Study on the Effect of Ultrasonic Wave Amplitude on De-emulsification of Crude Oil to enhance Production Process

by

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16304

Dissertation submitted in partial fulfilment of

the requirements for the

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Mechanical Engineering

JANUARY 2016

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

Mechanical Engineering Programme

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BACHELOR OF ENGINEERING (Hons)

MECHANICAL ENGINEERING

Approved by,

____

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JANUARY 2016

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgement, and the original work contained herein have not been undertaken or done by unspecified sources or persons.

LIM CHUN HAUR

ABSTRACT

One of the most challenging issues faced by the oil and gas industry is the formation of crude oil emulsion. The emulsion formation will lead to inconsistency in the production performance, which directly affects the economic growth of the industry. Based on previous researches, traditional practices by the industry mainly focus on the thermal, demulsifiers, and electrical methods on crude oil de-emulsification process. Current de-emulsification methods are less effective as they long time for the separation process to complete. Thus, this research is intended to study the effect of the ultrasonic wave on demulsification process as a new approach in solving crude oil emulsion related problem. Ultrasonic wave has high potential in enhancing the separation rate as it has been used in oil sludge treatment. Three tests were conducted on each treated emulsion to study the behaviour for more intensive analysis which are Bottle Test, Cross- Polarized Microscope (CPM) and Karl Fischer (KF) titration. Crude oil from Terengganu Crude Oil Terminal (TCOT) produced by PETRONAS Carigali Sdn Bhd were utilised throughout the research. The combination of the parameters were studied and analysed to identify the optimum demulsification process by using the Design Expert 6 software. Ultrasonic irradiation was performed and compared with base sample. The result showed that de-emulsification worked best at heating temperature of 60℃ at 40 μm of ultrasonic wave amplitude. From the optimization part, it was discovered that crude oil and water layers were strongly affected by the change of operating temperature and ultrasonic wave amplitude. Increase in the operating temperature to 60℃ enhanced the separation rate by 73.33%. However decreasing the threshold amplitude to 40% caused increase in water layer thickness by 22% of volume fraction. At 40% of ultrasonic wave amplitude, the water droplets were able to coalescence and flocculation at the fastest rate with the assistance of gravitational force. The threshold ultrasonic amplitude at 40 μm gave optimum cavitation effect to the de-emulsification by providing sufficient energy to crude oil emulsion for new interface formation. At the optimum parameter of 60℃ at 40 μm of ultrasonic wave amplitude resulted 73% of water separation compared to base sample at the end of the eight hours bottle test and achieved 4.016% of water content in the oil layers. Therefore, ultrasonic wave proved to show promising results to the de-emulsification process.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The largest oil and gas development in Malaysia is Angsi field. It is equipped with one Central Processing Platform (CPP) and four drilling platforms and located at the southern region of Malay Basin at 170 km away from East Coast of Peninsular Malaysia with the water depth of 69 m [1, 2]. Chemical flooding have been used in Angsi field to increase the production and act as pressure maintenance to the reservoir as the aquifer is weak in the region [1, 2]. Angsi field is facing an emulsion problem as the excess water have been injected to the well for the Enhance Oil Recovery (EOR) purposes. Besides, five oil fields of Esso Production Malaysian Incorporated (EPMI) which is known as Guntong, Tabu, Palas, Semangkok and Iron Barat are also facing the problem of formation of crude oil emulsion [3]. Figure 1.1 shows the location of Angsi field in East Coast of Peninsular Malaysia.

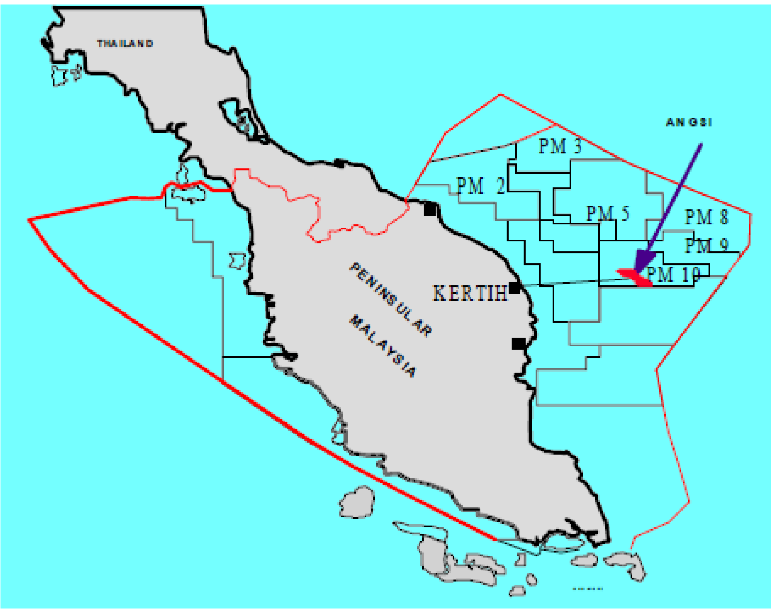


Figure 1.1: Angsi location map in Malaysia [4]

Throughout the extraction of crude oil from the reservoir, various injections and artificial lifting approaches have been adapted to enhance the oil recovery. Chemical injected for EOR will lead to the formation and stability of water in oil (w/o) emulsion [1]. The emulsion will create flow assurance issue to the oil production pipelines. Surfactants and polymers used in EOR will lower the crude oil and water interfacial film and increase water solubility [1]. It contributes greatly to the formation of crude oil emulsion. During crude oil transmission from reservoir to facilities or platform, the water and oil will be mixed vigorously due to the high turbulence flow which is affected by the high drawdown pressure in the well. This process will trigger agitation energy and form a crude oil emulsion.

Formation of the crude oil emulsion is undesired in the oil production. Most of the emulsion formation are water-in-oil (w/o) emulsion. The characteristics and physical properties of the crude oil will change significantly due to the w/o formation. The formation of emulsion is induced by the turbulence effect during oil extraction especially at the choke valve [5]. Separation of the emulsion is required to reach the desired product quality (<0.5% w/o) [6].

The formation of crude oil emulsion will increase the hydrocarbon cumulative viscosity resulting in a high pressure loss in the flow lines during the production. Additional energy input for the pumping process for transportation in pipelines is required. Crude oil emulsion must be treated to separate the water phase and other solid particles by mean of demulsification process. Demulsification process plays an important role to ensure crude oil reached its specifications of (<0.5% w/o) before being transported, stored and exported [1].

Crude oil emulsion are governed by three main elements which are surfactant, mixing energy and two immiscible liquids [3]. Nowadays, most of the oil and gas production companies are facing the similar problem whereby they are required to spend additional cost to separate crude oil emulsion to oil and water phases without compromising the chemical properties of the oil. Thus, emulsion stability mechanism, characteristics and behaviour need to be identified for effective demulsification process.

The crude oil emulsion is required to be de-emulsified to obtain good quality of crude oil. Although various methods have been conducted by the industry such as applying electrical current, demulsifier and thermal or the combination of the treatments [7]. Emulsion still remains a challenging issue in flow assurance to break up the emulsion by understanding the mechanism of crude oil emulsion stability. Therefore, stability of emulsion needs to be studied in order to have high separation of crude oil and water.

1.2 Problem Statement

The use of ultrasonic wave application received a lot of attention from researchers in China as part of Enhanced Oil Recovery (EOR) for improving oil production as ultrasonic wave is one of the most promising wave methods. According to Wang et al. [8], ultrasonic wave application is relatively cheaper compared to conventional chemical methods and it is reliable to apply ultrasonic treatment to enhance the oil production [8]. Besides, ultrasonic wave application have also been used widely in the food industry in nano emulsion preparation [9]. Ultrasonic is known as sonic wave and it causes cavitation when passed through a liquid medium and have multiple effects such as emulsification, de-emulsification and dispersion effects [10]. However, current de-emulsification methods such as thermal, electric field and gravity separation cannot solve the emulsion problem effectively and require more than 26 hours duration for separation [2]. In addition, there have been no ultrasonic applications on waxy crude oil from the Malay Basin at South China Sea.

1.3 Objectives

The objectives of this research are:-

i. to study the effect of the ultrasonic wave de-emulsification process of crude oil at different temperature and ultrasonic wave amplitude.
ii. to optimize crude oil de-emulsification efficiency.

By having this work, the crude oil emulsion problem faced in Malaysia can be solved by using ultrasonic wave application and hence separation of crude oil and water in crude oil emulsion can be performed more effectively.

1.4 Scope of Study

This research project is part of the flow assurance project under Universiti Teknologi PETRONAS (UTP). This study involves one type of waxy crude oil which is identified as “waxy crude oil A” obtained from Malaysia East Coast region produced by PETRONAS Carigali Sdn Bhd (PCSB). Firstly, the study focused on the experimental research and no numerical stimulation involved. Emulsion behaviour can only be analysed using experimental method and validated with Design Expert 6 software.

Secondly, the research project mainly focused on two parameters which are crude oil temperature and ultrasonic wave amplitude as variables to investigate the effect of ultrasonic wave toward the crude oil de-emulsification process. The water to oil ratio used throughout the research was 30:70. Other variables were set constant and high pressure environment was excluded. The experiments were conducted under atmospheric pressure condition.

Subsequently, the emulsion separation was assessed via Cross Polarized Microscope (CPM) observation to capture the microscopic image of the crude oil emulsion layer, Karl Fischer titration was used to identify the water content in the emulsion and bottle test was used to monitor the settling time of the crude oil emulsion. The results obtained were optimized by using Design Expert 6 software.

CHAPTER 2

LITERATURE REVIEW

This chapter elaborates the characteristic, classification and composition of the crude oil. Crude oil contains natural emulsifiers such as asphaltenes and resins which stabilized the crude oil during extraction. This chapter also covers the formation of crude oil emulsion and drawbacks of crude oil emulsion to the production operation system. Crude oil can be categorised as stable and unstable emulsion based on its stability. The four main processes that governed the crude oil emulsion stability are also presented in this chapter. The introduction of ultrasonic wave application and its working principle of past researches in the petroleum industry are elaborated.

2.1 Introduction to behaviour of Waxy Crude Oil in pipelines

Multiphase flow is a common phenomenon found in petroleum industry. Waxy crude oil is mainly found in the Malay Basin region and its temperature dependent crude oil [11]. High wax content in the crude oil causes rheological problem in the pipelines and separators [12, 13]. The crystallization of wax forms interlocking gel-like structure in the system and reduce the flow rate in the pipelines (waxy crude oil). It exhibits high pour point temperature (PPT) and wax appearance temperature (WAT).Temperature dropped below pour point temperature, it will completely form gel structure and retard the movement of the crude oil in the pipelines [12, 13].

2.1.1 Classification of Crude Oil

Crude oil is classified and differentiated based on the sulphur content and its density. American Petroleum Institute (API) has set a standard to measure the density of the crude oil and known as API gravity. Crude oil can be categorized into three main categories which are light crude oil (>31.1 °API), medium crude oil (22.3 °API to 31.1 °API) and heavy crude oil (< 22.3 °API) based on it API gravity. It is identified at 60 ° Fahrenheit by the specific gravity of an oil to the ratio of its density and to that of water. The formula for the calculation of API gravity is given by [14]:

$$\text{API gravity} = (141.5/\text{Specific Gravity}) - 131.5 \tag{2.1}$$

2.1.2 Crude Oil Composition

Crude oil is known as petroleum existed naturally within the earth crust and consisting of hydrocarbons, sulphur, nitrogen and metals. Crude oil can vary based on reservoir location, depth and age [3]. Crude oil composition contain organic compounds such as sulphur, oxygen and nitrogen whereas metals are copper, nickel, vanadium and iron [3]. Wolicka and Borkowski [15] claimed that crude oil is one of the most essential resources in the world. It has been used world widely in various industries such as refinery-petrochemical industry and power plant. Crude oil is converted to consumer product like lubrication, gasoline, oils, and polymers to serve the mankind [15].

Based on the fundamental of molecular basis, crude oil is a mixture of hydrocarbons, organic compounds and various types of metallic components. For instance, organic compounds consists of sulphur, oxygen, and nitrogen whereas metallic components comprise of vanadium nickel, copper and iron [16]. Fan et al. [17] used saturates, aromatics, resin and asphaltenes (SARA) analysis to divide crude oil components based on it polarizing ability and its polarity. SARA analysis method involves gravity-driven chromatographic separation, high pressure liquid chromatography (HPLC) and thin layer chromatography (TLC). As a result, crude oil composition can be separated into 4 major fractions which are saturates, aromatics, resin and asphaltenes. Presence of asphaltenes played an important roles in crude oil in the fluid process ability [18].

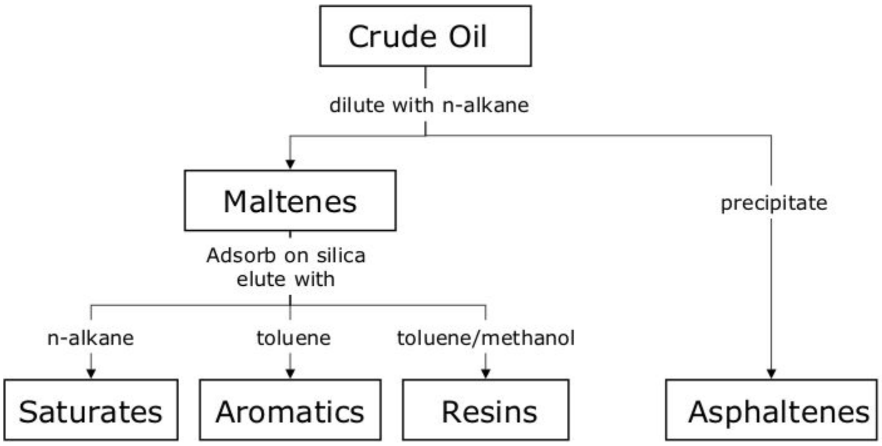


Figure 2.1: Crude oil composition into Saturates, Aromatics, Resins and Asphaltenes based on SARA analysis [18]

Asphaltenes is removed by using the precipitation method in a paraffinic solvent and other classes of compound are separated by using Chromatographic Fractionation. Among the four elements, saturates is the most significant in the hydrocarbon mixture based the fact of the absence of π-bonds in the crude oil while aromatics is differentiated by the polarities [19]. The formation of saturated hydrocarbons chain from straight chained paraffin to cycloparaffins is known as saturates whereas hydrocarbon contain aromatic nuclei which may be replaced by napthenes categorised as aromatic. In addition, resin is soluble in light alkanes but insoluble in propane [19].

2.1.3 Natural Emulsifiers in Crude Oil

In oil and gas exploitation, extraction and production, the formation of emulsion is always stabilized due to the presence of natural emulsifiers in the crude oil. Natural emulsifiers such as asphaltenes and resins have the ability to stabilize the oil and water interface [5].

Asphaltenes is a good emulsifier because it is a surface active agent. From a molecular structure perspective, asphaltenes can be separated into 2 parts which are polar head and nonpolar tail. Polar head will be attracted to the water and the nonpolar will be attracted to oil. This orientation will result in rigid film around the water molecules. The formation of the film will inhibit coalescence of droplets. In order to coalesce, the film must be ruptured. Therefore, asphaltenes naturally act as inhibitor for coalescence and the effect of polar fraction on the film properties will increase the interfacial viscosity in the oil and water interface [20]. According to Strassner's study, reducing asphaltenes from the crude oil composition will result in a looser emulsion. However, increasing of asphaltenes to crude oil will enhance the formation of rigid film and increased the stability of crude oil emulsion [20]. Water separation rate depends on the amount of asphaltenes in the crude oil. Increasing of asphaltenes will reduce the emulsification tendency [20]. Figure 2.2 illustrates the effect of asphaltenes concentration in Strassner study.

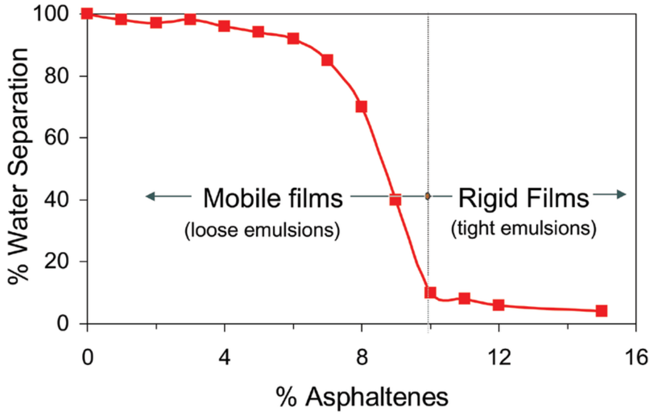


Figure 2.2: Effect of asphaltenes concentrate on water separation in the crude oil emulsion [20]

Resins is soluble in n-pentane, n-heptane and aromatic solvents whereas it is insoluble in propanol and methanol and is a non-volatile and polar fraction of petroleum. The resin acts as a stabilizing agent for asphaltenes. Resin can be found in long paraffin chain molecules or condensed with aromatic and naphtenic ring. Resin plays an important role in stabilizing the crude oil emulsion. According to Leontaritis [21], in crude oil emulsion, resin always act as a peptizing agents and associate with asphaltenes to form micelle. Hence, it is able to stop the coalescence process and achieve a stable emulsion state. Figure 2.3 shows the peptization of resin to the asphaltenes particles.

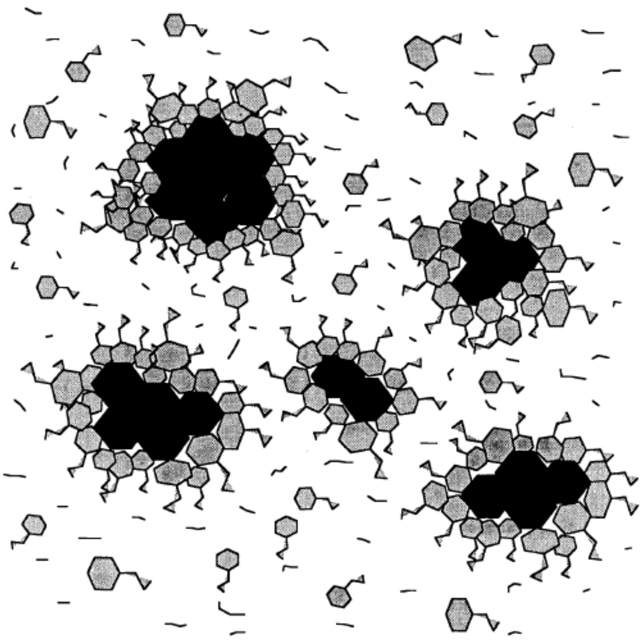


Figure 2.3: Peptization of asphaltenes with resin [21]

2.2 Composition of Formation and Produced Water

According to Ekins et al. [22], formation water is the natural water found inside the oil and gas reservoirs. Furthermore, produced water is defined as the water that produced along with oil and gas extraction from reservoirs and throughout the transportation lines. Additionally, enhanced oil recovery process is done by injecting chemical substances and water to force the crude oil out from reservoirs to production well. This action leads to the increase of produced water as it consists of the formation water and the additional water. Produced water are also used to re-inject into the wells as part of the enhanced oil recovery process and partial of the water is been treated and discharge into the sea.

Composition of the water in reservoir are strongly affected by the crude oil emulsion in the reservoir. Some of the components in hydrocarbon such as benzene, toluene, ethylbenzene and xylene dissolve partially in produced water [22]. These phenomena caused either de-emulsification or emulsification based on its quantity. Table 2.1 shows the example of the composition of formation water in Nigeria.

Table 2.1: Properties of formation water in producing oilfields in Nigeria [23]

Composition	K^++Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO^{3-}	CO_3^{2-}
Concentration (mg/L)	1452.2	5.6	16.8	425.5	20.2	2927.7	121.1

2.3 Crude Oil Emulsion

Crude oil emulsions is a heterogeneous liquids system that consists of two immiscible liquids that came into contact and not dissolved with each other [24]. Emulsion can be identified by the dispersion process between one liquid in another [24]. Emulsion is formed when oil and water are mixed vigorously in the process of entering perforation in the casing with the presence of huge different in pressure between the reservoir and well head [24]. However, Akpabio and Ekott [25] claimed that emulsion are naturally formed at the well head, chokes and valves section due to the action of the shear stress and the pressure drop in the system.

2.3.1 Classification of Crude Oil Emulsion

According to Akpabio and Ekott [25], crude oil emulsion can be divided into three major categories which are stable emulsion, unstable emulsion and meso-stable emulsion based on its stability and operation. Emulsion will achieve its stability when crude oil comprises of natural surfactants. Besides, crude oil emulsion behaviour is strongly affected by the temperature. Sefton and Sinton [26] proved that at high temperatures (>70℃), crude oil emulsion behave like Newtonian fluid and vice versa.

Stable emulsion is defined as no change in physical appearance of the colour and phases over time. In fact, the viscosity of the stable emulsion will increase over a long duration as it displays a strong viscoelastic properties and viscosities that is caused by the presence of asphaltenes and resins in the crude oil [25]. At molecular structure view, the position and alignment of the asphaltenes at the oil and water interface can cause the change in the viscosity.

Unstable emulsion normally preserve its emulsion state for few hours after the mixing process stops. The crude oil emulsion will separate into oil and water phases once the external force is lifted. It is a natural tendency for two immiscible liquids to separate in order to reduce its interfacial area. Nonetheless, the segment of the oil will retain a small amount of water as the oil is viscous [25].

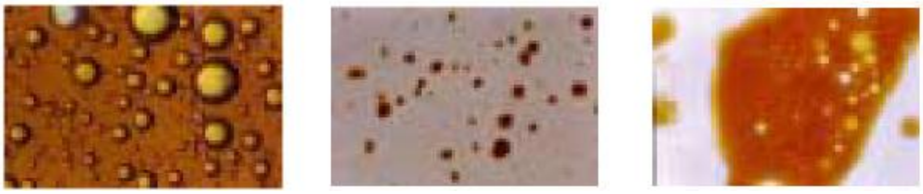
Meso-stable emulsion is the most common emulsion formation in the oil fields and production lines. Meso- stable emulsion have the appearance colour in red or black. It contains both properties of stable and unstable emulsion. These formation of emulsion is initiated by either two conditions. The first condition is that the crude oil emulsion contains low concentration of asphaltenes that is not sufficient to hinder the coalescence process. Second condition is that the high viscosity in the oil stabilized the water droplets for a period of time [25].

In agreement with stable, unstable and meso-stable emulsion, Opawale and Osisanya [23] deduced emulsion tightness index (ETI) formula:

$$ETI = \frac{M_1 - M_2}{M_{total}} \times 100\% \tag{2.2}$$

where M_1 is the amount of water blended, M_2 is the amount of water separated after special time and M_{total} is the total amount of water blended. Based on Equation (2.2), ETI will generate the values in the range of 0 to 100 percent. Zero percent ETI implies a loose emulsion and a 100 percent ETI implies a tight emulsion. Loose emulsion is an unstable emulsion whereby it will separate within a day and tight emulsion is a stable emulsion which requires days or weeks to separate [23].

In a study by Kokal [7], crude oil emulsion was classified into three main groups which were water-in-oil (W/O), oil-in-water (O/W) and multiple or complex emulsions. Figure 2.4 shows typical molecular structures of crude oil emulsions.



(a) (b) (c)

Figure 2.4: Photomicrographs (a) water-in-oil, (b) oil-in-water, and (c) water-in-oil-in-water Emulsion [7]

In water-in-oil (W/O) emulsion, water droplets exist in a continuous oil phase whereas in oil-in-water (O/W) emulsion, oil exists in a continuous water phase. Water-in-oil (w/o) emulsion is one of the crucial problem faced by the oil and gas industry [7, 23, 26]. However, for multiple emulsion it normally refers to water-in-oil-in-water (W/O/W) emulsion which made up of water droplets that clogged large oil droplets in a continuous water phase [7]. Dispersed phase and continuous phases depends on the volume fraction in the crude oil emulsion. The smaller volume fraction of liquid in crude oil emulsion is known as dispersed phase and the other will form the continuous phase [7].

2.3.2 Formation of Emulsion and Effect to Production Operation

Crude oil emulsion is crucial to the petroleum industry. The emulsion formation within the pore spaces could hinder the production rate. Emulsion formation frequently occur from the mixing and shearing process at area of chokes and valves in the flow stream [25]. The mixing of two immiscible liquids at high velocity and shear rate result in the formation of emulsion [7]. It will significantly reduce the flow rate of the hydrocarbon due to the presence of emulsion. In production and transportation lines, massive volumes of surfactants such as clays, paraffins, and asphaltenes are used as corrosion inhibitors and dispersants in acid treatments. Consequence of surfactant and acid treatment will trigger and enhance the emulsion formation and caused unnecessary blockage [1]. In general, several methods have been used to prevent the formation of emulsion in the pipelines.

2.3.3 Emulsion Stability Mechanism

Understanding the fundamental of the emulsion stability mechanism is very important before conducting any test and experiment. Stability is defined as the persistency of a crude oil emulsion toward the environment. Hence, stability have been acknowledged as the important characteristic in crude oil emulsion. Emulsion stability are governed by four main processes which are creaming, flocculation, coalescence and Ostwald ripening [3].

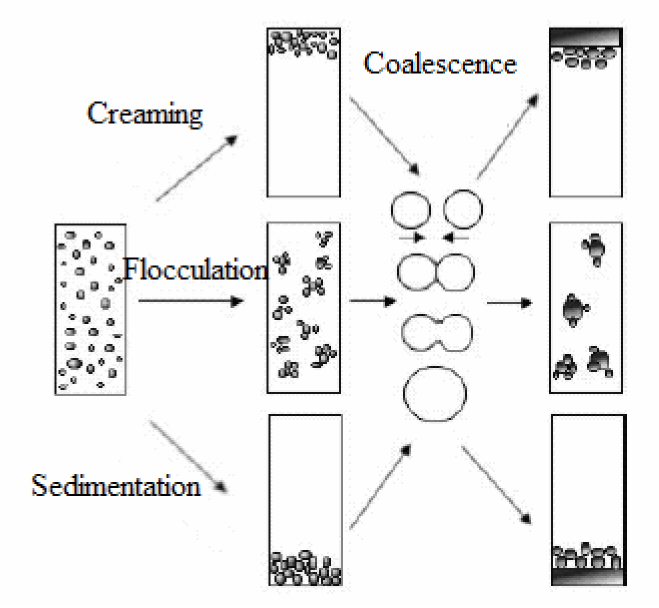


Figure 2.5: Illustration on creaming, flocculation and coalescence process [3]

Creaming is the opposite process of sedimentation which depends on the density difference between two liquid phases. The difference in density will cause the change in concentration gradient and form a close pack of droplets based on its identity [3]. Flocculation process will trigger the aggregation process to hold group of particles to form a large molecular structure due to the van der Waals attractive energy surpassing the repulsive energy in the emulsion [3]. Creaming is the first phenomena in crude oil emulsion that took place in low electrolyte concentration and is governed by the Ostwald ripening. The next stage is the flocculation process that takes place in high electrolyte concentration. Once both processes reach completion, coalescence will start [27].

The mechanism of coalescence consists of two stages which are film drainage and film rupture [3]. The interfacial film as discussed in Section 2.1.3 is made up of surface-active agent such as asphaltenes to prevent the coalescence process [3]. Asphaltenes will reduce the interfacial tension by creating an interfacial gradients in the crude oil emulsion. In order for coalescence mechanism to occur, the interfacial film in the emulsion needs to be ruptured by increasing the pressure gradient in the fluid [3].

Langevin et al., [28] state that emulsion stability mechanism is also influenced by the presence of Ostwald ripening. It is defined as the growth process that occurred in the dispersed phase by migrating between each other to form bigger droplets [28, 29]. The diffusion rate of monomers to a larger monomer droplets are directly depending on the volume fraction of the emulsion. For instance, the process of diffusion rate is low when the solubility of the water and oil are low in the heavy crude oil [29].

Emulsion stability mechanism is also influenced by the viscosity and density factors. Crude oil with high density and low API gravity is more stable compared to the low density and high API gravity crude oil [30]. Heavy crude oil is known as stable crude oil as it has a high viscosity and retard the movement of the dispersed water in the crude oil emulsion [30].

The fine solid particle have the capability in maintaining the emulsion state depending on the three factors such as size of solid particle, interparticle interaction and wettability of the fine solids [31]. Solid particles exist in submicron or micron in diameter by diffusing into the oil and water interface and stabilize the emulsion. The diffusion process allow them to form a rigid film with the aid of asphaltenes to inhibit the coalescence of the droplets. Furthermore, solid particle in crude oil emulsion may contain electrical charge that can enhance stability of the emulsion [31].

Stability of the emulsion are strongly affected by the wettability of the particle in the crude oil emulsion. Wettability is defined as the degree of the fine solid particle wetted either by the oil or water when both are present in the emulsion. Oil-in-water (o/w) emulsions are formed when the contact angle is less than 90 ° whereas water-in-oil (w/o) emulsion are formed when the contact angle is more than 90 ° [31]. According to Levine and Stanford [31], as the solid particles must be smaller than emulsion droplets to act as emulsion stabilizer. Hence, solid particles must be present at the interface and must be wetted by both phases equally. In crude oil emulsion, the oil-wet solids are asphaltenes and waxes whereas water-wet solids are sands, inorganic scales such as calcium carbonate, $CaCO_3$, and calcium sulphate, $CaSO_4$ formed in the pipelines and by-product of the corrosion [31].

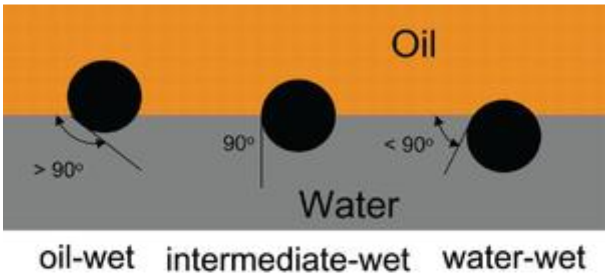


Figure 2.6: Wetting behaviour of the fine solid particles [31]

2.4 Current De-emulsification Methods

According to Kokal [7], demulsification is a mandatory process in the separator as the crude oil emulsion must be separated to its own phase completely before the crude oil can be processed and transported. Typically, stable emulsion are broken down into its phases by several combination processes such as gravitational separation, application of chemical demulsifiers, increasing the temperature of crude oil emulsion and application of electrical field to enhance coalescence [24, 25]. However, other alternative methods are also used such as pH adjustment, filtration and membrane separation [29].

Gravity separation process is based on the difference in the density of the crude oil and water [29]. For instance, gravity separation requires time for coalescence in the crude oil emulsion by reducing the flow rate in the system. This process can be achieved by altering the flow pattern in the vessel to enhance the separation process. Equipment such as gravity settling tanks, cyclones and centrifugal separators are used for the demulsification process [24, 29].

Besides, demulsifiers are used in the demulsification process to assist the separation of the crude oil emulsion into oil and water [7]. Typically, demulsifiers are made up of polymers that act as surfactants in retarding the emulsion. It has been designed to neutralize the emulsion agents in the crude oil [24]. The task of the demulsifers are to retard, weaken and destroy the interfacial film inside the crude oil emulsion and enhance the coalescence. Selection of the right demulsifers and dosage are still under research and development [7].

Thermal methods are performed in the separator to heat up the crude oil emulsion [7]. Increasing the temperature of the emulsion can reduce the viscosity of the crude oil and water settling rate. In molecular structure view, heating effect will resulting in weakening the interfacial film and interfacial viscosity. Therefore, it will enhance the coalescence rate in the crude oil emulsion. Nevertheless, the application of the heating process needs to tally with the overall economic analysis against treatment time and installation costs [7].

Lastly, application of the electrical field is used to enhance the separation of the crude oil and water [7]. Theoretically, water droplets in the crude oil emulsion will be charged when high voltage electricity is applied. Consequently, water droplets will vibrate rapidly and collide with each other. Furthermore, electrical fields could retard the interfacial film of the particles. Generally, application of electrical field is used together with chemical demulsifiers and heating process [7], [29].

2.5 Application of Ultrasonic Wave

Ultrasonic has been used in wide application such as cosmetic, environmental, architectural, musical and so for. It is a well-established equipment used in reducing the particle size in dispersion and emulsion applications [32]. According to Issaka et al. [33], ultrasonic has been proven as one of the effective applications in demulsification by enhancing the rate of mechanical effect in the crude oil emulsion. The basic components to generate ultrasonic are transducer and medium. Transducer is used to convert the electrical charges into mechanical wave while the medium is to allow the wave to propagate. Ultrasonic waves are similar to sound waves [33].

Ultrasound are categorized into low and high frequencies ultrasound. In sonochemistry, low frequency ultrasound ranges from 20 kHz to 100 kHz while above 100 kHz are considered as high frequency. Low frequency ultrasound is the main focus in the demulsification process as it induced mechanical effect instead of high frequency ultrasound which induces chemical effect to the emulsion. Cavitation effects are easy to produce in low frequency because the particles are subjected to compression and rarefaction in a long period. Consequently, large radius bubbles are more significant in low frequency ultrasound and the bubbles will collapse when it reached maximum radius size and burst more energy compared to high frequency ultrasound in inducing coalescence effect [34].

Besides, amplitude of ultrasonic also contribute significant effect to the crude oil emulsion stability [32, 35, 36]. A certain value of amplitude (P_A) pass through a medium at hydrostatic pressure (P_h) caused oscillation to the molecules [37]. During the oscillation cycle, the pressure is positive and the distance between the molecules decrease in compression cycle, whereas it is vice versa in rarefaction cycle. Thus, it yield and equation of, $P_C = P_h - P_A$ [37]. At certain amplitude, the average distance between molecules exceeds the critical distance and it will form a void and induce cavitation bubble in it as the droplets are not intact with each other [37]. A higher amplitude of ultrasonic will result in a large formation of bubbles known as cavitation effect [32]. As the bubbles absorbs sufficient energy and reach its maximum size, it will burst in the system [32, 35]. Subsequently, shock waves will be produced violently in the system [32]. In order to have an effective emulsification process, an optimum pressure amplitude threshold must be reached at a certain minimum value [36]. The process of emulsification can be initial with the right cavitation threshold only [36]. Figure 2.7 shows the formation of cavitation bubbles under threshold of ultrasonic amplitude.

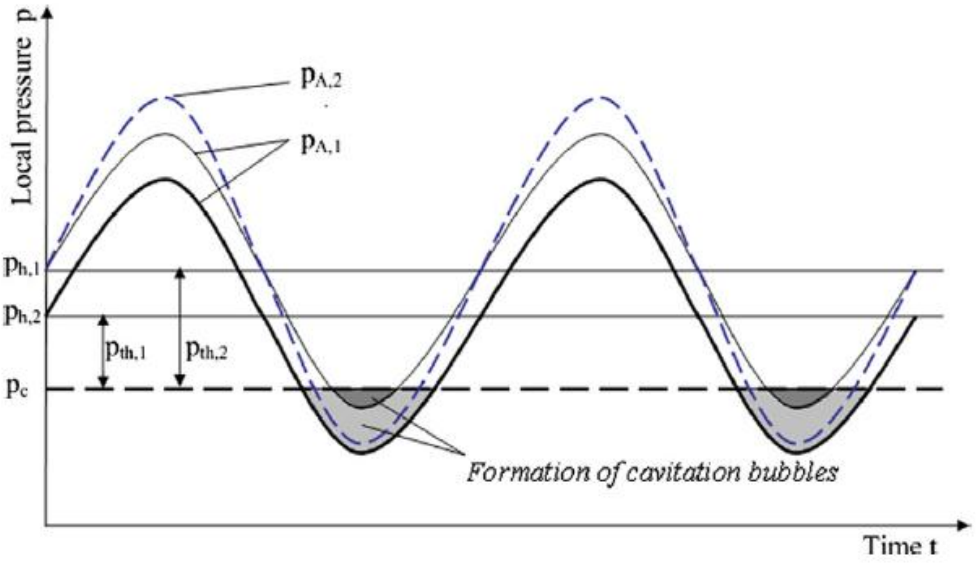


Figure 2.7: Relation of local pressure with cavitation [37]

Xu et al. [38] experimented on oil sludge to study the effect of ultrasonic treatment on de-oiling process. Under the ultrasonic irradiation process, the oil mud are able to separate from solid particle easily. These phenomena occurred because of the mechanical vibration on the oil sludge and cavitation effect at the interphase boundary of the oil and solid particle [38]. Based on their findings, cavitation increases when the ultrasonic intensity increases. At threshold ultrasonic intensity, it will induce a high cavitation rate and boost the separation rate. However, overwhelming ultrasonic intensity creates high intensity of shock wave and causes cavitation retardation [38].

Besides, ultrasonic application are also used in asphaltenes deposition treatment. Shedid [39] experiment, used low ultrasonic frequency 10 to 20 kHz to analyse crude oil viscosity and asphaltenes deposition. The ultrasonic treatment have drastically improved the oil permeability of core sample by increasing the ultrasonic irradiation time and its frequency. As a result, the asphaltic crude oil decomposed into smaller size of asphaltenes clusters [39].

The indirect ultrasonic application by using low frequency (35 kHz) was conducted by Antes et al. [40] on the water removal from crude oil. They discovered that the main contribution to the demulsification process is the cavitation effects. Based on their experiments, water was used as a medium of propagation of the ultrasonic wave [40]. During irradiation period, the cavitation effect will induce turbulence in the emulsion which will enhance the coalescence by bringing the water droplets close together. However, a longer irradiation time brings a negative impact to the emulsion whereby intensity of the turbulence will break the water droplets into smaller size and reduce the demulsification effect. Optimum irradiation time needs to be identified and associated with the intensity of the ultrasonic wave [40].

2.5.1 Ultrasonic Wave Working Principal and Mechanism

Yang, et al. [41] stated that the ultrasonic demulsification uses the principal mechanism of displacement. Ultrasonic is emitted in the mechanical wave formed. Under the irradiation effects, the water and oil in the crude oil emulsion will move in the wave loops direction and collide to each other. Hence, it will enhance the coalescence effect and bigger particle will be formed and separated by either creaming or sedimentation.

The mechanical wave generated will also induce heat to the crude oil emulsion. The heating effect will increase the crude oil emulsion temperature and reduce the viscosity of the system. In the water-in-oil emulsion, oil is the continuous phase and the water dispersed phase. The settling velocity can be calculated by using the Stokes' laws equation [41]:

$$V_m = \frac{D^2(P_w - P_0)}{18U_0} g \tag{2.3}$$

where V_m is velocity of water droplets, m/s, $(P_w - P_0)$is differential in the density of water and oil, kg/m^3$, D$ is the diameter of water droplets, $U_0$is the viscosity of the oil, kg $\mathrm{m}^{-1}\mathrm{s}^{-1}$ and g is the gravity acceleration, 9.8 m/s^2.

According to Hamidi et al. [42], ultrasonic application have been used in enhanced oil recovery process. Sound waves with frequency of 40 to 15 kHz were used to increase the oil production by losing the saturated oil in the reservoir. This phenomena is known as the "sono-capillary effect" whereby extra pressures is created inside the well by the P-waves [42]. The demulsification process under ultrasonic wave composed of two main processes which are the interfacial instability of the crude oil emulsion and induced cavitation bubble to the system. Based on their study, ultrasonic application can enhance the diffusion and coalescence between the small dispersed droplets [42].

Ultrasonic method is able to provide external energy to the w/o emulsion to agitate the dispersed phase to move and increase the efficiency of the separation. The effect of the ultrasonic application towards the emulsion are mainly governed by three factors which are ultrasonic intensity, irradiation time and temperature of the emulsion. These factors have significantly affect the behaviour of the crude oil emulsion [43].

Based on Issaka et al., [33], emulsion breaking are based on the three main mechanisms that are flocculation, coagulation and coalescence processes. By using the ultrasonic wave application, the wave energy will increase the speed of the mechanism effect through mechanical wave. Subsequently, the droplets will absorb the wave energy and increase the temperature and pressure of the crude oil emulsion. Thus, the temperature will reduce the viscosity of the emulsion and pressure will cause acoustic streaming that enhances coalescence effect by pushing the water droplets towards the pressure nodes [33]. Ultrasonic wave also involve acoustic force that is able to manipulate and alter the particle in the suspended medium. The wave is propagated throughout the medium in the mean of pressure wave. For instance, pressure force exerted on the particle is completely depending on the medium and the characteristics of the particle. Figure 2.8 shows the particle behaviour under acoustic forces.

The droplets in the emulsion is exposed to two forces which are primary acoustic force and secondary acoustic force [43]. Primary force helps in the flocculation process at the pressure nodes and antinodes while secondary force is an attractive force that combine two or more droplets into big droplets by compression. According to Luo et al., [43], smaller droplets are highly subjected to primary acoustic force. It is affected by a time-average force in the parallel direction to the sound propagate. Acoustic force will be more significant when the volume and size of the droplets grew bigger [44]. Below is the primary acoustic force equation in a one-dimension field:

$$F_{1,ac} = 4\pi a^3 k E_{ac} F \sin(2kx) \tag{2.4}$$

where k is the wave number of the acoustic field, E_{ac}, a is the droplet radius, x is the distance between droplet and the pressure antinode and F is the contract factor in finding the direction of droplet motion. Thus, F can be expressed by [44]:

$$F = \frac{p_r + (\frac{2}{3})(p_r - 1)}{1 + 2p_r} - \frac{1}{3\partial^2 p_r} \tag{2.5}$$

where p_r is the density ratio between the droplets and it continuous phases in the crude oil emulsion whereas ∂ is the speed ratio of the sound in droplet phase to the continuous phase. However, the motion of the droplets can be influenced by the intensity and the size of the droplets.

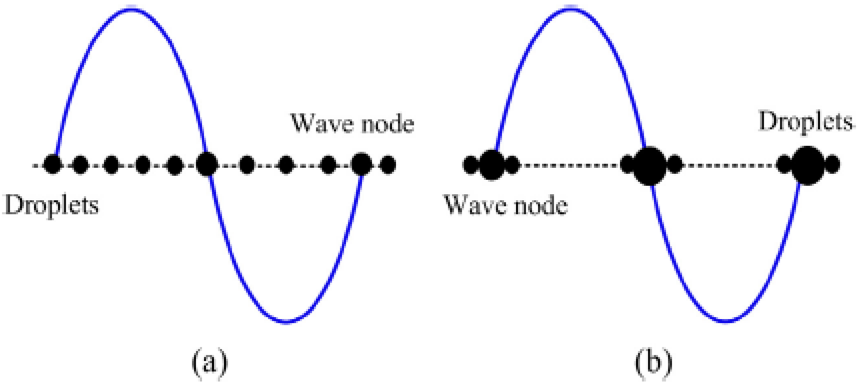


Figure 2.8: Schematic diagram of water droplets in oil. (a) The initial distribution of droplets and (b) the droplets after the ultrasonic irradiation [43]

Luo et al., [43] concluded that water droplets moved in quasi-sinusoidal oscillation. In addition, ultrasonic wave application will drive the water droplets to move vigorously and collide with each other. This will enhance the separation process.

CHAPTER 3

METHODOLOGY

In order to achieve the scope of study and the objectives of the research, several materials, equipment and experimental procedures used throughout the research are presented and discussed in the following sections. The research was carried out in four stages namely, Design of experiments, crude oil emulsion preparation, Ultrasonic treatment and optimization.

First stage is to design the run of the experiments based on the Design Expert Software. Second and third stages are experimental phases which consists of ultrasonic irradiation and samples characterisation. For ultrasonic irradiation, it involves ultrasonic equipment and double jacket reactor set-up. For samples characterisation, it involves bottle test, Cross Polarized Microscope BX53, Karl Fischer Titration C30 set-up for the measurement of crude oil emulsion samples. Optimization is the last stage of the research in order to identify the optimum parameters and validate the data.

This chapter discuss the overview of experiments, Gantt chart, and experiment methodology. The purpose of this research is to study the effect of the ultrasonic wave application towards the crude oil de-emulsification process

3.1 Overview of Study

The study has been conducted by using “waxy crude oil A” produced by PETRONAS Carigali Sdn Bhd. The flow of the research is shows in Figure 3.1. Basically, this study was started with project planning by taking consideration of the crude oil availability and process parameters. Two parameters which are operating temperature and ultrasonic amplitude were analysed throughout the studies.

Firstly, crude oil emulsion was prepared depending on the volume fraction of water to oil ratio. Ultrasonic wave treatment was conducted to the crude oil emulsion and followed by three tests. The most effective methods were determined by the water separation rate. For the optimization part, the parameters would be optimized by using Design Expert 6 software.

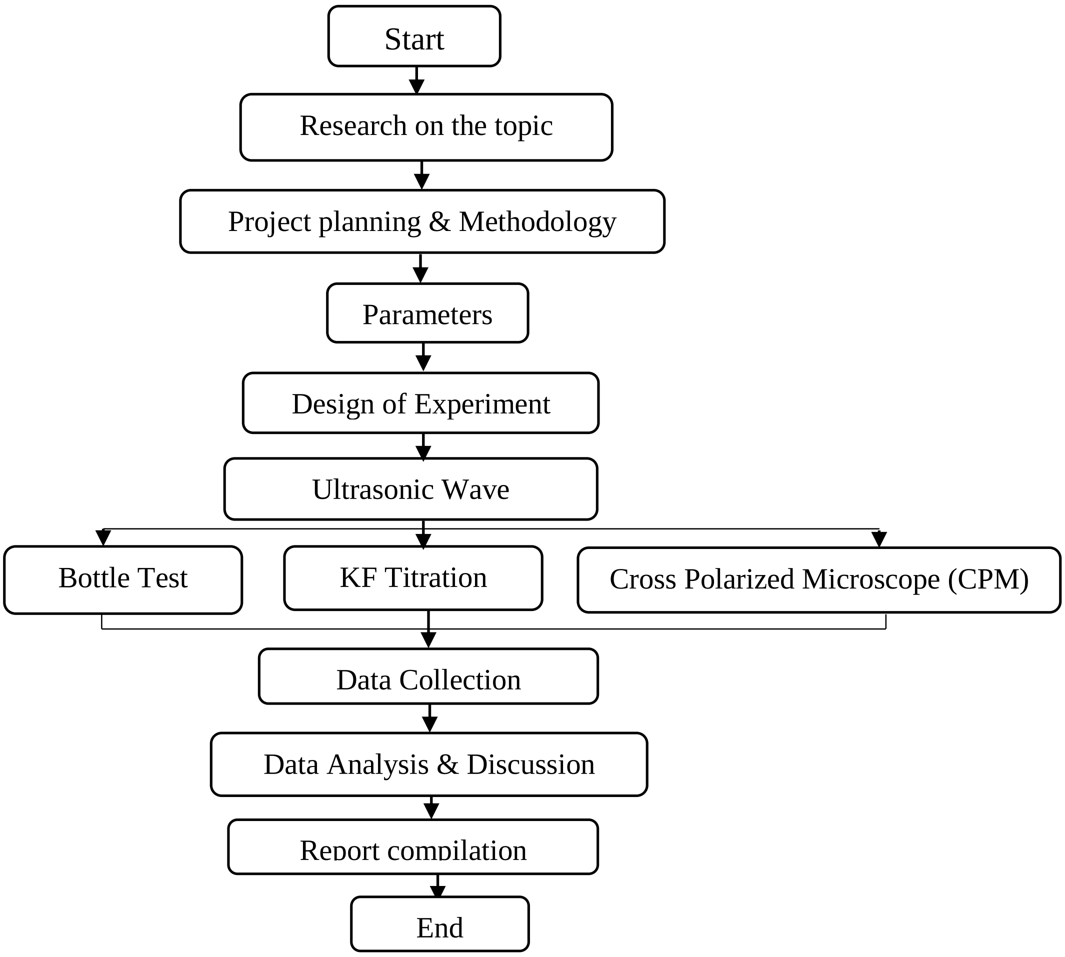
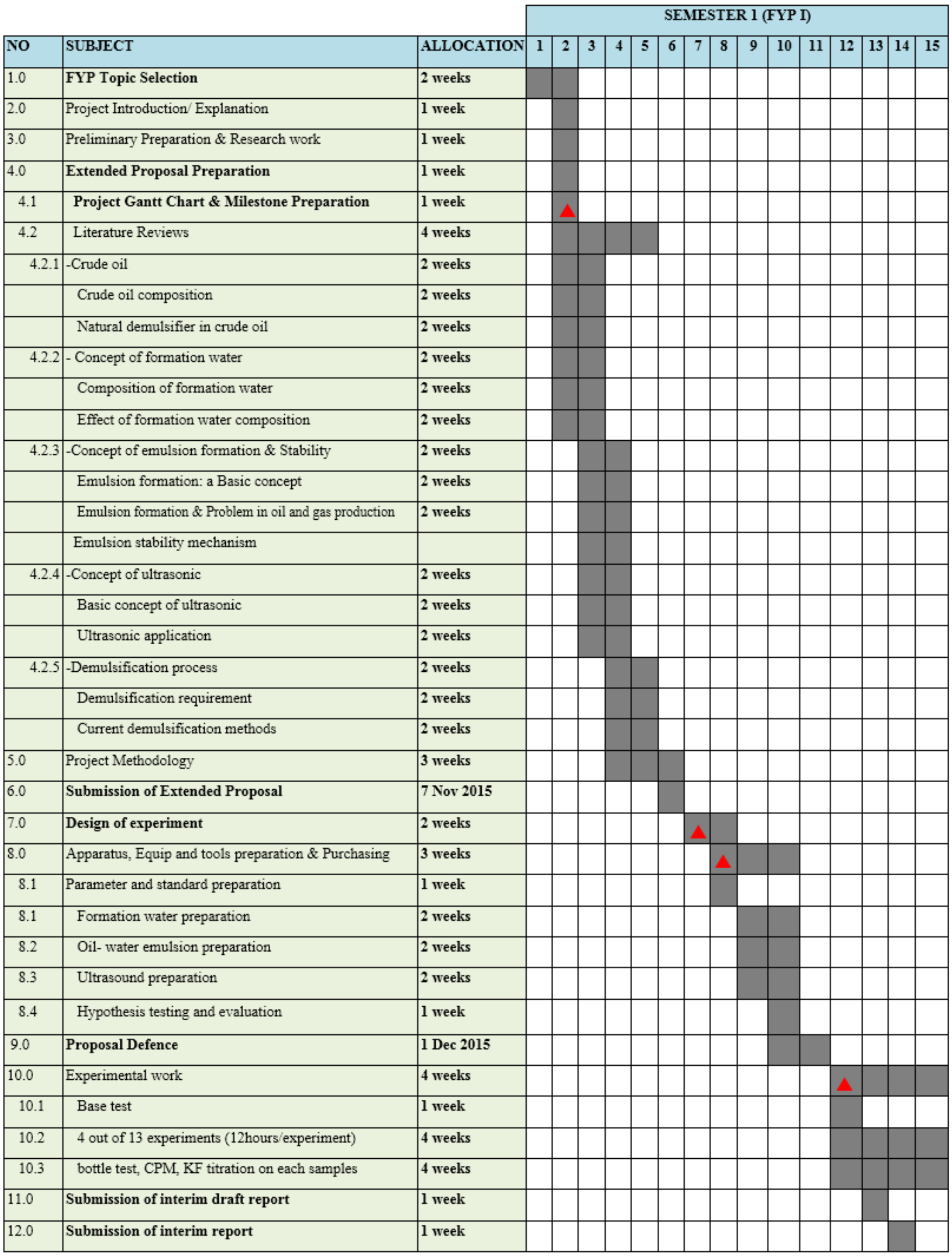


Figure 3.1: Overview of the study

3.1.1 Gantt Chart and Key Milestones

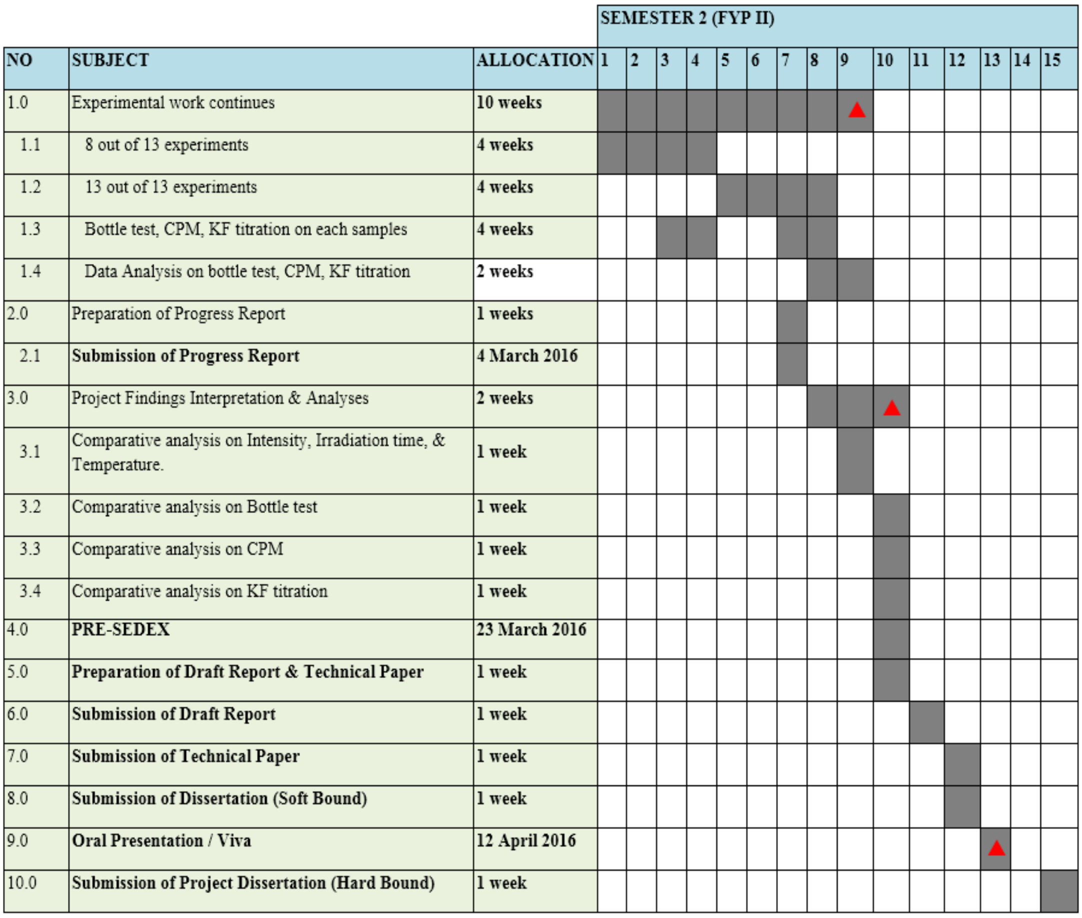
Figure 3.2 shows the Gantt chart of Final Year Project in semester 1. There were few milestones that were achieved throughout FYP 1 and were denoted as red triangles in Gantt chart. It started with the project Gantt chart preparation. It gave a clear picture and avoid downtime during the research. Second milestones were the design of experiments and equipment preparation. The next milestone was the ultrasonic irradiation treatment experiments start-up.



			SEMESTER 1 (FYP I)														
NO	SUBJECT	ALLOCATION	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1.0	**FYP Topic Selection**	**2 weeks**	▨	▨													
2.0	Project Introduction/ Explanation	**1 week**		▨													
3.0	Preliminary Preparation & Research work	**1 week**		▨													
4.0	**Extended Proposal Preparation**	**1 week**		▨													
4.1	**Project Gantt Chart & Milestone Preparation**	**1 week**		▲													
4.2	Literature Reviews	**4 weeks**		▨	▨	▨	▨										
4.2.1	-Crude oil	**2 weeks**		▨	▨												
	Crude oil composition	**2 weeks**		▨	▨												
	Natural demulsifier in crude oil	**2 weeks**		▨	▨												
4.2.2	- Concept of formation water	**2 weeks**		▨	▨												
	Composition of formation water	**2 weeks**		▨	▨												
	Effect of formation water composition	**2 weeks**		▨	▨												
4.2.3	-Concept of emulsion formation & Stability	**2 weeks**			▨	▨											
	Emulsion formation: a Basic concept	**2 weeks**			▨	▨											
	Emulsion formation & Problem in oil and gas production	**2 weeks**			▨	▨											
	Emulsion stability mechanism				▨	▨											
4.2.4	-Concept of ultrasonic	**2 weeks**			▨	▨											
	Basic concept of ultrasonic	**2 weeks**			▨	▨											
	Ultrasonic application	**2 weeks**			▨	▨											
4.2.5	-Demulsification process	**2 weeks**				▨	▨										
	Demulsification requirement	**2 weeks**				▨	▨										
	Current demulsification methods	**2 weeks**				▨	▨										
5.0	Project Methodology	**3 weeks**				▨	▨	▨									
6.0	**Submission of Extended Proposal**	**7 Nov 2015**						▨									
7.0	**Design of experiment**	**2 weeks**							▲	▨							
8.0	Apparatus, Equip and tools preparation & Purchasing	**3 weeks**								▲	▨	▨					
8.1	Parameter and standard preparation	**1 week**								▨							
8.1	Formation water preparation	**2 weeks**									▨	▨					
8.2	Oil- water emulsion preparation	**2 weeks**									▨	▨					
8.3	Ultrasound preparation	**2 weeks**									▨	▨					
8.4	Hypothesis testing and evaluation	**1 week**										▨					
9.0	**Proposal Defence**	**1 Dec 2015**										▨	▨				
10.0	Experimental work	**4 weeks**												▲	▨	▨	▨
10.1	Base test	**1 week**												▨			
10.2	4 out of 13 experiments (12hours/experiment)	**4 weeks**												▨	▨	▨	▨
10.3	bottle test, CPM, KF titration on each samples	**4 weeks**												▨	▨	▨	▨
11.0	**Submission of interim draft report**	**1 week**													▨		
12.0	**Submission of interim report**	**1 week**														▨	

Figure 3.2: Semester 1

Figure 3.3 shows the Gantt chart of Final Year Project in semester 2. The milestones of experiments were continued until the project reached its completion. The next milestone was the completion of data analyses and interpretation. The last milestone involved viva presentation on the finding and objectives of the research.



			SEMESTER 2 (FYP II)														
NO	SUBJECT	ALLOCATION	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1.0	Experimental work continues	**10 weeks**	▨	▨	▨	▨	▨	▨	▨	▨	▨▲						
1.1	8 out of 13 experiments	**4 weeks**	▨	▨	▨	▨											
1.2	13 out of 13 experiments	**4 weeks**					▨	▨	▨	▨							
1.3	Bottle test, CPM, KF titration on each samples	**4 weeks**			▨	▨			▨	▨							
1.4	Data Analysis on bottle test, CPM, KF titration	**2 weeks**								▨	▨						
2.0	Preparation of Progress Report	**1 weeks**							▨								
2.1	**Submission of Progress Report**	**4 March 2016**							▨								
3.0	Project Findings Interpretation & Analyses	**2 weeks**								▨	▨	▨▲					
3.1	Comparative analysis on Intensity, Irradiation time, & Temperature.	**1 week**									▨						
3.2	Comparative analysis on Bottle test	**1 week**										▨					
3.3	Comparative analysis on CPM	**1 week**										▨					
3.4	Comparative analysis on KF titration	**1 week**										▨					
4.0	**PRE-SEDEX**	**23 March 2016**										▨					
5.0	**Preparation of Draft Report & Technical Paper**	**1 week**										▨					
6.0	**Submission of Draft Report**	**1 week**											▨				
7.0	**Submission of Technical Paper**	**1 week**												▨			
8.0	**Submission of Dissertation (Soft Bound)**	**1 week**												▨			
9.0	**Oral Presentation / Viva**	**12 April 2016**													▨▲		
10.0	**Submission of Project Dissertation (Hard Bound)**	**1 week**															▨

Figure 3.3: Semester 2

3.2 Experiment Methodology

This section discusses the two sections of experimental procedures. The first section discussed about the crude oil emulsion preparation and ultrasonic irradiation treatment procedure. The second section focused on the testing of the crude oil emulsion samples and data analysing. All the findings were optimised by using response surface methodology in the design expert software.

3.2.1 Preparation of Formation Water

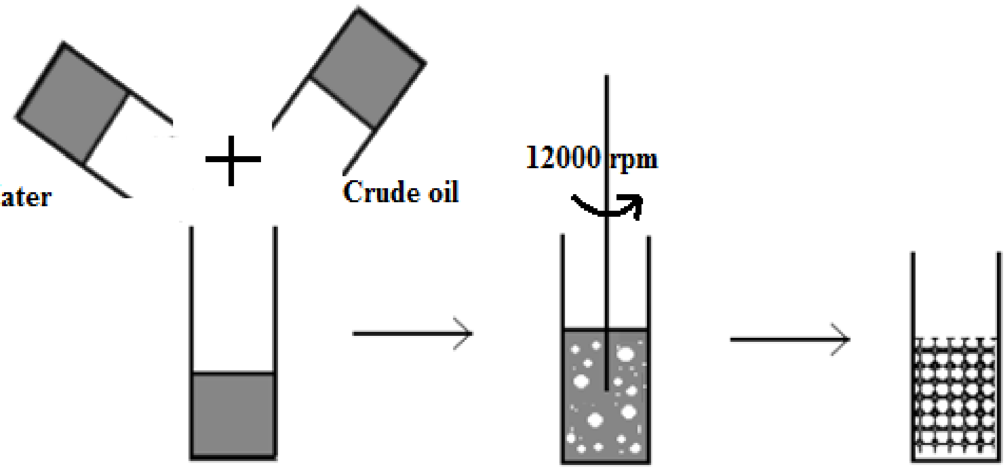
One litre of synthesis formation water was prepared to model the formation water in the oil field environment in Malay Basin field. Firstly, seven chemical components were measured in g/L and poured into one litre beaker. The chemical selection were based on PETRONAS reservoir data in East Coast of Peninsular Malaysia. Table 3.1 shows the chemical components used to prepare the formation water. One litre of ultra-pure water was obtained from Elga PURELAB Flex 3 Water Purification System. Ultra-pure water is water that contains no biologically active molecules where the H_2O, H^+ and OH^- ions are in equilibrium state. One litre of ultra-pure water was added gradually to the beaker. The mixture was agitated vigorously using IKA R 1389, a three blade propeller at the speed of 400 rpm at 23℃ of room temperature for a duration of one hour. Water that contains foreign substances and impurities are not applicable to this application.

Table 3.1: Composition in formation water

Chemical Substance	Concentration (g/L)
Sodium Bicarbonate ($NaHCO_3$)	5.1260
Potassium Chloride (KCl)	0.2646
Sodium Chloride (NaCl)	6.0114
Barium Chloride Dihydrate ($BaCl{:}2H_2O$)	0.0067
Strontium Chloride Hexahydrate ($SrCl2{:}6H_2O$)	0.0141
Magnesium Chloride Hexahydrate ($MgCl{:}6\ H_2O$)	0.0750
Calcium Chloride Dihydrate ($CaCl{:}2\ H_2O$)	0.2344

3.2.2 Formation of Crude Oil Emulsion

50 ml of water in oil (w/o) emulsion was prepared in 100 ml breaker in the ratio of 30:70 of water and oil. 35 ml of crude oil was poured into 100 ml beaker and followed by 15 ml of synthesis formation water. The crude oil and water mixture were heated up to 60℃ by using oil bath. Oil bath was used compared to water bath because it provides a more uniform heat distribution throughout the mixture and the heat capacity of oil is relatively lower than water. Once the mixture temperature reached 60℃, the crude oil mixture was heated for another 20 minutes to achieved homogenous temperature. Next, the crude oil mixture was stirred with IKA T25 DS2 stirrer at 12000 rpm for a duration of 15 minutes at mixing temperature of 60℃. 12000 rpm was utilized to mix the mixture as well as to avoid splashing due to the small volume of sample. Crude oil emulsion was mixed at atmospheric pressure by assuming no change of pressure throughout the research. The aim of stirring was to form a stable water-in-oil emulsion before undergoing ultrasonic treatment. The parameter selection and equipment used on crude oil emulsion preparation were based on the Anisa [45] research and aligned with PETRONAS Carigali Sdn Bhd data. A stable emulsion was formed and underwent ultrasonic irradiation treatment instantly to prevent the change of crude oil emulsion stated. Figure 3.4 illustrates the process of preparing the crude oil emulsion.



Mixture Stirred by using IKA T25 DS2 (w/o) emulsion

Figure 3.4: Process of preparing water-in-oil (w/o) emulsion preparation

3.2.3 Direct Ultrasonic Wave Application

Ultrasonic processor used was Cole-Parmer® 500-Watt Ultrasonic Homogenizer, 115VAC, 20 kHz, in combination with a standard probe in 15mm Titanium alloy Ti-6A1-4V. The ultrasonic equipment dimensions were: 8 inch (H) × 7.5 inch (W) × 13.5 inch (D). Double jacket reactor of 500 ml capacity was used to store crude oil emulsion during ultrasonic irradiation and avoid splashing of the sample to the surrounding. Thermocouple was inserted into emulsion samples to detect the change of the temperature in crude oil emulsion. It acts as a temperature control system to regulate the chilled water across the test tube. Any change in temperature in crude oil emulsion, will trigger the circulation of chilled water temperature which maintain the operating temperature of the system. According to Wang et al. [8], ultrasonic wave application had been used in viscosity reduction in oil recovery by inducing cavitation effect. Therefore, ultrasonic cavitation effect needs to be investigated under de-emulsification methods as it is interrelated with oil recovery process. The emulsion samples were poured into a 500 ml double jacket reactor and heated up by chilled water to its designated temperature based on data given by design expert software. Ultrasonic probe was immersed 2.5 cm down the surface of crude oil emulsion. The ultrasonic power was transmitted by irradiation in the function of amplitude percentage of the probe for duration of 15 minutes. After the ultrasonic wave irradiation, the samples were stored in centrifugal tube for bottle test observation in accordance with ASTM D1401-09.

Irradiation time at 15 minutes were in agreement with Hamidi et al. [42]. In a study by Hamidi et al. [42], the de-emulsification work best in the range of 12 to 30 minutes. In other words, increasing of irradiation time, caused emulsification to become more dominant compared to de-emulsification process [42]. The demulsification efficiency was evaluated by observing the free water formed at the bottle of centrifugal tube and by calculating the percentage of water separated from the emulsion through bottle test as a function of time in Section 3.4. Besides, Cross Polarized Microscope and Karl Fischer Titration were conducted before and after bottle test in Section 3.4. Figure 3.5 shows the ultrasonic wave equipment set-up. All the samples were stored into bottles for eight hours of bottle test.

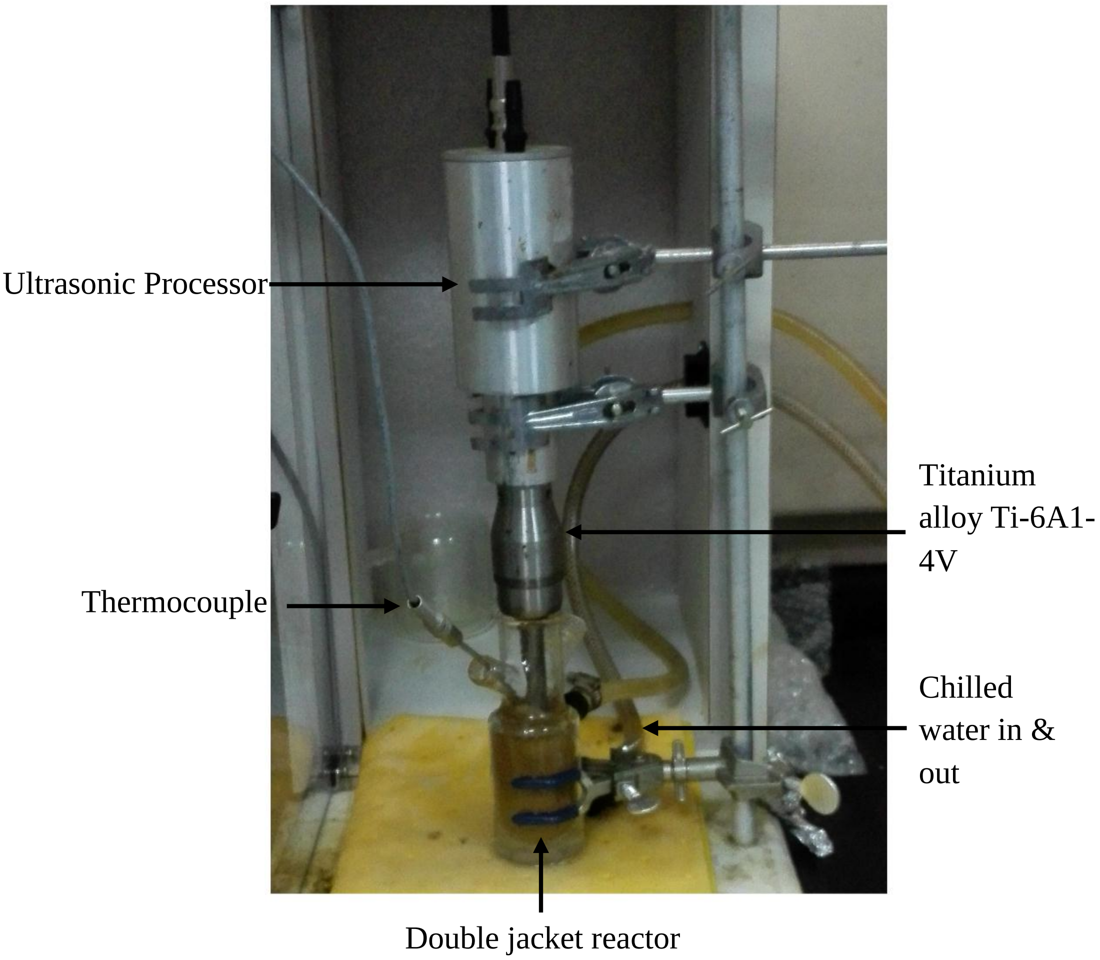


Figure 3.5: Ultrasonic wave equipment set-up

3.2.4 Cross-Polarised Microscope (CPM)

Cross-Polarised Microscope (CPM) model: Olympus BX53 was used in combination with analySISdocu software. CPM used polarised light to observe the water droplets structure and software used to measure the water droplets size in rag layer before and after bottle test. Crude oil, water and basic sediment have different refractive index. Thus, by utilizing polarised light, the quality of the image obtained with birefringent materials was improved with contract-enhancing technique. Under cross-polarised light, the liquid crude oil appeared dark in colour because polarised right bad been reflected by the crude oil. However, water droplets appear colourless which allowed the light pass-through the water droplets [46]. Cross-Polarised Microscope have been used in our study because it has several advantages over ASTM D2500 and ASTM-D3117 such as using magnification lens to extend the detection limit and ability to detect basic sediment in the crude oil samples [46]. In a study by Li et al. [47], droplet size distribution and wax appearance analysis were done by using cross-polarised microscope considering the change of temperature, oil viscosity and interfacial tension in crude oil emulsion.

For the CPM procedure, a drop of the crude oil emulsion sample was extracted by pipette and put onto microscope glass slide. The samples was cover with top glass to form 50 μm liquid firm. This is to ensure the size and structure of water droplets remain the same throughout the transferring process from centrifugal tube to glass slide. The specimen was placed on the hot stage of the observation point. The liquid film was maintained at the operating temperature. Lens and knob adjuster were adjusted until clear view of structure is obtained. Images were captured and size of the water droplets were measured at 100 μm.

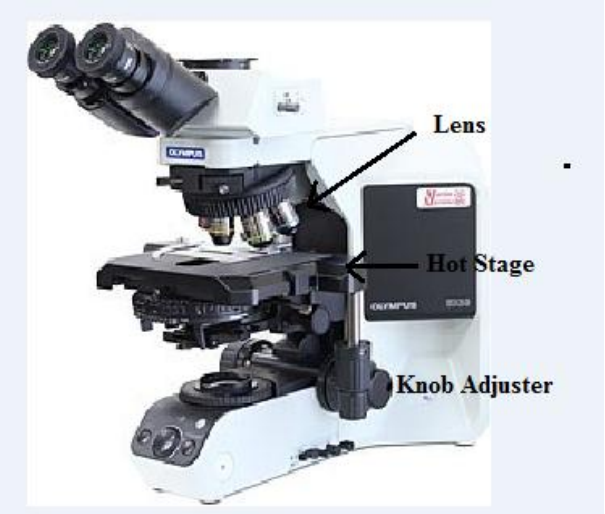


Figure 3.6: Cross-Polarised Microscope BX53

3.2.5 Karl Fischer (KF) Titration

Karl Fischer (KF) titration C30 model: Mettler Toledo was used to measure the water content in each layer extracted from crude oil emulsion, accordance with ASTM D-1744 standard. Fortuny et al. [48] applied Karl Fischer's titration method to analysis water content of the microwave de-emulsification of crude oil emulsion. The importance of this measurement is to identify the water content in oil layer relativity with the operating temperature and ultrasonic wave amplitude. In de-emulsification process, the water content in oil layer must be lower than rag layer and water layer. This is because sedimentation process caused the water droplets to move downward and form a larger droplets at the bottom of the centrifugal tube.

The water content was determined by the drift. The drift values were calculated based on moisture content in titration cell by purge gas. 0.3 grams of samples from crude oil, water and rag layers were weighted and inserted into vial and seal immediately to prevent contamination entering the vials. Stromboli oven was turned on throughout the measurement. Two empty vials with seals were inserted before samples vials to act as controlled variables. The samples were analysed when the drift value drop to less than 20 $\mu\text{g/min}$. The measurements were done automatically by Karl Fischer software by taking the difference in water content between sample vials and empty vials. The water contents were recorded.

Figure 3.7: Karl Fischer titration C30

3.3 Data Analysis

This section discusses the number of experiments and selection methods on conducting de-emulsification process by using ultrasonic wave application. It also covers the calculation of the separation efficiency by using bottle test, measurement of water droplets size and water content. Each data collection from bottle test result would be used in Design Expert Software to identify the optimum parameters of ultrasonic wave application in treating the crude oil emulsion.

3.3.1 Experiment Method and Selection

Number of experiments were generated by Design Expert Software based on the formulation of factorial design by involving several parameters. This method optimized the number of the experiments based on its variable to be investigated. It provides an insight of the “main effects” and “interaction effects” of the changing of value from low, medium to high level.

Three level factorial design are used in design of the experiments. The parameters are identified as crude oil temperature and ultrasonic amplitude. Overall, 13 experiments were generated by using Design Expert software as shown in Table 3.3 and each experiments requires 12 hours completion. Table 3.2 shows the three level factorial design of 13 experiments based on two parameters, crude oil temperature and ultrasonic amplitude. The experiments for Sample B2 were repeated four times by design expert software to validate the results and ensure that the results obtained are accurate.

Table 3.2: Experimental variables in three level factorial design

Experiments variables	Level of experiments variables			
	Units	$\alpha = -1$	$\alpha = 0$	$\alpha = 1$
Crude oil Temperature	℃	30	45	60
Ultrasonic Amplitude	%	40	60	80

Table 3.3: Thirteen experiments generated by Design Expert Software

Sample	Crude oil Temperature (℃)	Ultrasonic Amplitude (%)
A1	30	40
A2	30	60
A3	30	80
B1	45	40
B2	45	60
B2-1	45	60
B2-2	45	60
B2-3	45	60
B2-4	45	60
B3	45	80
C1	60	40
C2	60	60
C3	60	80

Table 3.4 shows the nomenclatures in ultrasonic wave de-emulsification process. Each nomenclature will be used in Chapter 4 to plot the graph of volume fraction the crude oil, water and rag layers.

Table 3.4: Nomenclatures description on ultrasonic wave de-emulsification

Nomenclature	Layer	Sample	Heating Temperature (℃)	Ultrasonic Amplitude (%)
40% Oil_Lyr	Oil	A1	30	40
60% Oil_Lyr	Oil	A2	30	60
80% Oil_Lyr	Oil	A3	30	80
40% Rag_Lyr	Rag	A1	30	40
60% Rag_Lyr	Rag	A2	30	60
80% Rag_Lyr	Rag	A3	30	80
40% Oil_Lyr	Oil	B1	60	40
60% Oil_Lyr	Oil	B2	60	60
80% Oil_Lyr	Oil	B3	60	80
40% Rag_Lyr	Rag	B1	60	40
60% Rag_Lyr	Rag	B2	60	60
80% Rag_Lyr	Rag	B3	60	80
40% Oil_Lyr	Oil	C1	80	40
60% Oil_Lyr	Oil	C2	80	60
80% Oil_Lyr	Oil	C3	80	80
40% Rag_Lyr	Rag	C1	80	40
60% Rag_Lyr	Rag	C2	80	60
80% Rag_Lyr	Rag	C3	80	80
40% H20_Lyr	Water	C1	80	40
60% H20_Lyr	Water	C2	80	60

3.4 Analytical Approach

3.4.1 Bottle Test

Bottle Tests were conducted after the ultrasonic treatments and base test. Bottle tests is an analytical and quantitative method to measure the water, oil and rag layers fraction based on the volume separation over the original volume fraction. Indirectly, the stability of the crude oil emulsion can be studied through bottle test. The longer the time required for the separation, the higher the stability and tightness of the crude oil emulsion. Throughout the bottle test, crude oil emulsion samples were prepared based on 30:70 in water to oil ratio. Bottle tests were known as a good indicator to calculate the water separation rate accordance with ASTM D1401–09.

The water separation were identify at each interval of time of 5 mins, 15 mins, 30 mins, 1 hour, 2 hours, 4 hours, 6 hours and 8 hours. The separation rate is calculated by:

$$\text{separation efficiency } (\%) = \frac{V_1}{V_2} \times 100 \tag{3.1}$$

where V_1 is the volume fraction of water layer and V_2 is the initial volume fraction of water. V_2 is a fix constant throughout the experiments and denoted as 30%.

Physical changes can be observed through the bottle test. For example, the colour and appearance of the crude oil emulsion, clarity of the water content, thickness of the rag layer and formation of sediment in the water layer if any.

3.4.2 Water Droplet Size

Measurement of water droplets size allowed the monitoring of the coalescence action of water droplets and understand the droplets size distribution. The water droplets size were measured by using the Olympus BX53 model, Cross Polarised Microscope (CPM) equipped with the digital camera and image analysis software. Measurement of the water droplets size were performed by capturing the clear image of the emulsion. Three images were randomly captured from the samples and 100 to 200 droplets were measured to obtain the average distribution of the droplets size.

In order to have a good judgement, water droplets size before and after base test were evaluated to act as a benchmark for the comparison. Water droplets size were measured after the ultrasonic test and after 8 hours of bottle test. The aim is to study the size and distribution of the water droplets under the effect of the treatment.

3.4.3 Water Content

The water content in oil and rag layer were used to study the effect of ultrasonic wave de-emulsification on the water content in each layer. This is very important in de-emulsification process, where the water content in oil layer is expected to be lower than water content in rag layer. Thus, the lower the water content in oil layer, the better would be the separation rate. According to Fortuny et al., [48], water content in crude oil layer affects the coalescence rate of oil droplets. The reduction of water content in crude oil layer, reduced the distance between the crude oil droplets and enhanced the flocculation and coalescence processes in the crude oil layer [48]. The water content of each layers was measured after the ultrasonic treatment and after an eight hours of bottle test by using Mettler Toledo C30 titration to study the different in the water content. The results of water content in each layer were measured in percentage (%).

CHAPTER 4

RESULT AND DISCUSSION

This section presents the result and finding throughout the experiment conducted based on the methodology in the previous section. The base test and thirteen experiments which underwent ultrasonic treatment was covered. All these experiments underwent three tests which were bottle test, Cross Polarised Microscope and Karl Fischer titration.

In this study, crude oil produced by PETRONAS Carigali Sdn Bhd from Terengganu Crude Oil Terminal (TCOT) was used throughout this research. The crude oil was selected and w/o emulsion was prepared to imitate the formation of waxy crude oil and formed w/o emulsion in Malaysia oilfield region. Volume fraction of 30% of water disperse phases and 70% of oil continuous phase w/o emulsion was prepared for the treatment testing.

To achieve and accomplish the objectives and scopes of this research project, this chapter was presented in three sections which are base test, ultrasonic de-emulsification and optimization of all the results. At the end of this chapter, the optimum parameter of ultrasonic wave application was identified.

4.1 Base Test

Base Sample test was conducted at 60℃ and the results were shown in Figure 4.1. The crude oil layer separation was slow and in-effective as volume fraction of oil layer only achieved 20% equivalent to 10 ml of crude oil after six hours of bottle test. The volume fraction of oil layer reached its stability at sixth hour and no increment of oil layer was observed. Besides, the oil layer formed was not clear as it contains slight amount of water droplets. Throughout the bottle test, water layer formation was not observed which indicates tight emulsion. This is because water droplets still existing in the rag layer (stable emulsion layer). It can concluded that the base sample was a stubborn emulsion and required de-emulsification process.

Subsequently, rag layer also posed a similar trend as compared with oil layer. It also reached stagnation point at sixth hours and achieved volume fraction of 80%. Throughout the base test, the rate decreased exponentially as it is a tight crude oil emulsion. Formation of rag layer acts as a mechanical barrier that accumulated the solid particles in the emulsion [49],[50].

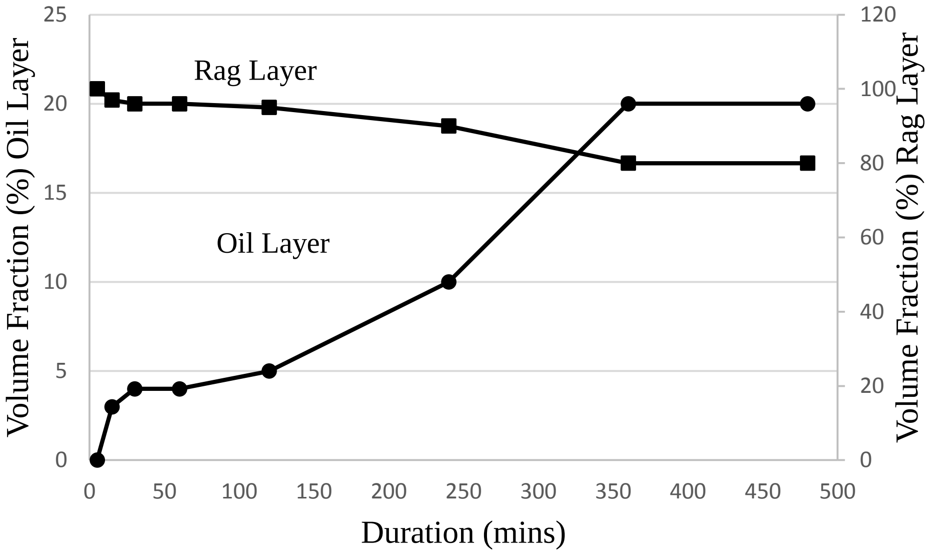
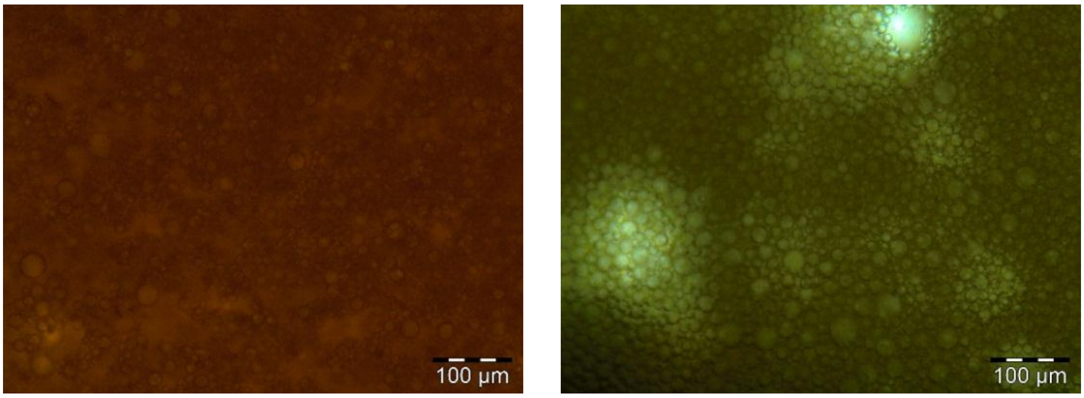


Figure 4.1: Volume fraction (%) of oil and rag layers in base sample

Table 4.1: CPM on base sample rag layer

Unit	Base sample water droplets size (μm)	
	Before 8hrs of Bottle Test	After 8hrs of Bottle Test
Mean	12.92	55.23
Minimum	4.48	25.00
Maximum	41.11	109.62

Based on the CPM result in Table 4.1, the size of the water droplets were increased drastically after eight hours of bottle test. Before bottle test, the water droplets were small due to the homogeneous mixing. The stirring process had dispersed into two phases which are water and crude oil into smaller cluster and cause a tight emulsion. Indirectly, small water droplets retard the coalescence effect. However, the water droplets size increased due to the presence of the gravitational force. Gravitational force is a slow process as it is a time dependent process. The force caused a difference in concentration gradient between two phases and induced creaming and sedimentation. However, the water droplets were loosely packed to each other and flocculation and coalescence effect was not significant. Figure 4.2 shows the water droplets in rag layer of the base sample before and after bottle test.



(a) (b)

Figure 4.2: Water droplets in rag layer (a) before bottle test and (b) 8 hours after bottle test

In Table 4.2, the mixture exist in water in oil emulsion before the bottle test, which was categorised as rag layer containing 16.8% of water content per droplets of the emulsion. After 8 hours of bottle test, it formed two layers which are oil layer and rag layer. In the oil layer, it contained 2.6% of water content while the rag layer contained 17.5% of water.

The water content in the rag layer increased by 0.7% after 8 hours as the water droplets have sediment to the bottom layer. The rag layer act as a mechanical barrier that trap the water droplets leading to no formation of water in the base sample.

Table 4.2: KF titration on the water content of base sample

Water content (%)		
Before bottle test	After bottle test (8 hours)	
Rag Layer	Oil Layer	Rag Layer
16.823	2.585	17.475

4.2 Ultrasonic De-emulsification Process

Figure 4.3 shows the relationship of the Water-in-oil (w/o) emulsion at temperature of 30℃ were investigated in volume fraction distribution based on ultrasonic amplitude. Based on the graph generated, the expected increase in oil layer was observed on the volume fraction with respect to the time. At the first hour, the oil layer in Sample A1 to A3 increased equally but started to behave differently after the first hour. Samples A1 and A3 crude oil layer reached its stability after six hours of bottle test. However, Sample A2 that underwent ultrasonic intensity of 60% have not achieved stability because most of the crude oil and water still exist in emulsion state and coalescence and flocculation process have not achieved completion stage. Water in oil (w/o) emulsion Sample A1 underwent 40% of ultrasonic irradiation showed the highest oil layer volume fraction of 16% compared to other ultrasonic intensity. Nevertheless, it is considered ineffective as the volume fraction of oil in base sample is only 20%.

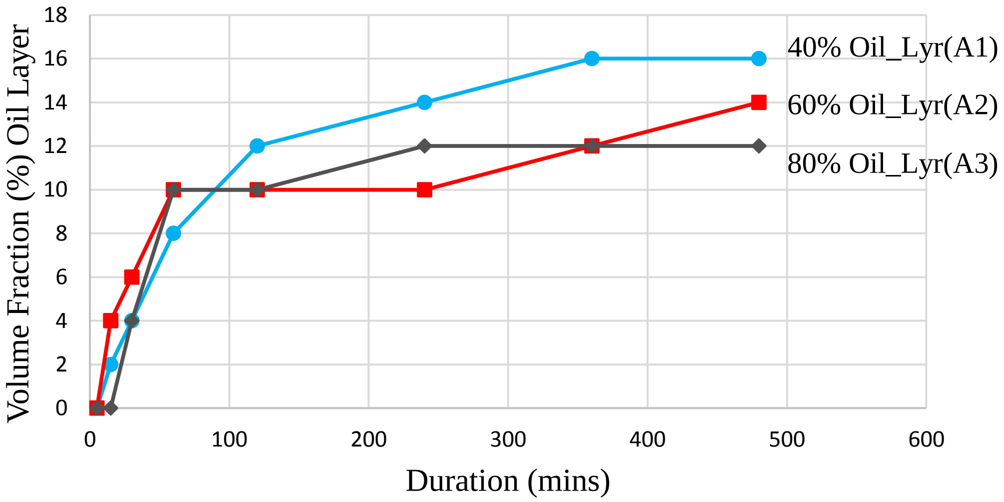


Figure 4.3: Volume fraction (%) of oil layer at heating temperature of 30℃ at different ultrasonic amplitude

Figure 4.4 shows the fluctuation in volume fraction of Rag layer of Samples A1 to A3 over the duration of time. Sample A1 to A3 showed drastic change in volume fraction of rag layer after one hour. All the samples have not achieved stability state as there was no water formation throughout the bottle test. Several portion of oil and water still exist in emulsion phase and trapped inside rag layer. At the eighth hour, Samples A2 and A3 present the similar trend of graph whereas Sample A1 have the lowest volume fraction of 84% compared to others.

Based on Figure 4.4, it is clearly shown that the rag layer formation in Sample A1 to A3 had the higher volume fraction compared to 80% volume fraction of rag layer in base sample. It can deduced that, operating temperature at 30℃ was not sufficient to heat up the crude oil emulsion. Most of the water and oil droplets were trapped inside the rag layer as no water layer formation at the end of eight hours of bottle test. To achieve the objective of this experiments, the volume fraction of rag layer under ultrasonic must lower than 80%.

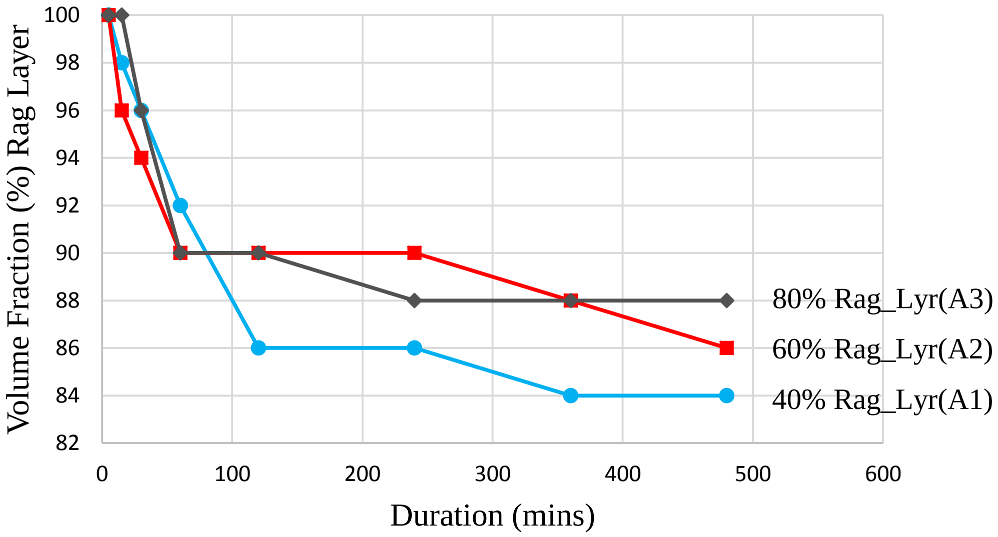


Figure 4.4: Volume fraction (%) of rag layer at heating temperature of 30℃ at different ultrasonic amplitude

Figure 4.5 illustrates the ultrasonic treatment at heating temperature of 45℃. Sample B2 was repeated four times based on the design expert software. Samples B2-1 to B2-4 data were recorded in Appendix A. The highest volume fraction of oil layer in sample B2 was selected and presented in the graph. Based on the graph, the volume fraction of oil layer increased gradually with respect to time. After eight hours of bottle test, oil layer thickness had not achieve stability state and increased exponentially. It indicated coalescence and flocculation process were in progress. Sample B1, B2 and B3 clearly showed that oil layer thickness were inversely proportional to the ultrasonic intensity. Hence, B1 showed the highest oil layer thickness whereas B3 have the lowest oil layer thickness were expected due to the differential in amplitude. Nevertheless, volume fraction of oil layer in Sample B1 (16%) had not surpassed the base sample (20%).

The oil layer formation for three samples are valid and in-line with the experiments of Gaikwad and Pandit [36]. The experimental result showed that the increase of the pressure amplitude of the ultrasonic prompted more cavitation effect. As a result, the formation of bubble and busting process increased aggressively and caused the w/o emulsion to breakup and enhance emulsification instead of de-emulsification process. Therefore, lower ultrasonic amplitude is desirable to provide sufficient energy for the new interface formation [36].

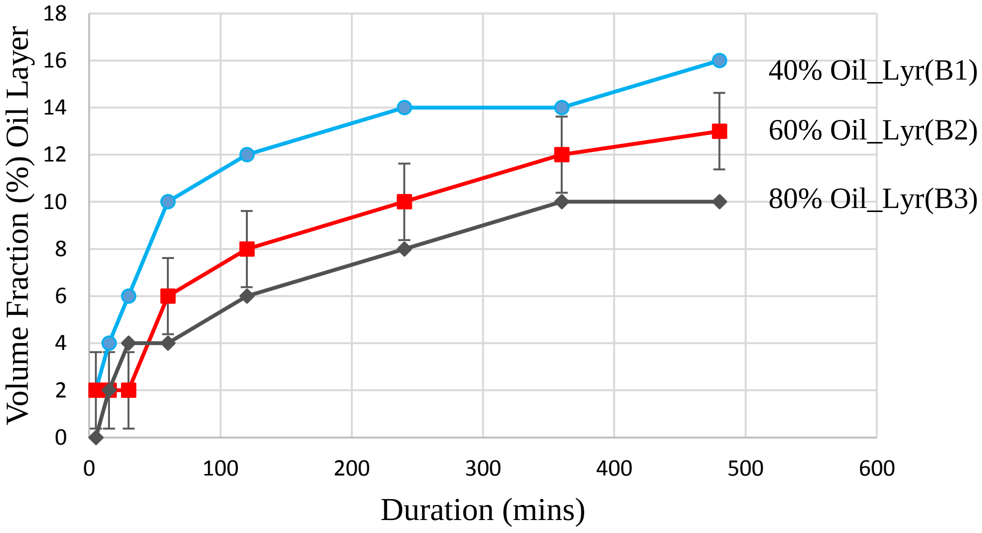


Figure 4.5: Volume fraction (%) of oil layer at heating temperature of 45℃ at different ultrasonic amplitude

As shown in Figure 4.6, the expected decrease in volume fraction of rag layer was observed over the period of eight hours. Water separation was yet to be seen as water droplets were remain in rag layer. Rag layer in Samples B1 to B3 decreased drastically after ten minutes of bottle tests compared to samples A1 to A2. These occurrences were due to the increase of the temperature of the emulsion from 30℃ to 45℃. The separation rate was strongly affected by the viscosity factor. As the temperature increased, the viscosity of the w/o emulsion decreased [7].

In the works of Kokal [7], and Smith and Arnold [30], they stated that heating effect enhanced the separation process of the emulsion. Increase of temperature greatly reduced the viscosity of the crude oil and increase the frequency of coalescence rate. In layman term, the heat energy speeds up the separation rate [7], [30]. Thus, the results obtained in Figure 4.6 are in agreement with Kokal [7], and Smith and Arnold [30]. Subsequently, the experiments were continue with Sample C1 to C3 at operating temperature of 60℃. The water layer formation was formed at 60℃, as presented in Figure 4.7.

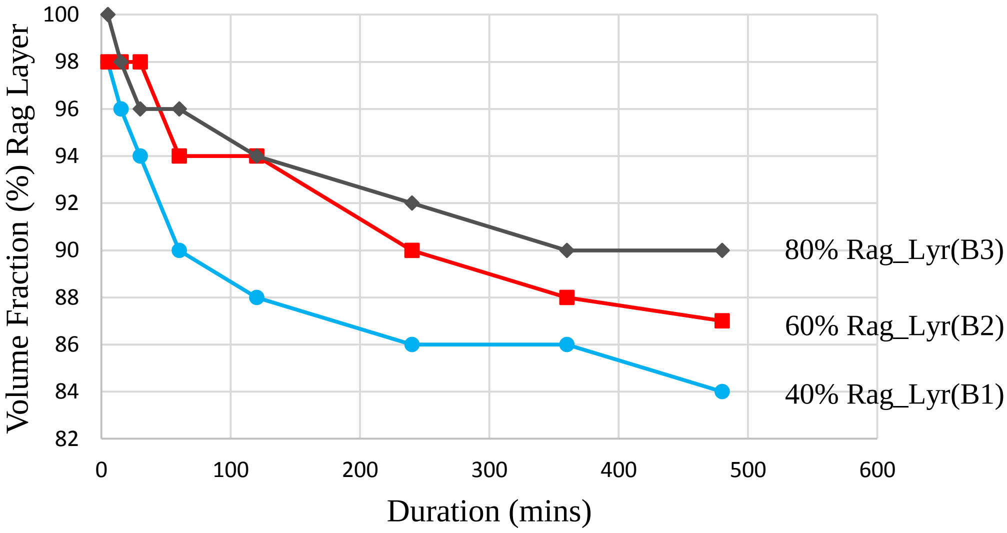


Figure 4.6: Volume fraction (%) of rag layer at heating temperature of 45℃ at different ultrasonic amplitude

Figure 4.7 illustrates the change of oil layer and water layer volume fraction of Samples C1, C2 and C3 over period of 8 hours. The formation of oil layer were increased rapidly after five minutes of bottle test in Samples C1 to C3. Samples C3 have the highest oil layer volume fraction of 24% which was higher than base sample by 4%. Besides, Samples C1 have the same oil layer volume fraction with base sample and was expected to increase after eight hours of bottle test.

The water layer formation were shown in Samples C1 and C2. Sample C3 does not exhibited any sign of water formation during eight hours of bottle test. Water layer can be observed after 15 minutes of bottle test with a volume fraction of 22% in sample C1 as compared to sample C2 which formed after 30 minutes with a volume fraction of 12% at the end of bottle test. The results at heating temperature of 60℃ showed significant improvement compared to no water separation in the base sample.

This phenomenon was proven true by Kokal [7], Smith and Arnold [30]. They stated that high temperature increased the collision rate between droplets by reducing the interfacial viscosity and enhanced coalescence rate. Sample C3 show no water layer formation due to high ultrasonic amplitude. These occurrence are due to the increasing in the intensity of shock wave and caused the emulsion to breaking up and reduced coalescence rate [35], [36]. It can be deduced that ultrasonic is able to accelerate the separation rate of crude oil emulsion at heating temperature of 60℃ at 40% amplitude.

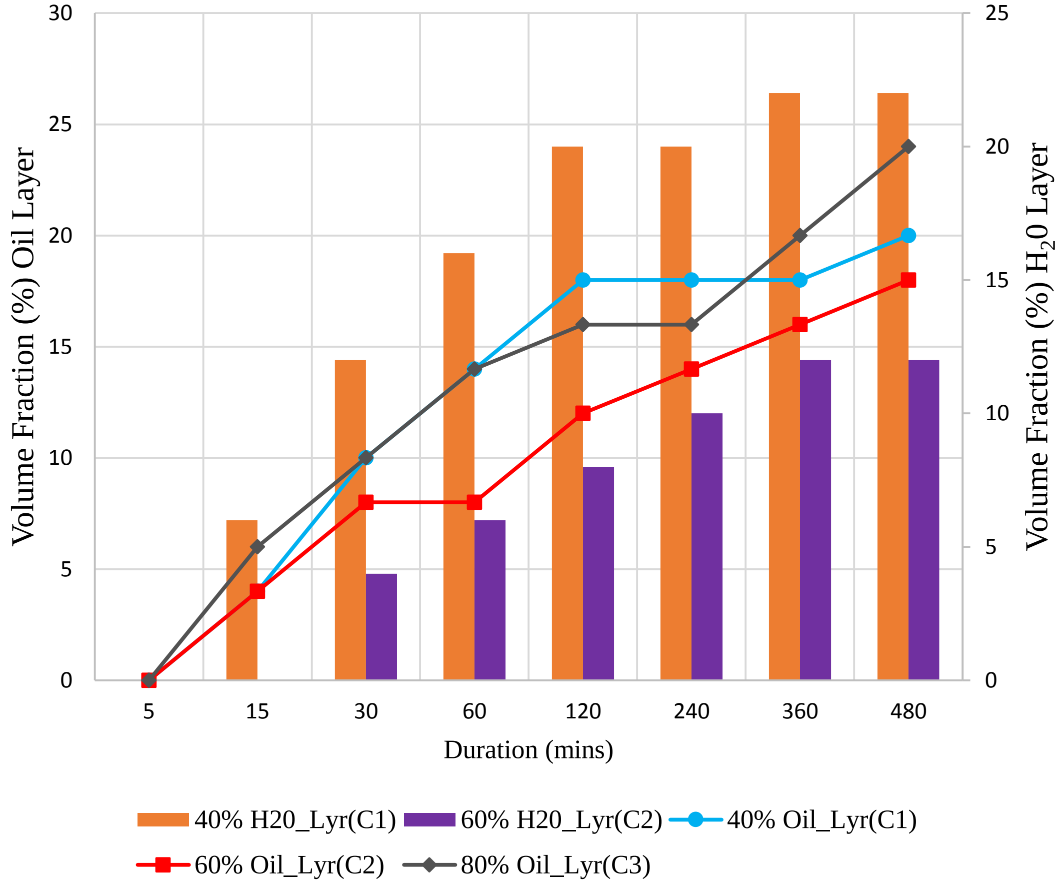


Figure 4.7: Volume fraction (%) of oil layer and water layer at heating temperature of 60℃ at different ultrasonic amplitude

Figure 4.8 demonstrates the similar trend behaviour with Figure 4.6. Samples C1 to C3 showed the overall lowest volume fraction of rag layer compared to other samples with heating temperature of 30℃ and 45℃. As previously discussed, the heating effect gave significant changes to the crude oil emulsion. Thus Figure 4.8 successfully illustrates the relationship between increased temperatures at threshold of amplitude on the separation rate to the crude oil emulsion.

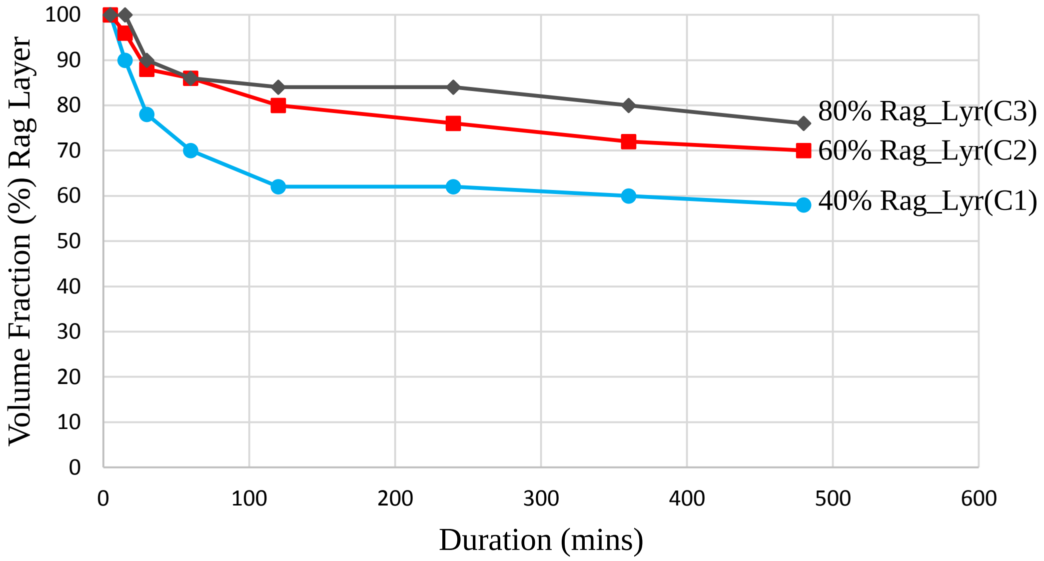


Figure 4.8: Volume fraction (%) of rag layer at heating temperature of 60℃ at different ultrasonic amplitude

Figure 4.9 shows the change of volume fraction of oil layer at different heating temperature at threshold amplitude of 40%. The threshold amplitude was focused because it gave the highest cavitation rate compared to other amplitude level. At operating temperature of 30℃ and 45℃, the volume fraction of oil layer achieved 15% at the end of eight hours of bottle test because insufficient heat energy was supplied to the system to trigger the coalescence and flocculation process. Based on Figure 4.9, Sample C1 showed the highest volume fraction of oil layer compared to other samples.

The trend was proven by Kokal's [7] finding that increased temperatures enhanced the separation rate of crude oil. As the temperature increases, crude oil particles will absorb the energy and converts to kinetic energy. It allowed crude oil to vibrate and move due to differential in density of crude oil and water. In molecular structure of view, increased operating temperature to 60℃ results in destabilization of interfacial film and allowed coalescence process to occur [7]. Hence, coalescence rate increased at high thermal energy. In short, heat accelerated the de-emulsification process.

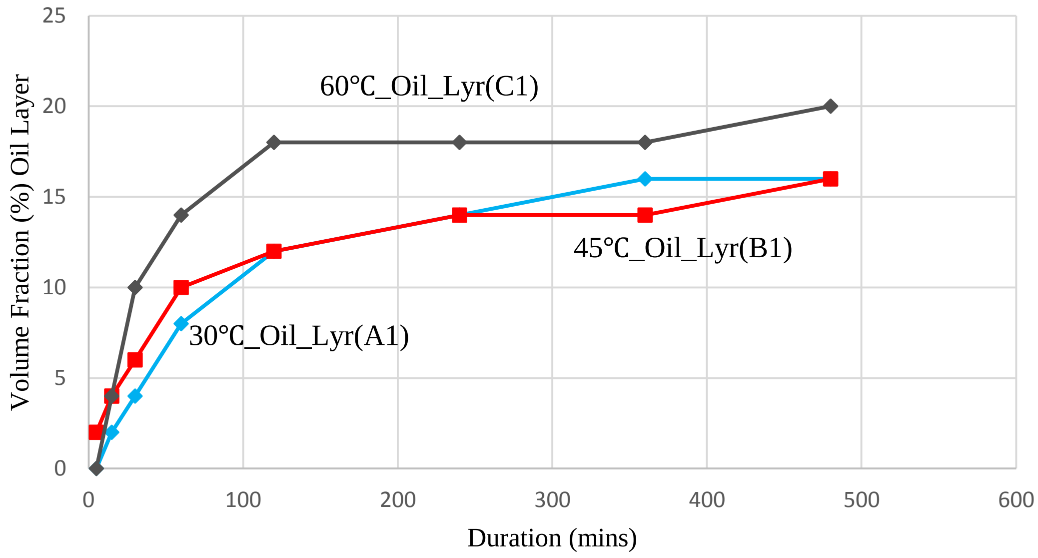


Figure 4.9: Volume fraction (%) of oil layer at threshold amplitude of 40% at different heating temperature

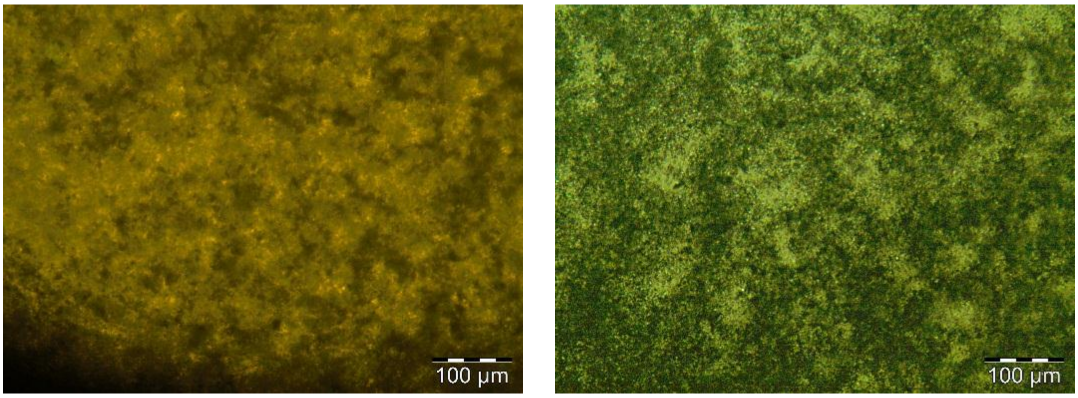
4.2.1 Water Droplets Size in Rag Layer

The mean size of water droplets were illustrated in Table 4.3. Most of the water droplets are small in size before bottle test were conducted. After eight hours bottle test, the water droplets increased in size because coalescence and flocculation had taken placed in the crude oil emulsion. Sedimentation process caused the water droplets to closely pack together for coalescence to occur due to the differential in density of the crude oil and water in the crude oil emulsion. Therefore, the size of water droplets had increased drastically after eight hours of duration.

Table 4.3: Water droplets size in rag layer

Sample	After treatment (μm)	After 8 hours bottle test (μm)
A1	2.41	4.06
A2	2.06	3.15
A3	2.12	7.78
B1	2.90	2.82
B2	3.44	3.81
B3	4.75	2.36
C1	5.22	11.13
C2	37.89	13.82
C3	2.73	3.76

Figure 4.10 shows the distribution of water droplets in crude oil emulsion before and after bottle test in Sample C1. The effectiveness of ultrasonic was determined by observing the change in size and tightness of water droplets in the rag layer. The larger the water droplets size, the better the coalescence and flocculation results [48]. After ultrasonic treatment in Sample C1, the mean size of water droplets were 5.2 μm and was scattered around the rag layer. Furthermore, the water droplets were not uniform in size distribution in the rag layer of crude oil emulsion. This is because the water droplets was in the initial stages of the flocculation and coalescence process.



(a) (b)

Figure 4.10: Water droplets in rag layer (a) before bottle test and (b) 8 hours after bottle test (b) in Sample C1

However, after eight hours of bottle test, the mean size of the water droplets were 11.13 μm and it formed more uniform water droplets distribution. The size of the water droplets were doubled after eight hours of duration and expected to increase as the time extended. Despite the size of water droplets diameter size, the tightness of droplets were observed in Figure 4.10 (b). The water droplets are clumped up together to form bigger clusters of water droplets as shown in Figure 4.10 (b). These clusters of water droplets are surrounded by oil and foreign solid particles.

This indicated that, ultrasonic wave application enhanced the de-emulsification process of water droplets by increasing the water droplets size and clumped the droplets tight together by forming a uniform shape.

4.2.1 Water Content

Table 4.4 shows the water content in oil and rag layers after eight hours of bottle test and after treatment. As the emulsion separated to its distinguished phase, water content were evaluated on each layer by using Karl Fischer titration. Water content in oil and rag layers need to be identified to prove the effectiveness of the ultrasonic application toward the de-emulsification process. Water content in each layer was indicted by using percentage.

Table 4.4: Karl Fischer titration on the water content of ultrasonic treatment samples

Sample	Temperature (C)	Amplitude (%)	After Treatment/ before bottle test (%)	After 8 Hours of bottle test (%)	
			H2O in Rag_Lyr	H2O in Oil_Lyr	H2O in Rag_Lyr
A1	30	40	25.761	1.686	23.547
A2	30	60	27.593	6.578	24.514
A3	30	80	26.676	13.001	23.119
B1	45	40	14.804	9.769	14.453
B2	45	60	28.231	7.953	26.153
B3	45	80	24.438	10.492	27.279
C1	60	40	16.833	4.016	13.664
C2	60	60	13.087	7.644	12.81
C3	60	80	14.572	4.831	14.432

At heating temperature of 30℃ of crude oil emulsion, the water content in rag layer remained high between 25% to 28% region compared to other samples. After eight hours of bottle test, the water contents dropped 2% to 3% in rag layer for Sample A1 to A3. Sample A1 had the lowest water content in oil layer compared to sample A2 and A3. Besides, the water content in oil layer in samples A3 persist at high water content among all the samples. It clearly proved that at threshold ultrasonic amplitude, it gave significant effect to the water content in oil layer by enhancing the coalescence process of the water droplets. However, the water content in the rag layer remains high due to insufficient heat energy supplied to the crude oil emulsion.

Subsequently, the increasing of operating temperature from 30℃ to 45℃ caused the reduction of water content in rag layer for Sample B1 to B3 before bottle test as compared to Sample A1 to A3. As agreed by Kokal [7], increase in temperature reduced the viscosity of crude oil and ease the movement of water droplets. Samples B1 to B3 showed high content of water in oil layer due to restrict of rag layer. Rag layer act as a barrier that inhibit the water droplet from oil layer to settle down into rag layer.

Sample C1 to C3 have overall lower water content in rag layer after the ultrasonic treatment at heating temperature of 60℃. After eight hours of bottle test, sample C1 contain 4.016% of water content in oil layer which was the lowest water content compared to samples C2 and C3. This occurrence was due to the optimum temperature and amplitude that enhance the coalescence rate and sedimentation of water by reducing the rag layer viscosity.

4.3 Optimization

To study the ultrasonic wave application in de-emulsification process, two parameters which are operating temperature and ultrasonic wave amplitude were investigated. The R-squared value was estimated by Analysis of Variance (ANOVA) to measure the variability in the observed response values could be explained by the experimental factors and their interactions. The value of R-squared is always between zero to one. A practical rule of thumb for evaluating the R-squared is that it should be at least 0.75 [51].

4.3.1 Optimization of Ultrasonic Wave De-emulsification

Optimization process was used to validate the emulsion de-emulsification process. Two variables which are temperature and amplitude were investigated in crude oil emulsion. As discussed in Section 4.2, Sample C1 showed the most significant effect whereby crude oil emulsion successfully separated into three phases; crude oil, rag layer and water. The oil, rag and water layers were tabulated into Design Expert software to be evaluated. Based on the optimization graph, interaction effect between temperature and amplitude collated with crude oil and water were able identified. This method is very important in creating new formulation between two parameters by knowing the optimum result. With the optimization data, empirical equation for oil, rag and water layers are able to be identified. Table 4.5 shows the data in three level factorial design.

Table 4.5: Three-level factorial design with response

Sample ID	Temperature (℃)	Amplitude (%)	Response1 Oil Layer (%)	Response1 Oil Layer (%)	Response1 Oil Layer (%)
A1	30	40	16	84	0
A2	30	60	16	84	0
A3	30	80	12	88	0
B1	45	40	16	84	0
B2	45	60	13	87	0
B2-1	45	60	12	88	0
B2-2	45	60	12	88	0
B2-3	45	60	11	89	0
B2-4	45	60	10	90	0
B3	45	80	10	90	0
C1	60	40	20	58	22
C2	60	60	18	70	12
C3	60	80	24	76	0

4.3.2 ANOVA for Response Surface Quadratic Model on Oil Layer

The analysis of variance (ANOVA) on oil layer was analysed from Design Expert Software to measure the variability of the observed response values as shown in Figure 4.11. The value of R-squared is 0.8921 which the second-order model explained about 89.21% of the variability observed in the gain. The R-squared symbolized how well the data was fitted to a statistical model. R-squared of 1 indicated perfect regression line fits to the well data. As R-squared approached value of 1 denoted that, the error were due to external factors such as random error and systematic error during the run of experiments.

Response: Oil Layer

ANOVA for Response Surface Quadratic Model

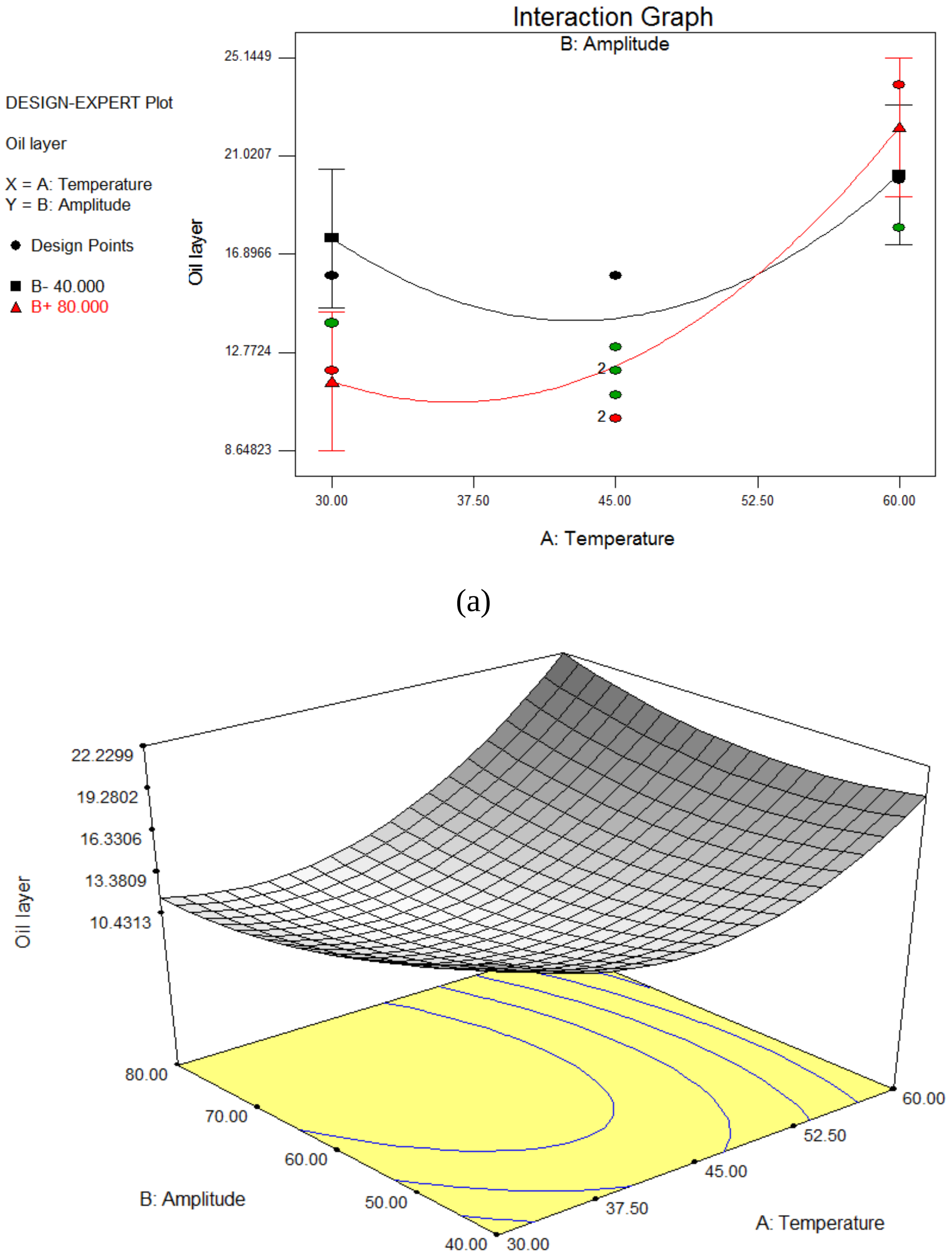
Analysis of variance table [Partial sum of squares]

Source	Sum of Square	DF	Mean Square	F Value	Prob>F	
Model	188.45	5	37.69	11.58	0.0028	significant
A	66.67	1	66.67	20.48	0.0027	
B	6.00	1	6.00	1.84	0.2167	
A^2	60.74	1	60.74	18.66	0.0035	
B^2	7.89	1	7.89	2.42	0.1635	
AB	16.00	1	16.00	4.92	0.0621	
Residual	22.78	7	3.25			
Lack of Fit	17.58	3	5.86	4.51	0.0899	Not significant
Pure Error	5.20	4	1.30			
Cor Total	211.23	12		R^2	0.8921	

The Model F-value of 11.58 implies the model is significant. There is only a 0.28% chance that a “Model F-value”this large could occur due to noise

Figure 4.11: ANOVA for Response Surface Quadratic Model on oil layer

Based on Figure 4.11, the F-value of the model on oil layer is 11.58 which implies that the result is valid and significant. The finding can be declared as significant as Prob>F is less than 0.05. The “Lack of Fit F-value” of the oil layer is 4.51 in Figure 4.11 implies that there is 8.99% chance that “Lack of Fit” occurred during the experiments and it entitled as “not significant” in ANOVA table mean the design model is fit. Figure 4.12 shows the interaction graph and 3D view of the oil layer behaviour under operating temperature and ultrasonic amplitude.



(a)

(b)

Figure 4.12: Response Surface of predicted oil layer (a) interaction graph (b) 3D model of interaction factor AB

Based on ANOVA response in oil layer, it yield an empirical relationship and model interaction between the variables:

$$Oil\ Layer = 79.93 - 2.054A - 0.86B + 0.021A^2 + 4.22 \times 10^{-3}\ B^2 + 6.67 \times 10^{-3}AB \tag{4.1}$$

where A is the heating temperature (℃) and B is the amplitude of the ultrasonic (%).

Referring Figure 4.12, increase of operating temperature gave significant effect to the increment of crude oil layer thickness. Based on Figure 4.12, crude oil layer at operating temperature of 60℃ showed higher in oil layer volume fraction compared to operating temperature of 30℃. Increase of ultrasonic amplitude percentage from 40% to 80% at operating temperature of 60℃ showed a slight improvement of 4% in oil layer volume fraction. However, increasing of ultrasonic amplitude in operating temperature of 30℃ showed low crude oil volume fraction. Hence, it is proved that crude oil layer thickness have strong correlation with operating temperature.

4.3.3 ANOVA for Response Surface Quadratic Model on Water Layer

Subsequently, the significance interaction of each factors were showed in an analysis of variance (ANOVA) for water layer in Figure 4.13. The value of R-squared is 0.92421 which the second-order model explained about 92.42% of the variability observed in the gain. R-squared of 0.92421 indicated a good fit and defined the true behaviour of water layer in crude oil emulsion separation. Figure 4.13 shows the F-value of the model on water layer is 17.08 implies the results are valid and significant as Prob>F is less than 0.05. This application yield a mathematical model equation:

$$Water\ Layer = -5.78 - 0.86A + 0.71B + 0.03A^2 - 6.04 \times 10^{-4}B^2 - 0.018AB \tag{4.2}$$

where A is the heating temperature (℃) and B is the amplitude of the ultrasonic (%).

Response: Water Layer

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Square	DF	Mean Square	F Value	Prob>F	
Model	498.24	5	99.65	17.08	0.0008	significant
A	192.67	1	192.67	33.02	0.0007	
B	80.67	1	80.67	13.83	0.0075	
A^2	91.59	1	91.59	15.70	0.0054	
B^2	0.16	1	0.16	0.028	0.8728	
AB	121.00	1	121.00	20.74	0.0026	
Residual	40.84	7	5.83			
Lack of Fit	40.84	3	13.61			
Pure Error	0.000	4	0.000			
Cor Total	539.08	12		R^2	0.9242	

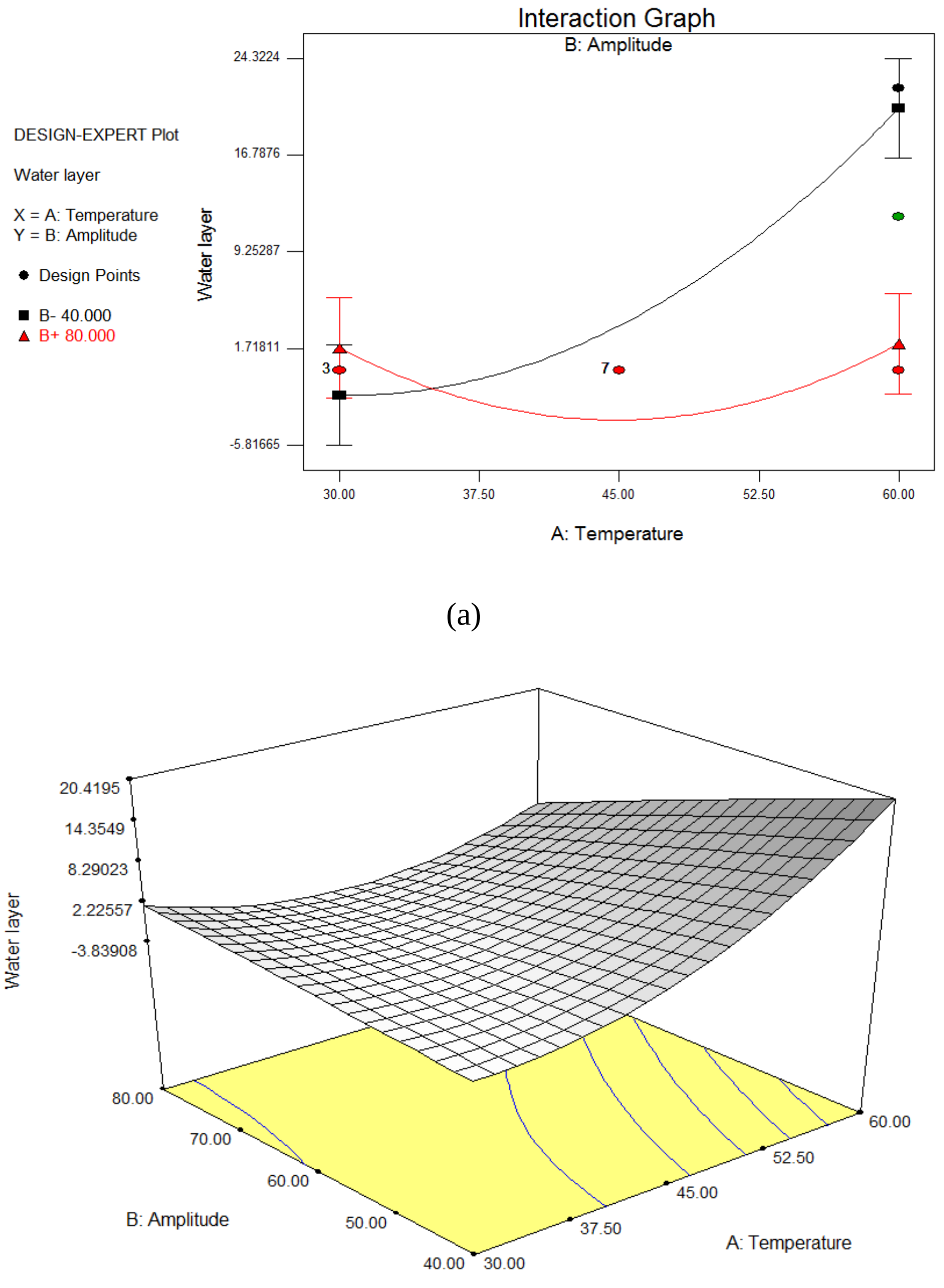
The Model F-value of 17.08 implies the model is significant. There is only a 0.08% chance that a “Model F-value”this large could occur due to noise

Figure 4.13: ANOVA for Response Surface Quadratic Model on water layer

Figure 4.14 summarizes the equation into interaction graph and 3D view of the water layer behaviour under the influence of the temperature and amplitude. Based on Figure 4.14 (a), the water layer thickness was strongly affected by the change of amplitude at heating temperature of 60℃. As deliberated in the literature review, amplitude at 40% is the threshold amplitude and it provides the optimum cavitation effect to droplets.

At threshold amplitude, water droplets experienced ideal ultrasonic irradiation. It induced sufficient shock wave that caused the cavitation bubble burst at ideal manner.

Therefore, it created a void for larger water droplets to form. Increment of amplitude to 80%, shows ineffectiveness in water layer separation. Figure 4.14 is inversely proportional to Figure 4.13. In general, increase in amplitude will induce excessive shock wave that break up all the water droplets into smaller droplets and formed a stable crude oil emulsion. The increase in amplitude also known as inhibition of de-emulsification process.



(a)

(b)

Figure 4.14: Response Surface of predicted water layer (a) interaction graph (b) 3D model of interaction factor AB

4.3.4 ANOVA for Response Surface Quadratic Model on Rag Layer

Based on Figure 4.15, the R-squared value is 0.9847. It indicated that the rag layer formation is very fit to the regression line or true value of the rag layer formation. The F-value of the model on rag layer is 89.92 imply the result is valid and significant because the Prob>F is less 0.05. The “Lack of Fit F-value” is 2.91 and probability of 0.1646 larger than 0.05 indicated that “Lack of Fit” is not significant. Therefore, the rag layer design model is fit.

Response: Rag Layer

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Square	DF	Mean Square	F Value	Prob>F	
Model	1062.38	5	212.48	89.92	< 0.0001	Significant
A	486.00	1	486.00	205.68	< 0.0001	
B	130.67	1	130.67	55.30	0.0001	
A^2	301.51	1	301.51	127.60	< 0.0001	
B^2	5.79	1	5.79	2.45	0.1614	
AB	49.00	1	49.00	20.74	0.0026	
Residual	16.54	7	2.36			
Lack of Fit	11.34	3	3.78	2.91	0.1646	Not significant
Pure Error	5.20	4	1.30			
Cor Total	1078.92	12		R^2	0.9847	

The Model F-value of 89.92 implies the model is significant. There is only a 0.01% chance that a “Model F-value”this large could occur due to noise

Figure 4.15: ANOVA for Response Surface Quadratic Model on rag layer

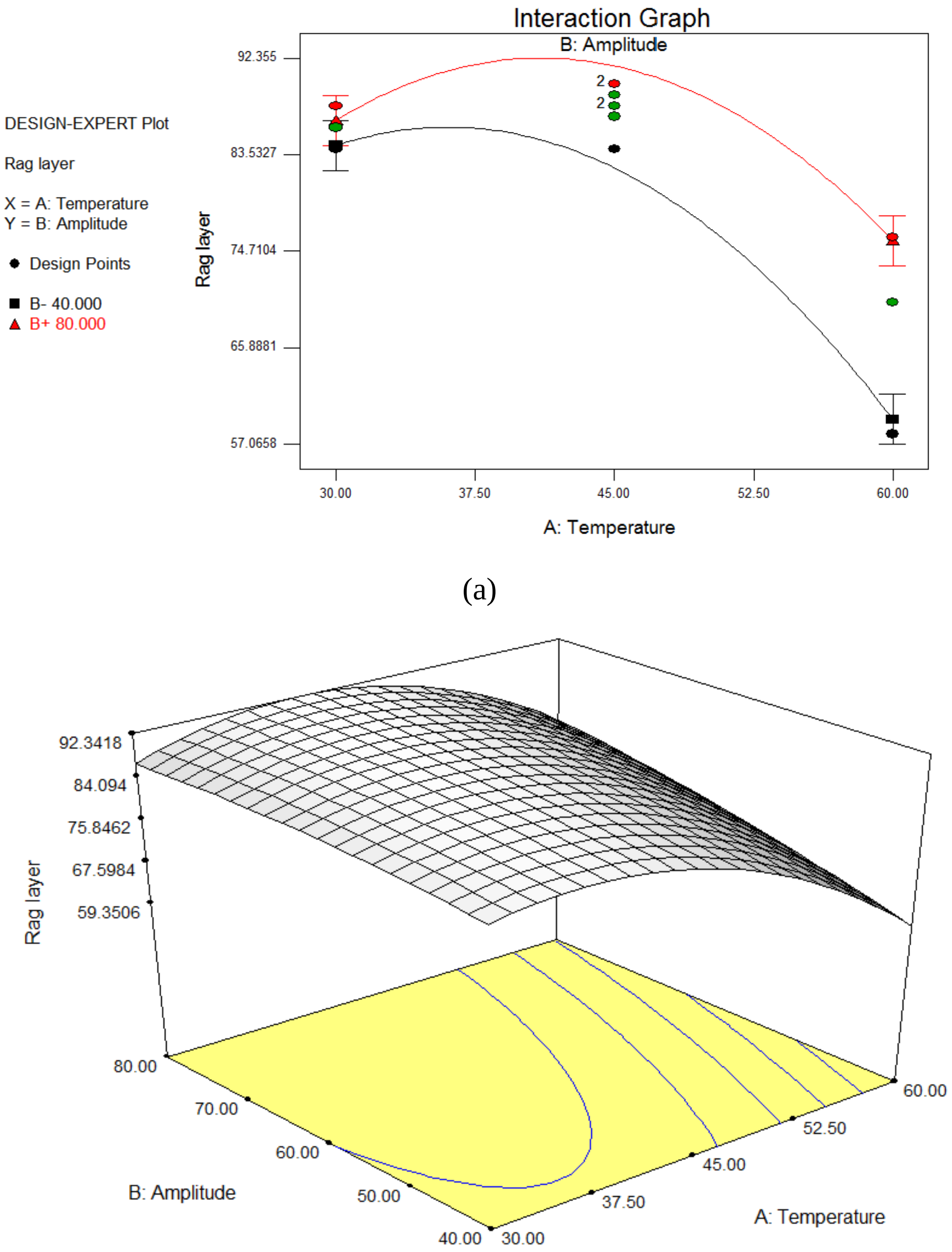
Based on Figure 4.15, the ANOVA for Response Surface Model on rag layer yield a mathematical model equation:

$$Rag\ Layer = 25.84 + 2.88A + 0.14B - 0.05A^2 - 3.32 \times 10^{-3}B^2 + 0.012AB \qquad (4.3)$$

where A is the heating temperature (℃) and B is the amplitude of the ultrasonic (%). The application of response surface generated interaction graph and 3D view of the rag layer behaviour under the influenced of the temperature and amplitude. Figure 4.16 shows the quadratic model graph obtained from the interaction between temperature and amplitude.

Based on Figure 4.16 (a), rag layer was greatly influenced by the heating temperature and amplitude. Both parameters gave significant effect to the formation of rag layer. Under ultrasonic irradiation, rag layer contain majority of water than crude oil particle. As discussed in Section 4.3.2 and Section 4.3.3, crude oil layer was affected by heating temperature and water was affected by the ultrasonic amplitude. Hence, it resulted in the rag layer achieving its minimum percentage of 58% of total crude oil emulsion at heating temperature of 60℃ at ultrasonic amplitude of 40%. The lower the rag layer, the more effective the separation rate.

Rag layer have the maximum thickness at heating temperature of 45℃ at 80% of ultrasonic amplitude. This was due to the insufficient heat energy supply and excessive of irradiation to the crude oil and water droplets. It caused high intensity shock wave and break the droplets into smaller droplets resulting in retardation of the de-emulsification process. Indirectly, the rag layer restrict the movement of the water droplets which results in large rag layer formation.



(a)

(b)

Figure 4.16: Response Surface of predicted rag layer (a) interaction graph (b) 3D model of interaction factor AB

4.4 Summary

By comparing the effectiveness of ultrasonic wave application and base sample in de-emulsification process. Ultrasonic irradiation showed the sign of separation in oil and water layers at heating temperature of 60℃. In optimization part (Section 4.3), at high temperature of 60℃, best separation of oil layer was obtained whereas at threshold of ultrasonic amplitude of 40% the best separation of water layer was achieved. Besides the rag layer also showed the lowest percentage at heating temperature of 60℃ and ultrasonic amplitude at 40%.

Overall, Sample C1 showed the highest recovery compared to other samples. Parameter at heating temperature of 60 ℃ and ultrasonic amplitude at 40% gave promising results in ultrasonic de-emulsification approach. Despite the original composition, Sample C1 showed water layer formation whereas no signs of water layer in base sample.

Table 4.6: Comparison on base sample and Sample C1

	Oil Layer (%)	Rag Layer (%)	Water Layer (%)
Original Composition	70	0	30
Base Sample	20	80	0
Sample C1	20	58	22

Separation efficiency was calculated based on volume fraction of water layer between base sample and ultrasonic Sample C1.

$$n_{Sep} = \text{Separation Efficiency} = \frac{22\ \%}{30\ \%} = 73.33\ \% \tag{4.4}$$

Based on Table 4.7, Sample C1 is recommended as the optimum operating condition under ultrasonic de-emulsification process because it achieved 73.33% separation efficiency in duration of eight hours bottle test as compared to base sample have no sign of water layer separation. Besides, under ultrasonic wave application the water content in oil layer had significantly dropped to 4.016% in Sample C1.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The efficiency of crude oil emulsion separation rate was investigated by studying the stability of the crude oil emulsion by conducting few testing such as bottle test, KF titration and Cross-Polarised Microscope. The objectives of the research are achieved through identifying the optimum parameter for ultrasonic wave application in de-emulsification process.

In conclusion, the ultrasonic irradiation and base sample experiments have successfully provided an insight on the effectiveness of ultrasonic de-emulsification method on the waxy crude oil. At heating temperature of 60℃ at 40% of amplitude of ultrasonic was identified as the best operating condition. The following conclusions can be drawn from this work:

1. There were no water separation in crude oil emulsion after eight hours of bottle test under ultrasonic irradiation treatment in Samples A and B which were conducted in heating temperature of 30℃ and 45℃. There was insufficient heat energy to initiate the separation process.

2. Heating temperature at 60℃ in Sample C was conducted to accelerate the water droplets formation based on the design expert software. This was justified by researchers which claimed that high temperature of 60℃ , reduced the viscosity of the crude oil emulsion. Therefore, it frees the movement of droplets and enhanced the flocculation and coalescence process.

3. Based on the interaction graph generated by design expert software, two findings have been discovered. Water formation in crude oil emulsion is strongly affected by the change of amplitude whereas oil layer formation is strongly affected by the change of crude oil temperature. Amplitude is a function of energy dissipation in the system. Thus, at 100% ultrasonic amplitude, the cavitation effect will increase and retard the movement of water from coalescing. Movement of crude oil was determined by the viscosity of the system. At high temperature of 60℃, the viscosity of crude oil was reduced and increased the crude oil separation rate in crude oil emulsion.

4. The optimum parameter for ultrasonic de-emulsification is at heating temperature of 60℃ at 40% ultrasonic amplitude. 40% ultrasonic amplitude at 20 kHz referred to 40 μm amplitude was applied to the crude oil emulsion. This statement is justified and proven by past researchers that the threshold amplitude and temperature are the key factors in affecting the quality of separation rate of crude oil emulsion. Threshold amplitude is the energy that provide optimum cavitation rate to the crude oil emulsion.

Ultrasonic application is an environmentally friendly technique for the effective de-emulsification on the crude oil emulsion. Based on the results obtain, ultrasonic application is a promising approach for crude oil de-emulsification process. Thus, the objectives of the research were achieved.

5.2 Recommendations

Throughout this research study, few recommendations can be done to improve the results and findings of the ultrasonic de-emulsification technique.

1. Performing continuous stirring process during ultrasonic irradiation. This will ensure even distribution of energy transmission from ultrasonic to crude oil emulsion.

2. Further research on crude oil emulsion at different water cut level such as 50:50, 70:30, and 90:30. This process will allow us to understand the effect of water in affecting the settling rate of crude oil.

3. Optimization of ultrasonic applications with right amount of de-emulsifier to enhance the crude oil and water separation rate. This will give further insight on oil recovery study in molecular structure view.

4. Evaluate the crude oil separation rate at different categories of crude oil emulsion such as oil-in-water (o/w) emulsion and water-in-oil-in-water (w/o/w) emulsion.

5. In order to obtain more accurate and effective water separation, the experiments should be conducted in pilot scale. This will provide a real and practical environment in treating crude oil emulsion.

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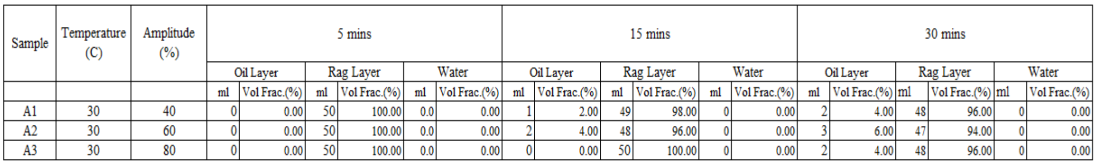
APPENDICES

Appendix A: Bottles Test Results

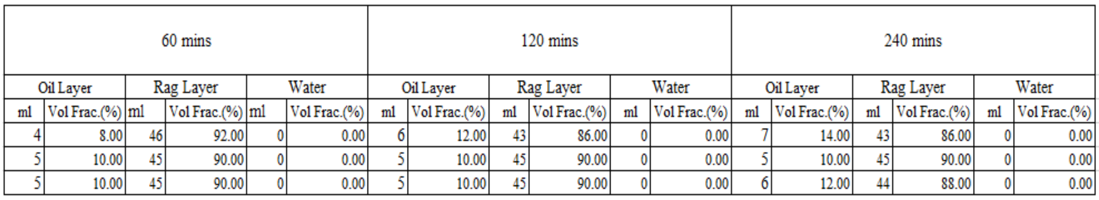
1. Bottle Test on Base Sample

Time (mins)	Thickness of layer (ml)					
	Crude oil Layer		Rag Layer		Water Layer	
	ml	%	ml	%	ml	%
5	0	0	50	100	0	0
15	1.5	3	48.5	97	0	0
30	2	4	48	96	0	0
60	2	4	48	96	0	0
120	2.5	5	47.5	95	0	0
240	5	10	45	90	0	0
360	10	20	40	80	0	0
480	10	20	40	80	0	0

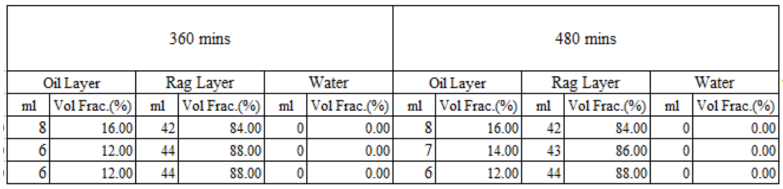
2. De-emulsification at Heating Temperature of 30°C



Sample	Temperature (C)	Amplitude (%)	5 mins						15 mins						30 mins					
			Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water	
			ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)
A1	30	40	0	0.00	50	100.00	0.0	0.00	1	2.00	49	98.00	0	0.00	2	4.00	48	96.00	0	0.00
A2	30	60	0	0.00	50	100.00	0.0	0.00	2	4.00	48	96.00	0	0.00	3	6.00	47	94.00	0	0.00
A3	30	80	0	0.00	50	100.00	0.0	0.00	0	0.00	50	100.00	0	0.00	2	4.00	48	96.00	0	0.00

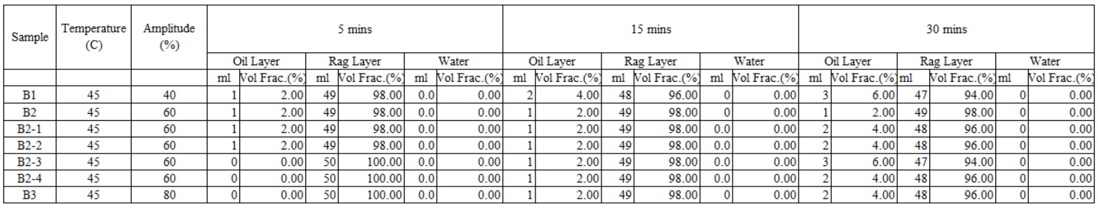


60 mins						120 mins						240 mins					
Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water	
ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)
4	8.00	46	92.00	0	0.00	6	12.00	43	86.00	0	0.00	7	14.00	43	86.00	0	0.00
5	10.00	45	90.00	0	0.00	5	10.00	45	90.00	0	0.00	5	10.00	45	90.00	0	0.00
5	10.00	45	90.00	0	0.00	5	10.00	45	90.00	0	0.00	6	12.00	44	88.00	0	0.00

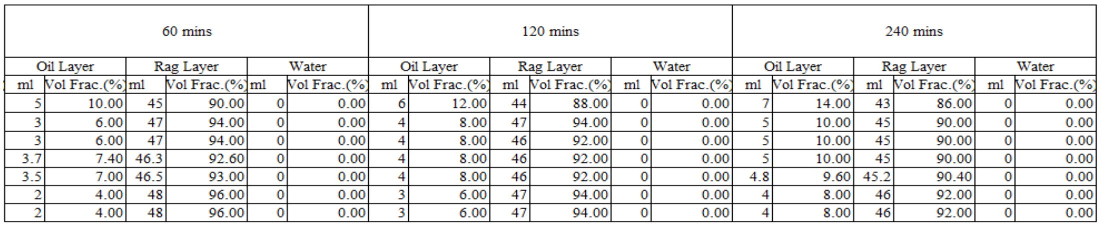


360 mins						480 mins					
Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water	
ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)
8	16.00	42	84.00	0	0.00	8	16.00	42	84.00	0	0.00
6	12.00	44	88.00	0	0.00	7	14.00	43	86.00	0	0.00
6	12.00	44	88.00	0	0.00	6	12.00	44	88.00	0	0.00

3. De-emulsification at Heating Temperature of 45°C



Sample	Temperature (C)	Amplitude (%)	5 mins						15 mins						30 mins					
			Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water	
			ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)
B1	45	40	1	2.00	49	98.00	0.0	0.00	2	4.00	48	96.00	0	0.00	3	6.00	47	94.00	0	0.00
B2	45	60	1	2.00	49	98.00	0.0	0.00	1	2.00	49	98.00	0	0.00	1	2.00	49	98.00	0	0.00
B2-1	45	60	1	2.00	49	98.00	0.0	0.00	1	2.00	49	98.00	0.0	0.00	2	4.00	48	96.00	0	0.00
B2-2	45	60	1	2.00	49	98.00	0.0	0.00	1	2.00	49	98.00	0.0	0.00	2	4.00	48	96.00	0	0.00
B2-3	45	60	0	0.00	50	100.00	0.0	0.00	1	2.00	49	98.00	0.0	0.00	3	6.00	47	94.00	0	0.00
B2-4	45	60	0	0.00	50	100.00	0.0	0.00	1	2.00	49	98.00	0.0	0.00	2	4.00	48	96.00	0	0.00
B3	45	80	0	0.00	50	100.00	0.0	0.00	1	2.00	49	98.00	0	0.00	2	4.00	48	96.00	0	0.00



60 mins						120 mins						240 mins					
Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water	
ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)
5	10.00	45	90.00	0	0.00	6	12.00	44	88.00	0	0.00	7	14.00	43	86.00	0	0.00
3	6.00	47	94.00	0	0.00	4	8.00	47	94.00	0	0.00	5	10.00	45	90.00	0	0.00
3	6.00	47	94.00	0	0.00	4	8.00	46	92.00	0	0.00	5	10.00	45	90.00	0	0.00
3.7	7.40	46.3	92.60	0	0.00	4	8.00	46	92.00	0	0.00	5	10.00	45	90.00	0	0.00
3.5	7.00	46.5	93.00	0	0.00	4	8.00	46	92.00	0	0.00	4.8	9.60	45.2	90.40	0	0.00
2	4.00	48	96.00	0	0.00	3	6.00	47	94.00	0	0.00	4	8.00	46	92.00	0	0.00
2	4.00	48	96.00	0	0.00	3	6.00	47	94.00	0	0.00	4	8.00	46	92.00	0	0.00

360 mins						480 mins					
Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water	
ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)
7	14.00	43	86.00	0	0.00	8	16.00	42	84.00	0	0.00
6	12.00	44	88.00	0	0.00	6.5	13.00	43.5	87.00	0	0.00
6	12.00	44	88.00	0	0.00	6	12.00	44	88.00	0	0.00
5	10.00	45	90.00	0	0.00	6	12.00	44	88.00	0	0.00
5	10.00	45	90.00	0	0.00	5.5	11.00	44.5	89.00	0	0.00
5	10.00	45	90.00	0	0.00	5	10.00	45	90.00	0	0.00
5	10.00	45	90.00	0	0.00	5	10.00	45	90.00	0	0.00

4. De-emulsification at Heating Temperature of 60℃

Sample	Temperature (C)	Amplitude (%)	5 mins						15 mins						30 mins					
			Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water	
			ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)
C1	60	40	0	0.00	50	100.00	0.0	0.00	2	4.00	45	90.00	3	6.00	5	10.00	39	78.00	6	12.00
C2	60	60	0	0.00	50	100.00	0.0	0.00	2	4.00	48	96.00	0	0.00	4	8.00	44	88.00	2	4.00
C3	60	80	0	0.00	50	100.00	0.0	0.00	3	6.00	50	100.00	0	0.00	5	10.00	45	90.00	0	0.00

60 mins						120 mins						240 mins					
Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water	
ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)
7	14.00	35	70.00	8	16.00	9	18.00	31	62.00	10	20.00	9	18.00	31	62.00	10	20.00
4	8.00	43	86.00	3	6.00	6	12.00	40	80.00	4	8.00	7	14.00	38	76.00	5	10.00
7	14.00	43	86.00	0	0.00	8	16.00	42	84.00	0	0.00	8	16.00	42	84.00	0	0.00

360 mins						480 mins					
Oil Layer		Rag Layer		Water		Oil Layer		Rag Layer		Water	
ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)	ml	Vol Frac.(%)
9	18.00	30	60.00	11	22.00	10	20.00	29	58.00	11	22.00
8	16.00	36	72.00	6	12.00	9	18.00	35	70.00	6	12.00
10	20.00	40	80.00	0	0.00	12	24.00	38	76.00	0	0.00

Appendix B: Cross Polarization Microscope Results on ultrasonic samples

Sample	After treatment			After 8 hours bottle test		
	Max	Mean	Min	Max	Mean	Min
A1 (30C 40%)	7.95	2.41	0.64	20.17	4.06	0.01
A2 (30C 60%)	4.35	2.06	0.02	21.10	3.15	0.64
A3 (30C 80%)	4.80	2.12	0.32	26.48	7.78	1.10
B1 (45C 40%)	20.41	2.90	0.32	13.31	2.82	0.45
B2 (45C 60%)	6.75	3.44	1.32	13.37	3.81	0.01
B3 (45C 80%)	38.35	4.75	1.01	18.78	2.36	0.32
C1 (60C 40%)	18.49	5.22	0.64	60.67	11.13	0.03
C2 (60C 60%)	105.77	37.89	5.66	68.01	13.82	0.10
C3 (60C 80%)	6.43	2.73	0.64	38.81	3.76	0.64