers. However, the smaller the concentration required for the given effect, the more efficient the demulsifier and betters the economics of the separation process (Efeovbokhan et al., 2010).

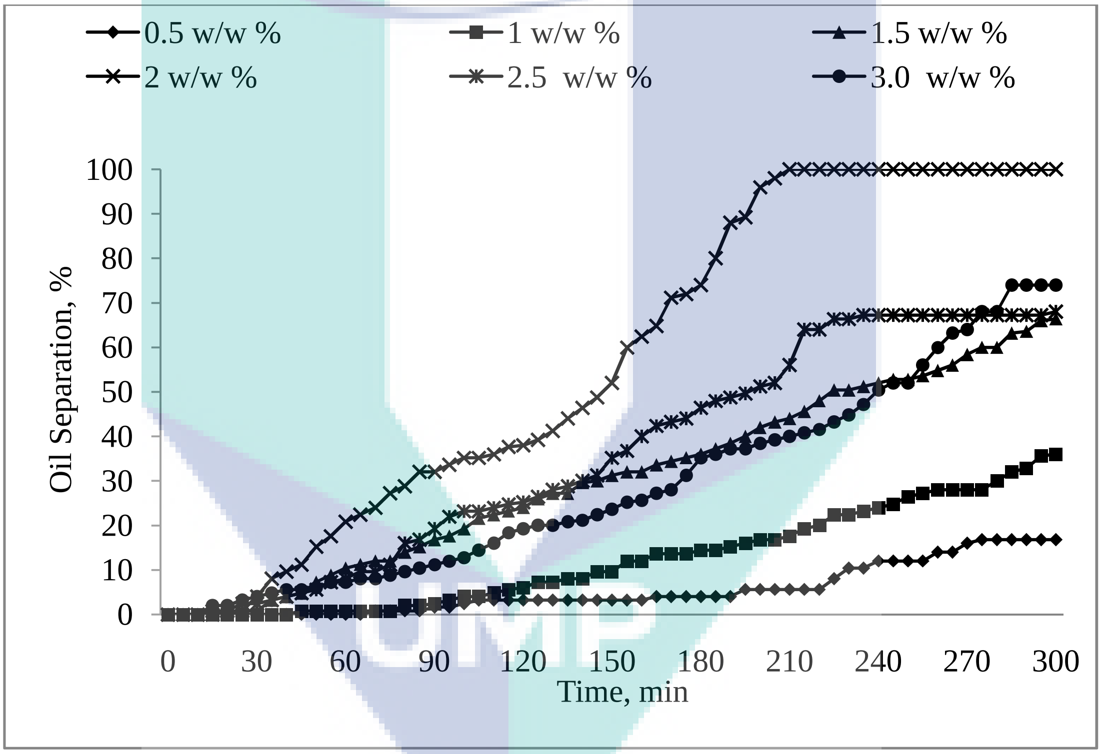


Figure 4.50: Oil separation at various concentration of octylamine for crude oil A

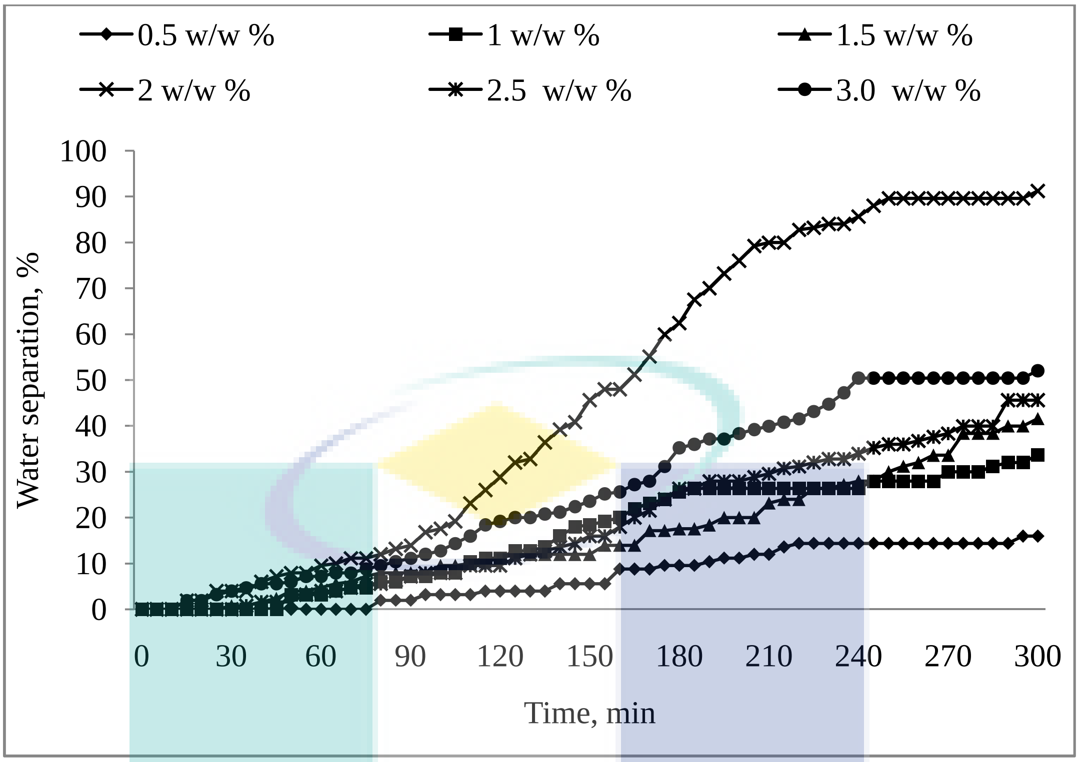


Figure 4.51: Water separation at various concentration of octylamine for crude oil A

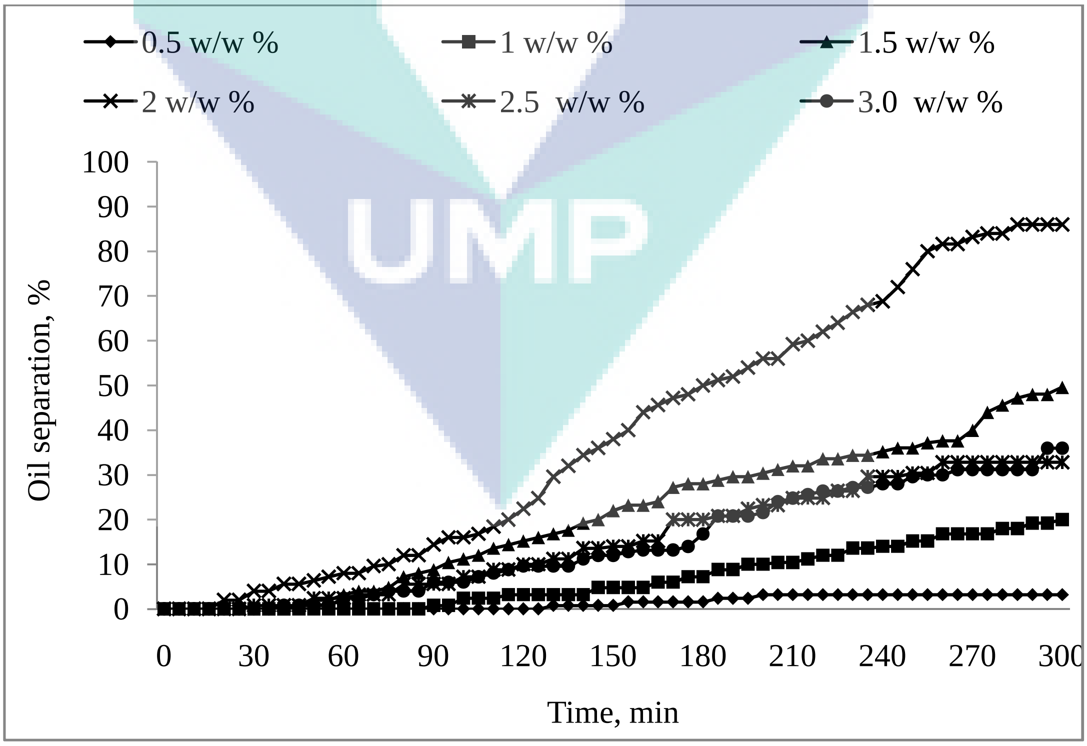


Figure 4.52: Oil separation at various concentration of octylamine for crude oil B

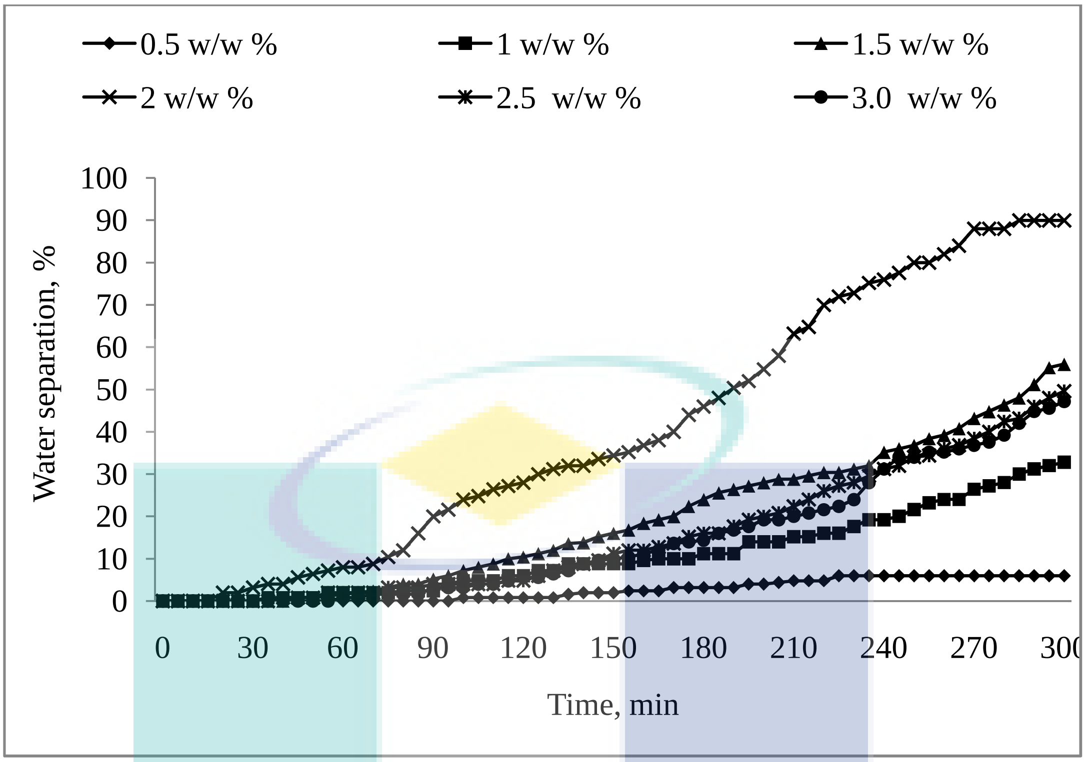


Figure 4.53: Water separation at various concentration of octylamine for crude oil B

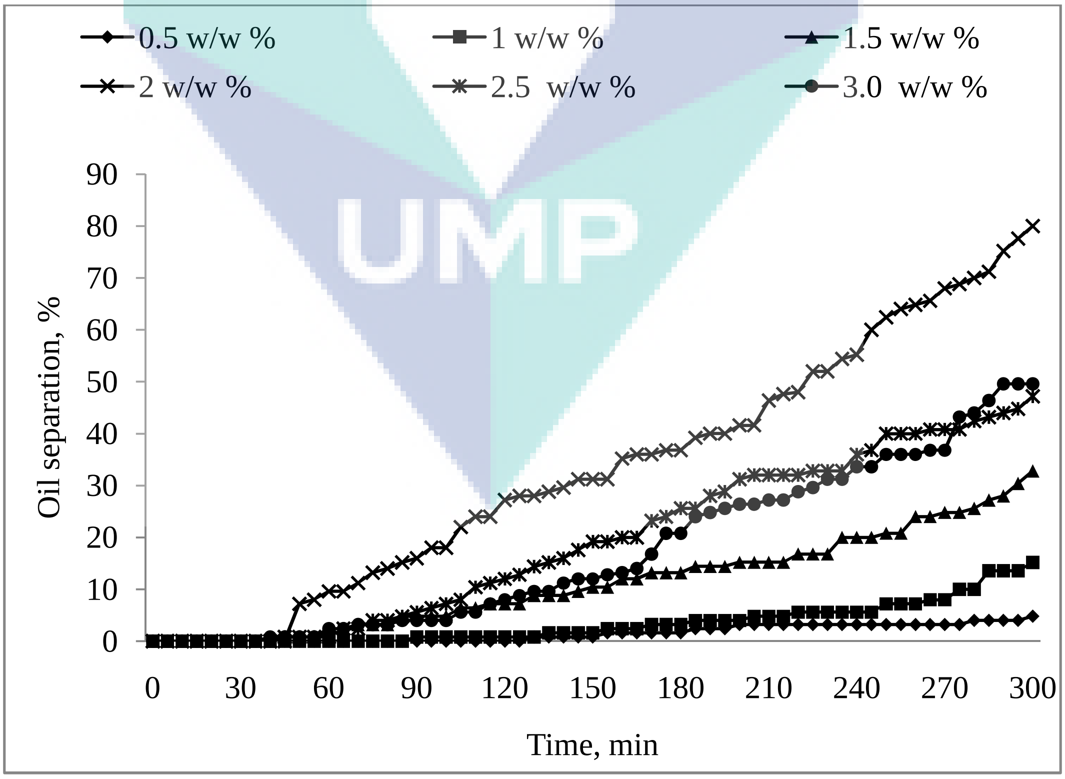


Figure 4.54: Oil separation at various concentration of octylamine for crude oil C

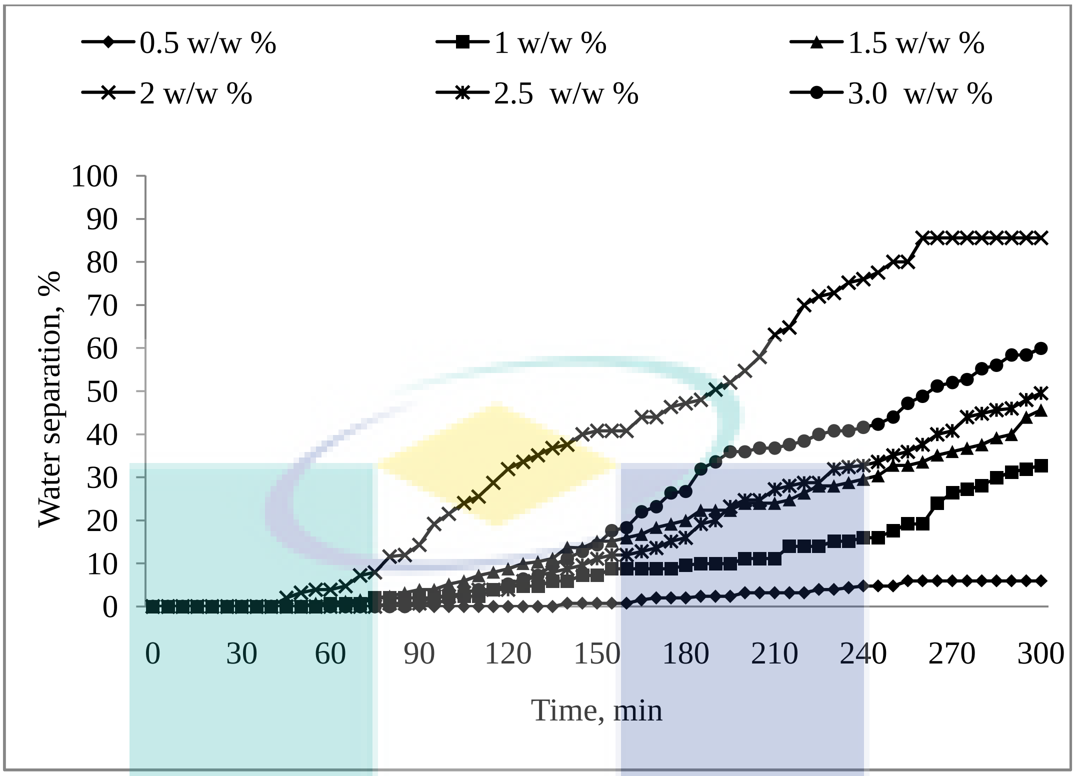


Figure 4.55: Water separation at various concentration of octylamine for crude oil C

4.4 OPTIMIZATION OF CHEMICAL DEMULSIFIER

Single demulsifiers that performed the best performance was selected from the preliminary study on demulsifiers effectiveness. Octylamine was shown good separation on water and oil compared to others. Thus, this demulsifier was carried out for optimization study in order to obtain an optimum condition to break down the emulsion with successful. An ideal experimental design was carried out based on Central Composite Design (CCD) with Response Surface Methodology (RSM). CCD and RSM were established with the assist of the Design Expert 6.0.8 software program. RSM was utilized to evaluate the effect of process variables and their interaction towards the attainment of their optimum conditions.

The two independent variables considered in this study were concentration of octylamine (A) and processing time (B), which was presented in Table 4.7. As illustrated in Table 4.7, the concentration variable was varied between 0.5 to 2.0 w/w percent and processing time variable was proceeded by varied the time consumes between 1 to 3 minutes. The determination range was based on preliminary experiments. This table was represented the independent variables for crude oil A and B.

Table 4.7: Independent variables of CCD design

	Name	Units	Low Level	High Level
A	: Concentration Octylamine	w/w %	0.5	2
B	: Processing time	minute	1	3

4.4.1 Response Surface Methodology (RSM) for Crude Oil A

A total of 13 runs of CCD experimental design and response based on the experimental runs were shown in Table 4.8. The models were considered as second order model for transistor gain data. The results tabled in Table 4.8 revealed that the relative effect of concentration as an operating parameter on water separation was clearly significant. The observed percent of water removal efficiencies varied between 13.6 and 96.8 %. The lowest water separation was exhibited at lower demulsifier dosage (Run 4). Run 1, 2, 3, 5, 9, 10 and 11 exhibited great separation of water with separation exceed 80 % as required.

Table 4.8: Response values for different experiment conditions for crude oil A

Run	**Factor 1 A: Concentration w/w %**	**Factor 2 B: Processing Time minute**	**Water Separation, %**	
			Predicted Response, Y_p	**Actual Response, Y_a**
1	1.25	2.00	85.28	88.00
2	2.00	1.00	89.72	92.80
3	2.00	3.00	95.62	96.00
4	0.19	2.00	11.38	13.60
5	2.31	2.00	91.12	86.40
6	1.25	0.59	66.09	60.00
7	1.25	2.00	85.28	81.20
8	0.50	3.00	49.98	45.60
9	1.25	2.00	85.28	85.60
10	1.25	2.00	85.28	83.60
11	1.25	2.00	85.28	88.00
12	0.50	1.00	22.88	25.20
13	1.25	3.41	89.41	92.80

Each of the observed values was compared with the predicted values obtained from the model. Each of the actual values, Y_a is compared with the predicted value, Y_p obtained from the model was shown in Table 4.9 and Figure 4.56. The values of residual were ranged from -6.09 to 3.39. The comparison of the residual with the residual variance (Means Square = 8.59) in Table 4.10 indicates that none of the individual residual exceeds twice the square root of the regression model.

Table 4.9: Actual responses and predicted values

Run	**Water Separation, %**		**Residual Y_a-Y_p**
	Predicted Value, Y_p	**Actual Value, Y_a**	
1	85.28	88.00	2.72
2	89.72	92.80	3.08
3	95.62	96.00	0.38
4	11.38	12.60	1.22
5	91.12	86.40	-4.72
6	66.09	60.00	-6.09
7	85.28	81.20	-4.08
8	49.98	45.60	-4.38
9	85.28	85.60	0.32
10	85.28	83.60	-1.68
11	85.28	88.00	2.72
12	22.88	25.20	2.32
13	89.41	92.80	3.39

4.4.1.1 Analysis of Variance (ANOVA) and Statistical Analysis

The application of the response surface methodology yielded the following regression equation which is an empirical relationship between water separation yield and the test variables in coded unit given in equation 4.2.

$$\text{Water separation, } Y = 85.28 + 27.62A + 8.75B - 17.21A^2 - 4.01B^2 - 4.30AB \qquad 4.2$$

Where, A and B was the concentration of demulsifiers (w/w %) and processing time (minute), respectively. A^2 and B^2 are the second-order effect of adding the concentration and processing time. AB represented the interaction term between A and B.

Table 4.10 shows the analysis of variance (ANOVA) of regression parameters of predicted response surface quadratic model for water removal efficiency. Table 4.10 inferred that, the computed F and Prob>F was 93.15 and <0.0001, respectively, which implied that the model was highly significant with low probability. Results obtained adequately suggesting that the present mathematical model was good prediction of the experimental results and as a matter of the terms in the model has a significant effect on the response. In a similar manner, the multiple correlation coefficient of R^2 was calculated to be 0.9852, indicating a good agreement existed between the experimental and predicted value as well as depicting that 98.52 % of the variability in the response could be well explained by the model while 1.48 % of total variation was poorly described by the model. According to Bashir et al. (2010a), for a good fit of model, the correlation coefficient should be at a minimum of 0.08. Moreover the "Lack of Fit" value was found insignificant (Prob>F= 0.1133) which denoted that the model was desirably fit. In this study, A, B, A^2 and B^2 are significant model terms. The main effect of concentration of demulsifier (A) was found to be the most significant factor to have the largest effect towards the water removal efficiency, and this was followed by the second order of concentration (A^2). The effect of interaction between concentration and processing time (AB) was found insignificant as the P value was over 0.05.

Table 4.10: Analysis of variance and adequacy of the quadratic model for crude oil A

Source	**Sum of Squares**	**Degree of Freedom**	**Means Square**	**F Value**	**Prob > F**
Model	8872.61	5	1774.52	93.15	< 0.0001
A	6102.63	1	6102.63	320.36	< 0.0001
B	612.26	1	612.26	32.14	0.0008
A^2	2061.61	1	2061.61	108.23	< 0.0001
B^2	112.14	1	112.14	5.89	0.0457
AB	73.96	1	73.96	3.88	0.0894
Residual	133.34	7	19.05		
Lack of Fit	98.98	3	32.99	3.84	0.1133
Pure Error	34.37	4	8.59		
Cor Total	9005.96	12			

SD= 4.36, Press= 757.53, R^2=0.9852, R^2_{adj}= 0.9746, Adeq Precision= 28.440

As applying the diagnostic plots provided by the Design-Expert 6.0.8 software, such a predicted versus actual value points, as well as the normal probability plots of the studentized residuals, the model adequacy can be judged. The second-order regression model obtained for the operating variable of water separation is satisfied as the predicted versus observed value plot approximates along a straight line as shown in Figure 4.56. The predicted value of water removal efficiency obtained from the model, and the actual experiment data were in good agreement. Figure 4.57 shows the analysis on normal propapability plots of the variables. The residuals' distribution depicted nearly a straight line which denoting errors are evenly distributed and therefore, support adequacy of the least-square fit.

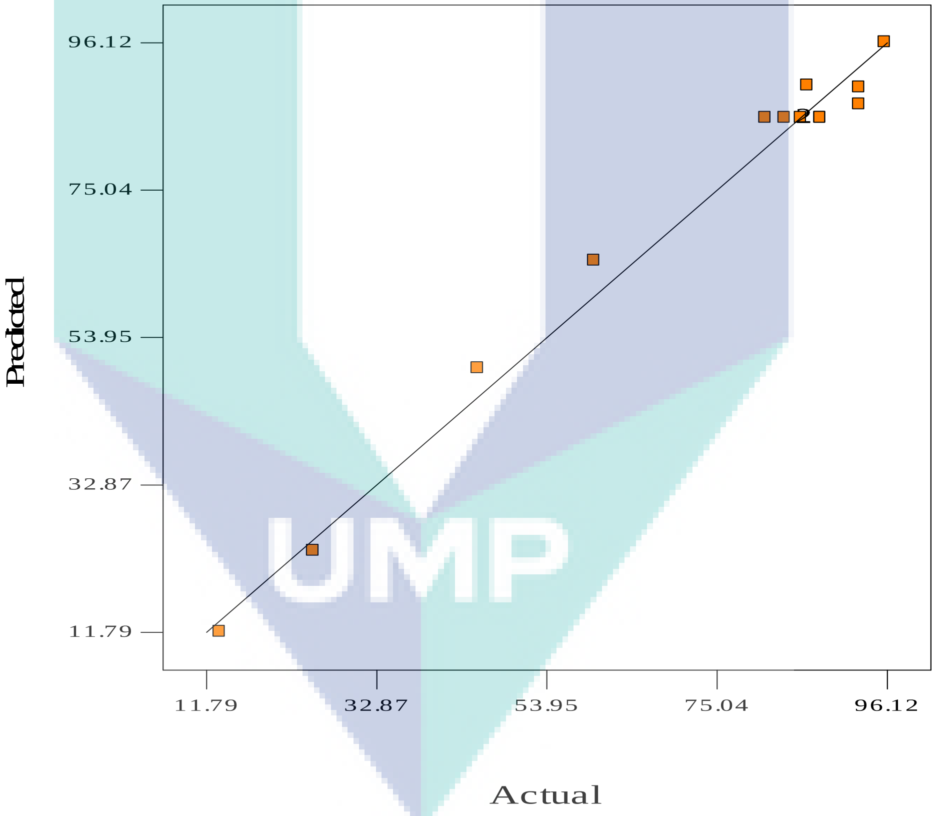


Figure 4.56: Predicted values versus actual values for the model

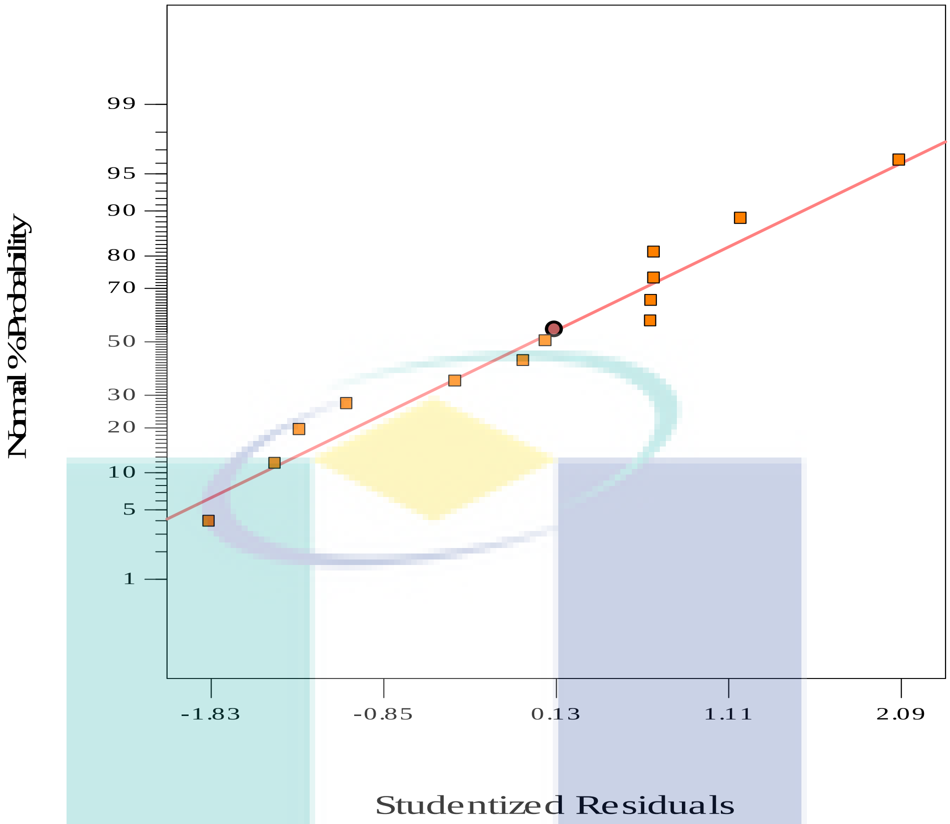


Figure 4.57: Design Expert plot-normal probability plot of the studentized residual for water separation

4.4.1.2 Response Surface Contour and Interaction Analysis on Each Variance

The 3D surface response and contour plots of the quadratic model were achieved by the Design-Expert 6.0.8 software and utilized to asses the interactive relationships between independent variables and response (Bashir et al, 2010a). 3D plots of the response function was represented in Figure 4.58. Figure 4.59 depicted the surface contour plots of the effect of concentration of demulsifier and processing time on water separation for crude oil A. As illustrated in Figure 4.58 and 4.59, increasing both concentrations of demulsifier and processing time can enhance water removal efficiency. Nevertheless, concentration of demulsifier exhibited a more powerful effect. The removal efficiency was found a maximum at high level factor. Based on the results, the maximum removal of 98.23 % was obtained when concentration and processing time were 2 w/w % and 3 minutes, respectively. However, lower water separation was exhibited at 0.19 w/w % and processing time were 2 minutes and suggesting that the performance of the process apply was essentially influenced by concentration of demulsifier and also processing time variables. Figure 4.60 shows the interaction between the variable involved. In fact, the interaction graphs indicated that there is insignificant interaction between concentration and processing time.

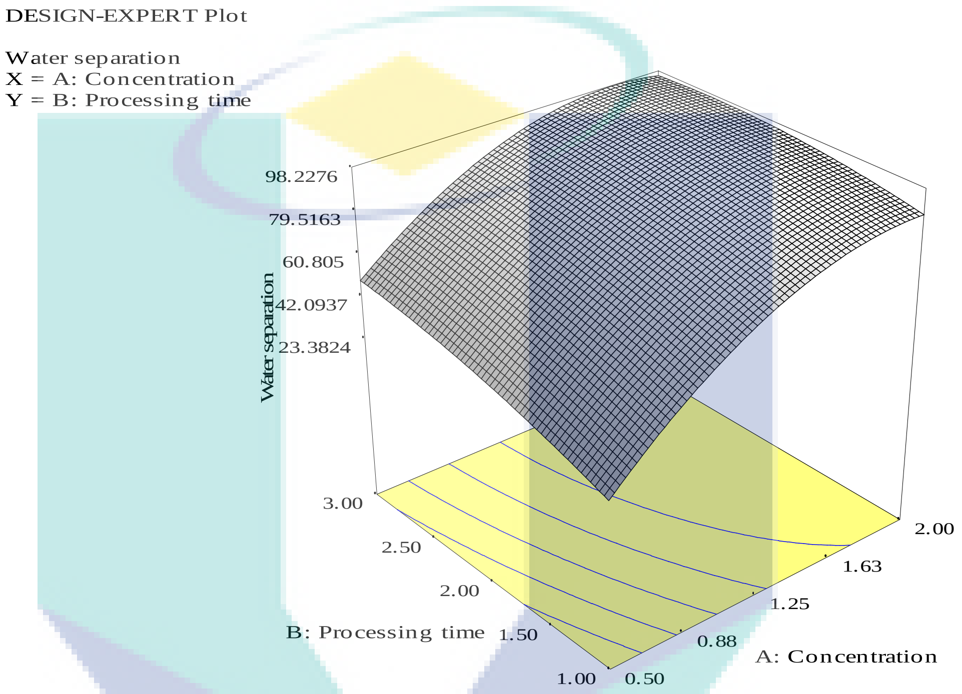


Figure 4.58: The 3D surface plots of water removal for crude oil A

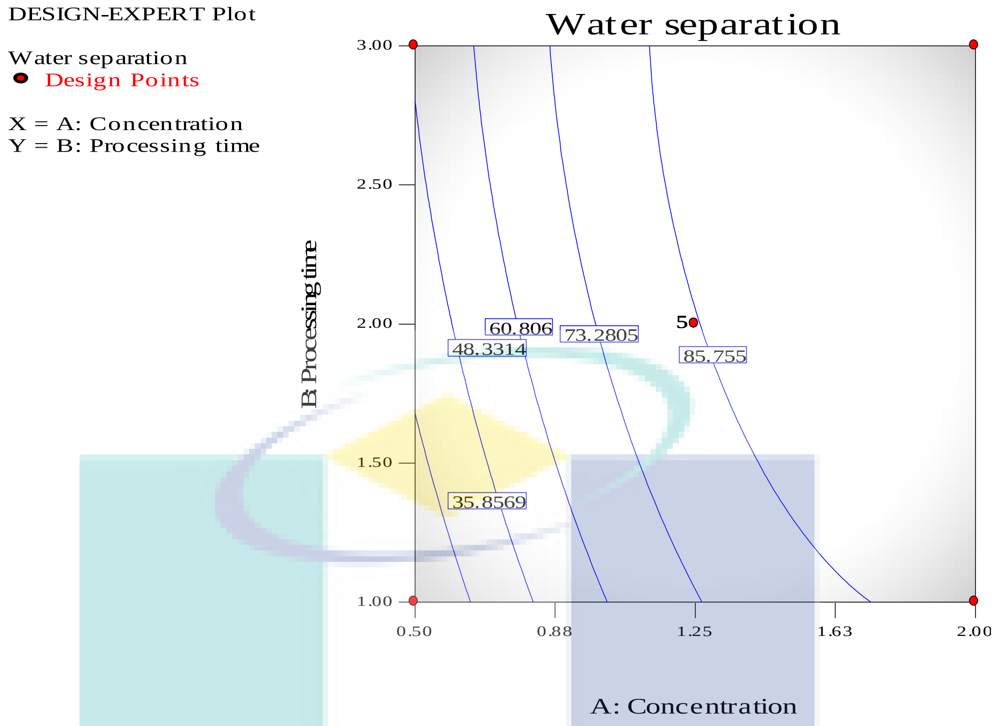


Figure 4.59: The water separation contour plots for crude oil A

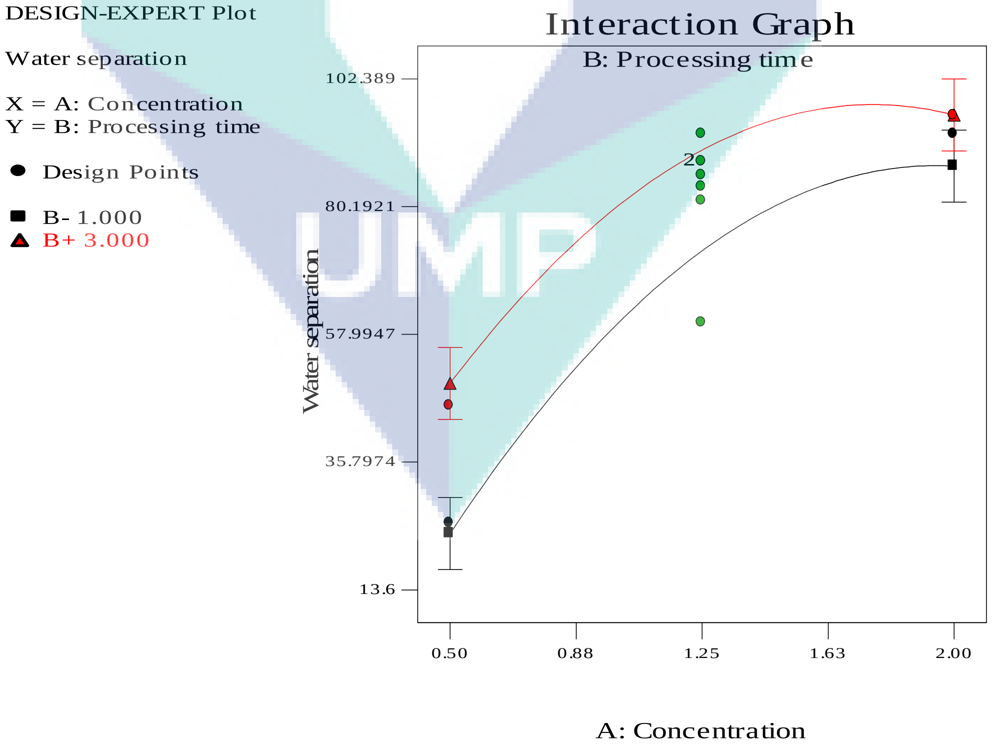


Figure 4.60: Interaction graph of water separation from the model equation for crude oil A

4.4.1.3 Validation Run of Empirical Model Adequacy

Adequacy of the developed empirical model needs to be verified or validated in order to confirm the prediction accuracy, which generated by the regression equation in predicting the removal efficiency (Zularisam et al., 2008). In order to validate the regression equation, experimental data were compared with data obtained by putting the same experimental condition in the regression equation.

The results tabulated in Table 4.11 shows that experimental data obtained by regression equation closely correlate with each other, which validate the regression equations developed. The percentage error between the actual and predicted value of both responses over a selected range of operating levels were calculated based on equation 4.3. The results had shown that the percentage error was 3.263 % for water removal. Thus, implied that the empirical model developed were considerably accurate to responding term as the percentage error between the actual and predicted values were well within the value of 5%, suggesting that the model adequacy is reasonably within the 95% of the prediction interval.

$$\%\, Error = \frac{Residual}{Actual\ value} \times 100\% \tag{4.3}$$

Table 4.11: Result of operating conditions with experimental design in validation run

Proposed optimal conditions		**Water Separation, %**		**Residual Y_a - Y_p**	**Error, %**
Factor 1: Concentration w/w %	**Factor 2: Processing time minute**	**Predicted value Y_p**	**Actual value Y_a**		
1.39	2.99	93.7636	90.8	-2.9636	3.263

4.4.2 Response Surface Methodology (RSM) for Crude Oil B

The analyzing of the correlation between the variables (concentration and processing time) was accomplished by using RSM. Considerable model terms were preferred to achieve the best fit in a particular model. The responses for water separation from CCD design for crude oil B were fitted with second order polynomial equation. CCD permitted the development of mathematical equation where predicted results were evaluated as a function of concentration of octylamine (A) and processing time (B) has been shown in equation 4.4.

There were 13 runs were designed by CCD as presented in Table 4.10. The results clearly indicated that concentration variable was strongly dependent on the water separation. The high level of concentration variable producing good results of water phase separation. As can be seen in Table 4.12, Run 1, 4, 6 were exhibited high water removal while the rest has show n less than 80 % of water separation. The comparison of each actual and predicted responses obtained from the model has shown in Table 4.13 and Figure 4.61. The residual values were ranging between -3.27 to 2.27. The residual values was compared with the residual variance (Means square = 3.15) indicated that none of the individual residual exceeds twice the square root of the residual variance. All these considerations designated a good adequacy of the regression model.

Table 4.12: Response values for different experiment conditions for crude oil B

Run	**Factor 1 A: Concentration w/w %**	**Factor 2 B: Processing Time minute**	**Water Separation, %**	
			Predicted Response, Y_p	**Actual Response, Y_a**
1	2.00	1.00	81.93	84.40
2	0.19	2.00	-2.17	0.00
3	0.50	1.00	6.97	5.60
4	2.00	3.00	93.13	95.60
5	1.25	3.41	58.15	57.60
6	2.31	2.00	103.27	100.00
7	0.50	3.00	18.97	17.60
8	1.25	2.00	62.08	62.00
9	1.25	2.00	62.08	64.00
10	1.25	2.00	62.08	62.80
11	1.25	0.59	41.75	41.20
12	1.25	2.00	62.08	59.20
13	1.25	2.00	62.08	62.40

Table 4.13: Actual responses and predicted values

Run	Water Separation, %		Residual Y_a-Y_p
	Predicted Value, Y_p	Actual Value, Y_a	
1	81.93	84.40	2.47
2	-2.17	0.00	2.17
3	6.97	5.60	-1.37
4	93.13	95.60	2.47
5	58.15	57.60	-0.55
6	103.27	100.00	-3.27
7	18.97	17.60	-1.37
8	62.08	62.00	-0.08
9	62.08	64.00	1.92
10	62.08	62.80	0.72
11	41.75	41.20	-0.55
12	62.08	59.20	-2.88
13	62.08	62.40	0.32

4.4.2.1 Analysis of Variance (ANOVA) and Statistical Analysis

The RSM gave the following regression equations for the water regression as a function of A and B. Final equation in terms of coded factors obtained is shown in equation 4.4.

$$\text{Water separation, } Y = 62.08 + 37.28A + 5.8B - 5.76A^2 - 6.06B^2 - 0.20AB \quad 4.4$$

The CCD matrix was analyzed by standard analysis of variance (ANOVA) as tabulated in Table 4.14. The model F-value of 371.02 implies the model is significant with Prob>F value below 0.05. In this case, A, B, A^2 and B^2 are significant model terms. Interaction between variable concentration and processing time (AB) was indicated as significant since the Prob> F value was greater than 0.100. The approximating function for the water separation response was attained with a high degree of fit (R^2=0.9962). A higher value of correlation coefficient; R indicated an excellent correlation between independent variables (Preeta et al., 2006). The Adequate Precision ratio of the model was 61.492, which are greater than 4 as desired. This ratio indicates an adequate signal and this model can be used to navigate the design space. The lack of fit F-statistic was statically significant as the Prob-value was over than 0.05. A significant lack of fit suggests that there may be some systematic variation unaccounted for in the hypothesized model (Bashir, et al., 2010a).

Table 4.14: Analysis of variance and adequacy of the quadratic model for crude oil B

Source	Sum of Squares	Degree of Freedom	Means Square	F Value	Prob > F
Model	11817.17	5	2363.43	371.02	< 0.0001
A	11117.00	1	11117.00	1745.18	< 0.0001
B	269.04	1	269.04	42.23	0.0003
A^2	231.20	1	231.20	36.29	0.0005
B^2	255.89	1	255.89	40.17	0.0004
AB	0.16	1	0.16	0.025	0.8786
Residual	44.59	7	6.37		
Lack of Fit	31.98	3	10.66	3.38	0.1349
Pure Error	12.61	4	3.15		
Cor Total	11861.76	12			

SD= 2.52, Press= 247.13, R^2=0.9962, R^2_{adj}= 0.9936, Adeq Precision= 61.492

The suitability of the model could be judged by diagnostic plots of predicted versus actual values as depicted in Figure 4.61. The figure has indicated that the plots signified a sufficient for agreement between the real, and the values achieved from the models. Analysis on the normal probability plot of the residuals was depicted in Figure 4.62. The results obtained exhibited nearly a straight- line residuals' distribution, which denoting errors were evenly distributed and therefore, support adequacy of the least-square fit (Zularisam et al, 2008).

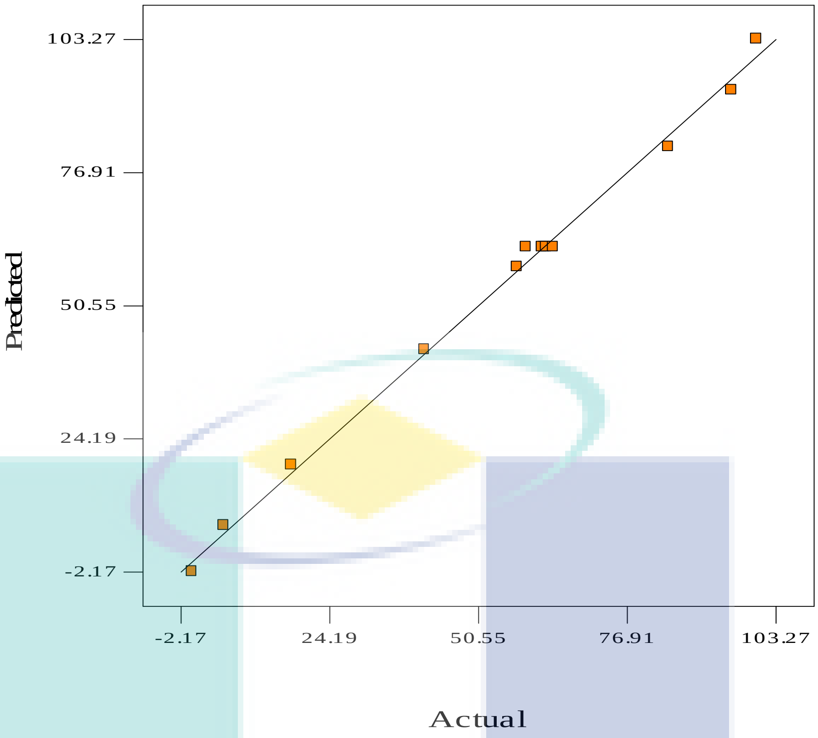


Figure 4.61: Compression between predicted and actual water regression

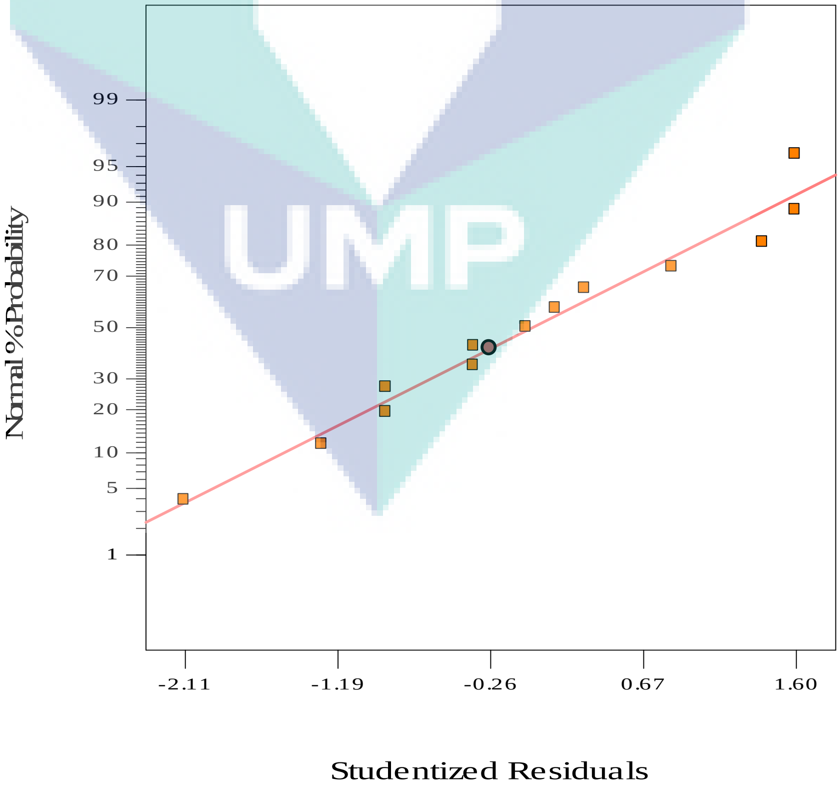


Figure 4.62: Normal probability plots of residuals for water removal for crude oil B

4.4.2.2 Response Surface Contour and Interaction Analysis on Each Variance

The optimal levels of variables were determined by constructing three-dimensional surface plots according to equation 4.4. Figures 4.63 and 4.64 show the effect of concentration of octylamine and processing time used on water separation for crude oil B. Figure 4.63 illustrated the 3D surface plot of water removal for crude oil B. The response surface plot in Figure 4.63 presents a very strong and significant positive effect on water regression. High level of concentration and processing time indicated high percentage of water separation. The contour plot for water removal is presented in Figure 4.66. The interaction graph between the variable A and B is shown in Figure 4.67. The interaction plots show that the lines are parallel to each other, so there is no interaction between the factors. The change in response mean from the low to the high level of tool replacement does not depend on the level of the water separation.

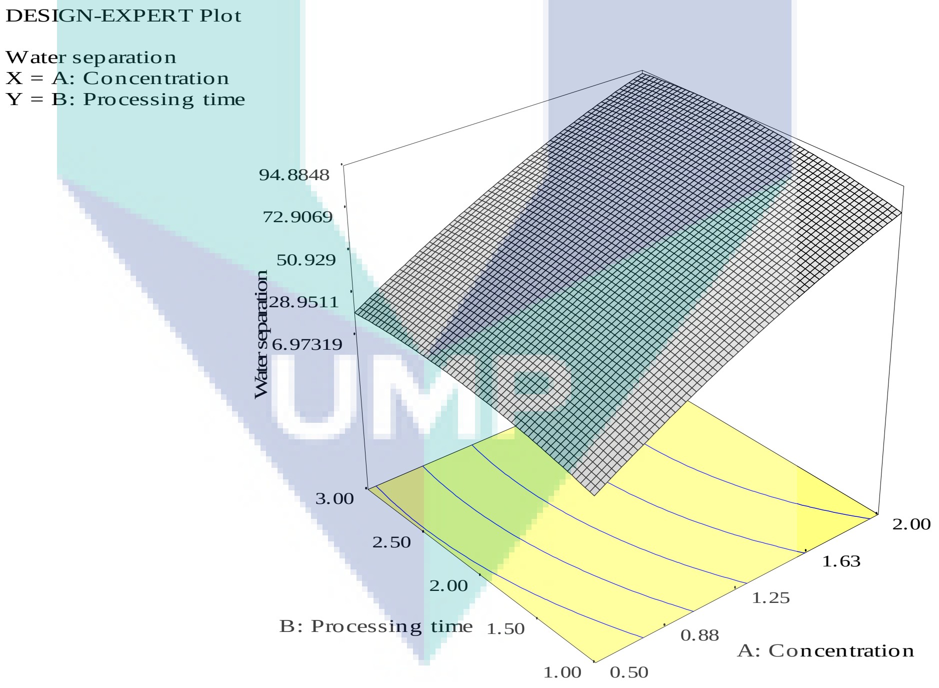


Figure 4.63: The 3D surface plots of water separation for crude oil B

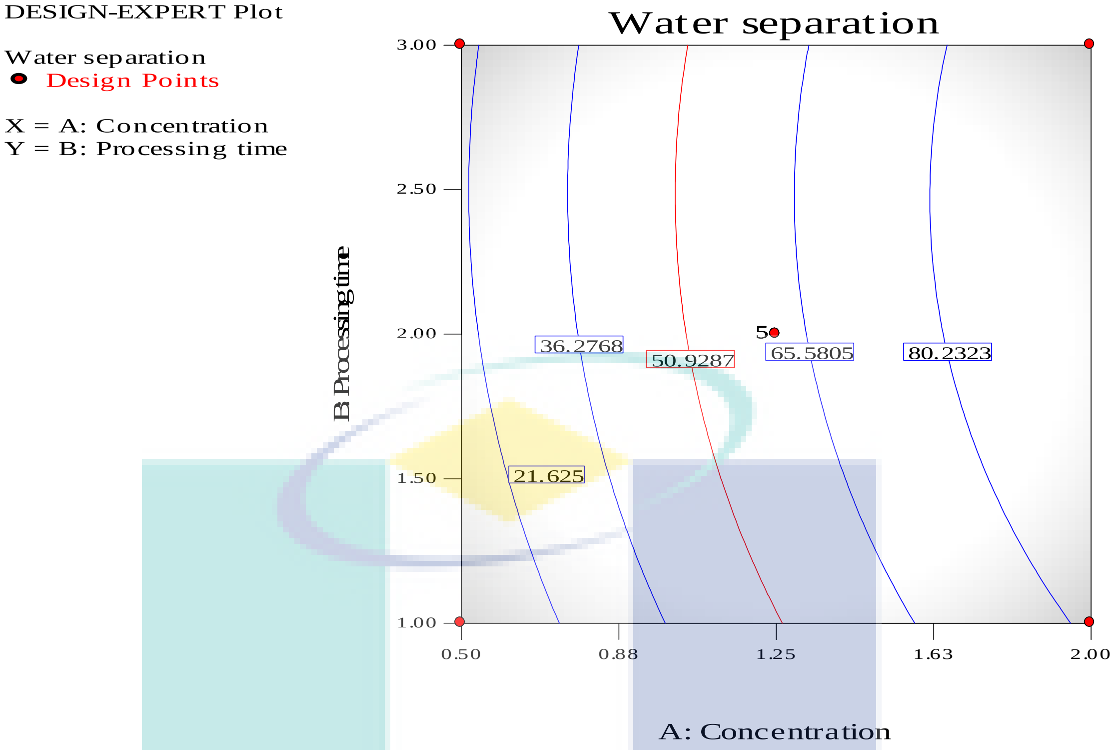


Figure 4.64: The contour plot of water separation for crude oil B

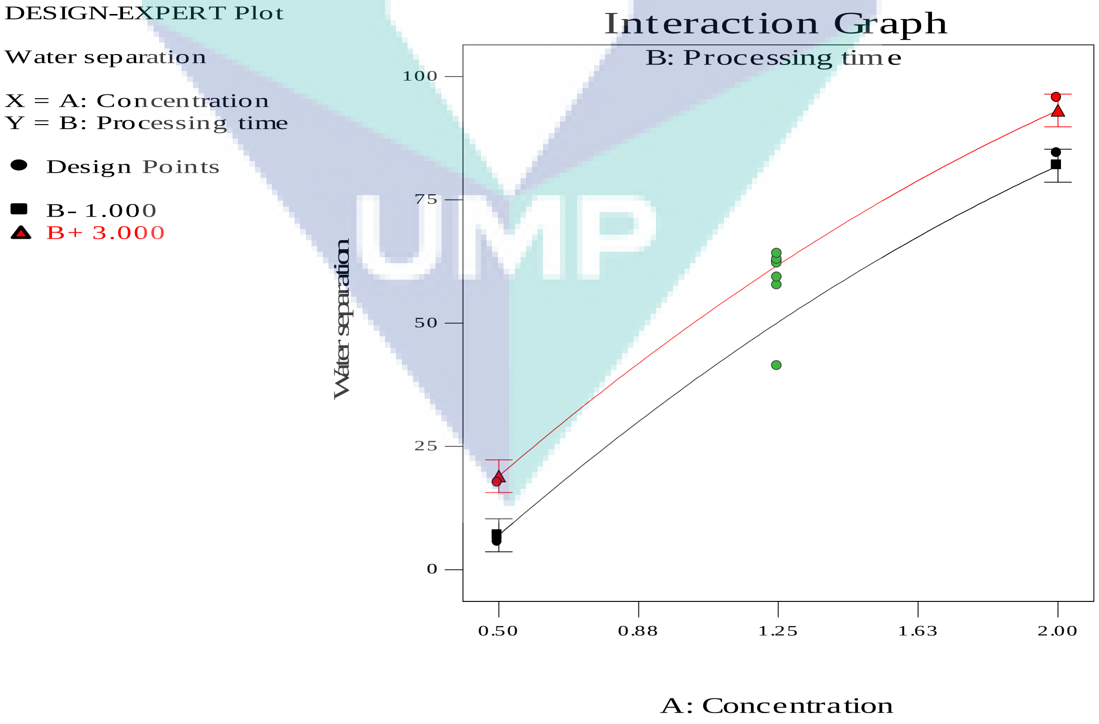


Figure 4.65: Interaction graph of water separation from the model equation for crude oil B

4.4.2.3 Validation Run of Empirical Model Adequacy

Optimization was carried out to determine the optimum value of water removal efficiency using Design-Expert 6.0.8 software. According to the software optimization step, the desired goal each operational condition was chosen “minimum” for concentration, “is in range” for processing time factor while the water separation efficiency was defined as “maximum” to achieve highest performance. There is only single solution of the optimum working condition and respective percent removal efficiency was established, and the result is presented in Table 4.15. According to Table 4.15, the 87.64 % removal of water phase was predicted according to the model under optimized operational condition. An additional experiment was then performed to confirm the optimum result. The actual response obtained is lower than the predicted value. According to the percentage or error between the actual and predicted value, the model is acceptable since the error is below than 5 %.

Table 4.15: Result of operating conditions with experimental design in validation run

Proposed optimal conditions		**Water Separation, %**			
Factor 1: Concentration w/w %	**Factor 2: Processing time minute**	**Predicted value Y_p**	**Actual value Y_a**	**Residual $Y_a - Y_p$**	**Error, %**
1.80	2.47	87.6444	84.4	-3.2444	3.844

4.4.3 Response Surface Methodology (RSM) for Crude Oil C

According to Bashir et al. (2010b), the application of RSM offered an empirical design to relate the response and test variables based on parameter estimation. In the present work, single regression analysis was carried out using response surface analysis to fit mathematical models to the experimental data aiming at an optimal region for the response variables studied and to define the relationship between two independent variables and the criteria of the variables as presented in Table 4.16. The results indicated that run 1, 3, 5, 6, 8, 9, 10, 11 and 12 have given high water removal percentage, which performed above 80 % of separation. Low concentration of octylamine gave low separation of water phase. The different of each actual and predicted responses gained from the model is illustrated in Table 4.17 and Figure 4.66.

The results show that the residual values are ranging between -4.70 to 4.76. The residual values is compared to the residual variance (Means Square = 5.73) indicated that none of the individual residual exceed twice the square root of the residual variance. All these considerations designated a good adequacy of the regression model.

Table 4.16: Response values for different experiment conditions for crude oil C

Run	**Factor 1 A: Concentration w/w %**	**Factor 2 B: Processing Time minute**	**Water Separation, %**	
			Predicted Response, Y_p	**Actual Response, Y_a**
1	2.31	2.00	84.56	86.40
2	1.25	2.00	41.90	40.80
3	2.00	3.00	84.56	85.60
4	2.00	1.00	93.96	0.40
5	1.25	2.00	87.20	90.40
6	1.25	3.41	87.40	90.00
7	1.25	2.00	67.10	62.40
8	0.19	2.00	84.56	84.80
9	1.25	2.00	84.56	80.40
10	0.50	1.00	86.44	86.00
11	1.25	0.59	93.96	92.00
12	0.50	3.00	84.56	85.60
13	1.25	2.00	19.94	24.00

Table 4.17: Actual responses and predicted values

Run	**Water Separation, %**		**Residual Y_a-Y_p**
	Predicted Value, Y_p	**Actual Value, Y_a**	
1	84.56	86.40	1.84
2	41.90	40.80	-1.10
3	84.56	85.60	1.04
4	93.96	0.40	-1.66
5	87.20	90.40	3.20
6	87.40	90.00	2.60
7	67.10	62.40	-4.70
8	84.56	84.80	0.24
9	84.56	80.40	-4.16
10	86.44	86.00	-0.44
11	93.96	92.00	-1.96
12	84.56	85.60	1.04
13	19.94	24.00	4.06

4.4.3.1 Analysis of Variance (ANOVA) and Statistical Analysis

By applying the factorial regression analysis on the experimental data, response and factor can be related by polynomial equation. The percentage of water separation as the response variable and the variables were used to determine the correlation between variables and result by using ANOVA. By running the ANOVA, the final equation of water separation in coded values was stated as given in equation 4.5. The result of equation indicated that the effect of the term A and second order of term A are highly significant than B and B^2. Besides, the derived model demonstrates statistical insignificant for the two-level interaction between A and B.

$$\text{Water separation, } Y = 84.56 + 29.83A + 7.18B - 20.15A^2 - 3.65B^2 - 3.80AB \qquad 4.5$$

Results of ANOVA for water separation are presented in Table 4.16. The model F-value of 168.82 and the small value of Probability F indicated that the model is sigificant. There is only 0.01 % chance that the model F-value this large could occur due to noise (Zahed et al., 2010). The results tabulated in table 4.18 also explained that the lack of fit value was insignificant suggested that the quadratic model is valid for this case. The R^2 value for this response variable was higher than 0.08 (0.9917), thus ensuring a satisfactory fitness of the regression model to the experimental data. The adequate precision gives a value measuring the signal-to-noise ratio (Ali et al., 2011). A ratio greater than 4 is desirable. The results revealed that the adequate precision value of 38.496 was very high compared to the desirable. This confirmed the possible use of the developed polynomial equation to navigate the design space. It was found that the values of Prob>F less than 0.05 indicated model terms are significant. In this case A, B, A^2 and B^2 are significant model terms. While, the interaction between variables (AB) indicate insignificant.

Table 4.18: Analysis of variance and adequacy of the quadratic model for crude oil B

Source	Sum of Squares	Degree of Freedom	Means Square	F Value	Prob > F
Model	10423.05	5	2084.61	168.82	<0.0001
A	7119.63	1	7119.63	576.57	<0.0001
B	412.31	1	412.31	33.39	0.0007
A^2	2825.91	1	2825.91	228.85	<0.0001
B^2	92.93	1	92.93	7.53	0.0288
AB	57.76	1	57.76	4.68	0.0673
Residual	86.44	7	12.348		
Lack of Fit	63.53	3	21.18	3.70	0.1195
Pure Error	22.91	4	5.73		
Cor Total	10509.49	12			

SD= 3.51, Press= 487.53, R^2=0.9917, R^2_{adj}= 0.9859, Adeq Precision= 38.496

The suitability of the model could be judged by diagnostic plots i.e predicted versus actual values (Aziz et al., 2011). Figure 4.66 illustrated the predicted value against the actual value for water regression. These plots signified a sufficient agreement between the real data, and the values achieved from the model. Normal plots of residuals indicate whether the residuals follow a normal distribution. Figure 4.67 depicted the normal probability plots of residual indicates that the residuals can be considered to fall on straight line implying that the error followed the line representing a normal distribution and support the assumptions of the empirical model (Bari et al., 2010).

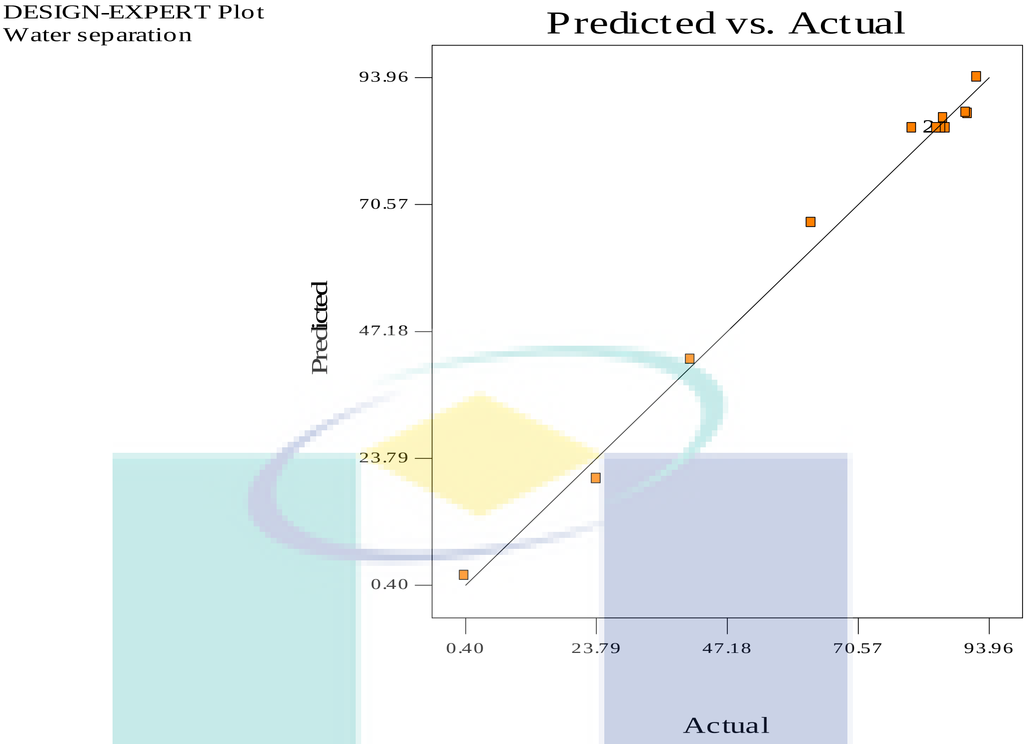


Figure 4.66: Predicted versus actual value of water regression for crude oil C

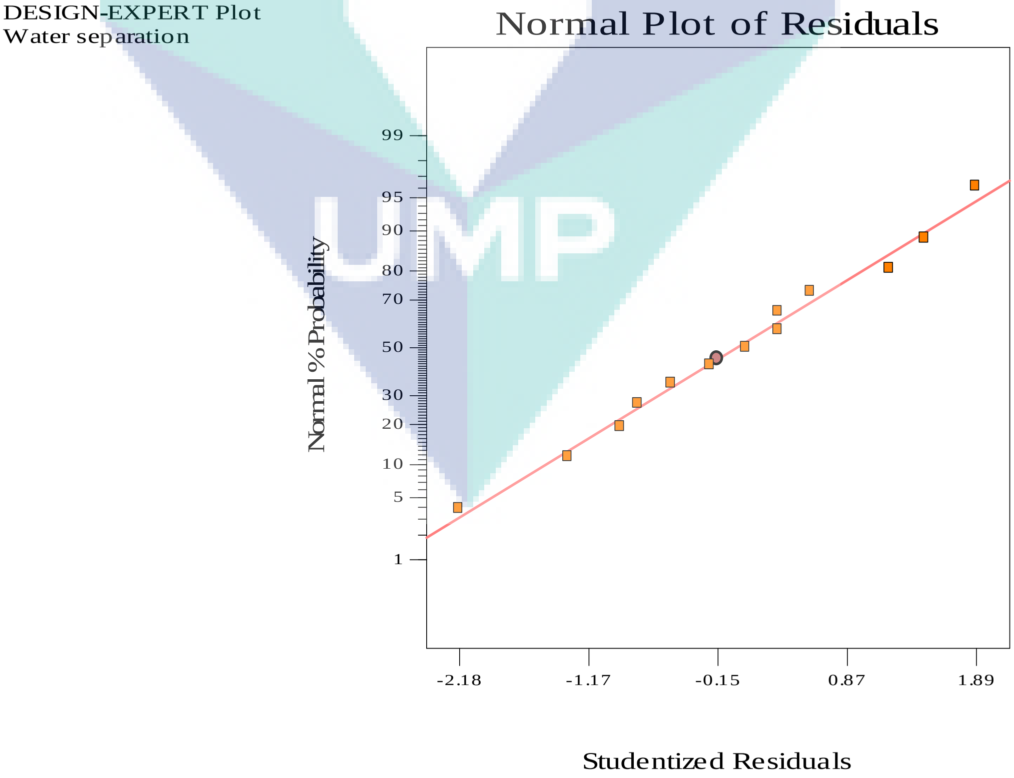


Figure 4.67: Normal plots of water regression for crude oil C

4.4.3.2 Response Surface Contour and Interaction Analysis on Each Variance

The 3D response and 2D contour plots are the graphical representation of the regression equation in order to determine the optimum values of the variables within the ranges considered (Tanyildizi et al., 2005). The 3D and contour plots for the interaction between two variables are presented in Figure 4.68, 4.69. The principal target of the response surface is to hunt efficiently for the optimum values of the variables such that the response is maximized. Figure 4.70 shows that the interaction lines are parallel to each other so, there are no interactions present between the factors.

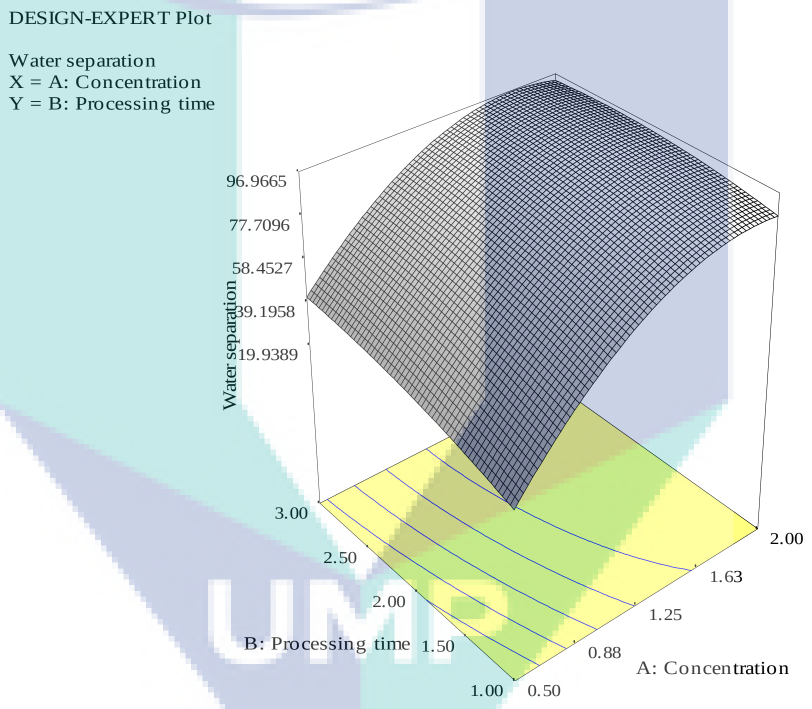


Figure 4.68: 3D response surface of water regression for crude oil C

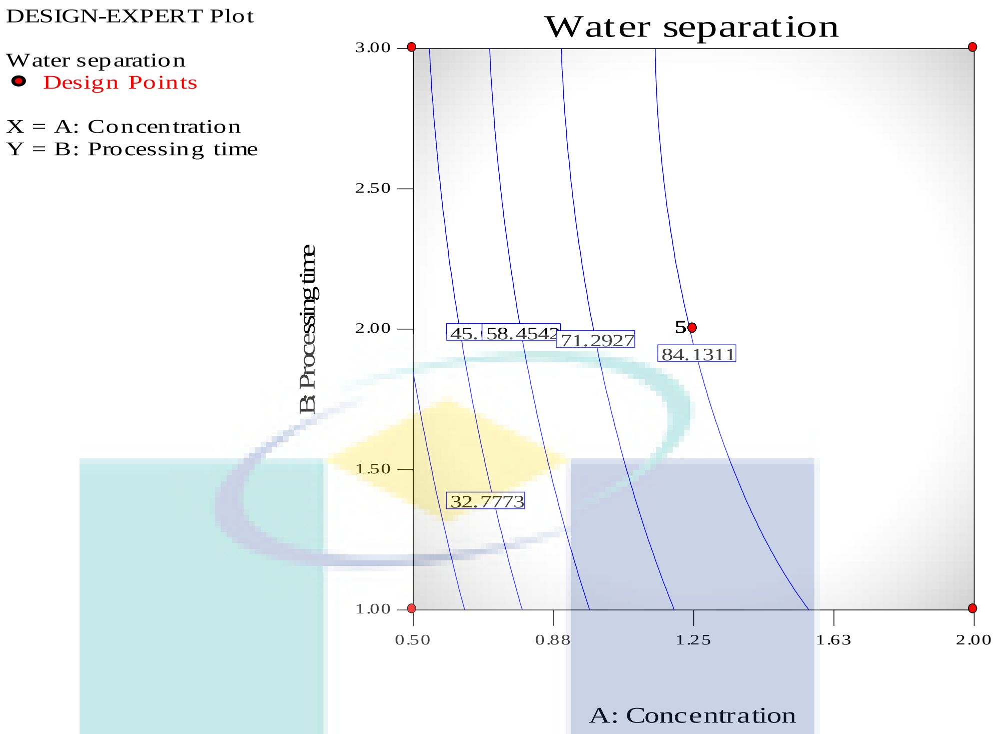


Figure 4.69: 2D plots of response surface of water regression for crude oil C

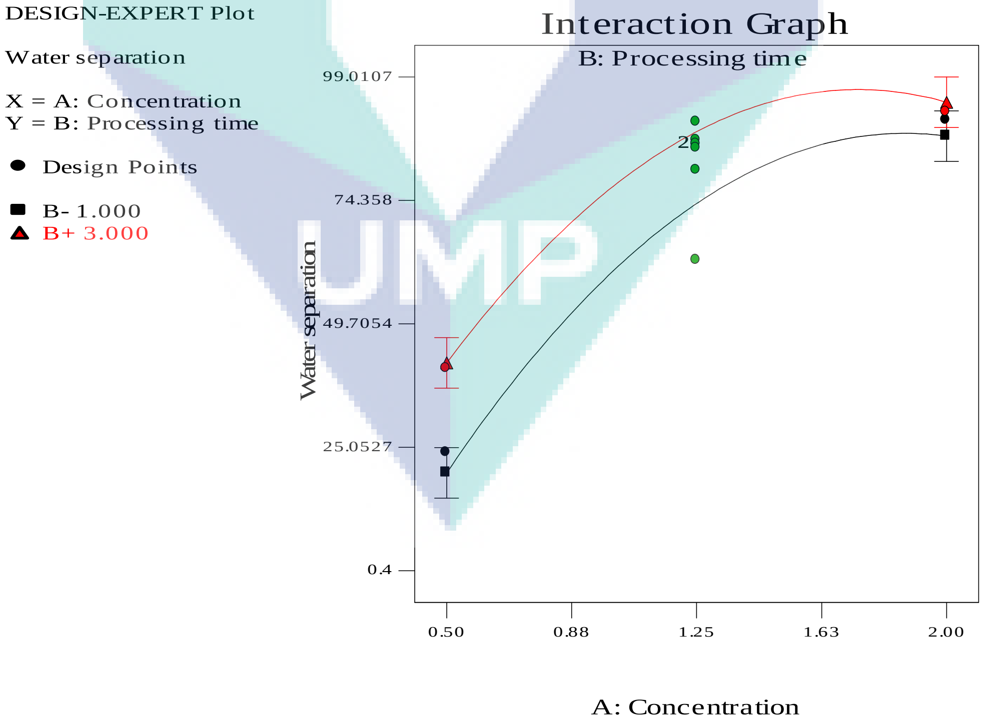


Figure 4.70: Interaction graph of response surface of water regression for crude oil C

4.4.3.3 Validation Run of Empirical Model Adequacy

Only one numerical solution suggested by using Design-Expert 6.0.8 software. The numerical solution of the developed model predicts the highest water removal. In order to verify the optimization and to validate the developed second order quadratic model, an experiment was performed according to the process conditions presented in Table 4.19. From the experiment, the highest water separation (90 %) was obtained in the optimum condition which is slightly less 3.49 % than the predicted value.

Table 4.19: Result of operating conditions with experimental design in validation run

Proposed optimal conditions		**Water Separation, %**			
Factor 1: Concentration w/w %	**Factor 2: Processing time minute**	**Predicted value Y_p**	**Actual value Y_a**	**Residual $Y_a - Y_p$**	**Error, %**
1.43	2.86	93.1403	90	-3.1403	3.489

4.5 COMPARISON BETWEEN CHEMICAL AND HEATING DEMULSIFICATION METHOD

There have two methods were carried out in the study of demulsification part namely chemical and thermal demulsification methods. The evaluations were based on the fast separation rate, and the highest water separated from the stable emulsion. The comparison was accomplished by using the chemical optimization results and thermal demulsification result. Table 4.20 has summarized the results obtained from the experimental work. The evaluation was taken 300 minutes of gravity settling observation. From the results obtained in destabilization part, found that the chemical demulsification has performed better compared to the thermal method. Chemical demulsification results show that it was capable to separate high water phase in a short time. Meanwhile, thermal demulsification has performed the oil separation only. It was expected that the water already evaporate during heating the emulsions. Theoretically, both methods are capable to enhance the acceleration of the droplets' coalescence of. However, Kokal (2002) has explained that the application of heat for emulsion breaking causes the loss of light ends from the crude oil reducing its API gravity and the treated oil volume.

Table 4.20: Separation performance of chemical and thermal demulsification methods

Demulsification method	Crude oil sample	Separation , %	
		Water	**Oil**
Chemical (Octylamine)	A	90.8	86.6
	B	84.4	80.4
	C	90	85.2
Thermal (Hot plate)	A	0	36
	B	0	25.6
	C	0	22

4.6 CHAPTER SUMMARY

Characterization of properties was applied on the crude oil samples. There have some correlation between physical and chemical properties of crude oil were shown that there is a dependency between them. The emulsion stability analysis was covered some parameter that influenced the formation of stable emulsion, and those parameters have shown a significant effect. In addition, demulsification of W/O emulsion was accomplished through thermal and chemical demulsification method. Both methods have been compared in terms of good water phase separation of. An optimization of chemical demulsifier was done via Design-Expert 6.0.8 software. The optimum condition to gain high water separation was revealed through this analytical software.

CHAPTER 5

CONCLUSIONS AND RECOMMANDATIONS

5.0 INTRODUCTION

This chapter has been divided into two main topic, which is covered the overall conclusion that can be made from the findings obtained during the research. Then, it followed by recommendation ideas for future work in order to gain better results.

5.1 CONCLUSIONS

Based on the objectives of this research, the conclusion can be derived into three main areas which consisted with characterization, stability and destabilization part. Besides, the finding of comparison between chemical and thermal demulsification method also included at the end of the conclusion part.

5.1.1 Characterization

Some of the important physical and chemical properties of crude oil samples have been determined. The physical properties of the crude oil samples showed that the °API density was in range of 30 to 41. All the samples have viscosity range between 3 to 17 cP at an ambient temperature. The analysis of surface and interfacial tension of the crude oil samples have show results in range of 27 till 34 mmN/m and 24 to 30 mmN/m, respectively. According to the chemical properties' analysis through open column chromatography, it can be concluded that the crude oils have saturates, aromatics, resins and asphaltenes content in between of 51.7 to 55.23 %, 23.8 to 27.67 %, 16.3 to 20.2 % and 0.58 to 3.44 %, respectively. The results gained have revealed that crude oil A has exhibited the lightest crude oil compared to crude oil B and C. Thus, crude oil A emulsions were less stable compared to crude oil B and C. Furthermore, crude oil C has acted as the heaviest crude oil which behaved more stable compared to other crude oil samples.

5.1.2 Stability

An investigation of water-oil-emulsion stability and separation was carried out in this thesis. The formations of W/O emulsions were influenced by several factors during preparing the emulsions. Some factors have been studied included mixing speed, processing time, volume phase ratio, emulsifier type and concentration of emulsifying agent. The effect of mixing speed, processing time and volume phase ratio have revealed that high mixing speed, long processing time and high volume phase ratio have been producing an emulsion with high viscosity and small droplets size, which enhances the stability of the emulsions. Furthermore, the effect of emulsifier types can be summarized as Span 83 is the better emulsifying agent for W/O emulsions compared to Tween 80, Triton X-100 and SDDS. Span 83 has great solubility towards oil, which was suitable for W/O emulsion formation. The concentration of emulsifier also played a significant role in formation of stable W/O emulsion. Where, high emulsifier dosages have given a good result in stability.

5.1.3 Demulsification

There have two types of demulsifier have been used in this study, which consisted with the oil-soluble and water-soluble demulsifier. Four groups of demulsifier were chosen to complete the destabilization study namely amine, polyhydric alcohol, alcohol, and natural demulsifier group. The screening results show that amine and natural demulsifier group have performed better in water and oil separation. Whereas low percentage of water and oil removal have been shown by other groups. A comparison of effectiveness in separation of water and oil among the best demulsifier of each group was revealed that octylamine has shown great efficiency in destabilized the W/O emulsion. This was due to low HLB value and high molecular weight of octylamine. The HLB value has influenced the solubility of octylamine onto oil phase which useful to enhance the droplets' coalescence. Based on a good performance of octylamine as demulsifying agent, it was proceeded to test the effect of demulsifier concentration in order to find a range of concentrations, which will be used in optimization part. The results gained have presented that the highest separation of water phase was obtained at 2 w/w % of octylamine. Over than that level, the emulsion has shows less separation. Thus, the concentrations in range of 0.5 to 2.0 w/w % have been carried out in response surface methodology (RSM) in sequence to find optimum condition of the demulsification process.

Optimization part was accomplished for crude oil A, B and C with assisted by Design-Expert 6.0.8 software. The results obtained have shows the optimum condition to remove water at maximum with low concentration of octylamine consumed. The optimum conditions that suggested by this method have been validated through experimental work. The validation results have shown less than 5 % error compared to predicted value.

In addition, demulsification through thermal method also has been determined via a hot plate. According to the results obtained, found that there was only oil phase separated from the emulsion. There was no water removed from the emulsion systems, and it was believed that the water was lost through the evaporation process during heating process.

Chemical demulsification have shows greater performance in water removal from the emulsions compared to the thermal method. This was due to the capability of the octylamine to separate the water and oil phase in a short period.

5.2 RECOMMANDATIONS FOR FUTURE WORK

This research goal was to separate the water and oil from the emulsion effectively by using chemical demulsification methods. The findings have shown that the emulsions were separated incompletely. Thus, suggested that to widen the range of demulsifier concentration in order to remove 100 % of water and oil phase from the emulsion. Additionally, this research has used Palm Based Oleyl Amine (PBOA) as demulsifier. It has performed greatly in water-oil separation during the experimental work. Therefore, it is proposed that PBOA studied in more detail because it is a natural product and its ability to separate relatively favorable.

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APPENDIX A

EFFECT OF MIXING SPEED ON EMULSION STABILITY

Table A.1: Effect of mixing speed on emulsion stability for crude oil A

Time, min	**Volume oil separation (mL)**				**Volume oil separation (%)**			
	RPM							
	500	**1000**	**1500**	**2000**	**500**	**1000**	**1500**	**2000**
0	0	0	0	0	0	0	0	0
5	2	0.5	0.6	0	8	2	2.4	0
10	4	0.8	1	0	16	3.2	4	0
15	5	1	1	0	20	4	4	0
20	6	1.5	1	0	24	6	4	0
25	7	2	1.4	0.1	28	8	5.6	0.4
30	8	2	2	0.1	32	8	8	0.4
35	9	2.8	2.3	0.2	36	11.2	9.2	0.8
40	10	3	2.5	0.3	40	12	10	1.2
45	11	4	2.8	0.5	44	16	11.2	2
50	12	4.5	2.8	0.5	48	18	11.2	2
55	13	5	2.8	0.5	52	20	11.2	2
60	14	6	3	0.6	56	24	12	2.4
65	15	6	3	0.6	60	24	12	2.4
70	15	6	3.5	0.6	60	24	14	2.4
75	15	6	3.5	0.8	60	24	14	3.2
80	15	6	4	0.8	60	24	16	3.2
85	15.5	6	4	0.8	62	24	16	3.2
90	15.5	7	4	1	62	28	16	4
95	15.5	7.5	5	1	62	30	20	4
100	15.5	8	5	1	62	32	20	4
105	16	9	5	1	64	36	20	4
110	16	9	6	1	64	36	24	4
115	16.4	9	6	1	65.6	36	24	4
120	16.4	9.3	6	1	65.6	37.2	24	4
125	16.4	9.5	6	1	65.6	38	24	4
130	16.8	9.8	6	1	67.2	39.2	24	4
135	17	9.8	6	1	68	39.2	24	4
140	17	9.8	6	1	68	39.2	24	4

Table A.1: Continued

Time, min	**Volume oil separation (mL)**				**Volume oil separation (%)**			
	RPM							
	500	**1000**	**1500**	**2000**	**500**	**1000**	**1500**	**2000**
145	17	10	7	1	68	40	28	4
150	17	10	7	1	68	40	28	4
155	17	10.5	7	1	68	42	28	4
160	17	10.5	7	1	68	42	28	4
165	17	10.5	7	1	68	42	28	4
170	17.5	10.5	7	1	70	42	28	4
175	17.5	10.5	7	1	70	42	28	4
180	17.5	10.5	8	1	70	42	32	4
185	17.5	11	8	1	70	44	32	4
190	17.5	11	8	1	70	44	32	4
195	18	11	8	1	72	44	32	4
200	18	11.5	8	1	72	46	32	4
205	18	11.5	8	1	72	46	32	4
210	18	11.5	8	1	72	46	32	4
215	18	11.5	8.5	1	72	46	34	4
220	18	12	8.5	1	72	48	34	4
225	18	12	8.5	1	72	48	34	4
230	18	12	8.8	1	72	48	35.2	4
235	18	12	8.8	1	72	48	35.2	4
240	18	12	9	1	72	48	36	4
245	18	12	9	1	72	48	36	4
250	18	12	9	1	72	48	36	4
255	18.5	12	9	1	74	48	36	4
260	18.5	12	9	1	74	48	36	4
265	18.5	12	9	1	74	48	36	4
270	18.5	12	9	1	74	48	36	4
275	18.5	12	9	1	74	48	36	4
280	18.5	12	9	1	74	48	36	4
285	18.5	12	9	1	74	48	36	4
290	19	12	9	1	76	48	36	4
295	19	12	9	1	76	48	36	4
300	19	12	9	1	76	48	36	4

Table A.2: Effect of mixing speed on emulsion stability for crude oil B

Time, hr	**Volume oil separation (mL)**				**Volume oil separation (%)**			
	RPM							
	500	**1000**	**1500**	**2000**	**500**	**1000**	**1500**	**2000**
0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0
2	0.35	0	0.2	0	1.4	0	0.8	0
3	1.15	0.2	0.2	0	4.6	0.8	0.8	0
4	2.25	0.2	0.2	0	9	0.8	0.8	0
5	3	0.2	0.2	0	12	0.8	0.8	0
6	3	0.4	0.2	0	12	1.6	0.8	0
7	3	0.4	0.2	0	12	1.6	0.8	0
8	3	0.4	0.2	0	12	1.6	0.8	0
9	3	0.5	0.2	0	12	2	0.8	0
10	3	0.5	0.2	0	12	2	0.8	0
11	3.25	0.5	0.4	0	13	2	1.6	0
12	3.5	0.8	0.4	0	14	3.2	1.6	0
13	3.5	0.8	0.4	0	14	3.2	1.6	0
14	3.8	0.8	0.5	0	15.2	3.2	2	0
15	4	1	0.5	0	16	4	2	0
16	4	1	0.5	0.2	16	4	2	0.8
17	4.5	1	0.5	0.4	18	4	2	1.6
18	4.8	1	0.5	0.5	19.2	4	2	2
19	5	1	0.5	0.5	20	4	2	2
20	5	1	0.6	0.5	20	4	2.4	2
21	5	1	0.6	0.5	20	4	2.4	2
22	5	1	0.6	0.5	20	4	2.4	2
23	5	1	0.6	0.5	20	4	2.4	2
24	5.2	1	0.6	0.5	20.8	4	2.4	2
25	5.2	1	0.6	0.5	20.8	4	2.4	2
26	5.2	1	0.8	0.5	20.8	4	3.2	2
27	5.5	1	0.8	0.5	22	4	3.2	2
28	5.5	1	0.8	0.5	22	4	3.2	2
29	5.5	1	0.8	0.5	22	4	3.2	2
30	6	1.2	0.8	0.5	24	4.8	3.2	2
31	6	1.2	0.8	0.5	24	4.8	3.2	2
32	6	1.2	0.8	0.5	24	4.8	3.2	2
33	6	1.2	0.8	0.5	24	4.8	3.2	2

Table A.2: Continued

Time, hr	**Volume oil separation (mL)**				**Volume oil separation (%)**			
	RPM							
	500	**1000**	**1500**	**2000**	**500**	**1000**	**1500**	**2000**
34	6	1.2	0.8	0.5	24	4.8	3.2	2
35	6	1.2	0.8	0.5	24	4.8	3.2	2
36	6	1.2	0.8	0.5	24	4.8	3.2	2
37	6	1.2	0.8	0.5	24	4.8	3.2	2
38	6	1.2	0.8	0.5	24	4.8	3.2	2
39	6	1.2	0.8	0.5	24	4.8	3.2	2
40	6	1.2	0.8	0.5	24	4.8	3.2	2
41	6.2	1.2	0.8	0.5	24.8	4.8	3.2	2
42	6.2	1.2	0.8	0.5	24.8	4.8	3.2	2
43	6.2	1.2	0.8	0.5	24.8	4.8	3.2	2
44	6.2	1.2	0.8	0.5	24.8	4.8	3.2	2
45	6.2	1.2	0.8	0.5	24.8	4.8	3.2	2
46	6.2	1.2	0.8	0.5	24.8	4.8	3.2	2
47	6.2	1.2	0.8	0.5	24.8	4.8	3.2	2
48	6.2	1.2	0.8	0.5	24.8	4.8	3.2	2

Table A.3: Effect of mixing speed on emulsion stability for crude oil C

Time, hr	Volume oil separation (mL)				Volume oil separation (%)			
	RPM							
	500	1000	1500	2000	500	1000	1500	2000
0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0
2	0.2	0.2	0	0	0.8	0.8	0	0
3	0.2	0.2	0	0	0.8	0.8	0	0
4	0.5	0.2	0.2	0	2	0.8	0.8	0
5	0.5	0.2	0.2	0	2	0.8	0.8	0
6	0.5	0.4	0.2	0	2	1.6	0.8	0
7	0.5	0.4	0.2	0	2	1.6	0.8	0
8	0.8	0.4	0.2	0	3.2	1.6	0.8	0
9	0.8	0.5	0.2	0	3.2	2	0.8	0
10	0.8	0.5	0.2	0	3.2	2	0.8	0
11	0.8	0.5	0.4	0	3.2	2	1.6	0
12	1	0.8	0.4	0	4	3.2	1.6	0
13	1	0.8	0.4	0	4	3.2	1.6	0
14	1	0.8	0.4	0	4	3.2	1.6	0
15	1	0.8	0.4	0	4	3.2	1.6	0
16	1.5	0.8	0.4	0	6	3.2	1.6	0
17	1.5	0.8	0.4	0	6	3.2	1.6	0
18	1.5	0.8	0.5	0.2	6	3.2	2	0.8
19	1.5	1	0.5	0.2	6	4	2	0.8
20	1.5	1	0.5	0.2	6	4	2	0.8
21	1.8	1	0.5	0.2	7.2	4	2	0.8
22	1.8	1	0.5	0.2	7.2	4	2	0.8
23	2	1	0.5	0.2	8	4	2	0.8
24	2	1	0.5	0.2	8	4	2	0.8
25	2.2	1	0.5	0.2	8.8	4	2	0.8
26	2.5	1	0.5	0.2	10	4	2	0.8
27	3	1	0.5	0.2	12	4	2	0.8
28	3.4	1.2	0.5	0.2	13.6	4.8	2	0.8
29	4	1.2	0.5	0.2	16	4.8	2	0.8
30	4.2	1.2	0.5	0.4	16.8	4.8	2	1.6
31	4.8	1.2	0.5	0.4	19.2	4.8	2	1.6
32	5.2	1.2	0.8	0.5	20.8	4.8	3.2	2
33	5.5	1.2	0.8	0.5	22	4.8	3.2	2

Table A.3: Continued

Time, hr	Volume oil separation (mL)				Volume oil separation (%)			
	RPM							
	500	**1000**	**1500**	**2000**	**500**	**1000**	**1500**	**2000**
34	5.8	1.2	0.8	0.5	23.2	4.8	3.2	2
35	5.8	1.2	0.8	0.5	23.2	4.8	3.2	2
36	5.8	1.2	0.8	0.5	23.2	4.8	3.2	2
37	5.8	1.2	0.8	0.8	23.2	4.8	3.2	3.2
38	5.8	1.2	1	0.8	23.2	4.8	4	3.2
39	5.8	1.2	1	0.8	23.2	4.8	4	3.2
40	5.8	1.2	1	0.8	23.2	4.8	4	3.2
41	5.8	1.2	1	0.8	23.2	4.8	4	3.2
42	5.8	1.2	1	0.8	23.2	4.8	4	3.2
43	5.8	1.2	1	0.8	23.2	4.8	4	3.2
44	5.8	1.2	1	0.8	23.2	4.8	4	3.2
45	5.8	1.2	1	0.8	23.2	4.8	4	3.2
46	5.8	1.2	1	0.8	23.2	4.8	4	3.2
47	5.8	1.2	1	0.8	23.2	4.8	4	3.2
48	5.8	1.2	1	0.8	23.2	4.8	4	3.2

Table A.4: Effect of mixing speed on droplets size

Mixing Speed, RPM	Mean Droplet Size		
	Crude Oil A	**Crude Oil B**	**Crude Oil C**
500	0.860	0.346	0.496
1000	0.370	0.134	0.123
1500	0.177	0.126	0.080
2000	0.077	0.059	0.034

Note: The viscosity is at 150 RPM at Temperature 50°C.

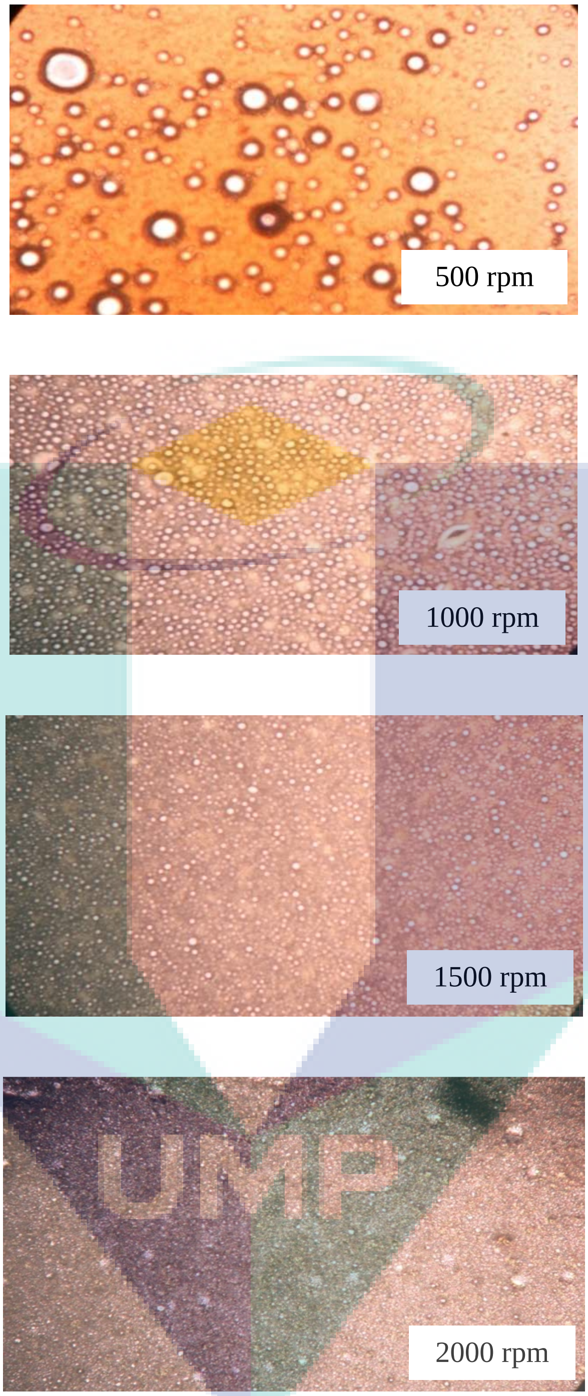

Figure A.1: Effect of mixing speed on droplet size for crude oil A

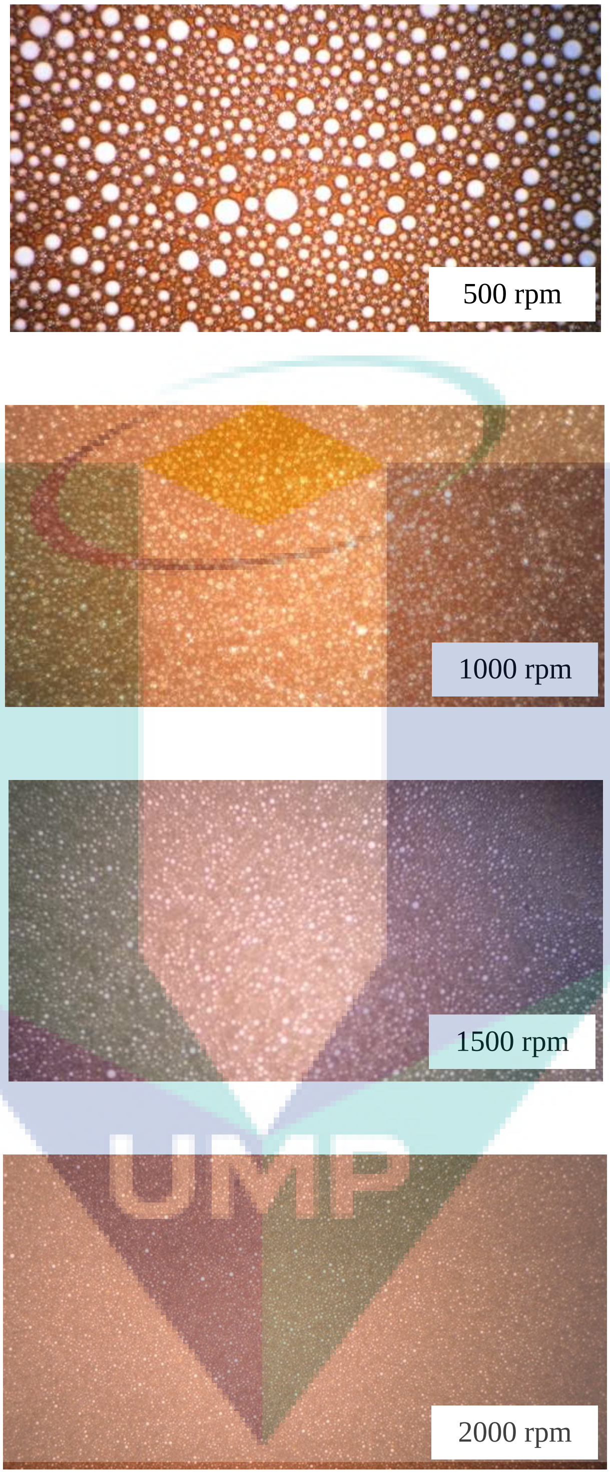

Figure A.2: Effect of mixing speed on droplet size for crude oil B

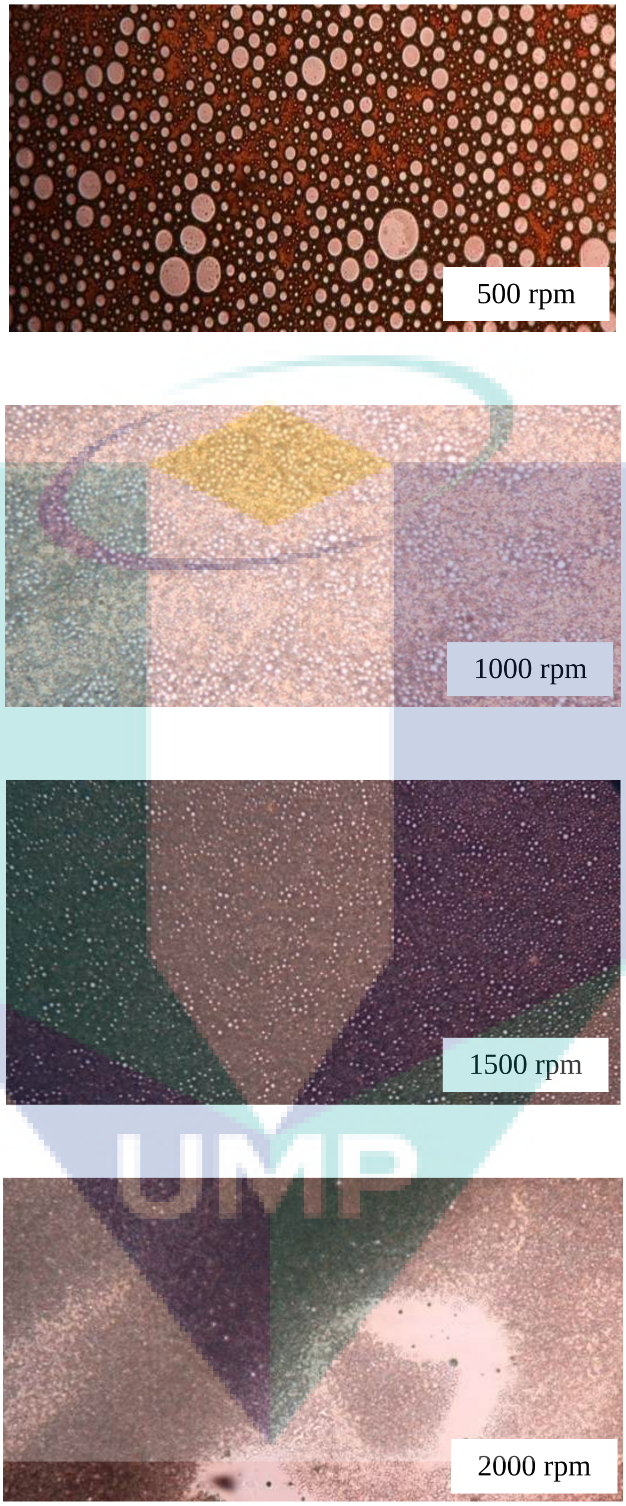

Figure A.3: Effect of mixing speed on droplet size for crude oil C

Table A.5: Effect of mixing speed on emulsion viscosity

Mixing speed	**Viscosity, cP**		
RPM	**Crude Oil A**	**Crude Oil B**	**Crude Oil C**
500	3.96	47.8	62.6
1000	27.2	62.4	89.4
1500	35.2	72.2	102.8
2000	44.6	88.8	139.2

Note: The viscosity is at 150 RPM at Temperature 50°C.

APPENDIX B

EFFECT OF PROCESSING TIME ON EMULSION STABILITY

Table B.1: Effect of processing time on emulsion stability for crude oil A

Time, min	**Volume oil separation (mL)**				**Volume oil separation (%)**			
	5 min	**7 min**	**9 min**	**12 min**	**5 min**	**7 min**	**9 min**	**12 min**
0	0	0	0	0	0	0	0	0
5	0.4	0	0	0	1.6	0	0	0
10	0.8	0	0	0	3.2	0	0	0
15	1	0.2	0	0	4	0.8	0	0
20	1.5	0.4	0.2	0	6	1.6	0.8	0
25	2	0.6	0.6	0	8	2.4	2.4	0
30	2.5	1	0.8	0	10	4	3.2	0
35	3	1.5	1	0	12	6	4	0
40	3.5	2	1.2	0	14	8	4.8	0
45	4	2.2	1.6	0	16	8.8	6.4	0
50	5	2.4	1.8	0	20	9.6	7.2	0
55	6	2.6	2.2	0.2	24	10.4	8.8	0.8
60	6	2.8	2.2	0.2	24	11.2	8.8	0.8
65	6.5	3	2.6	0.4	26	12	10.4	1.6
70	7	3.2	2.6	0.6	28	12.8	10.4	2.4
75	7	3.2	2.8	0.6	28	12.8	11.2	2.4
80	7.4	3.4	2.8	0.8	29.6	13.6	11.2	3.2
85	7.4	3.4	3	0.8	29.6	13.6	12	3.2
90	7.6	3.6	3.2	1	30.4	14.4	12.8	4
95	7.6	3.6	3.4	1.4	30.4	14.4	13.6	5.6
100	7.8	4	3.4	1.6	31.2	16	13.6	6.4
105	8	4	3.6	1.8	32	16	14.4	7.2
110	8	4.4	4	2	32	17.6	16	8
115	8.4	4.4	4.4	2	33.6	17.6	17.6	8
120	8.4	4.8	4.8	2	33.6	19.2	19.2	8
125	8.8	5	5	2	35.2	20	20	8
130	8.8	5	5	2	35.2	20	20	8
135	9	5	5	2	36	20	20	8
140	9	5	5	2	36	20	20	8
145	9	5	5.4	2	36	20	21.6	8
150	9	5	5.4	2	36	20	21.6	8

Table B.1: Continued

Time, min	Volume oil separation (mL)				Volume oil separation (%)			
	5 min	7 min	9 min	12 min	5 min	7 min	9 min	12 min
155	9	5	5.6	2.4	36	20	22.4	9.6
160	9	5	5.8	2.8	36	20	23.2	11.2
165	9	5.5	5.8	2.8	36	22	23.2	11.2
170	9.2	5.5	5.8	2.8	36.8	22	23.2	11.2
175	9.2	5.5	6	3	36.8	22	24	12
180	9.2	5.5	6	3	36.8	22	24	12
185	9.4	5.5	6	3	37.6	22	24	12
190	9.4	6	6	3	37.6	24	24	12
195	9.4	6	6	3	37.6	24	24	12
200	9.4	6	6	3	37.6	24	24	12
205	9.6	6	6	3	38.4	24	24	12
210	10	6	6	3	40	24	24	12
215	10	6	6	3	40	24	24	12
220	10	7	6	3	40	28	24	12
225	10	7	6	3	40	28	24	12
230	10	7	6	3	40	28	24	12
235	10	7	6	4	40	28	24	16
240	10	7	6	4	40	28	24	16
245	10	7	6	4	40	28	24	16
250	10	7.5	6	4	40	30	24	16
255	10	7.5	6	4	40	30	24	16
260	10	8	6	4	40	32	24	16
265	10	8	6	4	40	32	24	16
270	10	8	6	4	40	32	24	16
275	10	8	6	4	40	32	24	16
280	10	8	6	4	40	32	24	16
285	10	8	6	4	40	32	24	16
290	10	8.2	6	4	40	32.8	24	16
295	10	8.2	6	4	40	32.8	24	16
300	10	8.2	6	4	40	32.8	24	16

Table B.2: Effect of processing time on emulsion stability for crude oil B

Time, day	Volume oil separation, mL				Volume oil separation, %			
	5 min	7 min	9 min	12 min	5 min	7 min	9 min	12 min
0	0	0	0	0	0.0	0.0	0.0	0.0
1	0.5	0.5	0	0	2.0	2.0	0.0	0.0
2	0.8	1	0.5	0	3.2	4.0	2.0	0.0
3	1	1	0.5	0	4.0	4.0	2.0	0.0
4	1	1	1	1	4.0	4.0	4.0	4.0
5	1.4	1.2	1.2	1	5.6	4.8	4.8	4.0
6	1.4	1.2	1.4	1	5.6	4.8	5.6	4.0
7	1.6	1.2	1.4	1.2	6.4	4.8	5.6	4.8
8	1.6	1.2	1.6	1.2	6.4	4.8	6.4	4.8
9	1.8	1.2	1.6	1.4	7.2	4.8	6.4	5.6
10	1.8	1.4	1.6	1.4	7.2	5.6	6.4	5.6
11	2	1.4	1.8	1.6	8.0	5.6	7.2	6.4
12	2	1.4	1.8	1.6	8.0	5.6	7.2	6.4
13	2.2	1.4	1.8	1.8	8.8	5.6	7.2	7.2
14	2.2	1.4	1.8	1.8	8.8	5.6	7.2	7.2

Table B.3: Effect of processing on emulsion stability for crude oil C.

Time, day	Volume oil separation, mL				Volume oil separation, %			
	5 min	7 min	9 min	12 min	5 min	7 min	9 min	12 min
0	0	0	0	0	0.0	0.0	0.0	0.0
1	0.4	0.5	0	0	1.6	2.0	0.0	0.0
2	0.6	0.5	0.2	0	2.4	2.0	0.8	0.0
3	0.8	0.5	0.4	0	3.2	2.0	1.6	0.0
4	1	0.8	0.6	0.2	4.0	3.2	2.4	0.8
5	1.4	0.8	0.8	0.5	5.6	3.2	3.2	2.0
6	1.4	1	0.8	0.5	5.6	4.0	3.2	2.0
7	1.4	1.2	1	0.5	5.6	4.8	4.0	2.0
8	1.6	1.2	1	0.8	6.4	4.8	4.0	3.2
9	1.6	1.2	1.2	0.8	6.4	4.8	4.8	3.2
10	1.6	1.4	1.2	1	6.4	5.6	4.8	4.0
11	1.8	1.4	1.5	1	7.2	5.6	6.0	4.0
12	1.8	1.4	1.5	1	7.2	5.6	6.0	4.0
13	2	1.8	1.5	1	8.0	7.2	6.0	4.0
14	2.2	1.8	1.5	1	8.8	7.2	6.0	4.0

APPENDIX C

EFFECT OF VOLUME PHASE RATIO ON EMULSION STABILITY

Table C.1: Effect of volume phase ratio on emulsion stability for crude oil A

Time min	**Volume oil separation (mL)**				**Volume oil separation (%)**			
	Volume phase ratio, v/v %							
	20/80	**30/70**	**40/60**	**50/50**	**20/80**	**30/70**	**40/60**	**50/50**
0	0	0	0	0	0	0	0	0
5	0	0.5	1	0	0.0	1.4	3.3	0.0
10	0	1	2	0.4	0.5	2.9	6.7	1.6
15	0.2	2	3	0.6	0.5	5.7	10.0	2.4
20	0.2	3	3	0.8	0.5	8.6	10.0	3.2
25	0.2	4	4	1	1.0	11.4	13.3	4.0
30	0.4	4.4	5	1.4	1.0	12.6	16.7	5.6
35	0.4	6	6	2	1.0	17.1	20.0	8.0
40	0.4	9	7	3	1.0	25.7	23.3	12.0
45	0.4	10	8	3	1.0	28.6	26.7	12.0
50	0.4	11	8.4	4	1.0	31.4	28.0	16.0
55	0.4	12	8.6	4	1.0	34.3	28.7	16.0
60	0.4	13	8.8	4	1.0	37.1	29.3	16.0
65	0.4	13	9	0.4	1.0	37.1	30.0	16.0
70	0.4	14	9	5	2.0	40.0	30.0	20.0
75	0.8	14	10	5	2.5	40.0	33.3	20.0
80	1	15	10	5	2.5	42.9	33.3	20.0
85	1	15	10	5	2.5	42.9	33.3	20.0
90	1	16	10.2	5	2.5	45.7	34.0	20.0
95	1	16	10.2	5	2.5	45.7	34.0	20.0
100	1	16.2	10.2	5.4	2.5	46.3	34.0	21.6
105	1	16.2	10.6	5.4	2.5	46.3	35.3	21.6
110	1	16.4	10.6	5.4	2.5	46.9	35.3	21.6
115	1	16.4	10.6	5.6	2.5	46.9	35.3	22.4
120	1	16.4	10.6	5.6	2.5	46.9	35.3	22.4
125	1	16.8	10.8	5.6	2.5	48.0	36.0	22.4
130	1	16.8	10.8	5.8	2.5	48.0	36.0	23.2
135	1	16.8	10.8	5.8	2.5	48.0	36.0	23.2
140	1	17	10.8	6	2.5	48.6	36.0	24.0
145	1	17	10.8	6	2.5	48.6	36.0	24.0
150	1	17.2	11	6	2.5	49.1	36.7	24.0

Table C.1: Continued

Time min	**Volume oil separation (mL)**				**Volume oil separation (%)**			
	Volume phase ratio, v/v %							
	20/80	**30/70**	**40/60**	**50/50**	**20/80**	**30/70**	**40/60**	**50/50**
155	1	17.2	11	6.2	2.5	49.1	36.7	24.8
160	1	17.2	11	6.2	2.5	49.1	36.7	24.8
165	1	17.4	11	6.2	2.5	49.7	36.7	24.8
170	1	17.4	11	6.2	2.5	49.7	36.7	24.8
175	1	17.4	11	6.4	2.5	49.7	36.7	25.6
180	1	17.4	11	6.4	2.5	49.7	36.7	25.6
185	1	17.4	11	6.4	2.5	49.7	36.7	25.6
190	1	17.6	11	6.4	2.5	50.3	36.7	25.6
195	1	17.6	11	6.4	2.5	50.3	36.7	25.6
200	1	17.6	11.2	6.4	2.5	50.3	37.3	25.6
205	1	17.6	11.2	6.4	2.5	50.3	37.3	25.6
210	1	17.6	11.2	6.4	2.5	50.3	37.3	25.6
215	1	17.6	11.2	6.6	2.5	50.3	37.3	26.4
220	1	17.6	11.2	6.6	2.5	50.3	37.3	26.4
225	1	17.6	11.2	6.6	2.5	50.3	37.3	26.4
230	1	17.6	11.2	6.6	2.5	50.3	37.3	26.4
235	1	17.6	11.2	6.6	2.5	50.3	37.3	26.4
240	1	17.6	11.2	6.6	2.5	50.3	37.3	26.4
245	1	17.6	11.2	6.6	2.5	50.3	37.3	26.4
250	1	17.6	11.2	6.6	2.5	50.3	37.3	26.4
255	1	17.6	11.2	6.6	2.5	50.3	37.3	26.4
260	1	17.8	11.2	6.6	2.5	50.9	37.3	26.4
265	1	17.8	11.2	6.6	2.5	50.9	37.3	26.4
270	1	17.8	11.2	6.6	2.5	50.9	37.3	26.4
275	1	17.8	11.2	6.6	2.5	50.9	37.3	26.4
280	1	17.8	11.2	6.6	2.5	50.9	37.3	26.4
285	1	17.8	11.2	6.6	2.5	50.9	37.3	26.4
290	1	17.8	11.2	6.6	2.5	50.9	37.3	26.4
295	1	17.8	11.2	6.6	2.5	50.9	37.3	26.4
300	1	17.8	11.2	6.6	2.5	50.9	37.3	26.4

Table C.2: Effect of volume phase ratio on emulsion stability for crude oil B

Time, min	**Volume oil separation (mL)**				**Volume oil separation (%)**			
	Volume phase ratio, v/v %							
	20/80	**30/70**	**40/60**	**50/50**	**20/80**	**30/70**	**40/60**	**50/50**
0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0
30	0.2	0	0	0	1.25	0	0	0
40	0.4	0	0	0	2.5	0	0	0
50	0.8	0	0	0	5	0	0	0
60	1	0	0	0	6.25	0	0	0
70	1	0	0	0	6.25	0	0	0
80	1	0	0	0	6.25	0	0	0
90	1	0	0	0	6.25	0	0	0
100	1	0	0	0	6.25	0	0	0
110	1	0	0	0	6.25	0	0	0
120	1	0	0	0	6.25	0	0	0
130	1	0	0	0	6.25	0	0	0
140	1	0	0	0	6.25	0	0	0
150	1	0	0	0	6.25	0	0	0
160	1	0	0	0	6.25	0	0	0
170	1	0.2	0	0	6.25	1.43	0	0
180	1	0.2	0	0	6.25	1.43	0	0
190	1	0.2	0	0	6.25	1.43	0	0
200	1	0.2	0	0	6.25	1.43	0	0
210	1	0.5	0	0	6.25	3.57	0	0
220	1	0.5	0	0	6.25	3.57	0	0
230	1.5	0.5	0	0	9.38	3.57	0	0
240	1.5	0.5	0.2	0	9.38	3.57	1.67	0
250	1.5	0.5	0.2	0	9.38	3.57	1.67	0
260	1.5	0.5	0.2	0	9.38	3.57	1.67	0
270	2	1	0.2	0	12.5	7.14	1.67	0
280	2	1	0.2	0	12.5	7.14	1.67	0
290	2	1	0.5	0	12.5	7.14	4.17	0
300	2	1	0.5	0	12.5	7.14	4.17	0

Table C.3: Effect of volume phase ratio on emulsion stability for crude oil C

Time min	Volume oil separated (mL)				Volume oil separated (%)			
	Volume phase ratio, v/v %							
	20/80	30/70	40/60	50/50	20/80	30/70	40/60	50/50
0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0
10	1	0.2	0	0	4	0.8	0	0
15	2	0.2	0.2	0	8	0.8	0.8	0
20	3	0.2	0.2	0	12	0.8	0.8	0
25	3	0.4	0.2	0	12	1.6	0.8	0
30	6	0.4	0.2	0	24	1.6	0.8	0
35	6	0.6	0.4	0	24	2.4	1.6	0
40	8	0.6	0.4	0	32	2.4	1.6	0
45	8	0.6	0.4	0	32	2.4	1.6	0
50	8	0.8	0.4	0	32	3.2	1.6	0
55	9	0.8	0.4	0	36	3.2	1.6	0
60	9	0.8	0.4	0	36	3.2	1.6	0
65	10	1	0.6	0	40	4	2.4	0
70	10	1	0.6	0	40	4	2.4	0
75	10	1	0.6	0	40	4	2.4	0
80	10	1	0.8	0	40	4	3.2	0
85	13	1	0.8	0	52	4	3.2	0
90	13	1	0.8	0	52	4	3.2	0
95	13	1	0.8	0	52	4	3.2	0
100	13	2	0.8	0	52	8	3.2	0
105	14	2	0.8	0	56	8	3.2	0
110	14	2	0.8	0	56	8	3.2	0
115	14	2	1	0	56	8	4	0
120	14	3	1	0	56	12	4	0
125	14	3	1	0	56	12	4	0
130	14	3	1	0	56	12	4	0
135	14	3	1	0.6	56	12	4	2.4
140	14	4	1	0.6	56	16	4	2.4
145	14	4	1	0.8	56	16	4	3.2
150	14	4	1	0.8	56	16	4	3.2
155	14	5	1	0.8	56	20	4	3.2
160	14	5	1	0.8	56	20	4	3.2
165	14	5	1	0.8	56	20	4	3.2
170	14	5	1	0.8	56	20	4	3.2
175	14	5	1	1	56	20	4	4

Table C.3: Continued

Time min	Volume oil separated (mL)				Volume oil separated (%)			
	Volume phase ratio, v/v %							
	20/80	30/70	40/60	50/50	20/80	30/70	40/60	50/50
180	14	6	1.5	1	56	24	6	4
185	14	6	1.5	1	56	24	6	4
190	14	6	1.5	1	56	24	6	4
195	14	6	1.5	1	56	24	6	4
200	14	6	2	1	56	24	8	4
205	14	7	2	1	56	28	8	4
210	14	7	2	1	56	28	8	4
215	14	7	2	1	56	28	8	4
220	14	7	2	1.4	56	28	8	5.6
225	14	8	3	1.4	56	32	12	5.6
230	14	8	3	1.4	56	32	12	5.6
235	14	8	3	1.4	56	32	12	5.6
240	14	8	3	1.4	56	32	12	5.6
245	14	9	3	1.4	56	36	12	5.6
250	14	9	3	1.4	56	36	12	5.6
255	14	9	3	1.4	56	36	12	5.6
260	14	9	3	1.4	56	36	12	5.6
265	14	9	3	1.4	56	36	12	5.6
270	14	10	3	1.4	56	40	12	5.6
275	14	10	3	1.4	56	40	12	5.6
280	14	10	3	1.4	56	40	12	5.6
285	14	10	3	1.4	56	40	12	5.6
290	14	10	3	1.4	56	40	12	5.6
295	14	10	3	1.4	56	40	12	5.6
300	14	10	3	1.4	56	40	12	5.6

Table C.4: Effect of volume phase ratio on droplets size for crude oil A, B and C

Volume fraction v/v %	Mean Droplet Size, µm		
	Crude Oil A	Crude Oil B	Crude Oil C
20/80	0.103	0.091	0.089
30/70	0.093	0.086	0.070
40/60	0.077	0.059	0.044
50/50	0.049	0.044	0.037

Table C.5: Effect of volume phase ratio on emulsions viscosity for crude oil A, B and C

Volume phase ratio	**Viscosity, cP**		
v/v %	**Crude Oil A**	**Crude Oil B**	**Crude Oil C**
20/80	7.0	15.6	62.6
30/70	17.4	23.2	89.4
40/60	21.8	46.8	102.8
50/50	35.2	88.8	139.2

APPENDIX D

EFFECT OF EMULSIFIER TYPES ON EMULSION STABILITY

Table D.1: Effect of emulsifier types on emulsion stability for crude oil A

Time, min	Volume separated (mL)				Volume separated (%)			
	Span 83	Tween 80	Triton X-100	SDDS	Span 83	Tween 80	Triton X-100	SDDS
0	0	0	8	0	0	0	32	0
5	0	1	12	0	0	4	48	0
10	0.2	2	18	0	0.8	8	72	0
15	0.4	2	18	0	1.6	8	72	0
20	0.6	2	18	0	2.4	8	72	0
25	1	2	18	0	4	8	72	0
30	1	2	18	0	4	8	72	0
35	1	3	18	0	4	12	72	0
40	1	4	18	0	4	16	72	0
45	1	4	18	0	4	16	72	0
50	1.2	4	18	0	4.8	16	72	0
55	1.2	5	18	0	4.8	20	72	0
60	1.2	5	18	0	4.8	20	72	0
65	1.2	5	18	0	4.8	20	72	0
70	1.2	7	18	0	4.8	28	72	0
75	1.4	7	18	0	5.6	28	72	0
80	1.4	7	18	0	5.6	28	72	0
85	1.4	7	18	0	5.6	28	72	0
90	1.4	8	18	0	5.6	32	72	0
95	1.4	8	18	0	5.6	32	72	0
100	1.6	8	18	0	6.4	32	72	0
105	1.6	8	18	0	6.4	32	72	0
110	1.6	8	18	0	6.4	32	72	0
115	1.6	8	18	0	6.4	32	72	0
120	1.6	9	18	0	6.4	36	72	0
125	1.8	9	18	0	7.2	36	72	0
130	1.8	9	18	0	7.2	36	72	0
135	1.8	9	18	0	7.2	36	72	0
140	1.8	9	18	0	7.2	36	72	0
145	1.8	9	18	0	7.2	36	72	0
150	1.8	9	18	0	7.2	36	72	0
155	1.8	9	18	0	7.2	36	72	0
160	2	10	19	0	8	40	76	0

Table D.1: Continued

Time, min	Volume separated (mL)				Volume separated (%)			
	Span 83	Tween 80	Triton X-100	SDDS	Span 83	Tween 80	Triton X-100	SDDS
175	2.2	10	19	0	8.8	40	76	0
180	2.2	10	19	0	8.8	40	76	0
185	2.4	11	19	0	9.6	44	76	0
190	2.6	11	19	0	10.4	44	76	0
195	2.8	11	19	0	11.2	44	76	0
200	2.8	11	20	0	11.2	44	80	0
205	2.8	11	20	0	11.2	44	80	0
210	3	11	20	0	12	44	80	0
215	3.2	12	20	0	12.8	48	80	0
220	3.4	12	20	0	13.6	48	80	0
225	3.6	13	20	0	14.4	52	80	0
230	3.6	14	20	0	14.4	56	80	0
235	3.8	14	21	0	15.2	56	84	0
240	4	14	21	0	16	56	84	0
245	4	15	21	0	16	60	84	0
250	4.4	16	21	0	17.6	64	84	0
255	4.6	17	21	0	18.4	68	84	0
260	4.6	18	22	0	18.4	72	88	0
265	4.8	18	23	0	19.2	72	92	0
270	4.8	18	23	0	19.2	72	92	0
275	4.8	19	23	0	19.2	76	92	0
280	4.8	20	23	0	19.2	80	92	0
285	4.8	20	24	0	19.2	80	96	0
290	4.8	21	24	0	19.2	84	96	0
295	4.8	23	24	0	19.2	92	96	0
300	4.8	23	24	0	19.2	92	96	0

Table D.2: Effect of emulsifier types on emulsion stability for crude oil B

Time, min	Volume oil separated (mL)				Volume oil separated (%)			
	Span 83	Tween 80	Triton X-100	SDDS	Span 83	Tween 80	Triton X-100	SDDS
0	0	0	1	0	0	0	4	0
5	0	1	1.5	0	0	4	6	0
10	0	1	2	0	0	4	8	0
15	0	1	2	0	0	4	8	0
20	0	1	2	0.2	0	4	8	0.8
25	0	1.5	2	0.4	0	6	8	1.6
30	0	2	2	0.6	0	8	8	2.4
35	0.1	2	2	0.6	0.4	8	8	2.4
40	0.2	2	2	1	0.8	8	8	4
45	0.3	2	2	1	1.2	8	8	4
50	0.4	2.5	2	1	1.6	10	8	4
55	0.6	2.5	2	1	2.4	10	8	4
60	0.6	3	2	1	2.4	12	8	4
65	0.6	3	2.4	1	2.4	12	9.6	4
70	0.6	3	2.6	1	2.4	12	10.4	4
75	0.6	3	2.8	1	2.4	12	11.2	4
80	0.6	3	2.8	1	2.4	12	11.2	4
85	0.6	4	3	1	2.4	16	12	4
90	0.6	4.4	3	1	2.4	17.6	12	4
95	0.6	4.5	3	1	2.4	18	12	4
100	0.6	4.6	3	1	2.4	18.4	12	4
105	0.6	5	3	1	2.4	20	12	4
110	0.6	5	3	1	2.4	20	12	4
115	0.8	5	3	1	3.2	20	12	4
120	0.8	5	3	1	3.2	20	12	4
125	0.8	5	3	1	3.2	20	12	4
130	0.8	5	3	1	3.2	20	12	4
135	1	5	3	1	4	20	12	4
140	1	5.5	3	1.2	4	22	12	4.8
145	1	5.5	4	1.2	4	22	16	4.8
150	1	6	4	1.2	4	24	16	4.8
155	1	6	4	1.2	4	24	16	4.8
160	1	6	4	1.2	4	24	16	4.8
165	1	6.4	4	1.2	4	25.6	16	4.8
170	1	6.4	4	1.2	4	25.6	16	4.8

Table D.2: Continued

Time, min	Volume oil separated (mL)				Volume oil separated (%)			
	Span 83	**Tween 80**	**Triton X-100**	**SDDS**	**Span 83**	**Tween 80**	**Triton X-100**	**SDDS**
175	1	6.8	4	1.2	4	27.2	16	4.8
180	1	6.8	4	1.2	4	27.2	16	4.8
185	1	6.8	4	1.2	4	27.2	16	4.8
190	1	6.8	4	1.2	4	27.2	16	4.8
195	1	6.8	4	1.2	4	27.2	16	4.8
200	1	6.8	4	1.2	4	27.2	16	4.8
205	1	6.8	4	1.2	4	27.2	16	4.8
210	1	6.8	4	1.2	4	27.2	16	4.8
215	1	7	4	1.2	4	28	16	4.8
220	1	7	4	1.2	4	28	16	4.8
225	1	7.4	4	1.2	4	29.6	16	4.8
230	1	7.4	4	1.2	4	29.6	16	4.8
235	1	7.8	4	1.4	4	31.2	16	5.6
240	1	7.8	4	1.4	4	31.2	16	5.6
245	1	7.8	4	1.4	4	31.2	16	5.6
250	1	8	4	1.4	4	32	16	5.6
255	1	8.4	4	1.4	4	33.6	16	5.6
260	1	8.4	4	1.4	4	33.6	16	5.6
265	1	8.6	4	1.4	4	34.4	16	5.6
270	1	9	4	1.4	4	36	16	5.6
275	1	9	4	1.4	4	36	16	5.6
280	1	9.6	4	1.4	4	38.4	16	5.6
285	1	9.6	4	1.4	4	38.4	16	5.6
290	1	9.8	4	1.4	4	39.2	16	5.6
295	1	10	4	1.4	4	40	16	5.6
300	1	10	4	1.4	4	40	16	5.6

Table D.3: Effect of emulsifier types on emulsion stability for crude oil C

Time, Min	**Volume oil separated (mL)**				**Volume oil separated (%)**			
	Span 83	**Tween 80**	**Triton X-100**	**SDDS**	**Span 83**	**Tween 80**	**Triton X-100**	**SDDS**
0	0	0	0	0	0	0	0	0
5	0	0	1	0	0	0	4	0
10	0	0	1	0	0	0	4	0
15	0	0	1	0	0	0	4	0
20	0	0	1	0	0	0	4	0
25	0	0	1	0	0	0	4	0
30	0	0	1	0	0	0	4	0
35	0	0	1	0	0	0	4	0
40	0	0.2	1	0	0	0.8	4	0
45	0	0.2	1	0	0	0.8	4	0
50	0	0.2	1	0	0	0.8	4	0
55	0	0.2	2	0	0	0.8	8	0
60	0	0.2	2	0	0	0.8	8	0
65	0	0.4	2	0	0	1.6	8	0
70	0	0.4	2	0	0	1.6	8	0
75	0	0.4	2	0	0	1.6	8	0
80	0	0.4	2	0	0	1.6	8	0
85	0	0.6	2	0	0	2.4	8	0
90	0	0.6	2	0	0	2.4	8	0
95	0	0.6	2	0	0	2.4	8	0
100	0	0.8	2	0	0	3.2	8	0
105	0	0.8	2	0	0	3.2	8	0
110	0	0.8	2	0	0	3.2	8	0
115	0	0.8	2	0	0	3.2	8	0
120	0	0.8	3	0	0	3.2	12	0
125	0	1	3	0	0	4	12	0
130	0	1	3	0	0	4	12	0
135	0	1	3	0	0	4	12	0
140	0	1	3	0	0	4	12	0
145	0	1	3	0	0	4	12	0
150	0	1	3	0	0	4	12	0
155	0	1	3	0	0	4	12	0
160	0	1	3	0	0	4	12	0
165	0	1	3	0	0	4	12	0
170	0	1	3	0	0	4	12	0
175	0	1	3	0	0	4	12	0
180	0	1	3	0	0	4	12	0

Table D.3: Continued

Time, Min	Volume oil separated (mL)				Volume oil separated (%)			
	Span 83	**Tween 80**	**Triton X-100**	**SDDS**	**Span 83**	**Tween 80**	**Triton X-100**	**SDDS**
185	0	1	3	0	0	4	12	0
190	0	1	3	1	0	4	12	0
195	0	1	3	1	0	4	12	4
200	0	1	3	1	0	4	12	4
205	0	1	3	1	0	4	12	4
210	0	1	3	1	0	4	12	4
215	0	1	3	1	0	4	12	4
220	0	1	3	1	0	4	12	4
s225	0	1	3	1	0	4	12	4
230	0	1	3	1	0	4	12	4
235	0	1	3	1	0	4	12	4
240	0	1	3	1	0	4	12	4
245	0	1	3	1	0	4	12	4
250	0	1	3	1	0	4	12	4
255	0	1	3	1	0	4	12	4
260	0	1	4	1	0	4	16	4
265	0	1	4	1	0	4	16	4
270	0	1	4	1	0	4	16	4
275	0	1	4	1	0	4	16	4
280	0	1	4	1	0	4	16	4
285	0	1	4	1	0	4	16	4
290	0	1	4	1	0	4	16	4
295	0	1	4	1	0	4	16	4
300	0	1	4	1	0	4	16	4

APPENDIX E

EFFECT OF EMULSIFIERS CONCENTRATION ON EMULSIONS STABILITY

Table E.1: Effect of emulsifier concentration on emulsion stability for crude oil A

Time min	Volume oil separated (mL)					Volume oil separated (%)				
	Concentration of emulsifier (w/w %)									
	0.5	**1.0**	**1.5**	**2.0**	**2.5**	**0.5**	**1.0**	**1.5**	**2.0**	**2.5**
0	0	0	0	0	0	0	0	0	0	0
5	0.4	0.1	0	0	0	1.6	0.4	0	0	0
10	1	0.3	0.1	0	0	4	1.2	0.4	0	0
15	1	1	0.1	0	0	4	4	0.4	0	0
20	1.5	1	0.2	0.1	0	6	4	0.8	0.4	0
25	2	1.5	0.2	0.1	0.1	8	6	0.8	0.4	0.4
30	2	2	1	0.1	0.1	8	8	4	0.4	0.4
35	2.5	2	1.3	0.3	0.1	10	8	5.2	1.2	0.4
40	3	2	1.5	0.3	0.1	12	8	6	1.2	0.4
45	3	2	2	0.5	0.3	12	8	8	2	1.2
50	3.5	2.2	2	0.8	0.3	14	8.8	8	3.2	1.2
55	3.5	3	2	1	1	14	12	8	4	4
60	4	3	2	1	1	16	12	8	4	4
65	4.5	3	2	1	1	18	12	8	4	4
70	5	3.5	2	1	1.1	20	14	8	4	4.4
75	5.5	3.5	2.1	1	1.1	22	14	8.4	4	4.4
80	6	3.8	3	1	1.2	24	15.2	12	4	4.8
85	6	4	3.5	1	1.5	24	16	14	4	6
90	6.1	4	3.5	1	1.8	24.4	16	14	4	7.2
95	6.5	4	3.8	1	2	26	16	15.2	4	8
100	7	4.3	3.8	1	2	28	17.2	15.2	4	8
105	7	5	4	1	2.3	28	20	16	4	9.2
110	7.3	5	4	1	2.6	29.2	20	16	4	10.4
115	7.5	5	4	1.2	2.8	30	20	16	4.8	11.2
120	7.8	5.2	4	1.2	3	31.2	20.8	16	4.8	12
125	8	5.2	4	1.2	3	32	20.8	16	4.8	12
130	8	5.3	4	2	3	32	21.2	16	8	12
135	8	5.5	4	2	3.5	32	22	16	8	14
140	8	5.8	4	2	4	32	23.2	16	8	16
145	8.3	6	4.3	2	4	33.2	24	17.2	8	16
150	8.5	6	4.5	2	4	34	24	18	8	16

Table E.1: Continued

Time, min	Volume oil separated (mL)					Volume oil separated (%)				
	Concentration of emulsifier (w/w %)									
	0.5	**1.0**	**1.5**	**2.0**	**2.5**	**0.5**	**1.0**	**1.5**	**2.0**	**2.5**
155	8.5	6	4.8	2	4	34	24	19.2	8	16
160	9	6	4.8	2.5	4	36	24	19.2	10	16
165	9	6	5	2.5	4	36	24	20	10	16
170	9	6	5	3	4	36	24	20	12	16
175	9	6	5	3	4	36	24	20	12	16
180	9	6	5	3	4	36	24	20	12	16
185	9	6	5	3	4	36	24	20	12	16
190	9	6.3	5.5	3	4	36	25.2	22	12	16
195	9.5	6.5	5.5	3	4.3	38	26	22	12	17.2
200	9.5	6.5	5.5	3	4.8	38	26	22	12	19.2
205	9.5	6.5	6	3	5	38	26	24	12	20
210	9.5	6.8	6	3	5	38	27.2	24	12	20
215	9.5	6.8	6	3	5	38	27.2	24	12	20
220	9.7	7	6	3	5	38.8	28	24	12	20
225	10	7	6	3.5	5	40	28	24	14	20
230	10	7	6	3.5	5	40	28	24	14	20
235	10	7	6	3.5	5	40	28	24	14	20
240	10	7	6.1	3.5	5	40	28	24.4	14	20
245	10	7	6.1	4	5	40	28	24.4	16	20
250	10	7.1	6.1	4	5	40	28.4	24.4	16	20
255	10	7.1	6.1	4	5.5	40	28.4	24.4	16	22
260	10	7.1	6.3	4	5.5	40	28.4	25.2	16	22
265	10	7.3	6.5	4	6	40	29.2	26	16	24
270	10	7.3	6.5	4	6	40	29.2	26	16	24
275	10	7.3	6.5	4	6	40	29.2	26	16	24
280	10	7.5	7	4.5	6	40	30	28	18	24
285	10	7.5	7	5	6	40	30	28	20	24
290	10	7.5	7	5	6.5	40	30	28	20	26
295	10	8	7	5	6.5	40	32	28	20	26
300	10	8	7	5	6.5	40	32	28	20	26

Table E.2: Effect of emulsifier concentration on emulsion stability for crude oil B

Time, min	Volume oil separated (mL)					Volume oil separated (%)				
	Concentration of emulsifier (w/w %)									
	0.5	**1.0**	**1.5**	**2.0**	**2.5**	**0.5**	**1.0**	**1.5**	**2.0**	**2.5**
0	0	0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0
25	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0	0
35	0	0	0	0	0	0	0	0	0	0
40	0	0	0	0	0	0	0	0	0	0
45	0	0	0	0.2	0	0	0	0	0.8	0
50	0	0	0.2	0.2	0	0	0	0.8	0.8	0
55	0.2	0	0.2	0.2	0.2	0.8	0	0.8	0.8	0.8
60	0.2	0	0.2	0.2	0.2	0.8	0	0.8	0.8	0.8
65	0.2	0	0.2	0.2	0.2	0.8	0	0.8	0.8	0.8
70	0.2	0.2	0.2	0.2	0.2	0.8	0.8	0.8	0.8	0.8
75	0.4	0.2	0.2	0.2	0.2	1.6	0.8	0.8	0.8	0.8
80	0.4	0.2	0.2	0.2	0.2	1.6	0.8	0.8	0.8	0.8
85	0.4	0.2	0.4	0.2	0.2	1.6	0.8	1.6	0.8	0.8
90	0.4	0.2	0.4	0.2	0.2	1.6	0.8	1.6	0.8	0.8
95	0.6	0.2	0.4	0.2	0.2	2.4	0.8	1.6	0.8	0.8
100	0.6	0.4	0.4	0.2	0.2	2.4	1.6	1.6	0.8	0.8
105	0.6	0.4	0.4	0.2	0.2	2.4	1.6	1.6	0.8	0.8
110	0.6	0.4	0.4	0.2	0.2	2.4	1.6	1.6	0.8	0.8
115	0.8	0.6	0.4	0.2	0.4	3.2	2.4	1.6	0.8	1.6
120	0.8	0.6	0.4	0.2	0.4	3.2	2.4	1.6	0.8	1.6
125	0.8	0.6	0.4	0.2	0.4	3.2	2.4	1.6	0.8	1.6
130	0.8	0.6	0.6	0.2	0.4	3.2	2.4	2.4	0.8	1.6
135	0.8	0.6	0.6	0.4	0.8	3.2	2.4	2.4	1.6	3.2
140	0.8	0.6	0.6	0.4	0.8	3.2	2.4	2.4	1.6	3.2
145	0.8	0.8	0.8	0.4	0.8	3.2	3.2	3.2	1.6	3.2
150	0.8	0.8	0.8	0.4	0.8	3.2	3.2	3.2	1.6	3.2
155	0.8	0.8	1	0.4	1	3.2	3.2	4	1.6	4
160	0.8	0.8	1	0.4	1	3.2	3.2	4	1.6	4
165	0.8	0.8	1	0.4	1	3.2	3.2	4	1.6	4

Table E.2: Continued

Time, min	**Volume oil separated (mL)**					**Volume oil separated (%)**				
	Concentration of emulsifier (w/w %)									
	0.5	**1.0**	**1.5**	**2.0**	**2.5**	**0.5**	**1.0**	**1.5**	**2.0**	**2.5**
170	0.8	0.8	1	0.4	1	3.2	3.2	4	1.6	4
175	1	0.8	1	0.4	1	4	3.2	4	1.6	4
180	1	0.8	1	0.4	1	4	3.2	4	1.6	4
185	1	0.8	1	0.4	1	4	3.2	4	1.6	4
190	1	0.8	1	0.4	1	4	3.2	4	1.6	4
195	1	0.8	1	0.4	1	4	3.2	4	1.6	4
200	1	0.8	1	0.4	1	4	3.2	4	1.6	4
205	1.4	0.8	1	0.4	1	5.6	3.2	4	1.6	4
210	1.4	0.8	1	0.4	1	5.6	3.2	4	1.6	4
215	1.4	0.8	1	0.4	1	5.6	3.2	4	1.6	4
220	1.4	0.8	1	0.4	1	5.6	3.2	4	1.6	4
225	1.4	1.2	1	0.4	1	5.6	4.8	4	1.6	4
230	1.6	1.2	1	0.4	1	6.4	4.8	4	1.6	4
235	1.6	1.2	1	0.4	1	6.4	4.8	4	1.6	4
240	1.6	1.2	1	0.4	1	6.4	4.8	4	1.6	4
245	1.8	1.2	1	0.4	1	7.2	4.8	4	1.6	4
250	1.8	1.2	1	0.4	1	7.2	4.8	4	1.6	4
255	1.8	1.2	1	0.4	1	7.2	4.8	4	1.6	4
260	1.8	1.2	1	0.4	1	7.2	4.8	4	1.6	4
265	1.8	1.2	1	0.4	1	7.2	4.8	4	1.6	4
270	1.8	1.2	1	0.4	1	7.2	4.8	4	1.6	4
275	1.8	1.2	1	0.4	1	7.2	4.8	4	1.6	4
280	2	1.2	1	0.4	1	8	4.8	4	1.6	4
285	2	1.2	1	0.4	1	8	4.8	4	1.6	4
290	2	1.2	1	0.4	1	8	4.8	4	1.6	4
295	2	1.2	1	0.4	1	8	4.8	4	1.6	4
300	2	1.2	1	0.4	1	8	4.8	4	1.6	4

Table E.3: Effect of emulsifier concentration on emulsion stability for crude oil C

Time, min	**Volume of oil separated (mL)**					**Volume of oil separated (%)**				
	Concentration of emulsifier (w/w %)									
	0.5	**1.0**	**1.5**	**2.0**	**2.5**	**0.5**	**1.0**	**1.5**	**2.0**	**2.5**
0	0	0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0.2	0	0	0	0	0.8
15	0	0	0	0	0.4	0	0	0	0	1.6
20	0.2	0	0	0	0.4	0.8	0	0	0	1.6
25	0.2	0	0	0	0.4	0.8	0	0	0	1.6
30	0.4	0	0	0	0.5	1.6	0	0	0	2
35	0.4	0	0	0	0.5	1.6	0	0	0	2
40	0.4	0	0	0	0.6	1.6	0	0	0	2.4
45	0.6	0.2	0	0	0.6	2.4	0.8	0	0	2.4
50	0.6	0.2	0	0	0.8	2.4	0.8	0	0	3.2
55	0.6	0.2	0	0	0.8	2.4	0.8	0	0	3.2
60	0.6	0.2	0	0	0.8	2.4	0.8	0	0	3.2
65	0.8	0.2	0.2	0	1	3.2	0.8	0.8	0	4
70	0.8	0.2	0.2	0	1	3.2	0.8	0.8	0	4
75	0.8	0.2	0.2	0	1	3.2	0.8	0.8	0	4
80	0.8	0.2	0.2	0	1	3.2	0.8	0.8	0	4
85	1	0.2	0.2	0	1.2	4	0.8	0.8	0	4.8
90	1	0.2	0.2	0	1.2	4	0.8	0.8	0	4.8
95	1	0.2	0.2	0	1.2	4	0.8	0.8	0	4.8
100	1	0.2	0.2	0	1.2	4	0.8	0.8	0	4.8
105	1	0.2	0.2	0	1.2	4	0.8	0.8	0	4.8
110	1	0.2	0.2	0	1.2	4	0.8	0.8	0	4.8
115	1	0.4	0.4	0	1.2	4	1.6	1.6	0	4.8
120	1	0.4	0.4	0	1.2	4	1.6	1.6	0	4.8
125	1	0.4	0.4	0	1.2	4	1.6	1.6	0	4.8
130	1	0.8	0.6	0.2	1.2	4	3.2	2.4	0.8	4.8
135	1	0.8	0.6	0.2	1.2	4	3.2	2.4	0.8	4.8
140	1	0.8	0.8	0.2	1.2	4	3.2	3.2	0.8	4.8
145	1	0.8	0.8	0.2	1.2	4	3.2	3.2	0.8	4.8
150	1	1	0.8	0.2	1.2	4	4	3.2	0.8	4.8
155	1	1	0.8	0.2	1.2	4	4	3.2	0.8	4.8
160	1	1	0.8	0.2	1.2	4	4	3.2	0.8	4.8
165	1	1	0.8	0.2	1.2	4	4	3.2	0.8	4.8
170	1	1	0.8	0.2	1.2	4	4	3.2	0.8	4.8

Table E.3: Continued

Time, min	Volume of oil separated (mL)					Volume of oil separated (%)				
	Concentration of emulsifier (w/w %)									
	0.5	1.0	1.5	2.0	2.5	0.5	1.0	1.5	2.0	2.5
175	1	1	0.8	0.2	1.2	4	4	3.2	0.8	4.8
180	1	1	0.8	0.2	1.2	4	4	3.2	0.8	4.8
185	1	1	0.8	0.4	1.2	4	4	3.2	1.6	4.8
190	1	1	1	0.4	1.2	4	4	4	1.6	4.8
195	1	1	1	0.4	1.2	4	4	4	1.6	4.8
200	1	1	1	0.4	1.2	4	4	4	1.6	4.8
205	1	1	1	0.4	1.2	4	4	4	1.6	4.8
210	1	1	1	0.4	1.2	4	4	4	1.6	4.8
215	1	1	1	0.4	1.2	4	4	4	1.6	4.8
220	1	1	1	0.4	1.2	4	4	4	1.6	4.8
225	1	1	1	0.4	1.2	4	4	4	1.6	4.8
230	1	1	1	0.4	1.2	4	4	4	1.6	4.8
235	1	1	1	0.4	1.2	4	4	4	1.6	4.8
240	1	1	1	0.4	1.2	4	4	4	1.6	4.8
245	1	1	1	0.4	1.2	4	4	4	1.6	4.8
250	1	1	1	0.4	1.2	4	4	4	1.6	4.8
255	1	1	1	0.6	1.2	4	4	4	2.4	4.8
260	1	1	1	0.6	1.2	4	4	4	2.4	4.8
265	1	1	1	0.6	1.2	4	4	4	2.4	4.8
270	1	1	1	0.6	1.2	4	4	4	2.4	4.8
275	1	1	1	0.6	1.2	4	4	4	2.4	4.8
280	1	1	1	0.6	1.2	4	4	4	2.4	4.8
285	1	1	1	0.6	1.2	4	4	4	2.4	4.8
290	1	1	1	0.6	1.2	4	4	4	2.4	4.8
295	1	1	1	0.6	1.2	4	4	4	2.4	4.8
300	1	1	1	0.6	1.2	4	4	4	2.4	4.8

APPENDIX F

THERMAL DEMULSIFICATION METHOD

Table F.1: Heating rate during demulsification of W/O emulsion

Time, sec	Crude oil A		Crude oil B		Crude oil C	
	Temp. T (°C)	Heating rate dT/s	Temp. T (°C)	Heating rate dT/s	Temp. T (°C)	Heating rate dT/s
0	31	0	30.4	0	31.2	0
30	31.8	1.060	31.4	1.047	35.4	1.180
60	34.3	0.572	33.8	0.563	43.3	0.722
90	41.5	0.461	35	0.389	54	0.600
120	43.2	0.360	37.4	0.312	61.6	0.513
150	44.2	0.295	44.4	0.296	63.7	0.425
150	44.9	0.299	50.2	0.335	68.8	0.459
210	48.1	0.229	60	0.286	76.7	0.365
240	53.7	0.224	66.3	0.276	83.8	0.349
270	55.9	0.207	69.1	0.256	89.9	0.333
300	59.6	0.199	67	0.223	92.4	0.308
330	50.3	0.152	99.9	0.303	97.3	0.295
360	55	0.153	101.9	0.283	109.2	0.303
390	68	0.174	102.8	0.264	113	0.290
420	64	0.152	70.1	0.167	112.2	0.267
450	65.4	0.145	73.2	0.163	112.9	0.251
480	62.1	0.129	76.7	0.160	114.2	0.238
510	62.9	0.123	71.9	0.141	113.6	0.223
540	66.4	0.123	88.5	0.164	110.6	0.205
570	62.7	0.110	105.9	0.186	111.6	0.196
600	55.5	0.093	61	0.102	111.2	0.185
630	67.9	0.108	59.5	0.094	112.2	0.178
660	76.2	0.115	60.5	0.092	116	0.176
690	76.2	0.110	59.3	0.086	121.4	0.176
720	80.5	0.112	60.4	0.084	111.1	0.154
750	73.4	0.098	58.9	0.079	110.7	0.148
780	62.6	0.080	60.12	0.077	111.8	0.143
810	63.1	0.078	60.7	0.075	114.1	0.141
840	64.1	0.076	68.7	0.082	112.7	0.134
870	59.7	0.069	55	0.063	116.3	0.134
900	57.6	0.064	60	0.067	115.1	0.128

Table F.1: Continued

	Crude oil A		Crude oil B		Crude oil C	
Time, sec	**Temp. T (°C)**	**Heating rate dT/s**	**Temp. T (°C)**	**Heating rate dT/s**	**Temp. T (°C)**	**Heating rate dT/s**
930	66.7	0.072	67	0.072	114.3	0.123
960	72	0.075	60.9	0.063	113.6	0.118
990	65.1	0.066	63.3	0.064	117.8	0.119
1120	69.4	0.062	66.3	0.059	121.9	0.109
1150	58.2	0.051	66	0.057	132.9	0.116
1180	60	0.051	53.7	0.046	126	0.107
1210	56.6	0.047	77.9	0.064	123.4	0.102
1240	68.9	0.056	61.3	0.049	122.1	0.098
1270	67.8	0.053	70	0.055	124.7	0.098
1300	60.6	0.047	60.7	0.047	122.2	0.094

Table F.2: Effect of heating on emulsion stability

Time	Crude oil A		Crude oil B		Crude oil C	
min	mL	%	mL	%	mL	%
15	0.5	2	0.2	0.8	0.2	0.8
30	0.8	3.2	0.2	0.8	0.2	0.8
45	1	4	0.4	1.6	0.5	2
60	1.5	6	0.6	2.4	0.5	2
75	1.8	7.2	0.8	3.2	0.8	3.2
90	2	8	1.2	4.8	1	4
105	2.4	9.6	1.8	7.2	1	4
120	2.6	10.4	2	8	1.2	4.8
135	2.8	11.2	2.3	9.2	1.3	5.2
150	3.4	13.6	2.5	10	1.5	6
165	3.6	14.4	2.6	10.4	1.6	6.4
180	4	16	2.8	11.2	1.9	7.6
195	4.2	16.8	3	12	2.1	8.4
210	4.4	17.6	3.2	12.8	2.4	9.6
225	4.8	19.2	3.4	13.6	2.6	10.4
240	5.2	20.8	3.8	15.2	2.7	10.8
255	5.6	22.4	4	16	3.2	12.8
270	5.9	23.6	4.1	16.4	3.5	14
285	6.6	26.4	4.5	18	3.7	14.8
300	7.2	28.8	4.9	19.6	4	16
315	7.5	30	5.2	20.8	4.2	16.8
330	8.1	32.4	5.4	21.6	4.4	17.6
345	8.8	35.2	5.6	22.4	4.7	18.8
360	9	36	6.4	25.6	5.5	22

APPENDIX G

EFFECT OF AMINE GROUP DEMULSIFIERS ON EMULSION STABILITY

Table G.1: Effect of amine group demulsifiers on oil separation for crude oil A emulsions

Time day	**Oil Separation**							
	Dioctylamine		**Octylamine**		**Hexylamine**		**Pentylamine**	
	mL	**%**	**mL**	**%**	**mL**	**%**	**mL**	**%**
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	4.0	20.0	2.0	10.0	1.0	5.0	0.2	1.0
3	4.0	20.0	3.0	15.0	1.0	5.0	0.5	2.5
4	7.0	35.0	16.0	80.0	10.0	50.0	1.5	7.5
5	8.5	42.5	18.0	90.0	14.0	70.0	2.0	10.0
6	10.0	50.0	19.0	95.0	16.0	80.0	3.0	15.0
7	11.0	55.0	19.5	97.5	17.0	85.0	4.0	20.0

Table G.2: Effect of amine group demulsifiers on water separation for crude oil A emulsions

Time, Day	**Water Separation**							
	Dioctylamine		**Octylamine**		**Hexylamine**		**Pentylamine**	
	mL	%	mL	%	mL	%	mL	%
0	0.0	0.0	0	0	0	0	0	0
1	0.0	0.0	0	0	0	0	0	0
2	0.0	0.0	1	5	1	5	0	0
3	0.0	0.0	2	10	2	10	0	0
4	0.0	0.0	5	25	4	20	0	0
5	0.0	0.0	17	85	12	60	0	0
6	0.0	0.0	18	90	13	65	1	5
7	0.0	0.0	19.8	99	15	75	1	5

Table G.3: Effect of amine group demulsifiers on oil separation for crude oil B emulsions

Time, Day	**Oil Separation**							
	Dioctylamine		**Octylamine**		**Hexylamine**		**Pentylamine**	
	mL	**%**	**mL**	**%**	**mL**	**%**	**mL**	**%**
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	1.0	5.0	18.0	91.0	5.0	25.0	0.3	1.5
2	1.0	5.0	19.0	95.0	18.0	90.0	1.0	5.0
3	1.8	9.0	19.0	95.0	19.2	96.0	1.0	5.0
4	1.8	9.0	19.0	95.0	19.6	98.0	2.2	11.0
5	2.5	12.5	19.4	97.0	19.6	98.0	3.0	15.0
6	3.3	16.5	19.5	97.5	19.8	99.0	4.8	24.0
7	5.4	27.0	19.6	98.0	19.8	99.0	7.2	36.0

Table G.4: Effect of amine group demulsifiers on water separation for crude oil B emulsions

Time, Day	**Water Separation**							
	Dioctylamine		**Octylamine**		**Hexylamine**		**Pentylamine**	
	mL	**%**	**mL**	**%**	**mL**	**%**	**mL**	**%**
0	0	0	0	0	0	0	0	0
1	0	0	18.0	90.0	0	0	0	0
2	0	0	18.4	92.0	16	80	0	0
3	0	0	18.4	94.0	17	85	0	0
4	0	0	19.0	95.0	18.0	90.0	0	0
5	0	0	19.0	95.0	18.8	94.0	0	0
6	0	0	19.4	97.0	19.4	97.0	0	0
7	0	0	19.5	97.5	19.6	98.0	0	0

Table G.5: Effect of amine group demulsifiers on oil separation for crude oil C emulsions

Time day	Oil Separation							
	Dioctylamine		**Octylamine**		**Hexylamine**		**Pentylamine**	
	mL	**%**	**mL**	**%**	**mL**	**%**	**mL**	**%**
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.0	0.0	18.2	91.0	0.0	0.0	0.0	0.0
2	0.0	0.0	18.6	93.0	18.0	90.0	0.0	0.0
3	0.0	0.0	19.0	95.0	18.4	92.0	0.0	0.0
4	3.0	15.0	19.4	97.0	18.6	93.0	3.0	15.0
5	3.0	15.0	19.6	98.0	19.0	95.0	4.0	20.0
6	5.0	25.0	19.8	99.0	19.2	96.0	5.0	25.0
7	5.0	25.0	19.8	99.0	19.2	96.0	6.0	30.0

Table G.6: Effect of amine group demulsifiers on water separation for crude oil C emulsions

Time day	Water Separation							
	Dioctylamine		**Octylamine**		**Hexylamine**		**Pentylamine**	
	mL	**%**	**mL**	**%**	**mL**	**%**	**mL**	**%**
0	0.0	0.0	0.0	0.0	0.0	0.0	0	0
1	0.0	0.0	19.8	99.0	0.0	0.0	0	0
2	0.0	0.0	19.8	99.0	18.0	90.0	0	0
3	0.0	0.0	19.8	99.0	18.0	90.0	0	0
4	0.0	0.0	19.8	99.0	18.6	93.0	0	0
5	0.0	0.0	19.8	99.0	19.0	95.0	0	0
6	0.0	0.0	19.8	99.0	19.0	95.0	1	5
7	0.0	0.0	19.8	99.0	19.6	98.0	1	5

APPENDIX H

EFFECT OF POLYDRIC ALCOHOL GROUP DEMULSIFIERS ON EMULSION STABILITY

Table H.1: Effect of polyhydric alcohol group demulsifier on oil separation performance for crude oil A

Time, Day	Oil Separation							
	Dioctylamine		Octylamine		Hexylamine		Pentylamine	
	mL	%	mL	%	mL	%	mL	%
0	0.0	0.0	0.0	0.0	0.1	0.5	0.0	0.0
1	0.0	0.0	1.0	5.0	2.0	10.0	0.0	0.0
2	4.0	20.0	2.0	10.0	4.0	20.0	0.0	0.0
3	4.0	20.0	5.0	25.0	12.0	60.0	0.2	1.0
4	7.0	35.0	17.0	85.0	15.0	75.0	0.5	2.5
5	8.5	42.5	20.0	100.0	17.0	85.0	0.7	3.5
6	10.0	50.0	20.0	100.0	20.0	100.0	1.0	5.0
7	11.0	55.0	20.0	100.0	20.0	100.0	1.0	5.0

Table H.2: Effect of polyhydric alcohol group demulsifier on water separation performance for crude oil A

Time, Day	Water Separation							
	Dioctylamine		Octylamine		Hexylamine		Pentylamine	
	mL	%	mL	%	mL	%	mL	%
0	0.0	0.0	0	0	0	0	0	0
1	4.0	20.0	2	10	1	5	0.2	1
2	7.0	35.0	3	15	1	5	0.5	2.5
3	8.5	42.5	16	80	10	50	1.5	7.5
4	10.0	50.0	18	90	14	70	2	10
5	11.2	56.0	20	100	18	90	2.8	14
6	11.8	59.0	20	100	20	100	3.5	17.5
7	12.0	60.0	20	100	20	100	4.2	21

Table H.3: Effect of polyhydric alcohol group demulsifier on oil separation performance for crude oil B

Time, Day	Oil Separation							
	Dioctylamine		Octylamine		Hexylamine		Pentylamine	
	mL	**%**	**mL**	**%**	**mL**	**%**	**mL**	**%**
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	1.0	5.0	20.0	100.0	5.0	25.0	0.3	1.5
2	1.0	5.0	20.0	100.0	19.0	95.0	1.0	5.0
3	1.8	9.0	20.0	100.0	20.0	100.0	1.0	5.0
4	1.8	9.0	20.0	100.0	20.0	100.0	2.2	11.0
5	2.5	12.5	20.0	100.0	20.0	100.0	3.0	15.0
6	3.3	16.5	20.0	100.0	20.0	100.0	4.8	24.0
7	5.4	27.0	20.0	100.0	20.0	100.0	7.2	36.0

Table H.4: Effect of polyhydric alcohol group demulsifier on water separation performance for crude oil B

Time, Day	Water Separation							
	Dioctylamine		Octylamine		Hexylamine		Pentylamine	
	mL	**%**	**mL**	**%**	**mL**	**%**	**mL**	**%**
0	0	0.0	0	0	0	0	0	0
1	0	25.0	20	100	0	0	0	0
2	0	25.0	20	100	16	80	0	0
3	0	45.0	20	100	17	85	0	0
4	0	45.0	20	100	20	100	0	0
5	0	62.5	20	100	20	100	0	0
6	0	82.5	20	100	20	100	0	0
7	0	135.0	20	100	20	100	0	0

Table H.5: Effect of polyhydric alcohol group demulsifier on oil separation performance for crude oil C

Time, Day	**Oil Separation**							
	Dioctylamine		**Octylamine**		**Hexylamine**		**Pentylamine**	
	mL	**%**	**mL**	**%**	**mL**	**%**	**mL**	**%**
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.0	0.0	20.0	100.0	0.0	0.0	1.0	5.0
2	0.0	0.0	20.0	100.0	20.0	100.0	1.0	5.0
3	0.0	0.0	20.0	100.0	20.0	100.0	1.0	5.0
4	2.0	10.0	20.0	100.0	20.0	100.0	1.0	5.0
5	2.5	12.5	20.0	100.0	20.0	100.0	2.0	10.0
6	4.0	20.0	20.0	100.0	20.0	100.0	2.0	10.0
7	5.0	25.0	20.0	100.0	20.0	100.0	2.5	12.5

Table H.6: Effect of polyhydric alcohol group demulsifier on water separation performance for crude oil C

Time, Day	**Water Separation**							
	Dioctylamine		**Octylamine**		**Hexylamine**		**Pentylamine**	
	mL	**%**	**mL**	**%**	**mL**	**%**	**mL**	**%**
0	0.0	0.0	0	0	0	0	0	0
1	0.0	0.0	20	100	0	0	0	0
2	0.0	0.0	20	100	18	90	0	0
3	0.0	0.0	20	100	20	100	0	0
4	0.0	0.0	20	100	20	100	0	0
5	0.0	0.0	20	100	20	100	0.2	1
6	1.0	5.0	20	100	20	100	0.5	2.5
7	1.5	7.5	20	100	20	100	1	5

APPENDIX I

EFFECT OF NATURAL GROUP DEMULSIFIERS ON EMULSION STABILITY

Table I.1: Effect of natural surfactant on oil separation for crude oil A

Time, Day	**Oil Separation**			
	PBOA		**Coco amine**	
	mL	**%**	**mL**	**%**
0	0.0	0.0	0.0	0.0
1	2.5	12.5	0.5	2.5
2	3.0	15.0	0.5	2.5
3	6.6	33.0	1.0	5.0
4	19.6	98.0	8.0	40.0
5	19.8	99.0	11.0	55.0
6	19.8	99.0	19.5	97.5
7	19.8	99.0	19.5	97.5

Table I.2: Effect of natural surfactant on water separation for crude oil A

Time, Day	**Water Separation**			
	PBOA		**Coco amine**	
	mL	**%**	**mL**	**%**
0	0.0	0.0	0.0	0.0
1	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0
4	19.8	99.0	0.0	0.0
5	19.8	99.0	5.0	25.0
6	19.8	99.0	19.0	95.0
7	19.8	99.0	19.0	95.0

Table I.3: Effect of natural surfactant on oil separation for crude oil B

Time, Day	Oil Separation			
	PBOA		Coco amine	
	mL	%	mL	%
0	0.5	2.5	0	0
1	0.5	2.5	0.5	2.5
2	1	5	0.5	2.5
3	8	40	1	5
4	11	55	8	40
5	15	75	11	55
6	19.6	98.0	19.5	97.5
7	19.8	99.0	19.7	98.5

Table I.4: Effect of natural surfactant on water separation for crude oil B

Time, Day	Water Separation			
	PBOA		Coco amine	
	mL	%	mL	%
0	0	0	0	0
1	0	0	0	0
2	9	45	0	0
3	15	75	10	50
4	19.8	99.0	17	85
5	19.8	99.0	19.6	98.0
6	19.8	99.0	19.6	98.0
7	19.8	99.0	19.6	98.0

Table I.5: Effect of natural surfactant on oil separation for crude oil C

Time, Day	Oil Separation			
	PBOA		Coco amine	
	mL	%	mL	%
0	0	0.0	0	0.0
1	0	0.0	0	0.0
2	0.4	2.0	2	10.0
3	2	10.0	4	20.0
4	4	20.0	8	40.0
5	11	55.0	10	50.0
6	18	90.0	16	80.0
7	19.8	99.0	19.6	98.0

Table I.6: Effect of natural surfactant on water separation for crude oil C

Time, Day	Water Separation			
	PBOA		Coco amine	
	mL	%	mL	%
0	0	0	0	0
1	0	0	0	0
2	10	50	0	0
3	19.8	99.0	12	60
4	19.8	99.0	17	85
5	19.8	99.0	19.5	97.5
6	19.8	99.0	19.5	97.5
7	19.8	99.0	19.5	97.5

APPENDIX J

EFFECT OF ALCOHOL GROUP ON EMULSION STABILITY

Table J.1: Effect of alcohol group demulsifiers on emulsion stability for crude oil A

Time, Day	Oil Separation					
	Ethanol		Butanol		Heptanol	
	mL	%	mL	%	mL	%
0	0	0	0	0	0	0
1	0	0	0	0	0	0
2	0	0	0.2	1	0.5	2.5
3	0.5	2.5	0.8	4	1	5
4	1.2	6	1.5	7.5	1.6	8
5	1.8	9	2.2	11	2.4	12
6	2.4	12	3.6	18	3	15
7	3.2	16	4	20	5.4	27

Table J.2: Effect of alcohol group demulsifiers on emulsion stability for crude oil B

Time, Day	Oil Separation					
	Ethanol		Butanol		Heptanol	
	mL	%	mL	%	mL	%
0	0	0	0	0	0	0
1	0	0	0	0	0	0
2	0	0	0.2	1	0.5	2.5
3	0.2	1	0.8	4	0.8	4
4	0.5	2.5	1	5	1	5
5	1	5	1	5	1.4	7
6	1.5	7.5	2.4	12	3	15
7	2.7	13.5	3.8	19	5	25

Table J.3: Effect of alcohol group demulsifiers on emulsion stability for crude oil C

Time, Day	**Oil Separation**					
	Ethanol		**Butanol**		**Heptanol**	
	mL	**%**	**mL**	**%**	**mL**	**%**
0	0	0	0	0	0	0
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0.8	4	1	5
4	0.8	4	1	5	1.2	6
5	1	5	1.2	6	1.8	9
6	1.5	7.5	2	10	2.5	12.5
7	1.8	9	3.5	17.5	4	20

APPENDIX K

OPTIMIZATION: DIAGNOSTICS CASE STATISTICS

Table K.1: Diagnostics Case Statistics for crude oil A

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	25.2	23.3824	1.81762	0.625	0.68006	0.12847	0.65151	12
2	92.8	87.2211	5.57893	0.625	2.08736	1.2103	3.14507	2
3	45.6	49.4789	-3.8789	0.625	-1.4513	0.58508	-1.607	8
4	96	96.1176	-0.1176	0.625	-0.044	0.00054	-0.0407	3
5	13.6	11.7903	1.80965	0.625	0.67708	0.12734	0.64845	4
6	86.4	89.9097	-3.5097	0.625	-1.3131	0.47898	-1.4004	5
7	60	64.8781	-4.8781	0.625	-1.8251	0.92531	-2.334	6
8	92.8	89.6219	3.17807	0.625	1.18908	0.39275	1.23234	13
9	88	85.28	2.72	0.2	0.69676	0.02023	0.66868	11
10	81.2	85.28	-4.08	0.2	-1.0451	0.04551	-1.0533	7
11	85.6	85.28	0.32	0.2	0.08197	0.00028	0.07593	9
12	88	85.28	2.72	0.2	0.69676	0.02023	0.66868	1
13	83.6	85.28	-1.68	0.2	-0.4304	0.00772	-0.4038	10

Table K.2: Diagnostics Case Statistics for crude oil B

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	5.6	6.97319	-1.3732	0.625	-0.8885	0.21927	-0.8733	3
2	84.4	81.9285	2.47147	0.625	1.59906	0.71028	1.85825	1
3	17.6	18.9715	-1.3715	0.625	-0.8874	0.21872	-0.872	7
4	95.6	93.1268	2.47319	0.625	1.60018	0.71127	1.86029	4
5	0	-2.1686	2.16859	0.625	1.4031	0.54685	1.53222	2
6	100	103.269	-3.2686	0.625	-2.1148	1.24233	-3.2583	6
7	41.2	41.7488	-0.5488	0.625	-0.3551	0.03502	-0.3317	11
8	57.6	58.1512	-0.5512	0.625	-0.3566	0.03533	-0.3332	5
9	62.4	62.08	0.32	0.2	0.14175	0.00084	0.13143	13
10	62	62.08	-0.08	0.2	-0.0354	5.2E-05	-0.0328	8
11	62.8	62.08	0.72	0.2	0.31894	0.00424	0.29745	10
12	59.2	62.08	-2.88	0.2	-1.2758	0.06782	-1.3482	12
13	64	62.08	1.92	0.2	0.85052	0.03014	0.83156	9

Table K.3: Diagnostics Case Statistics for crude oil C

Standard Order	**Actual Value**	**Predicted Value**	**Residual**	**Leverage**	**Student Residual**	**Cook's Distance**	**Outlier t**	**Run Order**
1	24	19.9389	4.06112	0.625	1.88725	0.98936	2.49307	13
2	90.4	87.203	3.19695	0.625	1.48566	0.61311	1.66226	5
3	40.8	41.897	-1.097	0.625	-0.5098	0.07218	-0.481	2
4	92	93.9611	-1.9611	0.625	-0.9114	0.23071	-0.8988	11
5	0.4	2.06106	-1.6611	0.625	-0.7719	0.16551	-0.7472	4
6	86	86.4389	-0.4389	0.625	-0.204	0.01156	-0.1894	10
7	62.4	67.0973	-4.6973	0.625	-2.1829	1.32362	-3.577 *	7
8	90	87.4027	2.59731	0.625	1.207	0.40468	1.25575	6
9	85.6	84.56	1.04	0.2	0.33089	0.00456	0.30877	3
10	80.4	84.56	-4.16	0.2	-1.3236	0.07299	-1.4152	9
11	86.4	84.56	1.84	0.2	0.58543	0.01428	0.55578	1
12	85.6	84.56	1.04	0.2	0.33089	0.00456	0.30877	12
13	84.8	84.56	0.24	0.2	0.07636	0.00024	0.07072	8

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