DEMULSIFICATION OF WATER-IN- OIL (W/O) EMULSION BY MICROWAVE HEATING TECHNOLOGY

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STATEMENT OF AWARD FOR DEGREE

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SUPERVISOR'S DECLARATION

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

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STUDENT'S DECLARATION

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

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To my beloved parents, brothers, sisters, fiance, lecturers and friends

ABSTRACT

Traditional ways of breaking emulsion using heat and chemicals are disadvantageous from both economic and environmental perspectives. In this thesis, the potentials of microwave technology in demulsification of water-in-oil emulsion is investigated. The work began with some characterisation studies to provide understandings of fundamental issues such as formation, formulation and breaking of emulsions by both chemical and microwave approaches. The aim was to obtain optimised operating condition as well as fundamental understanding of water-in-oil stability, upon which further developments on demulsification processes could be developed. The stability studies were carried out by analysing operating conditions such as stirring time, types of surfactant used, temperature, phase inversion, water-oil-ratio (10-90%) and stirring intensity. In this study, also for microwave and chemical demulsification performance tests, three crude oils, namely crude oil A, B and C were utilised. These crude oils were obtained from Petronas Penapisan Melaka, Malaysia. Among of these oils, crude oil C was found to be the heaviest and best for stability and followed by crude oil A and B, respectively. Results also showed that microwave heating of emulsions is advantageous as it was faster and more uniform. A microwave-assisted chemical system was then developed in crude oil A and C, and then successfully applied on demulsification of water-in-oil emulsions. Its performance was compared with conventional demulsification methods such as hotplate, chemical demulsifiers and gravity separation. For microwave irradiation, it was found that the microwave power was proportional to the volume rate of heat generation, rate of temperature increases, wavelength and penetration depth, while the volume fraction is proportional to dielectric properties and inversely proportional to the penetration depth and wavelength. In optimisation part, crude oil A and C obtained 2^3 factorial designs with microwave power, microwave processing time and demulsifier concentration. The percentage of water separated from the model crude oil A was 45.10% at 710 watt in 2.40 minutes with 0.15 wt% demulsifier, while for crude oil C was 38.03% at 767 watt in 2.50 minutes with 0.14 wt% demulsifier, respectively. Crude oil B acquired 2^2 factorial design with microwave power and time processing; the percentage of water separated was 64.07% at 692 watt in 2.56 minutes. The results obtained in this study have exposed the capability of microwave technology in demulsification of water-in-oil emulsion. Further works are nevertheless required to provide deeper understanding the mechanisms involved to facilitate the development of an optimum system applicable to the industry.

ABSTRAK

Kaedah tradisional dalam memisahkan emulsi menggunakan haba dan bahan kimia adalah merugikan dari segi ekonomi and alam sekitar. Dalam tesis ini, potensi teknologi gelombang mikro dalam demulsifikasi oleh air-dalam-minyak emulsi dikaji. Pekerjaan bermula dengan beberapa kajian mengenai ciri-ciri untuk memberikan pemahaman tentang isu-isu asas seperti pembentukan, perumusan dan memecahkan emulsi oleh kedua-dua pendekatan kimia dan gelombang mikro. Tujuannya adalah untuk mendapatkan keadaan operasi dioptimumkan serta pemahaman dasar air-dalam kestabilan-minyak, atas mana perkembangan lebih lanjut atas proses demulsification dapat dikembangkan. Pengajian kestabilan dilakukan dengan menganalisis keadaan operasi seperti waktu pengadukan, jenis surfaktan yang digunakan, suhu, fasa inversi , nisbah air-minyak (10-90%) dan adukan intensitas. Dalam kajian ini, juga untuk ujian gelombang mikro dan demulsifikasi kimia, tiga minyak mentah, dinamakan sebagai minyak mentah A,B dan C telah digunakan. Minyak mentah ini diperolehi dari Petronas Penapisan Melaka, Malaysia. Di antara minyak mentah ini, minyak mentah C adalah yang terberat and baik untuk kestabilan dan masing-masing diikuti oleh minyak mentah A and B. Keputusan juga telah menunjukkan bahawa pemanasan emulsi oleh gelombang mikro ini menguntungkan kerana lebih cepat dan seragam. Sebuah sistem gelombang mikro-kimia kemudian dikembangkan di minyak mentah A dan C, dan kemudiannya berjaya dalam aplikasi ke atas demulsifikasi oleh emulsi air-dalam-minyak. Prestasinya telah dibandingkan dengan kaedah demulsifikasi konvensional seperti piring pemanas, demulsifi kimia dan pemisahan graviti. Untuk iridiasi gelombang mikro, didapati bahawa kuasa gelombang mikro adalah berkadar terus dengan kadar isipadu oleh generasi haba, kadar peningkatan suhu, panjang gelombang dan kadalaman penetrasi, manakala fraksi isipadu adalah berkadar terus dengan sifat dielektrik dan berkadar songsang dengan kedalaman penetrasi dan panjang gelombang. Dalam bahagian pengoptimuman, minyak mentah A dan C memperolehi 2^3 rancangan faktorial dengan kuasa gelombang mikro, masa pemprosesan gelombang mikro dan konsentrasi demulsifer. Peratusan pemisahan air daripada model minyak mentah A ialah 43.11% pada 710 watt dalam 2.40 minit dengan 0.15 wt% konsentrasi demulsifer, manakala untuk minyak mentah C ialah 38.03 % pada 767 watt dalam 2.50 minit bersama 0.14 wt% demulsifer. Minyak mentah B memperolehi 2^2 rancangan faktorial dengan kuasa gelombang mikro dan masa memprosesan; peratusan pemisahan air ialah 64.10 % pada 692 watt dalam 2.56 minit. Keputusan yang diperolehi dari kajian ini telah mengembangkan keupayaan teknologi gelombang mikro dalam demulsifikasi emulsi air-dalam-minyak. Lebih banyak kerja tetap diperlukan untuk memberikan pemahaman yang lebih dalam mekanisme yang terlibat untuk memudahkan pembangunan sistem yang optimum yang sesuai untuk industri.

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LIST OF ABBREVIATIONS

A	asphaltenes
API	American Petroleum Institute
^{o}C	^{O}Celcius
^{o}C/min	^{o}C per minute
CH	conventional heating
cm	centimetre
CMC	critical micelle concentration
cP	centipoises
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infra Red
g	gram
GHz	giga hertz
HLB	hydrophile-lipophile balance
HPLC	High-Performance Liquid Chromatogram
min	minute
mL	mili litre
mg	mili gram
MW	microwave
O/W	oil-in-water
O/W/O	oil-in-water-in-oil
R	resin
R/A	resin to asphaltene ratio
rpm	rotate per minute
SARA	Saturated, Asphaltenes, Resin, Aromatic
SDDS	sodium dedocyl sulfate
Span 83	sorbitan sesquiolate
Tween 80	polysorbate 80
WAT	wax appearance temperature

W/O	water-in-oil
W/O/W	water-in-oil-in-water

LIST OF NOMENCLATURES

E	electric field intensity
f	frequency
H	magnetic field
S	surface
c_o	velocity
Dp	penetration depth
c	speed of light
V	volume of water separated
Cp	heat capacity
h	convective heat transfer coefficient
q_{mv}	volume rate of heat generation
P	microwave power dissipated per unit volume
W	watt

Greek Symbols

μ_O	viscosity of oil
ρ	liquid density, g/cm^3
µ	micron
Φ	volume fraction
ε’’	dielectric loss
ε’	dielectric properties
ε*	complex permittivity
λ	wavelength, cm
%	percent
σ	electric conductivity

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

It is well recognized that the energy consumption per capita and crude oil play and important role in providing energy supply of the world because crude oil is the most readily exploitable source of energy available to humankind, and also source of raw materials for feed stocks in many of the chemical industries (Holmberg; 2001). However, there are about 80% of exploited crude oils exist in an emulsion state, all over the world (Xia et al., 2004). Particularly, the emulsion presents in crude oil reduced the quality of crude oil and also may be encountered problems during the refinery process thus can lead to enormous financial losses if not treated correctly. Hence, emulsions have to be broken to reach specific values of product quality (<0.5% W/O), both for oil and produced water to avoid large economic penalties (Hannisdal, 2005).

The undesired emulsion is necessary to be demulsified to have good quality of the crude oil. Although great effort has been made to demulsified these emulsions, it remains a challenge to effectively break up undesired emulsions by understand the mechanism of formation and stabilisation of the emulsion. The stabilisation and formation of emulsion are crucial parts to study before demulsified the stable emulsion, results in higher separation of water presented in the crude oil.

1.2 PROBLEM STATEMENT

The major problem, when dealing with the crude oil is the formation of persistent water in the crude oil emulsion thus performed the stable emulsion. The present stable emulsion in crude oils encountered many problems especially when deals with the quality of crude oils. Emulsions occurred when there is water as immiscible liquids present in the crude oil. Water is normally present in crude oil reservoirs or is injected as steam to stimulate oil production. Water and oil can mix while rising through the well and when passing through valves and pumps to form in most cases relatively stable dispersions of water droplets in crude oil. Emulsions of crude oil and water can be encountered at many stages during drilling, producing, transporting and processing of crude oils and in many locations such as in hydrocarbon reservoirs, well bores, surface facilities, transportation system and refineries. Also, emulsions usually exhibit viscosities significantly higher than crude oil, thus increasing the energy input required for transport in pipeline (Alejandro et al., 2005). The formation of stable and persistent emulsions are typically undesirable and can result in high pumping costs, reduced throughput and special handling equipment in the production and refining of crude oil petroleum as a challenge which has defied broads and generic resolution for several decades.

A most recent technology which has received lots of attention from researchers is the application of microwave field in the demulsification process (Wolf, 1986; Rajaković and Skala, 2006). Microwave offer a fast heating treatment with uniform temperature distribution to the subjected sample. Because of the qualities of microwave discussed earlier in the other industry such as food industry and oil sands separation from previous researchers (Mutyala et al., 2010; Yanniotis and Sundén, 2006), study has been conducted regarding the use of electromagnetic energy to heat emulsion especially for stable emulsion. This present study is aimed to investigate the effect of microwave radiation in the breaking of the emulsion and separation of water from crude oil and compare it with conventional heating methods, to find an effective way of good separation, less energy consumption, and even cost effective. Thus, to fill this gaps in petroleum industry, three types of crude oil from light to heavy crude oil were selected to accomplish the problems in industry especially when covenant with stable emulsion for heavy crude oil . The emulsion was prepared by following the problems encountered in industry through screening the stability of emulsion before demulsified each emulsion.

1.3 DEFINITION OF TERMS

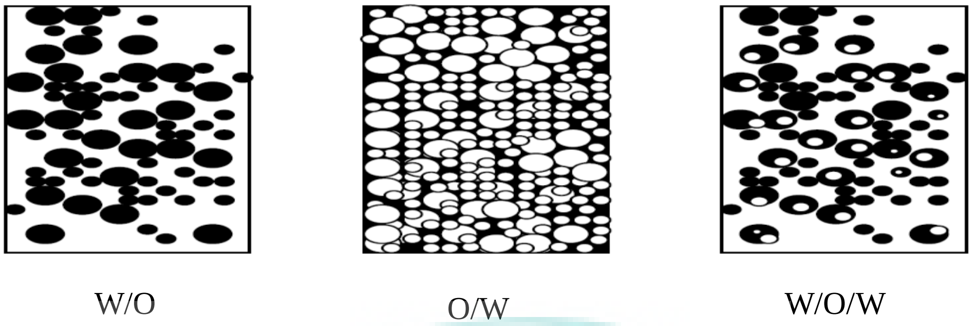
The terms of emulsion, types of emulsion, demulsification and microwave radiation are defined in generally and are listed below:-

1.3.1 Emulsion

Dispersions of a liquid phase in another will exhibit certain stability. The term significantly stable means relative to the intended use and may range from a few minutes to a few years. At least two immiscible liquid phases should be present to make an emulsion (Sjöblom, 2006; Rosen, 2004). The dispersed phase is sometimes referred to as the internal (disperse) phase and the continuous phase as the external phase (Schramm, 2005). In most emulsions, one of liquids is aqueous while the other is hydrocarbon and referred to as oil.

Emulsions are formed when one liquid is dispersed in a continuous liquid phase of a different composition. However, as studied by Rosen (2004), two immiscible pure liquids cannot form an emulsion. For a suspension of a liquid in another to be stable enough to be classified as an emulsion, a third component must be present to stabilise the system and called as emulsifying agent.

As reviewed from Holmberg (2001) as shown in Figure 1.1, the common types of emulsions are oil-in-water (O/W) and water-in-oil (W/O) emulsions, although water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O) multiple emulsions are sometimes encountered. However, in the petroleum industry, the common emulsion present is water-in-oil (W/O) types.



W/O O/W W/O/W

Figure 1.1: Commom Types of Crude Oil Emulsions (W/O and O/W) and Less Common (W/O/W)

Source: Holmberg (2001)

1.3.2 Demulsification

The breaking of emulsion is necessary in many applications such as environmental technology, painting, petroleum industry and waste-water treatments. The breaking of emulsion which is the process of oil and water separation from emulsion also can be identified as demulsification (Yang et al., 2009). As studied by Wu et al. (2003), demulsification can be achieved by three methods which are chemical, mechanical and electrical.

1.3.3 Microwave Irradiation

Microwave irradiation is one of the demulsification methods. Abdurahman et al. (2007), Tanmay and Ayappa (1997) as saying that microwave radiation is an electromagnetic radiation with frequency range within 300 MHz to 300 GHz or equivalently with wavelengths ranging from 1 m down to 1 mm Microwave is non-ionizing radiation that causes molecular motion by migration of ions and dipole rotation. However, it will not change the molecular structure.

1.4 OPERATIONAL DEFINITION

Microwave radiation terms need to be operated as follow this study.

1.4.1 Microwave

In this study, microwave was used as an alternative method to demulsified water-in-crude oil emulsion. Elba domestic microwave oven model: EMO 808 SS would be used in heating crude oil emulsion samples. The microwave was modified to put sample container. Two thermocouples were inserted in the emulsion samples at different locations. This study was investigated the capability of microwave compared with conventional methods at prescribed variables.

1.5 OBJECTIVES OF STUDY

The objectives of this present study are:-

i. To investigate the stability of emulsion using different crude oil samples.
ii. To investigate the performance of microwave application in demulsification of water-in-crude oil emulsions.
iii. To compare the performance of microwave application with conventional demulsification methods.

1.6 SCOPES OF STUDY

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

1. Characterisation of crude oil in terms of physical and chemical properties.
2. To investigate the factors affected stability and formation of W/O emulsion.
3. To examine the demulsification of emulsions by conventional methods (hotplate, chemical demulsifiers, and gravity separation).
4. To examine the demulsification of emulsions by microwave heating using batch process system.

5. To study the effect of varying the microwave power generation in demulsification of W/O emulsions.
6. Optimisation of process parameters in demulsification.

1.7 SIGNIFICANT OF STUDY

Demand of the crude oil especially in refinery industry causes the higher production of crude oil. However to date, crude oil exploitation has advanced to the point that the era of large fields with a high quantity and quality is over. Since the possibility of finding highly productive formations is small the corresponding strategy is focused on an improved exploitation of the existing large fields and to tie in, in an efficient way, small fields. The most important thing when focusing on existing large fields is to increase the recovery rate. To fill these gaps, this study is proposed an alternative method to demulsified the formation of emulsion by using different types of crude oil starting from lighter to heavier which each crude oil inventive from petroleum industry to accomplish the industry standard and requirement. Subsequently, the prepared emulsion was demulsified by comparing conventional and microwave irradiation. By the end of this study, the most effective method in demulsification could be identified and the process parameters also could be optimised using response surface methodology.

1.8 THESIS OUTLINE

This thesis was organized by seven chapters which begun with chapter 1. Chapter 1 presents in general information regarding the background, definition of terms. This chapter also listed the objectives and scopes of study covered in this study.

Chapter 2 discussed in details about water-in-crude oil emulsion and factors affect the stability of emulsion. In first section, the formation of emulsion different of W/O and O/W also foam were explained. As major problems investigated in this study, emulsions were explained the mechanisms of stability and instability. The introduction of application method such as heating, chemical and electrical in demulsification is engrossed in general.

The purpose of chapter 3 is to discuss, in general terms how microwave is generated. It also introduces the fundamental nature of microwaves include mechanisms of dielectric constant and loss and loss tangent. This chapter discuss about interact of microwave with materials, and how these interactions generate process heat.

Materials and experiment procedures used to achieve objectives in this study are presented in Chapter 4. These include the crude oil characteristics which involve the physical and chemical properties of crude oil. Then follow by the emulsion stability test at different phase ratio of emulsion. And finally demulsified the emulsion by comparing conventional and microwave methods. Demulsification by microwave heating technology was selected for further scope which optimisation part.

The main findings for emulsion stability are discussed in Chapter 5. The discussion covered the crude oil characteristics in physical and chemical properties. This chapter also discussed the factors affect on emulsion stability. Meanwhile for the demulsification part, results and discussion are conferred in Chapter 6. The optimisation part in microwave technology also covered in this chapter. Lastly, the conclusion and recommendations in this study are discussed and listed in Chapter 7.

1.9 SUMMARY

Emulsion problems in crude oil production and processing have gained serious consideration either from fundamental and practical aspects by oil companies as well as researchers for the last few decades. One of the focuses is on developing an effective method of breaking up W/O emulsions formed within reservoirs. This study will address some of the fundamental and practical aspects of these areas of interest.

CHAPTER 2

EMULSION STABILITY

2.1 INTRODUCTION

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

2.2 CRUDE OIL EMULSION COMPOSITION

Crude oil varies greatly in appearance depending on its composition. As postulated from Auflem (2002), crude oil is the complex mixture of hydrocarbons, with small amount of sulphur, oxygen and nitrogen, as well as various metallic constituents, particularly vanadium, nickel, iron and copper. Crude oils consist of light hydrocarbon such as gasoline, asphaltenes, resins, waxes and napthenic acid. Crude oils, especially heavy crude oils contain large quantities of asphaltenes (high molecular weight polar components) act as natural emulsifier or also called surface active agent. Besides, the other crude oil components such as resins, fatty acids, waxes and napthenic acid also act as surface active agent but cannot action alone in producing stable emulsion. The other particles in crude oils such as silica, clay and iron oxides naturally hydrophilic but they can become oil-wet (hydrophobic) due to long term exposure to the crude oil in the absence of water (Langevin et al., 2004).

The method of dividing crude oil into four major fractions: saturates (including waxes), aromatics, resins and asphaltenes is called SARA fractionation, based on their polarity and solubility in the solvent. Based on Hannisdal (2005), briefly, saturates are defined as the saturated hydrocarbons ranging from straight-chained paraffins to cycloparaffins (naphthenes) while the aromatic fraction includes those hydrocarbons containing one or more aromatic nuclei which may be substituted with naphthenes or paraffins. Asphaltenes are defined as the solubility class of crude oil that precipitates in the presence of aliphatic solvents while the resin fraction is defined as the fraction soluble in light alkanes, but insoluble in liquid propane. Both are the most aromatic and most polar compounds of petroleum with the greatest amount of sulphur, nitrogen, and oxygen. The method of dividing crude oil into these four fractions is illustrated in Figure 2.1.

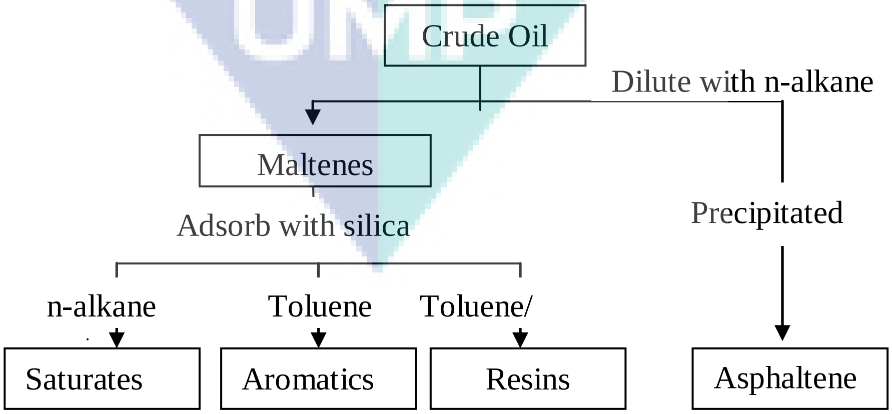


Figure 2.1: Schematic of Saturate, Aromatic, Resin and Asphaltene (SARA) Fractionation of Crude Oils

Source: Auflem (2002)

Crude oils from different regions have different properties. The physical properties that mainly affect the behaviour and persistence of crude oil are specific gravity, viscosity and pour point (Hannisdal, 2005).

2.3 EMULSION

Emulsions are colloidal dispersions in which a liquid is dispersed in a continuous liquid phase of different composition. The dispersed phase is sometimes referred as the internal (disperse) phase and the other one phase as the external phase (Schramm, 2005). Emulsions may contain not just oil, water and emulsifier (usually surfactant), but also solid particles and gas. Emulsions are created throughout the full range of processes in the petroleum producing industry including drilling and completion, fracturing and simulation, reservoir recovery, surface treating and transportation. During heating, as part of an oil recovery process such as hot-water flotation or in situ steam flooding, emulsions having a wide range of viscosities can be formed, particularly if they are water-in-oil (W/O) type.

2.4 EMULSION FORMATION

There are two stage processes formation of emulsions which are formation of new droplets and stabilisation of the droplets (Figure 2.2). For the formation of emulsion, at least two immiscible liquids are required (Ariany, 2004). The first process, formation of new droplets involves disrupting the stable bulk liquid to form dispersed phase by apply mechanical energy. The second process is the tendency of the droplets to coalesce and reform the stable bulk liquid must be overcome (Jennifer, 1999).

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

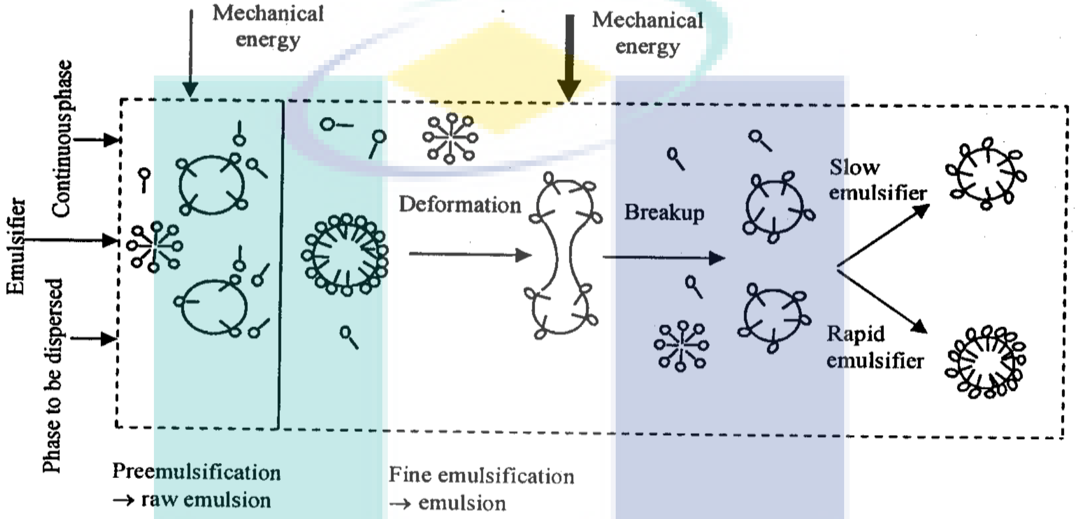


Figure 2.2: Processes of the Crude Oil Emulsion Formation

Source: Ariany (2004)

2.4.1 Physico-chemical Factors Affecting the Formation of Emulsions

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

2.5 TYPES OF EMULSION

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

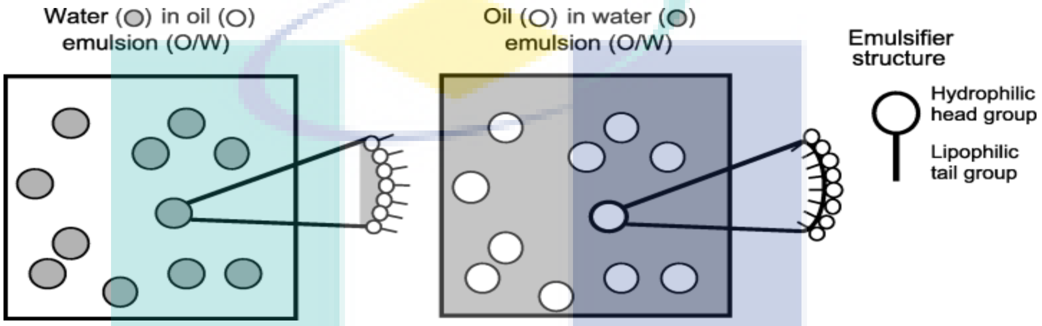


Figure 2.3: The Orientation of Emulsifier on the Surface of the Dispersed Phase.

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

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

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

In general, O/W is presented if the surfactant (emulsifying agents) is more soluble in water than oil. Emulsions are common colloidal systems in many industrial products such as food, cosmetics, and pharmaceutical or agrochemical preparations. O/W emulsion is often used to deliver functional molecules and nutritional benefits, or to create a certain texture to the consumer. Oil-in-water emulsions are made of oil droplets which are dispersed in an aqueous continuous phase and stabilised by surface active molecules.

2.5.3 Differences Between W/O and O/W Emulsions

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

2.6 TESTS FOR EMULSION TYPES

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

2.6.1 Dilution Method

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

2.6.2 Electrical Conductivity

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

2.6.3 Staining the Continuous Phase

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

2.7 EMULSION STABILITY

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

2.7.1 Electrostatic Forces

The approach of emulsion droplets to another one may be resisted by electrostatic forces. Sullivan and Kilpatrick (2002) as saying that electrostatic forces in emulsions arise from a surface charge on the droplet and then electric double layer may form around disperses phase droplet (Figure 2.4). Electrostatic forces do not play a significant role in the stabilization of water-in-oil emulsion because of the low dielectric constant of continuous phase.

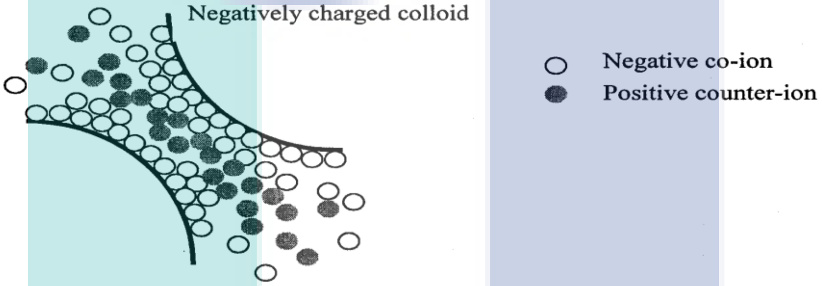


Figure 2.4: Electrostatic Forces

Source: Ariany (2000)

2.7.2 Steric Repulsion

Steric repulsion is one of the mechanisms in emulsion stability. Steric repulsion is the resistance of adsorbed species on droplet interfaces to interactions with adsorbed species on other droplets as shown in Figure 2.5 (Sullivan and Kilpatrick, 2002). This mechanism occurs when it is energetically favourable for the adsorbed material to interact with the solvent in the continuous phase rather than other adsorbed material. Steric repulsion is commonly found in systems stabilized by nonionic where salvation energies can be high as result of hydrogen-bonding interactions.

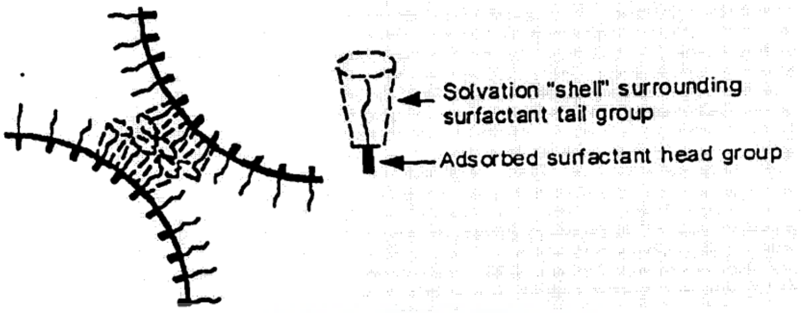


Figure 2.5: Steric Repulsion

Source: Ariany (2004)

2.7.3 Marangoni-Gibbs Effect

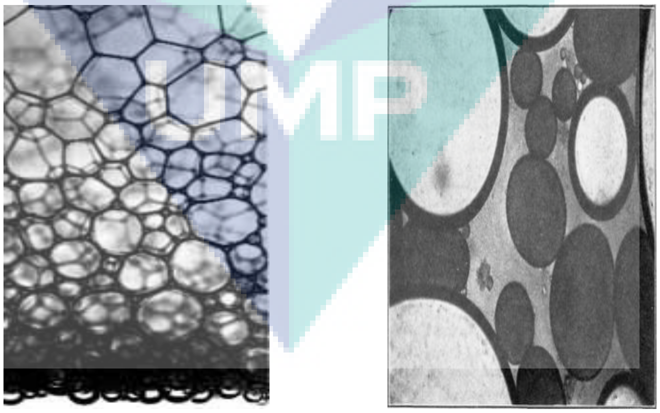
The effect on the surface tension by surfactant adsorption from the bulk solution (Gibbs effect) and by diffusion along the interface (Marangoni effect) is often referred to as combined Marangoni-Gibbs effect. The critical thickness for rupture of a thin film depends on the adsorption kinetics and interfacial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

2.7.4 Thin Film Stabilization

The formation of a mechanically rigid, viscoelastic and stagnant film around the droplets provides a physical barrier for droplet-droplet coalescence. Crude oil varies greatly in appearance depending on its composition. As postulated from Auflem (2002), crude oil, especially heavy crude oils contain large quantities of asphaltenes (high molecular weight polar components) act as natural emulsifier or also called surface active agent. Besides, the other crude oil components such as resins, fatty acids, waxes and napthenic acid also act as surface active agent but cannot action alone in producing stable emulsion (Langevin et al., 2004).

2.8 EMULSION AND FOAM

As mention above, emulsion is colloidal dispersion in which a liquid is dispersed in a continuous liquid phases. Foam is also deal with the colloidal dispersion. However, foam involve with gas is dispersed in a continuous liquid phase. Liquids foams and emulsions in general, unstable thermodynamic (Wilde, 2000). The creation of foams and emulsion essentially requires the formation of fine bubbles and droplets. Foam can be created by liquid which, the surface area of liquid is expand to form a thin film around gas bubbles. The liquid must be able to posse the correct rheological and surface properties to retard thinning of the lamellae which lead to bubble coalescence and also diffuse the trapped gas from small to large bubbles or to the surrounding atmosphere. Figure 2.5 illustrated the general foam and emulsion image. Bubbles in persistent foams are polyhedral and not spherical. In fact foam bubbles usually have diameters greater than 10 µm and may be larger than 1000 µm (Schramm, 2005).



(a) (b)

Figure 2.6: Illustration of a Generalised (a) Foam (b) Emulsion

Source: Schramm (2005)

2.9 EMULSION DESTABILISATION

The break-up of droplets depends strongly on the type and intensity of the flow which is determined by the rotational speed and geometry of the impeller, geometry of the vessel and material properties of the continuous phase such as viscosity and mass density (Hannisdal; 2005). The phenomenon of emulsion separation can be broadly categorized into four mechanisms for demulsification which are sedimentation/ creaming, aggregation coalescence and Ostwald ripening. Sedimentation or creaming occurs when there is density different between dispersed and continuous phase. Aggregation is when two or more droplet species are aggregated and clump together but separated by a thin film of continuous phase. While coalescence occurs when thin film between the droplets break and they fuse together to form single larger unit. From Figure 2.7, at low interfacial coverage of the stabilizing units, collision of the emulsion droplets (a-b) usually terminated their coalescence (b-c). The flocculation or aggregation (d) takes place before proceed with coalescence process.

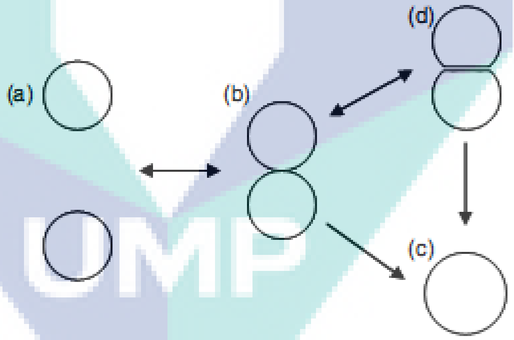


Figure 2.7: Possible Consequence from Collisions between Two Droplets.

Source: Hannisdal (2005)

2.9.1 Sedimentation

This is the phenomenon by which emulsions separate into two emulsions, one richer other is poorer in the dispersed phase. The more concentrated emulsion is commonly referred to as cream. The separation of cream from unhomogenised milk is very common example of cream phenomenon. The mechanism of creaming appears to be due to the slow sedimentation of the emulsified droplets (Paul and Daniel; 1985). The velocity of sedimentation of a drop, v_m of a radius, r and density, ρ_w in a liquid of viscosity, μ_o and density of continuous phase, ρ_o is given by Stoke's equation if oil is continuous phase.

$$V_m = \frac{gD^2(\rho_w - \rho_o)}{18\mu_o} \tag{2.1}$$

Larger dispersed particle radii and difference density, (ρ_w -ρ_o) give the faster sedimentation. This effect may be minimised by gentle mixing (Jennifer; 1999).

2.9.2 Aggregation

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

2.9.3 Coalescence

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

2.9.4 Ostwald Ripening

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

2.10 METHODS OF EMULSION BREAKING

The breaking of emulsion is necessary in emulsion treatment. Methods currently available for demulsification can be classified as chemical, electrical and mechanical (Abdurahman et al., 2007). In generally, methods to induce phase separation for water-in-oil emulsions can be applied using chemical or heating the emulsion. Chemical demulsifiation is common method used and since the 1930s, demulsifier has been used in treating emulsion (Wu et al., 2003). Conventional thermal heating involved the breaking of emulsion due to reduction of viscosity of continuous phase. However, currently microwave has been studied an alternative method to treat the emulsion. The concept of microwave demulsification is first introduced by Klaika (1978) and Wolf (1986).

2.10.1 Application of Chemical

Chemical demulsifier is a conventional method widely used in industry. However, the problems of using this method are environment problematic which involve with waste water stream and the cost of using chemical in large quantities volume could be enormous and may outweigh the benefits realized (Countinho et al., 2008; Rajaković and Skala , 2006; Arnoud, 2004). This method involves the use of chemical additives to accelerate the emulsion breaking process. As studied by Kang et al. (2006), the breaking through this method is based on the rupture of interfacial film and surfactant adsorption mechanisms. The dispersed phase (water droplets) approached each other and flattens to form a thin film of continuous phase between them. Demulsifier molecules and natural surfactants (asphaltenes) then compete each other to adsorb onto voids created because of the difference of interfacial tension inside and outside film (Figure 2.8). The outward drainage flow of the film can create gradients in the interfacial tension which then oppose and slow down to drainage (Djuve et al., 2001). In this way, the adsorption of demulsifier is continuous exponentially until the films become very thin and it ruptures due to close proximity of adjacent dispersed phase surfaces and local absence of surfactant molecules.

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

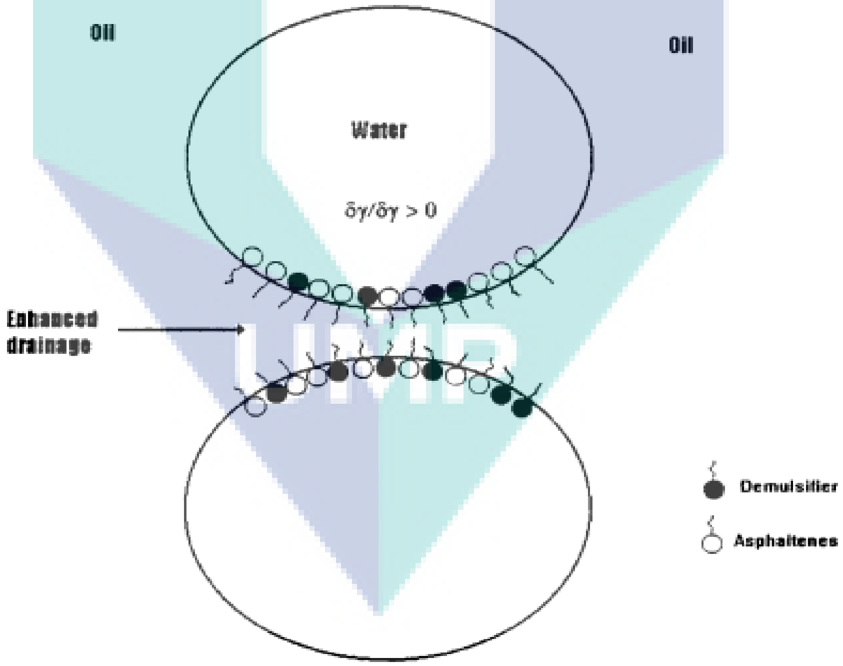


Figure 2.8: Process of Chemical Demulsification

Source: Djuve et al. (2001)

2.10.2 Application of Thermal Heating

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

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

2.10.3 Effects of Electric Current

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

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

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

2.11 SURFACTANTS

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

The adsorption of surfactant from a bulk phase to a surface or interface occurs at any concentration. As studied by Homberg (2001), the surface concentration increased gradually as soluble surfactant in water increased until reaches a maximum level at specific bulk concentration. Beyond this concentration, individual surfactant monomers begin to aggregate with their hydrophilic heads pointing outwards towards the solution and the hydrophobic tails pointing inwards away from the water in order to minimise the free energy of the system. The effects of association between adjacent hydrophobic or hydrophilic section of surfactant molecules are enhanced in aggregate structures such as micelles (Biresaw and Mittal, 2008). Hence, the concentration at this aggregation occurs is called the critical micelle concentration (CMC) as shown in Figure 2.9.

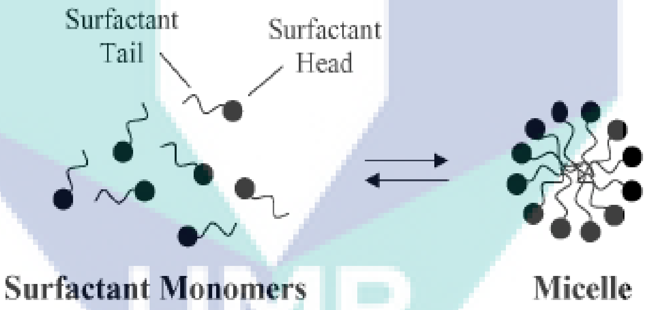


Figure 2.9: Typically Surfactant Structure

Source: Carlota et al. (2005)

By adding surfactant such as surface-active emulsifiers or demulsifiers that affect the molecular confirmation and arrangement at the interface, would alter the interfacial tension and changed the stability of the formed emulsions (Wang et al., 2004). The selection of surfactant in preparation of either W/O or O/W emulsions is often made by hydrophilic-lipophilic balance (HLB). This method was first introduced by Griffin (1954) to scale the relative percentage of hydrophilic to lipophlic (hydrophobic) groups in the surfactant molecules. For an O/W emulsion, droplets the hydrophobic chain exists in the oil phase, while the hydrophilic head resides in aqueous phase and vice versa for W/O emulsion. Table 2.1 provided the range of HLB in selection of surfactants for particular applications:-

Table 2.1: A Summary of Surfactant HLB Ranges and Applications

HLB range	Application
3-6	W/O emulsifier
7-9	Wetting agent
8-18	O/W emulsifier
13-15	Detergent
15-18	Solubiliser

Source: Hait and Moulik (2001)

2.12 SUMMARY

In the petroleum industry, the present of emulsion is undesirable because of problems encountered by forming this emulsion. Essentially breaking of emulsion is to improve the quality of emulsion. However, the stability of emulsion is crucial part to investigate first. This stability of emulsion depends on the properties of crude oil and factors affected on emulsion characteristics such as viscosity, temperature and concentration of dispersed phase.

CHAPTER 3

MECHANISMS OF MICROWAVE THEORY

3.4 INTRODUCTION

It has been known for long time that microwaves can be use for heat materials. In fact, the development of microwave oven for the heating food has been more than a 50-year history (Wu, 2003). Recently, microwave is investigated as an alternative method to break the emulsion. Microwave irradiation is being studied as tool for demulsification. In the electromagnetic spectrum, the microwave radiation is located between infrared radiation and radio waves. Microwaves have wavelengths of 1 mm -1m, corresponding to the frequencies between 0.3 and 300 GHz (Lidstrőm et al., 2001). From Lidstrőm et al. (2001), in general in order to avoid interference, the frequency at which industrial and domestic corresponding to 2.45 GHz, but other frequency allocations do exists (Figure 3.1). The heating of liquids using microwaves can be explained by the interaction of matter with the electric field of the incident radiation, causing the movement of ions as well as that of induced or permanent molecule dipoles. The movement of such species can cause heat generation.

3.5 MICROWAVE ENERGY AND MATERIALS INTERACTION

Microwave is very short waves of electromagnetic by penetrate the electromagnetic energy through materials. Since microwave energy transfer involve electric and magnetic field, the interaction materials is selected based on electric and magnetic component.

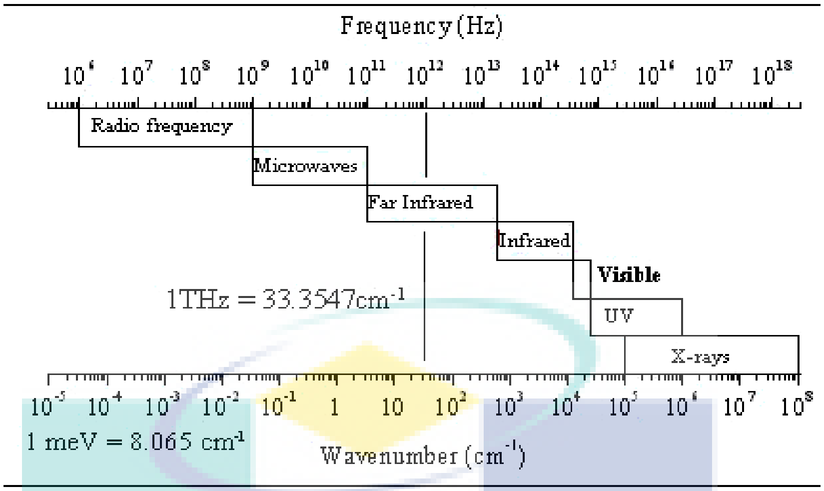


Figure 3.1: Frequency Ranges of Microwaves used in Microwave Oven

Source: Modified from National Materials Advisory Board (1994)

A propagating electromagnetic wave has two components which are an electric field, E (unit V/m) and magnetic field, H (unit A/m). There are vectors and always perpendicular with each other as illustrated in Figure 3.2. In free space the propagating wave has a velocity (c_o) of about 3.0 x 10^8 m/s and this is the maximum speed for energy to travel. Frequency (f) and wavelength (λ) are linked as in Equation 3.1;

$$c = \lambda f \tag{3.1}$$

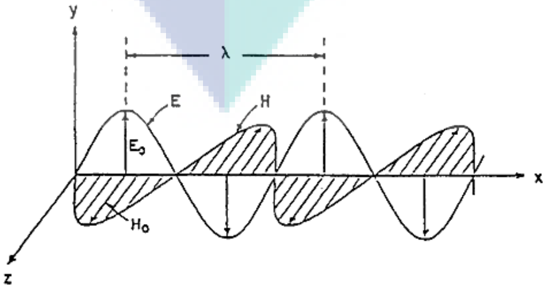
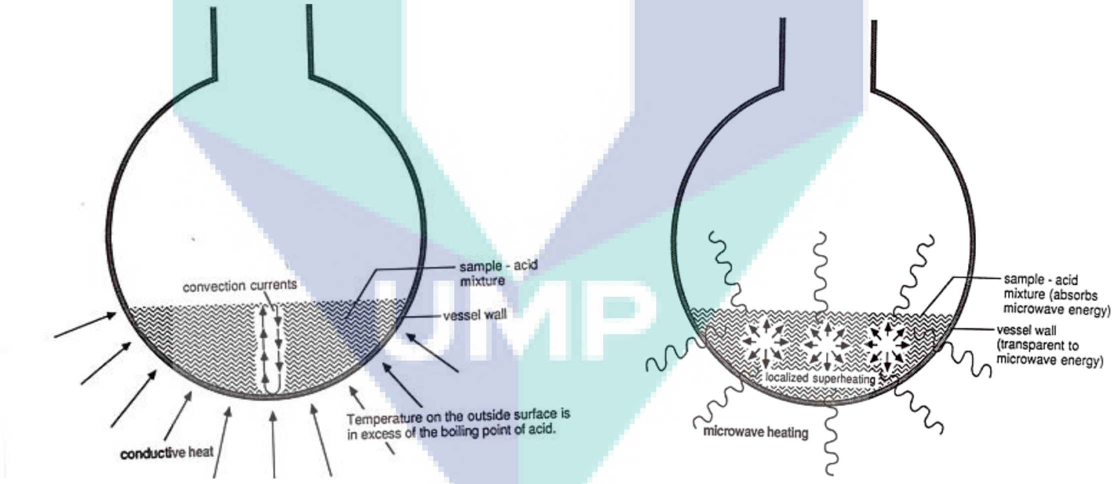


Figure 3.2: A Propagating Electromagnetic Wave

Source: Ryynänen (2002)

The most important thing in microwave heating is volumetric heating, which in a manner different with conventional heating. Volumetric heating means that materials can absorb microwave energy directly and convert into heat. This lead the advantages of microwave like rapid, selectively, control and uniform heating. While in conventional heating, heat must diffuse from the surface to material. As reported by Nadkarni (1984), for conventional thermal heating, typical time required to complete heat wet absorption by conductive heating is about 1-2 hours. While for microwave heating in open-vessel, the time required is less about 96% which 5-15 min. In conventional thermal heating, vessel used usually poor conductors of heat, thus it takes time to heat vessel and transfer it into the solution. Because vaporisation occurs at the surface of liquid, a thermal gradient is established by convection currents and only a small portion of solution is at the temperature of the heat applied. Therefore, when conductively heating occurs, only a small portion of the solution is above the boiling point temperature of the solution (Figure 3.3).



(a) (b)

Figure 3.3: Sample Heating by (a) Conventional Thermal Heating (b) Microwave Heating

Source: Kingston (1988)

3.3 MICROWAVE PROPERTIES

The main application of microwave processing of materials is heating. As studied by Lidstrőm et al. (2001), if two samples containing water and oil respectively are heated under microwave irradiation, the final temperature is higher in the water sample. In order to understand why this phenomenon occurs, it is necessary to understand the mechanisms of microwave dielectric heating. As with all electromagnetic radiation, microwave radiation can be divided into an electric field and magnetic field component. The former component is responsible to the dielectric heating is affected via two mechanisms which are dipole rotation and ionic conduction as illustrated in Figure 3.4 and 3.5 (Coutinho et al., 2008). Gas cannot be heated under microwave irradiation since the distance between two rotating molecules is long enough for molecules to be able to follow the electric field therefore, there are no phases different will be generated.

3.3.1 Dipole Rotation Mechanism

Electric dipoles are formed by the interaction of electric charge with the matrix. A dipole is sensitive to the external electric fields and will attempt to align itself with the electric field by rotation itself (Lidstrőm et al., 2001). Water molecule is an example of a posse dipole molecule.

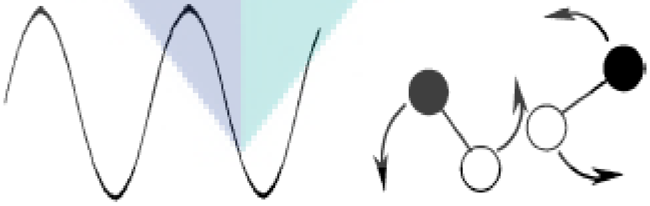


Figure 3.4: Alignment of Dipolar Molecules with an Oscillating Electric Field

Source: Lidstrőm et al. (2001)

Based on Coutinho et al. (2008), in liquids state, the electric dipoles cannot rotate instantaneously and the ability of molecules to align under influence of electric field will vary with different frequencies and viscosities of liquid. For low radiation frequencies, the time where the electric field changes direction is higher than the dipole response time. Molecules gain some energies but overall heating effect with full alignment is small. However, at very high frequency electric field, dipoles do not have sufficient time to follow the oscillating field and molecules do not rotate and move. When there is no motion, so there is no energy takes place and there also no heating occurs.

3.3.2 Ionic Conduction

A solution containing ions migrate through the solution under the influence of an electric field, resulting in expenditure of energy due to an increased collision rate, therefore converting the kinetic energy to heat (Lidstrőm et al., 2001). The resulting electrical currents heat the sample as a consequence of the electrical resistance

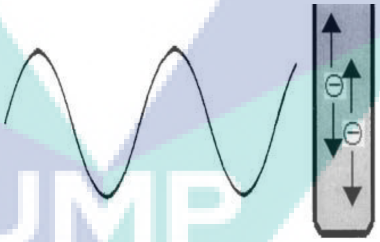


Figure 3.5: Charge Particles in the Solution Follow the Applied Electric Field

Source: Lidstrőm et al. (2001)

This ion migration is a flow of current that results in I^2R migration depend on size, charge and conductivity of the dissolved ions and are subject to the effects of ion interaction with the solvent molecules. The parameters affecting ionic conduction are ion concentration, ion mobility and temperature of solution.

3.3.3 Dielectric Properties

From the mechanisms above, polar solvents and/or ions are needed for the microwave heating. Dielectric response for various materials plays important role to carry out efficient material processing and a significant amount of earlier research was devoted to understand the physics on microwave assisted transport and heating characteristics (Lidstrőm et al., 2001; Basak and Meenakshi, 2006). The dielectric polarization depends on the ability of the dipoles reorientation in an applied electric field. In order to compare the abilities of different solvents to generate heat from microwave irradiation, their capabilities to absorb microwave energy and to convert the absorbed energy into heat must be accounted (Lidstrőm et al., 2001). These factors may be considered using the loss angle, δ which is usually expressed in the form of its tangent

$$\tan\delta = \frac{\varepsilon^{''}}{\varepsilon} \qquad (3.2)$$

The real permittivity or dielectric constant,ε' is characterising the penetration of microwaves into material and loss factor, ε'' indicating the material ability to store energy. The complex permittivity,ε* is a measure the ability of a dielectric to adsorb and store electrical potential energy with real permittivity,ε' and loss factor, ε''.

$$\varepsilon^{*} = \varepsilon' - i * \varepsilon'' \qquad (3.3)$$

The re-orientation of dipoles and displacement of charge are equivalent to an electric current as mention in Maxwell's displacement current. As postulated by Indra, (2007), the displacement current will be 90° out of phase with the electric field when a dielectric precisely follows the electric field whereas the flow of current is perpendicular to the electric field. A dielectric that does not follow the oscillating electric field will have a phase difference between the orientation and electric field. Hence, this will produces a component, *I sin* δ which cause energy is absorbed from the electric field and converted into heat; called as dielectric loss.

3.3.4 Energy Conversion

In microwaves, energy is converted into heat which, a process that involves interaction between microwave fields and the conductivity or dielectric properties of the material. As claimed by National Materials Advisory Board (1994), there are three processes interaction between microwave and materials; i) space charges due to electronic conduction ii) ionic polarization associated with far-infrared vibrations and iii) rotation of dielectric dipoles.

The dielectric properties of material in combination with the applied of electromagnetic field result in the conversion of the electromagnetic energy into heat. Power that transmitted through the material can be determined by Poynting's Vector (Equation 3.4) which is derived from Maxwell equation (Leszek, 2003). The flow of energy through the surface, S enclosing the volume, V to the cross product of the electric-field, E and magnetic field, H strength which can be explained by the flux of a vector:-

$$S = E \times H \tag{3.4}$$

Using the divergence theorem, the Maxwell equation by assuming material properties of the volume, the following equation can be acquired for the real portion of the Poynting Power Theorem:-

$$\int_S (E \times H)_n dS = -\int_V E.JdV - \frac{\partial}{\partial t}\int_V \left(\frac{1}{2} \in E^2 + \frac{1}{2}\mu H^2\right) dV \tag{3.5}$$

The rate loss of energy stored in electric and magnetic field within a region of space is state in left side. The right side represent the work done per second by the impressed forces, $E.JdV$, the sum of the rate of dissipation of electrical energy, $\frac{1}{2} \in E^2$ as heat and the rate of flow of electromagnetic energy outward, $\frac{1}{2}\mu H^2$ through the surface of region.

3.4 WORKING EQUATIONS FOR MICROWAVE DEMULSIFICATION STUDY

Microwave heating is an alternative method to demulsified the emulsion due to the fact that microwave offers a clean, cheap and convenient heating process that in most of the times results into better yield and shorter times. Since microwave heats material volumetrically, the volume rate of microwave heat generation from energy balance equation can be determined as:-

$$Q_{mw} = \frac{hA}{V}(T_m - T_a) + \frac{\varepsilon A\sigma}{V}\left[(T_m + 273.15)^4 - (T_a + 273.15)^4\right] + \rho C_p\left(\frac{dT}{dt}\right) \tag{3.6}$$

The right side comprises three terms, convection, conduction and radiation heat transfer through the sample. From Equation 3.7, the rate of heat transfer for conduction and convection are assume zero due to the rate of heat transfer from emulsified water droplets to continuous phase is very rapid; therefore, in practically temperature of water and oil almost same. Therefore, the heat generation of emulsion can be expressed as follows:-

$$Q_{mw} = \rho C_P\left(\frac{dT}{dt}\right) \tag{3.7}$$

where Q_{mw} (cal/s.cm^3) is the total dissipated microwave power in the material, heating rate, dT/dt (^{o}C/sec), density, ρ (g/cm^3) and heat capacity, C_p (cal/g. ^{o}C) respectively. Density and heat capacity of emulsion calculated from mixing rules as:

$$\rho_m = \rho_w\phi + \rho_o(1-\phi) \tag{3.8}$$

$$C_{pm} = C_{p,w}\phi + C_{p,o(}(1-\phi) \tag{3.9}$$

The rate of heat generation is depends on dielectric properties of the emulsion. For water, dielectric constant and loss are two important parameters. These parameters are represented by the following equations (Di et al., 2000):

$$\varepsilon'_w = 85.2 - 0.3358T \tag{3.10}$$

$$\varepsilon''_w = 320.66T^{-1.03} \tag{3.11}$$

However, as proposed by Von Hippel (1954) dielectric properties of various petroleum oils, in this regard dielectric constant and loss tangent of crude oil for this study calculated from the equation below:-

$$\varepsilon'_{oil} = 2.24 - 0.000727T \tag{3.12}$$

$$\tan\delta_o = 0.527T + 4.28x10^{-4} \tag{3.13}$$

From Lidstrőm et al. (2001), the dielectric constant can only change with temperature since the frequency for most types of microwave apparatus is set at 2.45 GHz, the wavelength, λ_m and penetration depth, D_p within a sample for a radiation is related to dielectric constant and dielectric loss as follows:

$$\lambda_m = \frac{c}{f}\left[\frac{\varepsilon_r'\left(\sqrt{1+\left(\frac{\varepsilon_r''}{\varepsilon_r'}\right)^2}+1\right)}{2}\right]^{-1/2} \tag{3.14}$$

Penetration depth has been generally related to temperature distribution in microwave heating. Penetration depth measures the distance from the surface of a dielectric material and given approximately by:-

$$D_p = \frac{c}{2\Pi f}\left[\frac{\varepsilon_r'\left(\sqrt{1+\left(\frac{\varepsilon_r''}{\varepsilon_r'}\right)^2}-1\right)}{2}\right]^{-1/2} \tag{3.15}$$

3.5 SUMMARY

The penetration of electromagnetic into materials was depends on the ability of materials to absorb the electromagnetic and convert it into heat. The ability of materials to absorb the electromagnetic was interpreted into dielectric properties equation of emulsion whereas using mixing rule for water and crude oil. The effectiveness of microwave radiation at different microwave power and ratio of water-crude oil was investigated through penetration depth and wavelength as discussed in equation above.

CHAPTER 4

MATERIALS AND METHODS

4.1 INTRODUCTION

This chapter describes the materials, equipment and methods followed to solve the problem of this study. To accomplish the objectives of scopes of this research, the study was carried out in three stages namely, emulsion stabilisation, microwave batch process and optimisation.

The first and second stages are experimental while third stage is optimisation. Experimental methods involve the procedure for emulsion sample preparations, experimental set-up for microwave equipment, sample characterisation using microwave processes (sample analysis, identification of emulsion type, measurement of emulsion stability, density, viscosity and dielectric properties of emulsions. Details of the experimental are discussed below.

4.2 FLOW OF STUDY

The study has been conducted by using three types of crude oil from lighter to heavier crude oil. The flow of study shows in Figure 4.1. Basically this study was summarised by six parts. Firstly each crude oil was characterised in term of physical and chemical properties. The emulsion would be prepared depend on the requirement of volume fraction and each prepared emulsion was checking either W/O or O/W emulsion by using dilution and conventional drop tests. Only W/O emulsion has been used in the emulsion stability part. The most stable emulsion was selected in this screening part before demulsified in demulsification part by comparing conventional and microwave irradiation. The most effective methods determined by observing the percentage of water separated. For the optimisation part, the process parameters in demulsification would be optimised using response surface methodology.

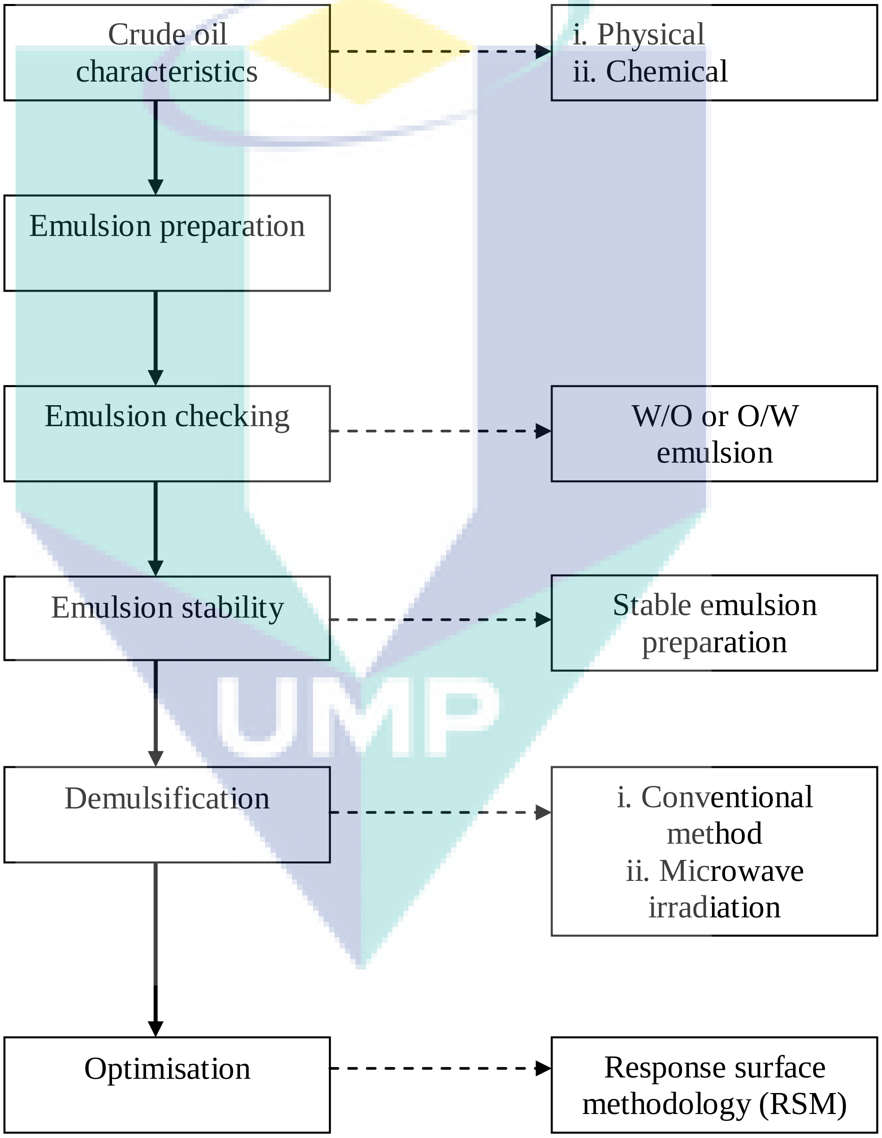


Figure 4.1: Flow of Study

4.3 MATERIAL SELECTION

Basically in this study, there were three types of crude oils were donated from Petronas Refinery at Melaka were used. The samples were denoted as crude oil A (Saudi), crude oil B (Kuwait) and C (United Arab Emirates). The samples were selected because of the types which were consisting heavy and light crude oil.

Several chemicals are selected while characterise and investigated the emulsion stability. In the preliminary study, four emulsifiers such as sodium dedocyl sulfate (SDDS) 10% in water from Merck, polysorbate 80 (Tween 80) from R&M chemicals, Triton X-100 (98-100% from Merck) and sorbitan sesquiolate (Span 83) from Sigma were selected to form the most stable emulsions depend on the type of crude oils. The emulsifiers contain of non-ionic and ionic groups to compare the most stable emulsion performed by emulsifiers. The reagent grade n-pentane (>99.0% from R&M Chemicals), n-hexane (99% from Merck) to decolourise crude oil, toluene (>99.5% from Systerm), methanol (≥99.9% from Merck), dichloromethane (≥99.6% from Merck) were used in separation of fraction components in crude oil. 99% hexylamine from Sigma-Aldrich, octylamine (≥98% from Merck) and pentylamine (98% from Merck) act as demulsifier.

4.3.1 Sample Preparation

Basically emulsion is prepared by added water to crude oil in prescribed ratio. About 50 mL of emulsion sample was prepared in this study. Figure 4.2 illustrates the schematic diagram in preparing the emulsion. Firstly, 0.1% emulsifier of crude oil added to crude oil (mixing solution) and it stirred using three blades propeller for 1 minute with ±500 rpm. Water is added gradually to the mixing solution and was agitated vigorously using a standard three blade propeller at speed 500 to 1500 rpm and temperature 28-30^{o}C for 5 minutes. Then, the type of emulsion (W/O or O/W) was inferred by a conventional drop test (Evdokimov et al., 2008). The concentrations of water (internal phase) in the samples were varied by volume. Emulsions were observed over a period of time to provide a qualitative measure of the stability. Details of these studies were reported in next chapter (results and discussion).

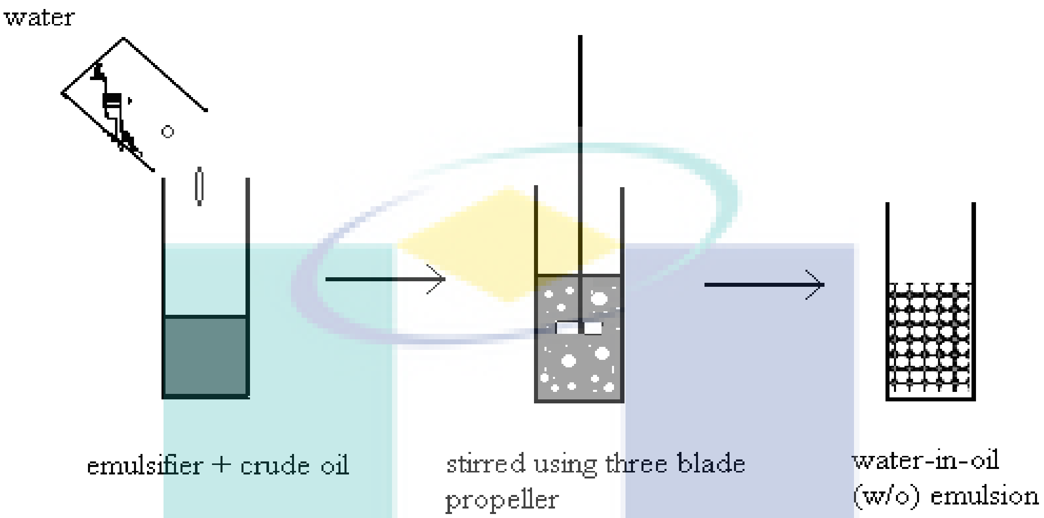


Figure 4.2: Schematic Diagram for Preparing W/O Emulsion System

4.4 ANALYTICAL PROCEDURE

4.4.1 Physical Characteristics

Density of Crude Oil

The density of crude oil is measured using pycnometer 20 mL (ASTM D70, NFT 66007). Pycnometer is a glass flask with a close fitting ground glass stopper with a capillary hole through it. This fine hole releases a spare liquid. The samples is introduced to equilibrate to room temperature (27 ^{o}C ± 0.2 ^{o}C) in pycnometer and weighted. The pycnometer also filled with distillate water and weighted at same temperature. While for ^{o}API density, both density of crude oil and water are measured at 15.6 ^{o}C as shown in Equation. 4.1. The petroleum gravity (^{o}API) is measured using the following equation:-

$$^{o}APIdensity = \frac{141.5}{d(at15.6^{o}C)} - 131.5 \tag{4.1}$$

$$d(at15.6^{o}C) = \frac{\rho_{sample}}{\rho_{water}} \tag{4.2}$$

Pour Point

Pour point bath model K46100 from Koehler Instrument Company which conforms to ASTM D9 used to measure pour point for each crude oil. Pour point bath required a pressure vessel and a water bath in addition. The pour point bath consisted of 4 litres water cooling bath with cover, which is equipped with an opening for one air jacket, a stopper and a borehole for thermometer. Crude oil was cooled at specified rate and examined the flow characteristics. The lowest temperature at which crude oil will flow is observed and stated as pour point.

Viscosity, Shear Rate and Shear Stress

Viscosity, shear rate, and shear stress of the water-in-crude oil emulsions in this study were determined by Brookfield Rotational Digital Viscometer Model LV/DV-III with UL adaptor. The Brookfield Viscometer apparatus was equipped with a water bath thermostat, a spindle set, and software of Brookfield Rheocalc Version 1.2. A smaller diameter spindle (type’s spindle 31) was used to measure the emulsions’ viscosities with a cell containing approximately 10 mL of sample. This type of measurement is usually referred as Couette method, and it measures the fluid parameters of shear stress and viscosity at given shear rates. The principle of operation of this unit is to drive a spindle which is immersed in the sample. The measuring range is determined by the rotational speed of the spindle, the container the spindle is rotating in and the full scale torque of the spring. The rheometer was thoroughly cleaned between measurements of different emulsion samples.

Water Content

The crude oil was injected using syringe 10mL in Karl Fisher Analyzer model 787 KF Titrano brand Metrohm to analyse water content in crude oil. Karl Fisher is calibrated to achieve standard drift value is below 20 or once condition of light remains on without blinking, the 787 KF Titrano was ready for sample injected. The syringe with sample was tare to zero and sample was injected through septum. The result of water content was measured in unit of percent (%).

Interfacial Tension and Surface Tension

Surface and interfacial tension measurement standard test method (ASTM) is used and the equipment is Surface Tension Analyzer model DST 60 A. This measurement was equipped with ring and glass sample. Crude oil was inserted into the glass sample and the ring was adjusted and the analyzer was calibrated at the surface of crude oil. Water was inserted into the crude oil and the reading of interfacial tension perform was recorded. The ring used in this method must kept under perfectly clean and dust free conditions. It was cleaned by 70% ethanol and burnt with a blue flame from a Bunsen burner after every application.

Droplet Size

The droplet size distribution of emulsion was observed and determined using Carl Zeiss research microscope equipped with the digital camera and AxioVission AC image analysis software. The measurement of emulsion was performed without further dilution of emulsion. Approximately 3 images were randomly taken for each distribution and 100-400 droplets were counted to obtain droplets size distribution.

Wax Appearance Temperature (WAT)

The wax appearance temperature of crude oil was performed using Differential Scanning Calorimetry (DSC) apparatus. Before experiment, all the crude oils are thermally pre-treated; namely, the samples were heated to 80^{o}C for 2 hours in water bath with closed containers and shaken thoroughly to ensure complete dissolution of wax. Then the closed containers are left to cool to room temperature. A 4-8 mg thermally pre-treated crude oil specimen was then transferred into an aluminium crucible, which was then sealed and weighed. The apparatus was continuously flushed with nitrogen at 20 mL/min, and an empty crucible was held in the reference cell (Díaz-Ponce et al., 2010). Experiments were carried out by heating the crucible to 80^{o}C and keeping temperature for 1 minute then cooled at a cooling rate of 5^{o}C/min from 80 to -30^{o}C.

4.4.2 Chemical Characteristics

Crude Oil Separation

The procedures in separating asphaltenes and resins were modified from Ariany(2004) and followed procedure from ASTM D2007-80. Crude oil was weighted about 100 g and hexane slowly added into the crude oil with ratio 1:10. The solution was stirred using magnetic stirrer and left in 6 hours to sediment precipitated. Two layers were observed. The solution was filtered using membrane filter paper (0.22 µm) at funnel filter. The precipitated was dried and evaporated at fumed hood. The precipitate contained asphaltenes and solid, was filtered and dried at room temperature. In order to separate asphaltene from solid, the dried precipitate was dissolved into toluene and centrifuged for 30 minutes at 3000 rpm. After supernatant liquid was separated from precipitate, the precipitated solids were rewashed with toluene until clear rewashed toluene flow. The asphaltene was acquired by evaporated the toluene of supernatant.

The supernatant liquid was poured onto the silica gel. The mixture was shaken using mechanical shaker for 15 minutes at room temperature to ensure resins (absorbed fraction) absorbed well onto the silica gel. The mixture was allowed stand for 30 minutes for sedimentation and followed by filtration process to separate oil and silica gel with absorbed fraction. After that, the mixture was dried by evaporating the solvent then the mixture dissolved with 7% methanol in dichloromethane to desorbed resins from silica. Lastly, the resins and clean silica was obtained after filtration and solvent evaporation.

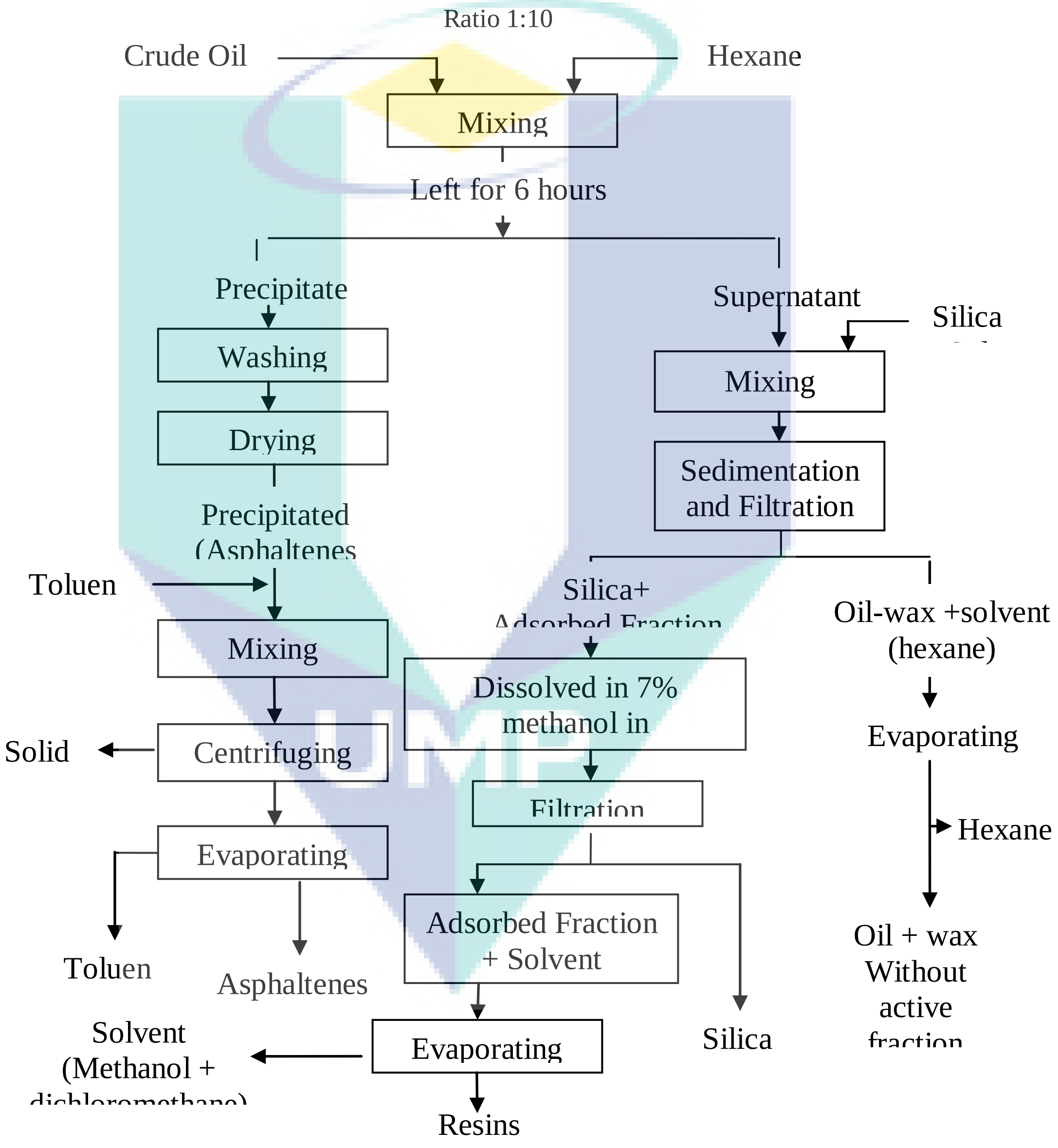


Figure 4.3: Procedures for Recovering Asphaltenes and Resins

Source: Ariany (2004)

Separation of Oil and Wax Precipitated

From sedimentation and filtration steps in supernatant liquid, the balance of sedimentation was oil, wax and hexane. Meanwhile after filtration, the filtrate was silica with absorbed fraction as shown in Figure 4.4 (Nemirosvkaya et al., 2005). Hexane was evaporated in room temperature to ensure only oil and wax was left in further steps. The oil-wax sample was weighted and petroleum ether was added as ratio 1:7. The mixing process was done using glass rod to dissolve the sample. A 110mL of acetone was inserted into the dissolved sample and stirred using magnetic stirrer in 5 minutes to execute the homogenous sample. The samples were cooled in 2 hours at -20^{o}C in the freezer. The next process was filtration which the samples were filtrated (using Whatman no.1 filter paper) through a Buchner funnel (d=15 cm). The precipitated sample was wax crystal and supernatant liquid consisted of crude oil with solvent (acetone and petroleum ether). The precipitated was washed with wash solvent until clean solvent flowed and dried in room temperature was about 24 hours. The precipitated wax crystal was weighted each hour after 24 hours sample was dried to ensure the solvent was evaporated with ±0.001g from previous weighted crystal wax. Meanwhile for pure oil, the supernatant liquid was evaporated to obtain pure oil.

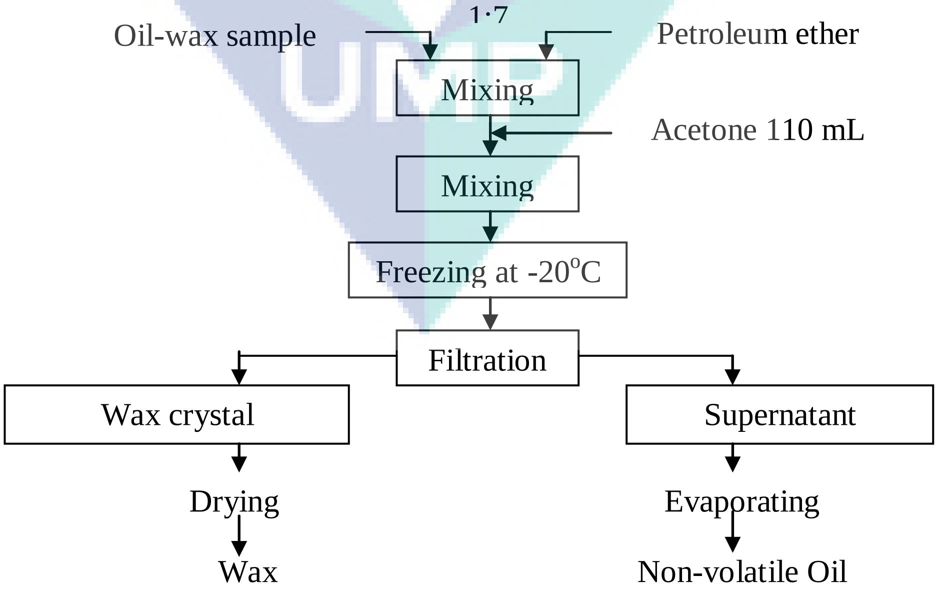


Figure 4.4: Separation Wax Crystal from Crude Oil

Functional Group Analysis

Fourier Transfer Infrared Spectrometer (FTIR) model Thermo Nicolet was used to analyse the content of various functional groups in main natural surfactant of crude oil which are asphaltenes and resins based on vibration of molecules. The sample was prepared and inserted into pellet beside KBr powder. This KBr powder was utilised as die set before recorded into FTIR spectrophotometer. The pellet was cleaned with acetone for each sample analysis. In infrared spectroscopy, IR was passed through the asphaltenes and resins. Infrared spectroscopy detects the vibration characteristics of chemical functional groups in a sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wavenumber (cm^{-1}) range regardless of the structure of the rest of the molecule. Table 4.1 listed the assignment of absorption bands in the 1800-1550 and 1100-950 cm^{-1} region of IR-spectra of the crude oil fractions.

Table 4.1: Assignment of Absorption Bands of IR-Spectra of the Crude Oil Fractions

Functional group	**Absorption band (cm^{-1})**
Ester	1750-1710
Ketone	1730-1700
Aldehyde	1730-1690
Amide	1670-1620
Aromatic	1600
Nitro	1600-1480
Ether	1150-1050
Sulfoxide	1060-1020

Source: Midttun and Kvalheim (2001)

Table 4.2 listed the types of hydrogen bonding presence in asphalatenes within 3170-3500 cm^{-1} region of FTIR spectra.

Table 4.2: Assignment for Hydrogen Bonding in Asphaltenes

Types of hydrogen bonding	Wavenumber (cm^{-1})
OH-π	3500
Self-associated OH	3370
OH-ether O	3300
Cyclic OH	3240
OH-N	3170

Source: Chen et al. (1998)

4.5 DEMULSIFICATION PROCEDURES

The stable emulsion would be treated in demulsification part. The demulsification experiments were performed using both methods; conventional heating and microwave irradiation at 2450 MHz. using batch process. For conventional heating, chemical and hotplate were selected as method in comparing with microwave radiation method. The demulsification efficiency was evaluated by measuring the percentage of water separated from the emulsion as a function of time. The amount of separated water is the most appropriate measure of the emulsion stability of water-in crude oil (W/O) emulsions (Jiang et al., 2007).

4.5.1 Microwave Oven

Elba domestic microwave oven model: EMO 808 SS was used in heating crude oil emulsion samples (for batch heating process). The details of the Elba domestic microwave oven was: its power consumption is 230 V~50Hz, 1400 Watts (microwave), 230 V at 1000 Watts (Heater) and its rated power outlet is 900 Watts at operation frequency of 2450 MHz. The oven cavity dimensions are: 215 mm (H)*350 mm (W)* 330 mm (D), and oven capacity 23 Litres.

For the batch microwave heating process, the top and bottom of the sample container was covered with aluminium foil and was placed in the centre of the microwave. Three thermocouples were inserted in the emulsion samples at different locations; top, middle, and bottom, as shown in Figure 4.5 respectively. The emulsion samples were heated with microwave radiation at 2450 MHz for a different microwave exposure time. Temperature profiles of emulsions inside the cylindrical container during the batch microwave heating were recorded by Pico-TC-08 data logger. In the conventional heating, a hotplate was used for samples heating.

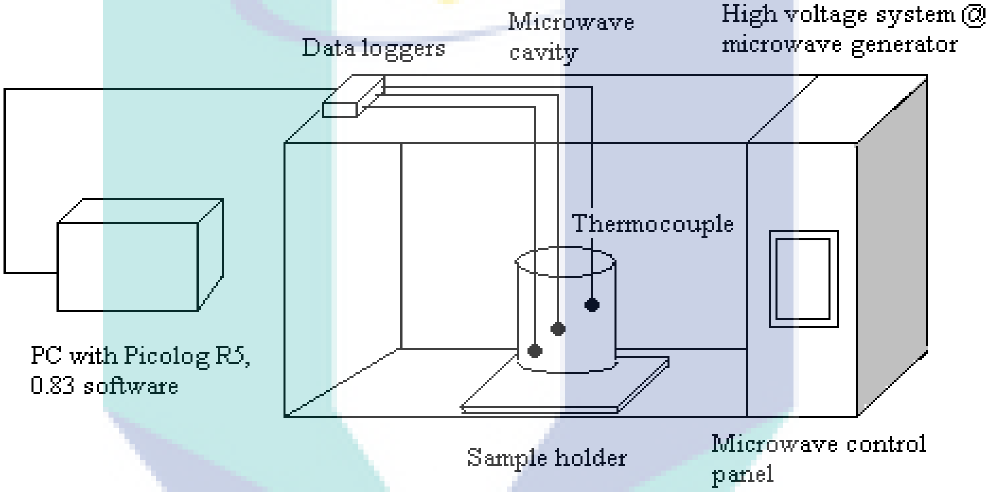


Figure 4.5: Schematic Diagram for Elba Microwave Model: EMO 808 SS

4.5.2 Conventional Methods

Emulsion was prepared by compared two ratios; 20-80 % W/O and 50-50 % W/O emulsion. The chemical demulsifier was added into the emulsion at 1500 rpm in 30 seconds to perform homogenous solution. The effectiveness of demulsifier was evaluated by observing the percentage of water separation from gravity settling. The most effective demulsifier in screening part was then compared with others demulsification methods. In conventional heating method, the prepared emulsion was heated using hotplate in prescribed condition to compare with microwave heating method. Temperatures at surface and bottom beaker were measured using thermometer. While for gravity settling, emulsion was prepared and separated by sedimentation.

4.6 DATA ANALYSIS

The experiment was analysed by observation free water forms at the bottom of measuring cylinder and calculated as percentage water separation as shown in Equation 4.3. This is the best indicator in measuring stability of emulsion and used from previous researcher (Jiang et al., 2007). The amount of water separated or response of yield (%) was calculated as equation below:-

$$\text{Water separated (\%)} = \frac{\text{volume of water (V), mL}}{\text{Original volume of water }(V_o)\text{, mL}} \times 100 \qquad (4.3)$$

Each data collection would be performed in MATLAB (matrix laboratory) in plotting functions of data collection.

4.7 OPTIMISATION

The results from the demulsification of microwave irradiation were used as the variable in optimising the formulation in order to produce the best results in breaking the prepared emulsion by using experimental design. An experimental design determined the effect of the independent variables on the dependent variable (response) which then the relation between them illustrated through a regression model. In this section, the software Design Expert (Trial Version 6.0.8, Stat-Ease Inc., Minneapolis, MN) was employed for experimental design, data analysis and modelling of experiment. The central composite design (CCD) of response surface methodology was used to obtain data that fits a full second order polynomial in five replicates at the centre of the design to allow for estimation the pure of sum squares (Wang et al., 2008).

4.7.1 The Method of Factorial Experiment

There are many types of factorial experiment, but only 2 levels, i.e. the 2^k factorial experiments used in this study. As denoted 2^k, 2 refer to level and k is for variable investigated in the study. The method of factorial experiments has been design to allow the effects of a number of experimental variables on the yield to be investigated simultaneously. It gives the 'main effects' and 'interaction effects' of the changing its value from lower to higher level. The main effect of an experimental variable is defined as average of the effects of changing its value from the lower level to upper level among all the experiments. It is derived by assuming that the experimental variable is an independent variable and all the variations in its effect due to experimental errors only. The interactive effects between two or more experimental variables are calculated on the assumption that the experimental variables are not independent but in fact interacting between them. In this study two levels of factorial design were selected which 2^2 and 2^3 designs. These factorial design were selected depend on the sample used after screening processes.

The 2^2 Design

For this type, emulsion prepared in crude oil B was used which two variables involved between microwave power and time processing. The levels of each variable may be arbitrarily called as 'low' and 'high' (Montgomery, 2001). The treatment combinations can be displayed graphically as in Figure 4.6. The level of experiment variables in 2^2 factorial design is shown in Table 4.3 which x_1 donates microwave power and x_2 is time processing of microwave, respectively.

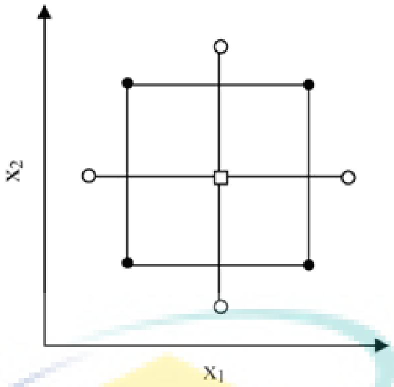


Figure 4.6: Central Composite Designs for Optimisation of 2^2 Factorial Design (●) Points of Factorial Design, (o) Axial Points and (□) Central Point

Source: Bezerra et al. (2008)

In the experimental design, all variables were coded. Once the desired range of values for the variables are defined, they were coded to lie at ±1 for the factorial points, 0 for the center points and $\pm \alpha_c$ for the axial points.

Table 4.3: Levels of the Experimental Variables in 2^2 Factorial Design

Experiment variables	**Level of Experiment Variables**			
	α= -1	**α= 0**	**α= +1**	**units**
Power (x_1)	540	720	900	Watt
Time (x_2)	2	2.5	3	min

The 2^3 Design

Supposing there were three variables for both screening emulsions (crude oil A and C) that are microwave power (x_1), time processing (x_2) and concentration of demulsifier (X_3). This design is known as 2^3 factorial design due to the number of variables involved (Montgomery, 2001). The treatment combinations can be displayed graphically as in Figure 4.7. The level of experiment variables in 2^3 factorial design is shown in Table 4.4.

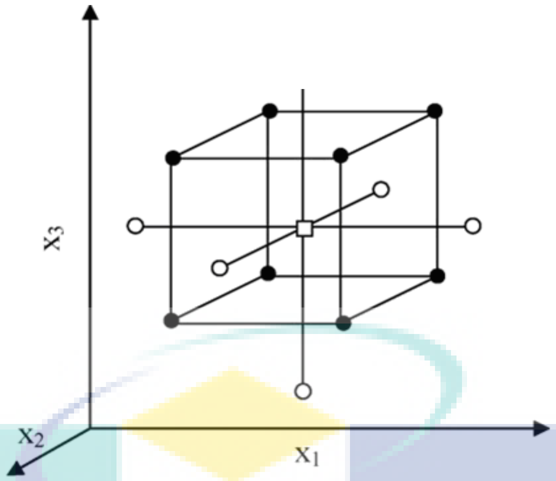


Figure 4.7: Central Composite Designs for the Optimisation of 2^3 Factorial Design (•) Points of Factorial Design, (o) Axial Points and (□) Central Point

Source: Bezerra et al. (2008)

Table 4.4: Levels of the Experimental Variables in 2^3 Factorial Design

Experiment variables	**Level of Experiment Variables**			
	α= -1	**α= 0**	**α= +1**	**units**
power	540	720	900	Watt
time	2	2.5	3	min
concentration	0.05	0.1	0.15	wt %

4.7.2 Optimisation Using Response Surface Methodology (RSM)

Respond surface methodology is a group of statistical techniques for empirical model building (Lenth, 2009). Usually the response surface model can be classified in first-order or second-order polynomial. The first-order function will be used if the response is well modelled by a linear function of the independent variables.

$$y = \beta_o + \beta_1 x_1 + \beta_2 x_2 + ... + \beta_k x_k + \varepsilon \tag{4.4}$$

If the model is curvature in the system, then equation below must be used for second and higher order level approximated:-

$$y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^{\ 2} + \sum_{i} \sum_{\substack{j \\ i<j}} \beta_{ij} x_i x_j + \varepsilon \qquad (4.5)$$

y represents the measured response and x_i, the value of variables. $\beta_{o,}$ $\beta_{i,}$ and β_{ij} are the constants representing the intercept, coefficients of the first-order term and coefficients of second-order interaction terms and ε is the residual associated to the experiments, respectively.

4.7.3 Evaluating the Model

The mathematical model found after fitting the function to the data sometimes not satisfactorily described the experimental domain studied. Thus, the model fitted was evaluated using the Analysis of Variance (ANOVA) obtained from Design of Expert (DOE). The analysis based on variance ratios to determine whether significant or not significant different exist among the means of observed parameters.

The analysis has begun with the estimation the effect of each experimental variable and their two variables interaction by estimation the regression and standard error for each coefficient. The significance of each coefficient was determined using p-value. Another way to evaluate the model is the lack of fit (Bezerra et al., 2008). A model will be well fitted to the experimental data if it presents a significant regression and non-significant lack-of-fit.

4.8 SUMMARY

Screening of the most stable emulsion is the most important test in this study. This test was run by using the well-known method, which is called emulsion stability test assisted equipments depend on the types of emulsion rheology have been chosen and the most stable emulsion was performed through percentage of water separated.

For the optimisation, parameters affected demulsification process in microwave was selected to locate the optimum point in enhancing the percentage of water separated. Crude oil A and C was used 2^3 factorial design while crude oil B occupied with 2^2 factorial design due to the results in demulsification using microwave irradiation.

CHAPTER 5

CRUDE OIL EMULSION STABILITY

5.1 INTRODUCTION

For emulsion dispersion, which is not thermodynamically stable, the degree of emulsion stability is very important. Thus, knowledge of the emulsion stability was investigated closely before proceed with demulsification process. The stability of emulsion was first determined by observing the physical separation of water after emulsion was prepared and left in room in a certain time. Generally, greater separation phase separation indicates lower emulsion stability with shorter shelf life.

5.2 CHARACTERISTICS OF CRUDE OIL

The stability of emulsion was investigated closely to the characteristic of crude oil. Determine physical and chemical properties of crude oil are essential to get better understanding of crude oil characteristics. The physical properties such as viscosity, shear stress, density and surface tension, as well as for chemical properties; weight percentage of asphaltenes, resins, solid particles and wax precipitated.

5.2.1 Physical Properties of Crude Oil

Each crude oil has own complexity nature in characteristics and offers individual problems. The properties of crude oil is one of the crucial parts need to be studied to solve and better understanding of emulsion problems encountered in oil field. Comparison studies among the crude oil were listed in Table 5.1.Results had shown that crude oil C was the heaviest and the lightest was crude oil B. Crude oil C acquired nearly density as crude oil A. The density of all the types of crude oil exhibit almost same density while crude oil C obtained the highest followed by crude oil A and B. This trend has good confirmation with Ariany (2004), which viscosity changes in small magnitude usually proportional to density change, whether caused by temperature or pressure. The different physical properties of crude oil are obviously showed from API density which strongly agreed that crude oil C is the heaviest crude oil.

The crude oil ceased to flow when reached pour point due to excessive amount of wax crystal forming due to the build up of network wax crystal forming and the crude oil gels under static condition (Zhu, 2008). From Table 5.1, crude oil A obtained the lowest pour point (-20.4^{o}C) while crude oil C acquired the highest pour point (-12^{o}C) whereas the lower pour point would mean the gelling of oil in the wells will not be expected. This is supported by Pedersen and R∅nningsen (2000) which the network of wax crystal build up was persuaded the value of pour point. As reported by Taraneh et al. (2008), the waxy crystal behaves as typical homogenous liquid at temperature above pour point and the amount of wax start to attain its saturation limit by forming a solid solution in the crude oil at temperature lower pour point. In contrast, temperature at which the dissolved solids are no longer completely soluble was measured using differential scanning calorimetry (DSC) as the onset temperature of the exothermal peak observed upon cooling and called as wax appearance temperature (WAT). Crude oil C, which presents the highest pour point, displays higher with sharp peak of exothermal (Appendix A). High WAT cause greater flow pressure and temperature drop, thus the WAT is good indicator of the pour point (Alghanduri et al., 2010). The properties of crude oil also investigated closely for surface tension analysis. From Table 5.1, crude oil C obtained the highest surface tension due to high viscosity of crude oil thus increase force attraction between molecules.

Table 5.1: Physical Properties of Crude Oil

	crude oil A	**crude oil B**	**crude oil C**
viscosity (cP) at 25°C	183.6	24.6	207.8
density (g/cm^3)	0.8459	0.8345	0.8494
°API density	29.226	33.819	26.481
pour point (°C)	-20.4	-19	-12
Wax Appearance Temperature (WAT),°C	-1.18	3.11	4.44
Water content (%)	7	0.65	2
Surface tension (m/Nm)	13.276	13.046	13.659

5.2.2 Chemical Properties of Crude Oil

The composition of crude oil as explained in Chapter 4 shown in Table 5.2. Results explained that crude oil C obtained the highest asphaltenes content followed by crude oil A and B. From Auflem (2002) and Langevin et al. (2004), the asphalteness content can be a good indicator in emulsion stability since asphaltenes play an important part in emulsion stability. As postulated from El Gamal et al. (2005), at the interface, asphaltenes self assemble to produce rigid film thus make a barrier in coalescence. The presence of resin also persuade in the emulsion stability. However, high content of resin reduced the emulsion stability due to the interaction of resins with asphaltenic aggregates render the aggregates less interfacially active. Therefore, the ratio of resin to asphaltenes (R/A) can be an important factor to identify the emulsion stability. As increasing R/A ratio, the asphaltenes molecularly dissolved (Ali and Alqam, 2000; Mclean and Kilpatrick, 1997). Results indicate crude oil B less stable crude oil compared to others crude oil. In contrast, as studied the content of wax precipitated in the crude oil, crude oil C performed the higher content of wax followed by crude oil B and A. This was proven by studied of physical properties of crude oil which the higher wax crystal exhibited higher wax appearance temperature. Solid particles have both hydrophilic and hydrophobic regions, so it would be located at the oil-water interface. Therefore, the presence of solid particles at the interface will enhance the stability of asphaltenes-resin film (El Gamal et al., 2005; Sullivan and Kilpatrick, 2002).

Table 5.2: Chemical Properties of Crude Oil

Types of crude oil	asphaltenes (A)	resin (R)	Oil		Wax	solid particles	R/A
			non-volatile	volatile			
crude oil A	11.00	21.60	33.49	16.97	2.74	14.20	2.70
crude oil B	5.94	32.33	45.51	0.32	5.11	9.77	11.0
crude oil C	14.7	23.80	29.01	5.28	11.81	15.27	2.03

Infrared analysis informs the functional groups exist in asphaltenes for crude oil A, B and C as shown in Figure 5.1. Crude oil A, B and C indicate the presence of hydrocarbon bonded such as OH due to the presence of hydrogen bonding between OH groups and various hydrogen bonding acceptors such as ether oxygen and pyridinic nitrogen. Both asphaltenes and resin had shown same trend with the spectra of crude oil (Appendix A). As listed in Table 4.2 (in previous chapter) there were five types of hydrogen bonding existed in asphaltenes (Chen, 1998). Figure 5.1 shows the strongest absorption ~ 3300 cm^{-1} that OH-ether oxygen was the main hydrogen bonds in all types of crude oil studied. These types of crude oil also contained large amounts of water, characterised by the large broad band at 3400 cm^{-1}. Hence, as postulated by Woods et al. (2004), the peak also is attributed to O-H or N-H stretching and associated hydrogen bonding. All crude oil also obtained peaks in the 2830 and 2850 cm^{-1} which corresponding to CH_2 and CH_3 group. The range of these peaks due to the CH bends for aliphatic group presented in asphaltenes. At~1600cm^{-1}, the crude oil contain of aromatic groups. However this functional group indicates stronger peak in crude oil B compared to other crude oils. The stronger peak of aromatic performs lower asphaltenes (Hannisdal et al., 2005; Ariany, 2004).

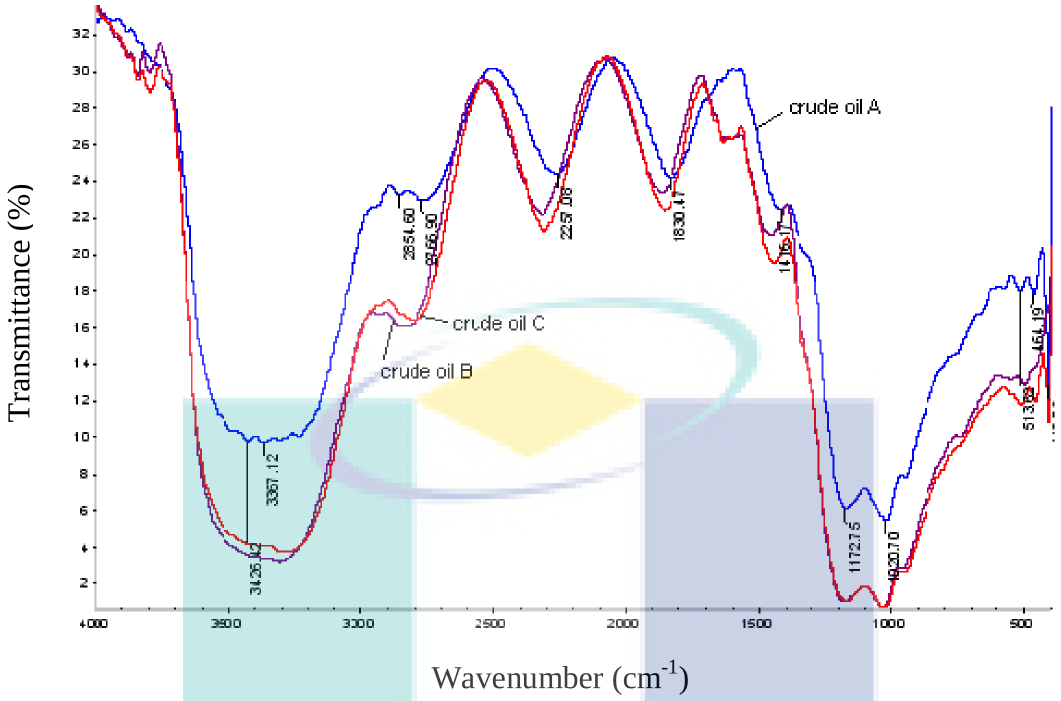


Figure 5.1: FTIR Spectra for Asphaltenes of Crude Oil A, B and C

Resin is a component in crude oil that has dark colour in liquid or semisolid. The functional groups of resin are also indicated in crude oil A, B and C. Figure 5.2 displays the spectra of resin analyse using FTIR. The overall trend of spectra has similarity with asphaltenes because resin also has polar group. A comparison of the subtracted spectra of the each crude oil shows that crude oil A and B displayed the same trend. However, crude oil C presents the aldehydes group at 2775.85 cm^{-1} which this interest area different with both crude oil A and B. Aldehydes is part of aromatic group whereas the heavy crude oil presents high aromatic content. This is supported by Hannisdal (2005) who studied the relation of aromatic groups in crude oil. Meanwhile, aromatic compound also rest in range 1600-1450 cm^{-1} the peaks on figure show that each crude oil resin have similar aromatics compound.

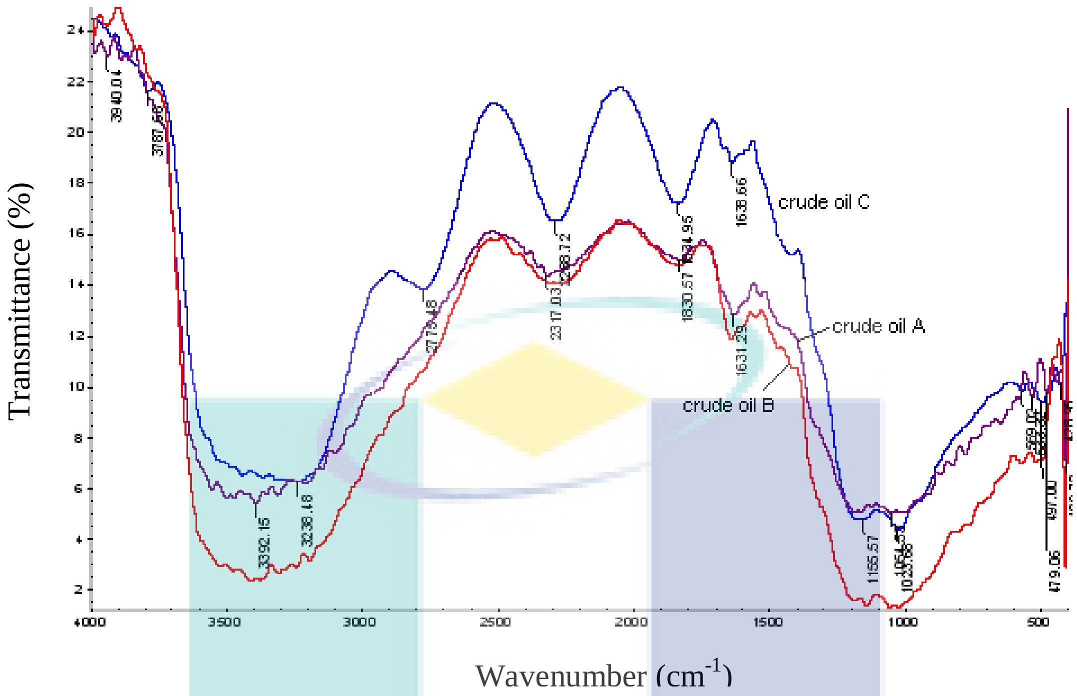


Figure 5.2: FTIR Spectra for Resin of Crude Oil A, Crude Oil B and Crude Oil C

5.3 STABILITY CHARACTERISTICS OF CRUDE OIL EMULSION

The stability of emulsion is main element of water-in-oil (W/O) emulsion. The characteristics of emulsion are investigated closely to better understand the effect of parameters such as surfactant, stirring intensity, droplets size and volume fraction on emulsion stability.

5.3.1 Effect of Surfactant Types on Stability of Emulsion

Emulsion was prepared at different surfactants to discover the most stable emulsion as problems encountered in industry. The most important task in preparation of emulsions is the selection of suitable surfactant which will satisfactorily emulsify the chosen ingredients at a given temperature. It has long been recognized that with a homologous series of surfactants, there is a relation between the contributions of the polar hydrophilic head and the nonpolar lipophilic tail which related to the polarity of surfactant (Chen and Tao, 2005).

Figure 5.3 shows various types of surfactants were compared to investigate the most stable emulsion performed in crude oil B. Span 83 (HLB=3.7) which is non-ionic group oil soluble executed the most stable emulsion compared to other types of surfactant. As studied by Opawale and Burgess (1998), who are investigated the rheological properties of sorbitan fatty acid ester (Span) at water-oil interface, the sorbitan fatty acid ester (Span) is typically used in preparing W/O emulsion. As observed until 180 minutes, there was no separation occurring by using Span 83. Span 83 adsorbed onto surfaces with hydrophobic group oriented toward the surfaces and making it more hydrophilic. This surfactant dissolved in the crude oil as continuous phase, essentially non-polar in nature as compared to water, the dispersed phase (water) in crude oil becomes covered with a single layer of surfactant molecules and increased dissimilarity between droplets. By increasing dissimilarity between two droplets, avoided droplets from coalesce and made system become stable.

As compared to the other types of surfactant, Tween 80 is non-ionic group and water-soluble obtained the highest percentage of water separation (60 % after 60 minutes) followed by Triton X-100 and SDDS. Triton X-100 (HLB= 13.5) same group as Tween 80 (15.0) with but Triton X-100 most soluble in water and miscible in most polar organic solvents & aromatic hydrocarbons (Hait and Moulik, 2001). However within 180 minutes, the percentage of water separated in the crude oil was only 56 % within 180 minutes by gravitational settling. SDDS from anionic group obtained the higher percentage of water separated compared with emulsion prepared in Span 83 due to the properties of surfactant which an anionic group. From Chern and Lin (1996), this types of surfactant can impart repulsive forces between similarity charged electric double layer to the particles of natural surfactant i.e. asphaltenes and resin.

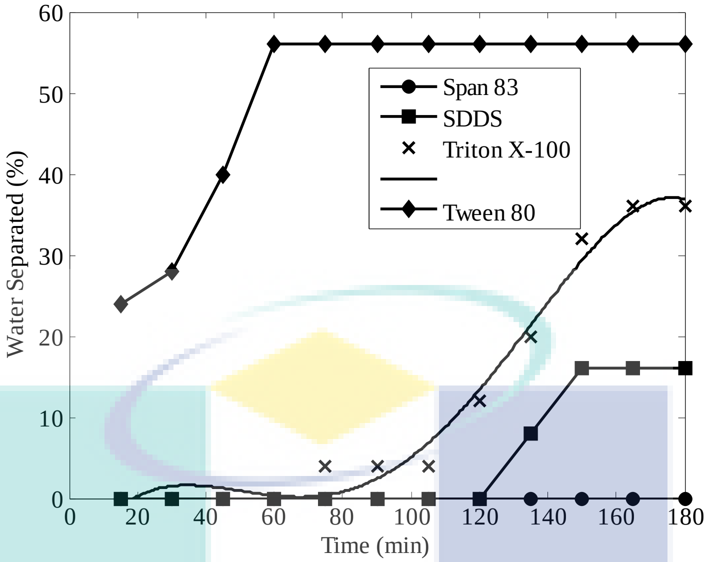


Figure 5.3: Effects of Types of Surfactant on W/O Emulsion Stability (Experimental Condition: Stirring Intensity = 1500 rpm; Processing Time=5 minutes)

5.3.2 Effect of Stirring Intensity (rpm) on Emulsion Stability

The stability of emulsion is also affected by stirring intensity. During emulsification, interfacial area between two phases increase, therefore mechanical energy is required to minimise the interfacial area and proceed with emulsification. The larger excess of energy required to produce small droplets size using very intense agitation thus makes a barrier of droplets to coalesce. The break-up of droplets depends strongly on the type and intensity of the flow which is determined by the rotational speed and geometry of the agitator (Hannisdal, 2005).

Figure 5.4 examines the effect of viscosity for crude oil A, B and C in 50-50 % W/O and 20-80 % W/O emulsion as varied stirring intensity. From figures, higher ratio (50-50 % W/O emulsion) has higher viscosity because the main attribution to the viscosity in emulsion system is dispersed droplets (Urdahl et al., 1997). When droplets are introduced, the flow system becomes distorted; hence the energy dissipation is increased. This increment energy will lead to an increase in the viscosity of emulsion. For 50-50 % W/O emulsion, crude oil C showed there was significantly increasing of viscosity. In contrast, crude oil A and B show only slightly increasing and at 1500 rpm, emulsion prepared from crude oil A and B began to form stable emulsion. This trend of results also can be determined at lower ratio (20-80 % W/O emulsion).

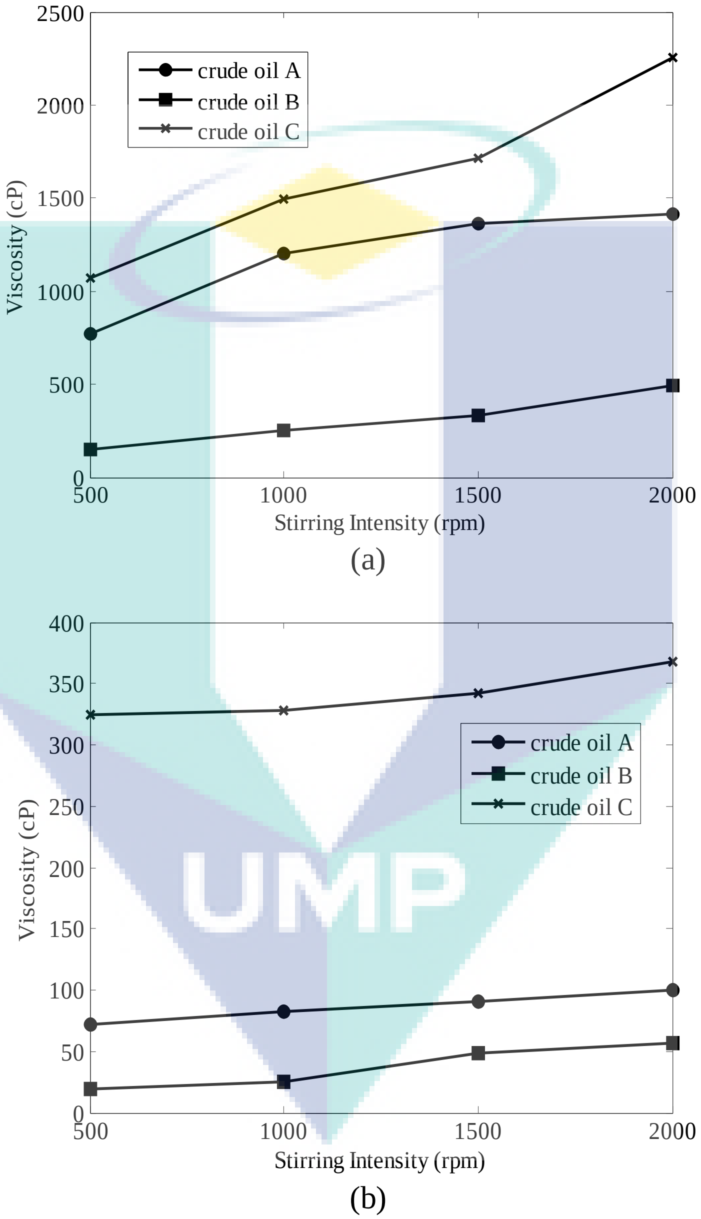


Figure 5.4: Viscosity Effect at Varied Stirring Intensity (a) 50-50 % W/O (b) 20-80 % W/O Emulsion

Further study of stirring intensity on water separated only could be observed in crude oil B due to the properties of crude oil and after screening, crude oil A and C do not separated through observation until 5 days. The percentage of water separated observed in varied stirring intensity shown in Figure 5.5. Emulsion was processed at 5 minutes for each mixing speed and using Span 83 as selected surfactant. Results acquired that higher stirring intensity indicated more stable emulsion by observing the percentage of water separation. At 500 rpm, after 15 minutes, the water resolved was 65 % as compared to 1500 rpm which only achieved 5%. At lower stirring intensity, the surfactant does not well mixed with the crude oil (not homogenous). Thus, the surfactant do not covered the droplets significantly and rigid film do not formed. However, for the higher stirring intensity, the effectiveness of surfactant to adsorb onto the droplets was increased. At higher stirring intensity, example for this study, the maximum speed has been studied was 2000 rpm, the surfactant and crude oil mixed well and the amphiphilic in the surfactant and play their parts very well and adsorbed onto the droplets.

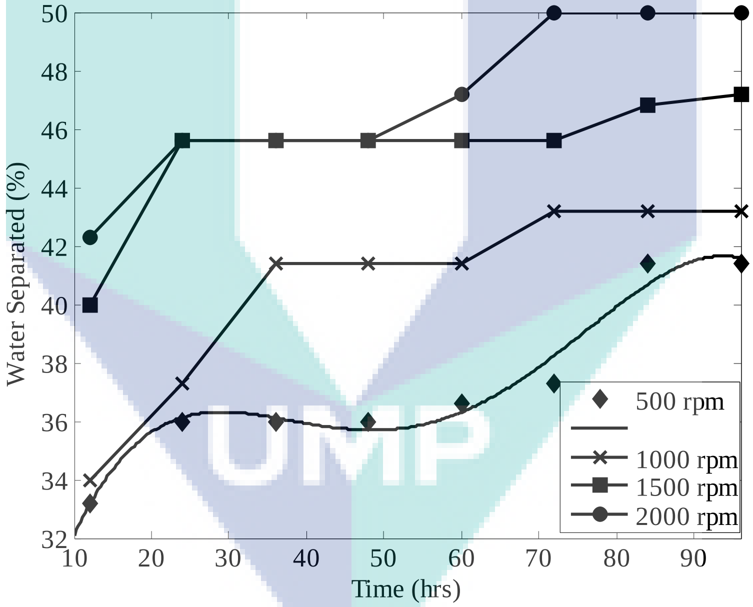


Figure 5.5: Effect of Stirring Intensity on Emulsification

In addition, the agitation speed also persuaded the diameter of droplets and provided information on the efficiency of emulsification process. Figure 5.6 demonstrates the mean of droplets diameter, *d* at varied phase ratio for crude oil B where the size of droplets (mean) is inversely proportional with stirring intensity. Both phases ratio showed high discrepancy for droplets mean diameter and viscosity where 50-50 % W/O emulsion obtained higher diameter and viscosity compared to 20-80 % W/O emulsion. For 50-50 %

W/O emulsion, the droplets mean diameter decrease significantly until 1500 rpm and slightly decreased at 2000 rpm while 20-80 % W/O emulsion, there was slightly decreased of droplets mean diameter within 1500 rpm and droplets decreased drastically at 2000 rpm. The intersection of mean droplet diameter for 20-80 % and 50-50 % W/O emulsion can be explained due to the stability of emulsion. Emulsion at this stirring intensity was believed began to form a stable emulsion and after this stirring intensity the emulsion took a long time to separate after left in room temperature. The higher stirring intensity also providing the two-phase-oil-water system which more energy can generate drastic shear strength as consequence leading to the water droplets being small.

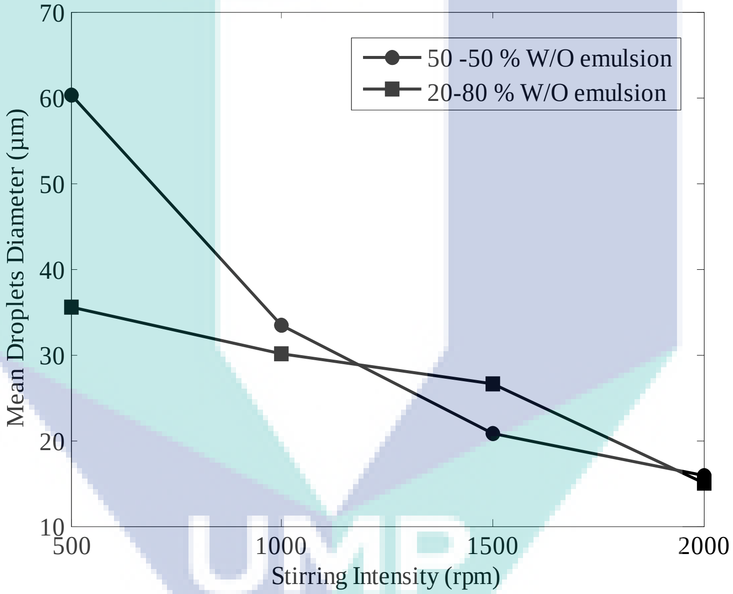


Figure 5.6: Mean of Droplet Diameter (µm) within 500 to 2000 rpm of Stirring Intensity

5.3.3 Effect of Temperature on Emulsion Stability

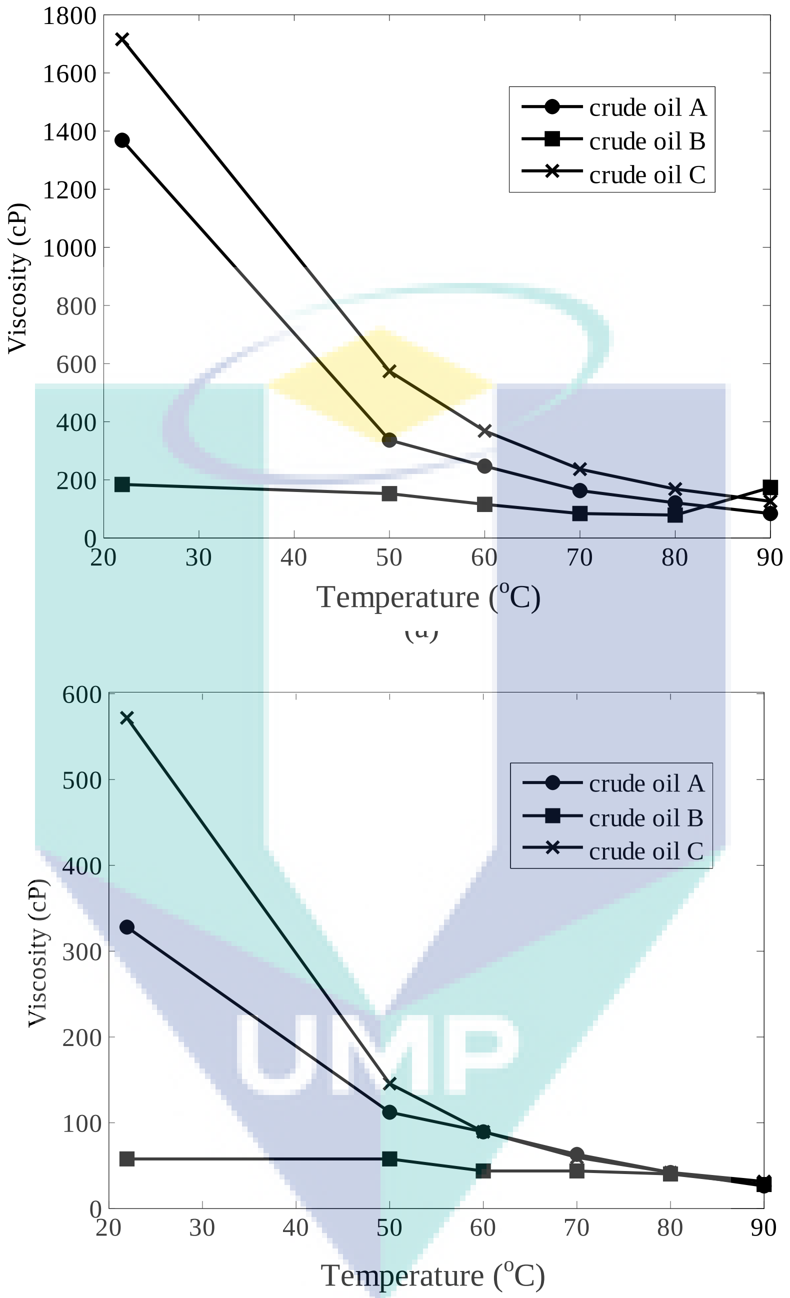
Temperature often has an indirect factor that affects the emulsion stability as results of altering the interfacial tension and viscosity of emulsion. The effect of temperature was examined at 20-80 % W/O and 50-50 % W/O emulsion. For both ratios, viscosity of W/O emulsion is strongly augmented by decreasing temperature. According to the ideal Stoke's Law for the creaming rate of emulsion, the gravitational instability rate of emulsion is directly proportional with density different of continuous and dispersed phases (ρ_o- ρ_w)

$$v_m = \frac{gD^2(\rho_O - \rho_w)}{18\mu_o} \tag{5.1}$$

If viscosity, μ_o (cP) is lower, the density different of continuous and dispersed phases increased. Thus, lead the higher velocity of droplets, v_m. As temperature increased, the movement of droplets (velocity) also higher therefore enhance the droplets to coalescence.

Figure 5.7 (a) and (b) show decreasing of viscosity as augmented temperature. However for crude oil B, at 90^{o}C the deformability limit for the droplets is over and the viscosity abruptly increased. The drastic increasing of viscosity in crude oil B is believed because of the phase inversion occurs from W/O to O/W emulsion. Temperature is one of factor changing the surfactant hydrophile-lipophile balance (HLB) in systematically varied from predominantly oil-soluble to water soluble. At lower temperature, Span 83 is mainly soluble in oil phase and as temperature increased to 90^{o}C (crude oil B), the surfactant is preferentially soluble in water phase.

Crude oil B obtained the lower viscosity compared to crude oil A and C. At inversion point, the interfacial tension decreases favour the breaking process thus, produced smaller droplets size and associated higher viscosity.



(a)

(b)

Figure 5.7: Effect of Temperature on Emulsion Stability at (a) 50-50 % W/O and (b) 20-80 % W/O Emulsion

Figure 5.8 illustrates the effects of mean droplets size diameter as increasing temperature when prepared at 1500 rpm for 20-80 % W/O and 50-50 % W/O emulsion. The emulsion with higher ratio shows bigger in mean of droplets size compared to lower ratio with increasing temperature as decipted in Figure 5.8. This results was discussed in previous figure (Figure 5.6) which at 1500 rpm, the mean droplet size has intersaction of 20-80 % and 50-50 % W/O emulsion. This is expected since higher ratio obtained the emulsion become more viscous thus reduce the interaction among droplets. However for 50-50 % W/O emulsion observed there was drastically decreasing for mean of droplets size from 27 µm to 7.5 µm at 90^{o}C. This results explained the study was proven by Rusli (2007), which the decreasing droplet size at higher temperature because of viscosity have no longer effects to temperature. As droplets size increased, the specific surface area of oil/water interface increased thus resulting strong interaction between them.

The emulsion which have relatively large droplet size (>10 µm), the relative temperature is independent of the droplet size. As temperature increased, the viscosity decreased thus the viscosity of emulsion is no longer independent factor. This result is correlated with Zaki (1997) which, at higher droplet size, the hydrodynamic forces (hard-sphere interaction) are dominant. While for smaller droplet size (<10 µm), the colloidal surfaces and Brownian motion can be dominant.

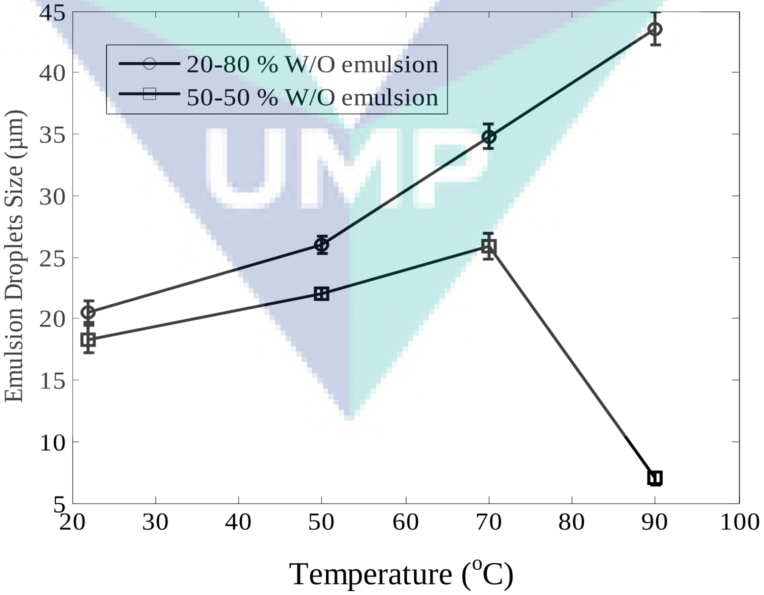


Figure 5.8: Effect of Mean Droplet Diameter (µm) in Increasing Temperature

5.4 OTHER FACTORS CONTROLLING EMULSION STABILITY

5.4.1 Rheological Properties of W/O Emulsions of Different Dispersed Volume Fractions

The discussion of rheology has deal with the deformability and flow properties which related to the viscosity of emulsion. Volume fraction of dispersed (water) phase is varied from lower (10-90 % W/O) until 60-40 % W/O emulsion to identify the effect of volume fraction of dispersed phase on emulsion stability.

Effects on Viscosity

As stated in literature part, viscosity can be though as resistance of fluid to flow. The affecting factors are numerous and viscosity is one of the expected. If the internal phase in an emulsion has a sufficiently high volume fraction, the emulsion viscosity increased due to droplet crowding or structural viscosity become non-Newtonian until achieved to the critical volume fraction. This expected result is proven by investigated the effects of viscosity when changing the volume fraction of emulsion.

The effects of volume fraction and maximum volume fraction on viscosity are described using the Krieger-Dougherty equation:-

$$\eta = \eta_c \left(\frac{1-\phi}{\phi_m} \right)^{-2} \tag{5.2}$$

Where η is viscosity of emulsion; η_c represents the viscosity of continuous phase (based on this study, crude oil is continuous phase); Φ is phase volume of dispersed phase and Φ_m denotes the maximum phase volume.

Effect of the viscosity on the volume fraction is shown in Figure 5.9 for all types of crude oil used in this study. At low volume fraction (~0.15), the viscosity increased linearly but as the volume fraction increased the viscosity increased steeper. However, when the droplets are closed enough and exceed the limitation, the viscosity decreased drastically due to changing the phase inversion of emulsion to oil-in-water. From Figure 5.9, the critical volume fraction point for crude oil A, B and C are 0.5, 0.6 and 0.68, respectively.

This results is supported by Tadros (2009) which, random packing droplets might start being in contact at a lower volume fraction. Earlier assumptions of phase inversion were based on packing parameters. When volume fraction exceeds of maximum packing (~ 0.64 for random packing and ~0.74 for hexagonal packing of monodisperse), critical point of volume fraction reached. However, these assumptions are not adequate because there are still emulsion invert at volume fraction values below than the maximum packing.

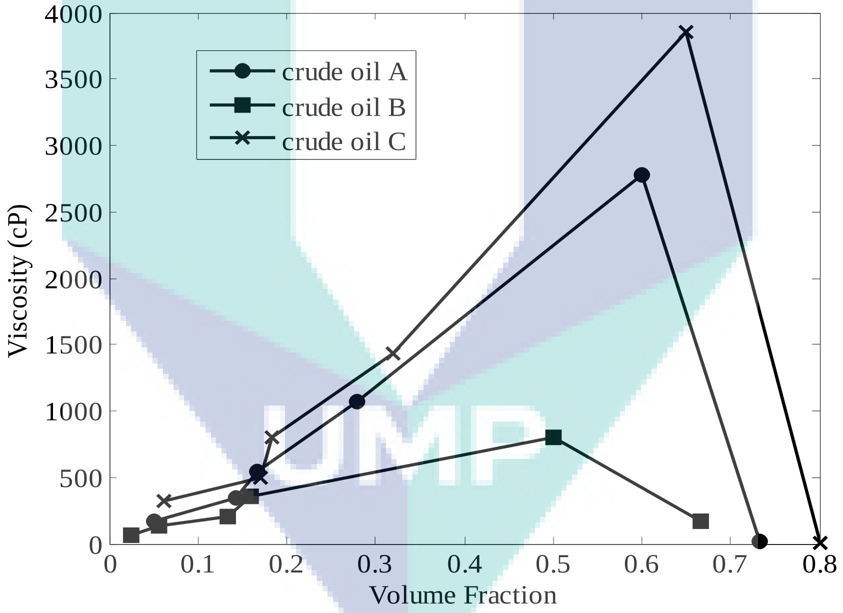


Figure 5.9: An Influence of Phase Volume Fraction on the Emulsion Type and Viscosity

Effect of Interfacial Tension

Surface tension is a measure of the force at a boundary between condenses and gas phase. If these attractive forces are between two immiscible liquids, which boundary between two condensed phases, like oil and water, they are referred to as interfacial tension. The interfacial tension of crude oil are important because they are also indicative the ease of formation and emulsion stability. Figure 5.10, the overall trend of graph shows that the interfacial tensions increased with density and drastically decrease as density is further increasing. Emulsion prepared in crude oil A and C demonstrated there are linear increasing of interfacial tension within density 0.923 and 0.92 g/mL and linearly decrease within 0.94 g/mL. Also, as can be seen from Figure 5.10, in crude oil B, two peaks are obtained before interfacial tension drastically decreases at 0.9172 g/mL. The increasing density of emulsion has correlation with volume fraction which emulsion has changing from a simple viscous solid at low volume fraction to an elastic solid having a substantial shear modulus at higher volume fraction. Also, this elasticity results from work done against interfacial tension to create additional droplet surface area when the shear further deforms the compressed droplets. Thus, the definition from Bancroft (1912) could be applied whereas the water acted as continuous phase due to the surfactant more soluble in water.

From Rosen (2004), the changing of W/O to O/W emulsion as increasing volume fraction due to the interfacial tension between the hydrophilic ends of the surfactant molecules with water phase and oil phase molecules. For W/O emulsion, the water-hydrophilic end tension was greater causing the film to be concave toward water. However, as droplets increased until reached a critical amount, the oil-hydrophobic end tension was greater causing the film toward the oil, resulting in the enclosure of the oil by the water.

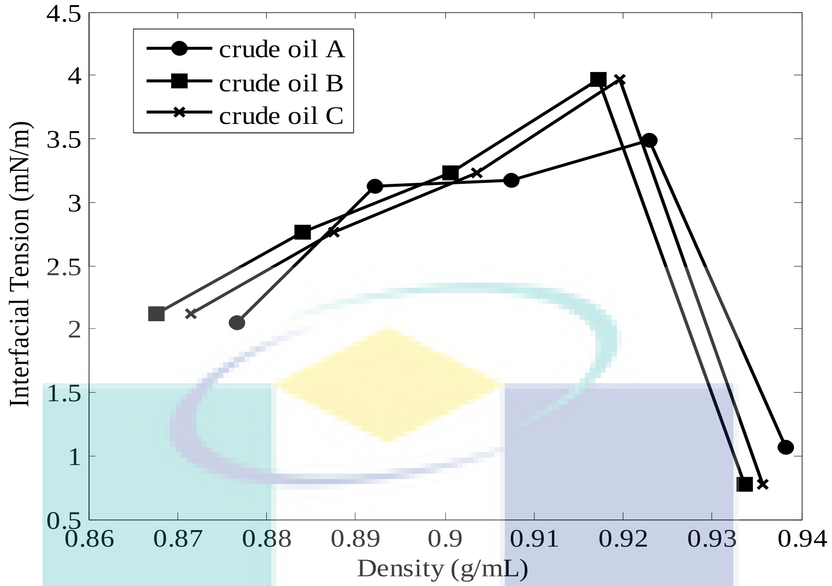
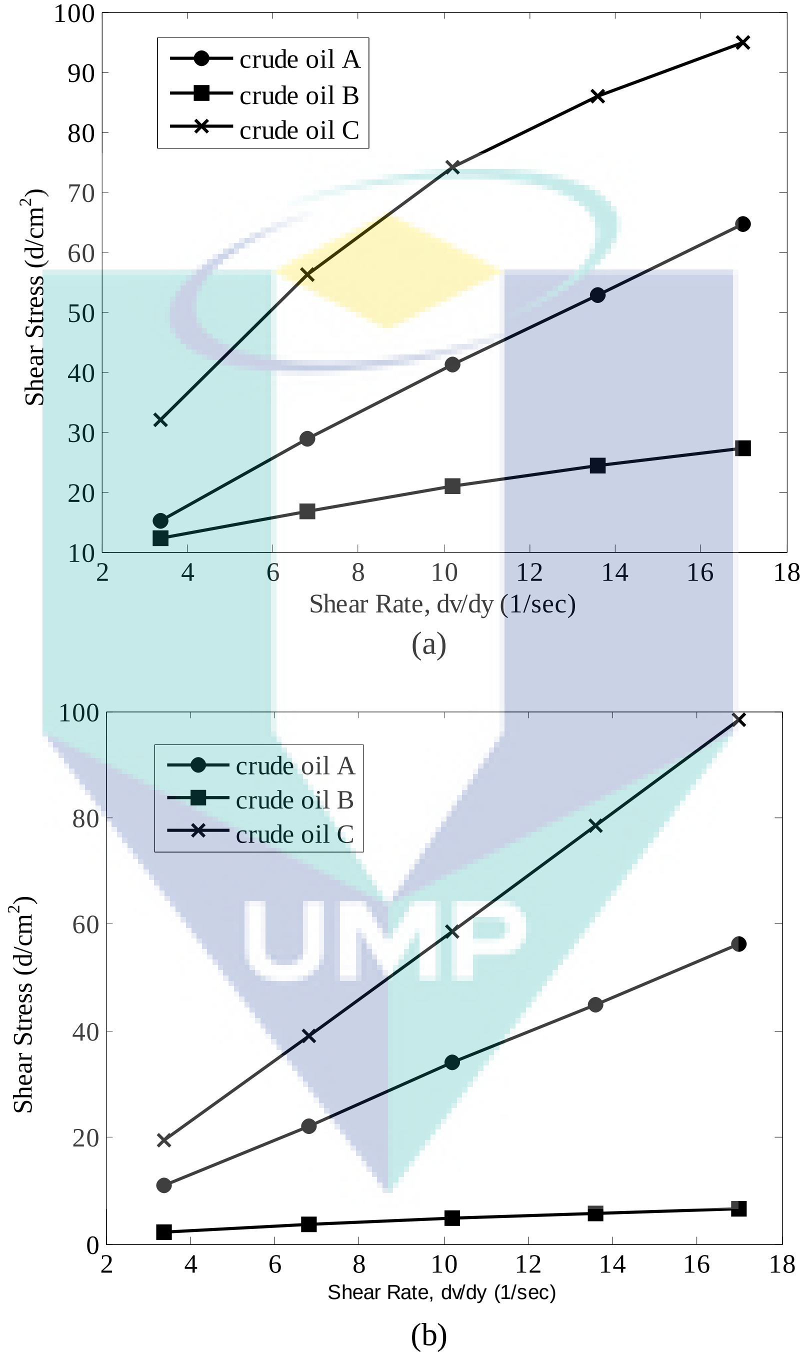


Figure 5.10: Interfacial Tension Effect of Emulsion by Varied Density

Effects of Shear Stress and Shear Rate

The shear stress versus shear rate profile is presented in Figure 5.11. The rheological behaviour of an emulsion may be either Newtonian or non-Newtonian depending upon its ratio. When shear stress is applied, Newtonian liquid flows as long as stress is applied even after stress is removed (McClements, 2005). Figure 5.11(a) and (b) show the shear stress is no longer linear as increasing the dispersed phase ratio which at 20-80 % W/O emulsion, a straight line graph observed from shear stress versus shear rate. While as increased the dispersed phase ratio, crude oil B and C obtained non-Newtonian behaviour. As proposed from Chhabra, (2007) and Lee et al. (1997), as increasing dispersed phase ratio, the emulsion behaviour more on non-Newtonian due to the alteration of rheological properties of fluid flow condition. However, at 50-50 % W/O emulsion for crude oil A, the emulsion follows Newtonian behaviour which as shear stress is applied, the crude oil is flow continuously. This is due to the wax appearance temperature (WAT) of crude oil higher (4.44^{o}C) compared to others crude oils. Above the WAT, wax crystal dissolved although chemically very complex crude oil and performed a simple Newtonian fluid (Li and Zhang, 2003).



(a)

(b)

Figure 5.11: Effect of Shear Stress on Shear Rate with Varied Phase Ratio (a) 50-50 % W/O (b) 20-80 % W/O Emulsion

The crude oil A was investigated closely by increasing the phase ratio of water-crude oil to 55-45 % W/O and 60-40 % W/O emulsion as shown in Figure 5.12. As increasing the phase ratio, the emulsion behaviour as pseudoplastic which emulsion was stretched and alignment while being sheared due to increasing the droplet content into the crude oil. This result verified that higher phase ratio required from crude oil A to behave as non-Newtonian due to the content of wax-precipitated in crude oil A was lower than crude oil C and B.

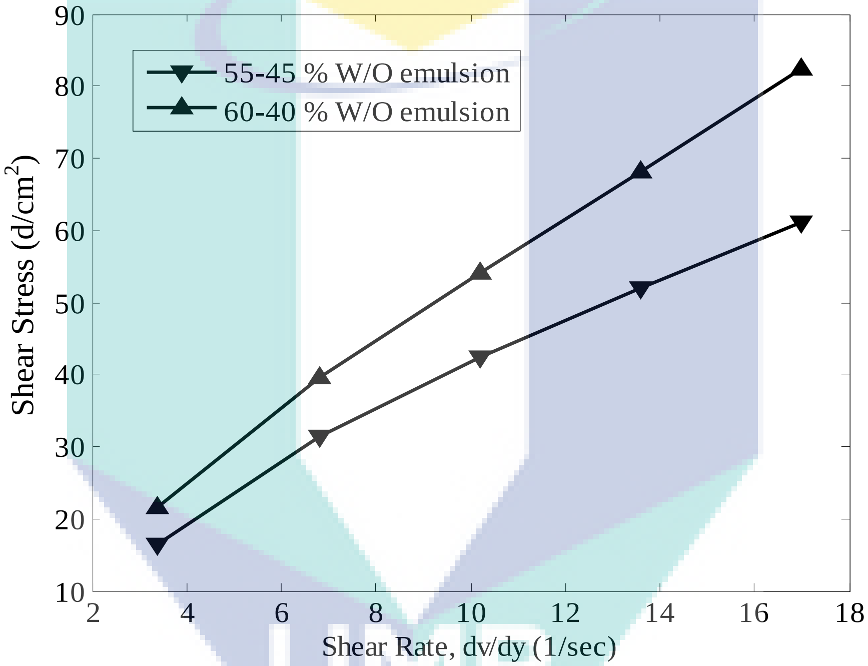
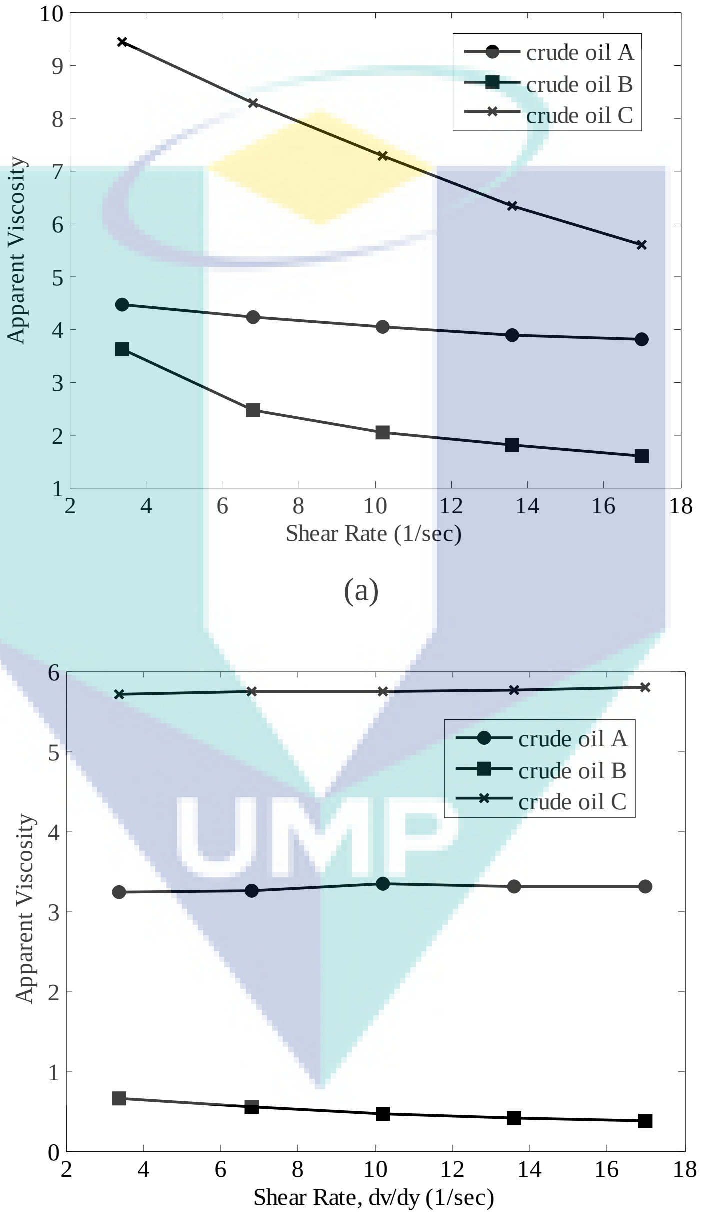


Figure 5.12: Effect of Shear Stress on Shear Rate in Crude Oil A by Increased the Ratio

The effect of phase ratio in examining the emulsion behaviour was confirmed by plotting apparent viscosity versus shear rate as shown in Figure 5.13. At higher phase ratio, the apparent viscosity of crude oil B and C clearly decreased as increasing shear rate thus verified the emulsion pursued pseudoplatic behaviour. The gradual break-up of interparticles structure may be primarily responsible for this behaviour. While, crude oil A obtained a slightly decreased of apparent viscosity at lower shear rate and begun to be constant at higher shear rate.

However, at lower phase ratio, all the crude oil confirmed act as Newtonian behaviour whereas the apparent viscosity is independent with shear rate because the flocculation of droplets does not take place due to the amount of droplets present in the emulsion was smaller.



(a)

(b)

Figure 5.13: Shear Rate Dependence on Viscosity of Emulsion with Varied Phase Ratio (a) 50-50 % W/O Emulsion (b) 20-80 % W/O Emulsion

Crude oil A was further investigated in behaviour of emulsion by increased phase ratio to 55-45 % W/O and 60-40 % W/O emulsion. The results display in Figure 5.14 was showed that the apparent viscosity decreased as increasing shear rate. Emulsion in both ratios exhibited non-Newtonian behaviour due to trend of graph obtained. This was supported the discussion of shear stress against shear rate at same ratios in crude oil A.

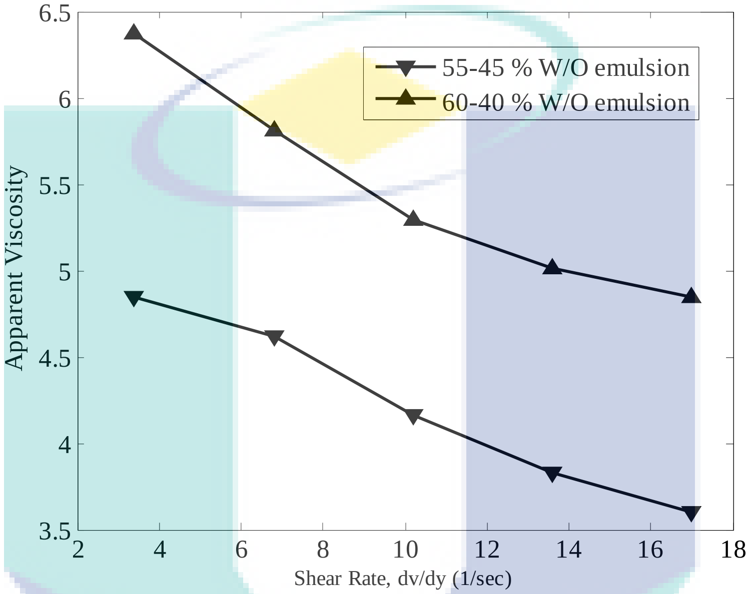


Figure 5.14: Effect of Apparent Viscosity on Shear Rate in Crude Oil A at 55-45 % and 60-40 % W/O emulsion

5.5 SUMMARY

The overall stability of emulsion was influenced by the characteristics of crude oil itself. The heavy crude oil obtained the higher percentage of asphaltenes and wax-precipitated thus enhance the non-Newtonian behaviour as increased the volume fraction of emulsion. Thus, from this study, crude oil C acquired the heaviest crude oil, followed by crude oil A and B. The rheological of emulsion plays an important role in the phase inversion of emulsion from water-in-oil (W/O) to oil-in-water (O/W).

CHAPTER 6

MICROWAVE DEMULSIFICATION STUDY ON WATER-IN OIL (W/O) EMULSION

6.1 INTRODUCTION

The types and mechanisms of demulsification process as reviewed in section 2.9 for the overall demulsification methods (Chapter 2) and details of microwave demulsification was discussed in Chapter 3. Chapter 5 was mainly concerned with the problems involved in the production, formation and stabilisation of water-in-oil (W/O) emulsions. This chapter on the other hand, focuses on reducing the stability of existing emulsions, i.e., demulsification or emulsion breaking.

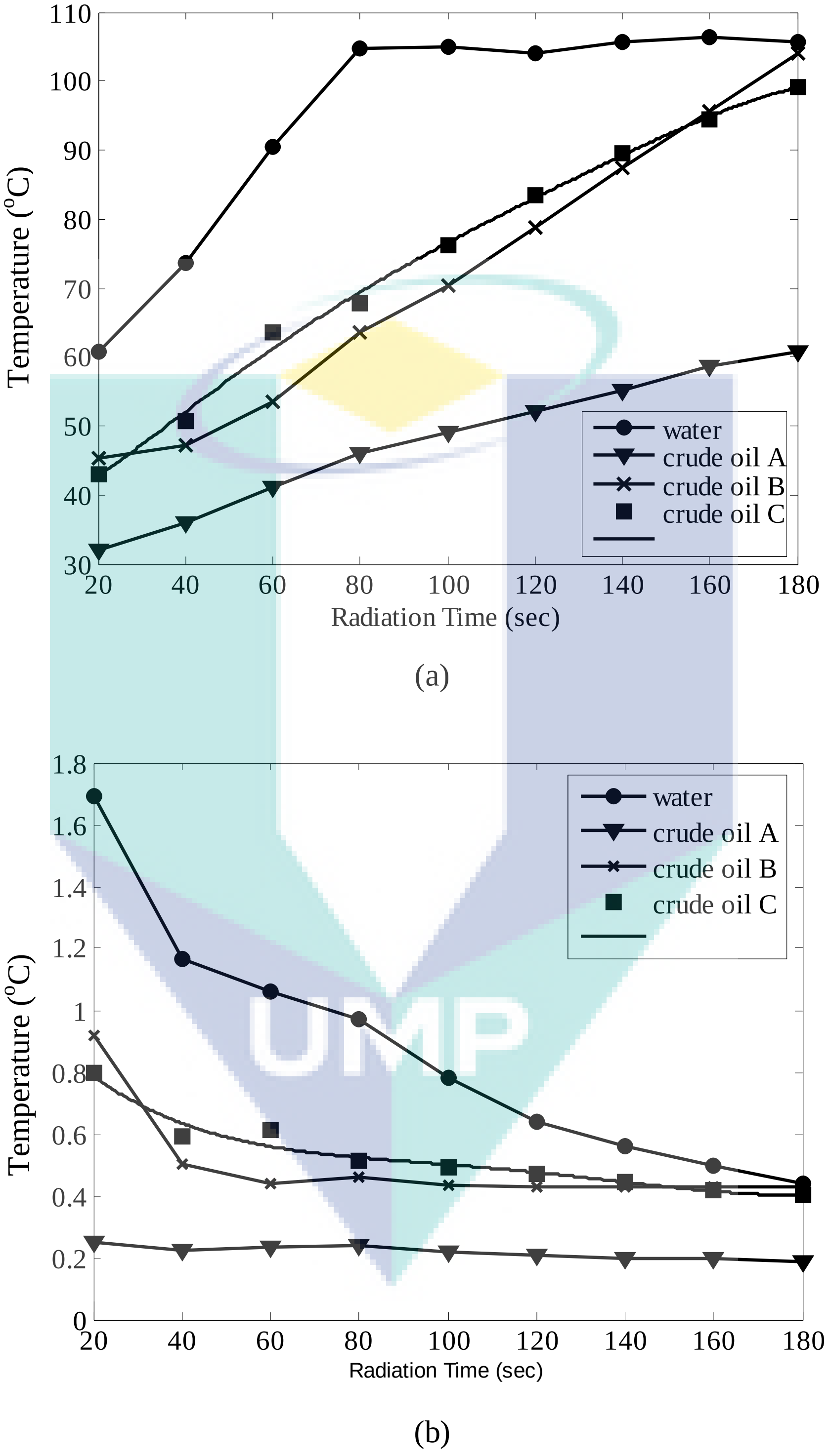
This chapter presents and analyses results of an alternative of cost effective technology of high frequency energy separation of crude oil emulsions via microwave field irradiation in comparison with the conventional breaking methods.

6.2 EXPERIMENTAL RESULTS FOR MICROWAVE IRRADIATION

Experiments were carried out using water and crude oils in microwave irradiation. It can be seen in Figure 6.1, water obtained higher temperature compared to crude oil because water has dipole moments thus more rapid temperature can be arises. However at 80 sec (T= 105^{o}C), temperature rise for water began to constant because temperature rise in water is more uniform than oil since more convective mechanisms existence in water.

Water is becoming a vapour but, temperature of crude oil is increasing. Temperature difference of water and crude oil are explained by polarisation. The temperature in crude oil B and C show higher increasing compared to crude oil A due to the content of wax precipitated in the crude oil. Wax is non-polar, thus in crude oil A the efficiency of crude oil in microwave is reduced thus correlated also with the temperature rise. By comparing crude oil B and C, it shows that crude oil C which exhibited highest asphaltenes content acquired the highest temperature rise between the others crude oil. This trend was first detected by Gunal and Islam (2000) who mentioned that under the influence of microwave irradiation, the temperature rise increases due to the greater impact at higher concentration values of asphaltenes.

The heating rate was calculated by divided temperature increasing with microwave radiation time. Results in Figure 6.1b show that the correlation of heating rate was inversely proportional with radiation. This is expected since the dielectric loss to the wall is small. The average of heating rate in water, crude oil A, B and C were 0.867, 0.218, 0.497 and 0.257 ^{o}C/sec. At early stage in microwave irradiation, crude oil B obtained the higher heating rate compared with crude oil C. However, as time increased the heating rate of crude oil B is reduced than crude oil C. This unstable heating in crude oil B obtained due to the properties of crude oil B itself was lighter than crude oil C. Al-Ayed (2009) has studied the contribution of heavy component into heating rate which heating rate higher at lower viscosity of crude oil and can be clarified as smaller heavy component.



(a)

(b)

Figure 6.1: Temperature (a) and Heating Rate (b) as Function Microwave Radiation Time by Comparing Water with Crude Oils

6.3 EFFECT OF WATER-OIL RATIO ON TEMPERATURE DISTRIBUTON

The heaviest crude oil, which crude oil C was further investigated in temperature distribution under microwave irradiation. Figure 6.2 shows that increasing ratio of water-oil phase caused the temperature distribution increased. 10-90 % W/O emulsion performed the lowest temperature increased within 220 seconds; the maximum temperature achieved was 85.11^{o}C. In contrast, for higher ratio, at 220 seconds, temperature distribution could be higher as 120^{o}C for 50-50 % W/O emulsion and 106^{o}C for 30-70 % W/O emulsion. This was due to the content of dispersed phase was lesser than 30-70 % W/O and 50-50 % W/O emulsion. However, the temperature distribution of 50-50 % W/O has same trend with 30-70 % W/O emulsion due to rapid heating at higher phase ratio. The average temperature distribution for 10-90 % W/O, 30-70 % W/O and 50-50 % W/O emulsion were 61.67, 80.52 and 83.14^{o}C. Thus, as phase ratio increased more readily microwave irradiation is absorbed and higher temperature is obtained.

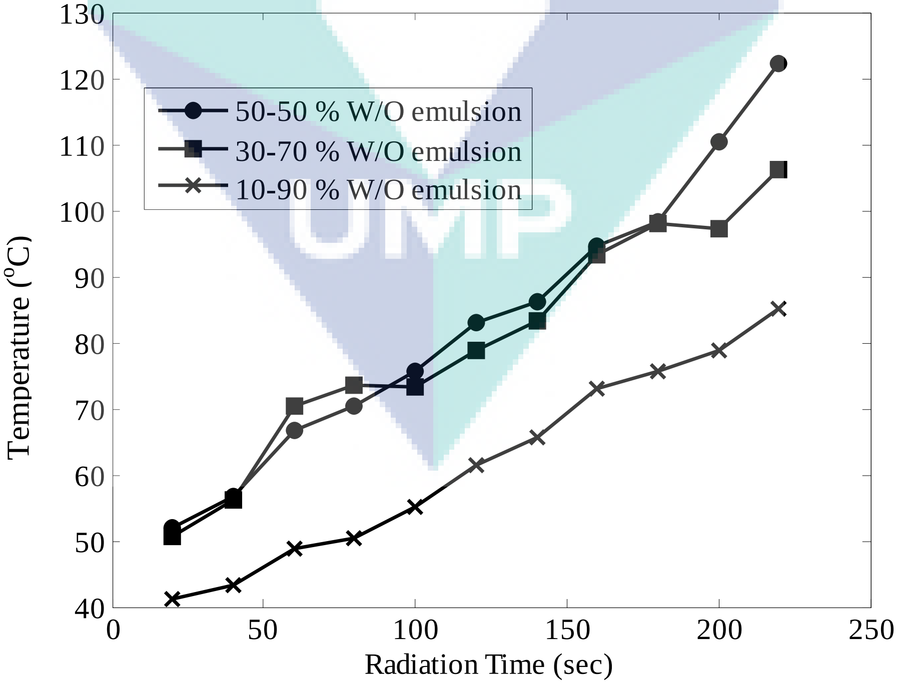


Figure 6.2: Effect of Temperature Distribution at Varied Phase Ratio

6.4 EFFECT OF MICROWAVE POWER ON W/O EMULSION

The effectiveness of microwave power was first determined by observing the physical phase separation which the higher percentage of water separated indicates the most effective microwave power in demulsified emulsion. Figure 6.3 presents the efficiency of water-oil separation by varying microwave power. Increasing microwave power up to 720 W (96 %) causes a substantial efficiency in phase separation. After that, the phase separation decreased to 80 % within 60 minutes. As microwave power increased, the percentage of water separated increases due to high dielectric properties. However, from Figure 6.3, at 900 W the percentage of water separated decreased because emulsion from crude oil A and C contained higher natural surfactant thus at higher power, temperature increases rapidly and thermal heating arises.

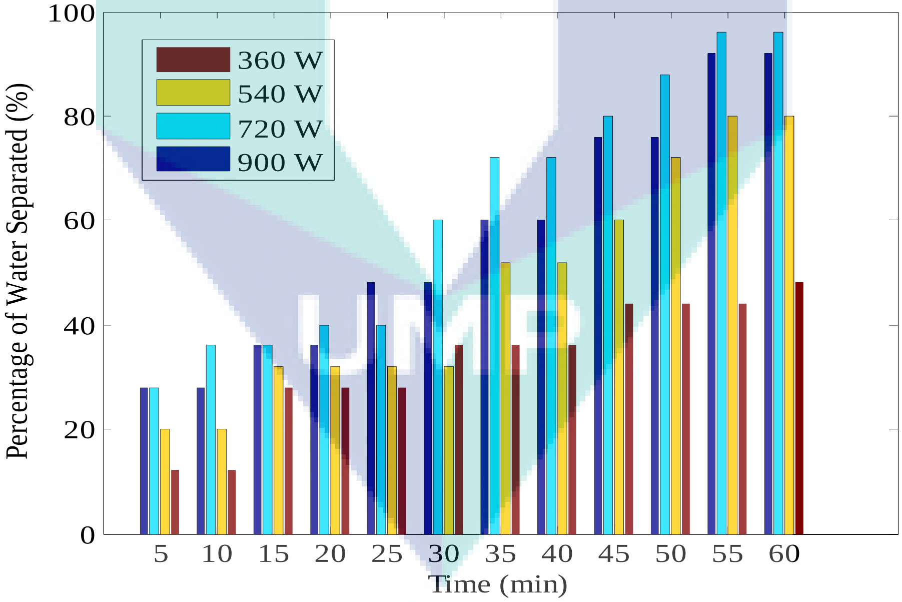


Figure 6.3: Microwave Power Effect on Water Separation

The effects of microwave power with radiation time was examined and results shown in Figure 6.4. Microwave power significantly influences the rate of temperature rise. When the emulsion was exposed to 900 W, the average heating rate is approximately

0.596°C/sec. The average heating rate decreased as microwave power decreased. With an increment microwave power from 360 W to 900 W, the heating reached 0.225°C/sec and 0.596°C/sec respectively with the same exposure time. For higher microwave power, the temperature is greater near the top surface and locally high inside the layer. Furthermore, this is evident that there has correlation between heating rate and microwave power. The increasing of heating rates with microwave power is caused by increasing the absorption of microwave energy because the power absorbed increases with the square of the internal electric intensity. The relation between microwave power dissipated absorbed by a material with dielectric field electric intensity has been given in Equation 6.1:-

$$P = 2\prod f\varepsilon_o\varepsilon^{''}E^2 = \sigma E^2 \tag{6.1}$$

where P is microwave power dissipated per unit volume, E is electrical field intensity and σ is electrical conductivity. This relationship shows that the energy dissipation is proportional to the electrical conductivity.

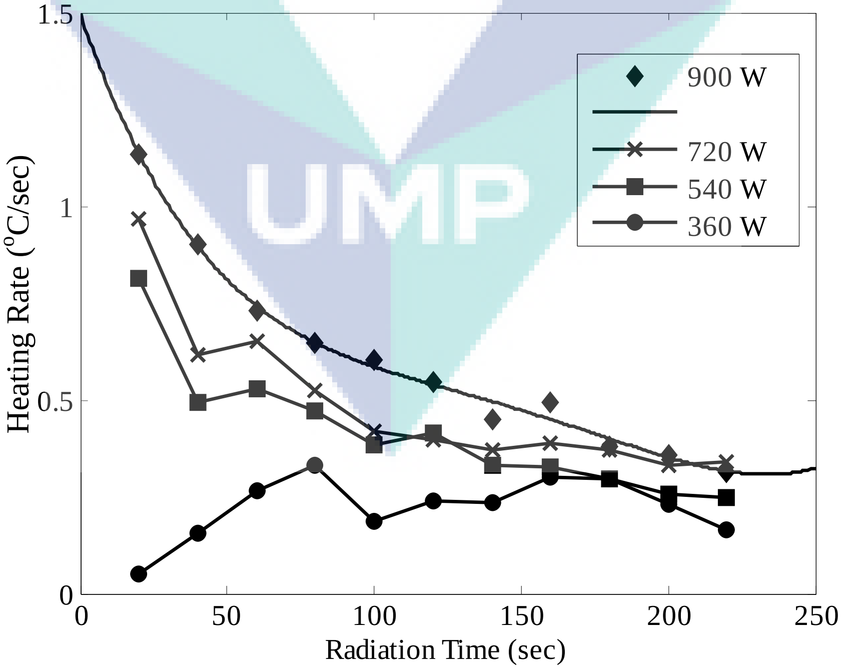


Figure 6.4: Heating Rate in Microwave Power with Variation Time

The effect of wavelength, λ and penetration depth, D_p at varied microwave power from 360 W to 900 W were investigated within radiation time as shown in Figure 6.5. From Figure 6.5, at high microwave power, 900 W, both wavelength and penetration depth were increased and their values were found to be 2.25 cm and 12.00 cm, respectively. Both wavelength and penetration depth significantly increased at 360 to 540 W and at higher microwave power, the wavelength and penetration depth showed slightly increasing because of more intense electromagnetic inside the molecules. At higher microwave power, waves can transmit through the water layer rapidly thereby less amount of waves loss at the wall of the sample's beaker due to the decreasing of dielectric constant. The decreasing in dielectric constant is attributed to the higher temperature within the water layer since the electromagnetic field is more intense.

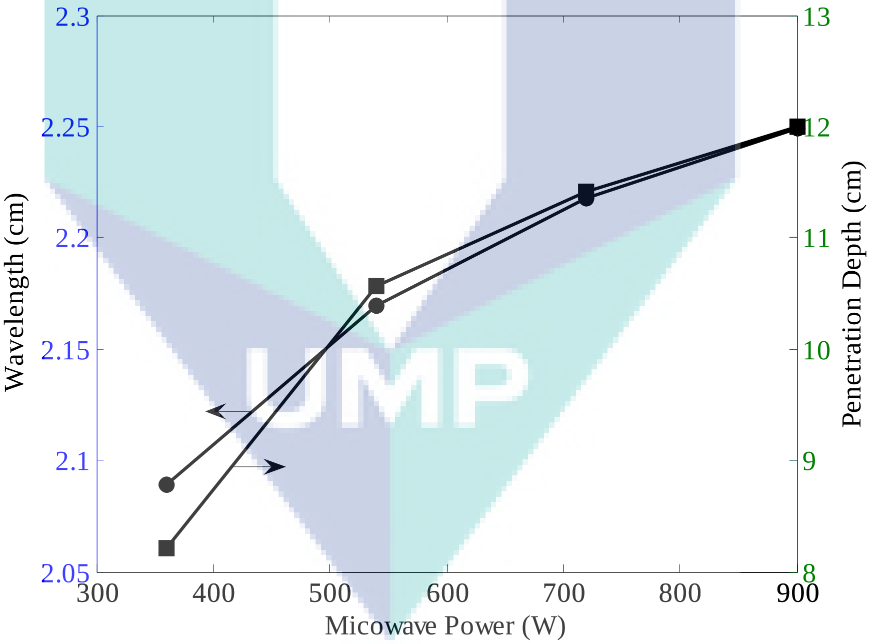


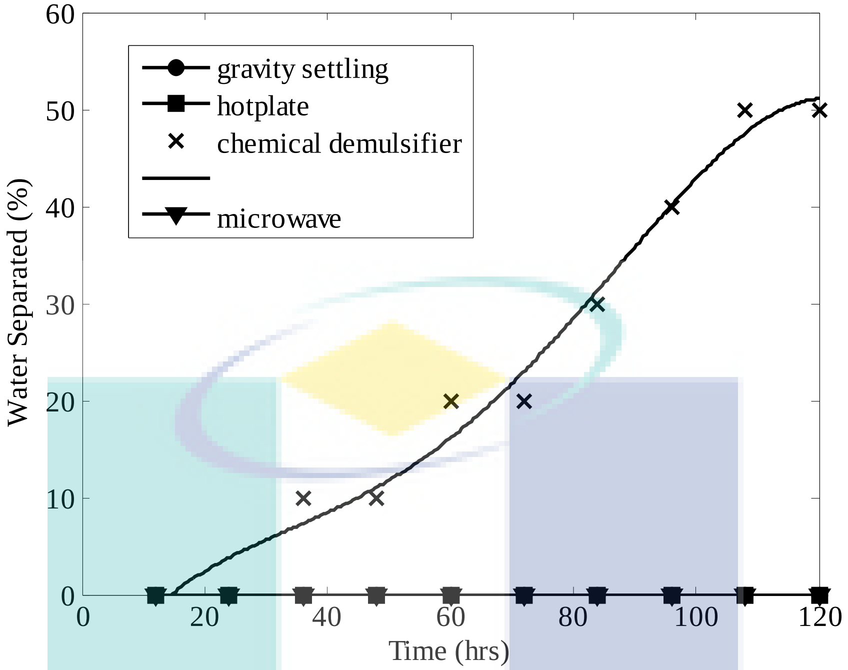
Figure 6.5: Wavelength (cm) and Penetration Depth (cm) Affected within 360 W to 900 W in Microwave Power

6.5 SEPARATION OF WATER FROM EMULSIONS

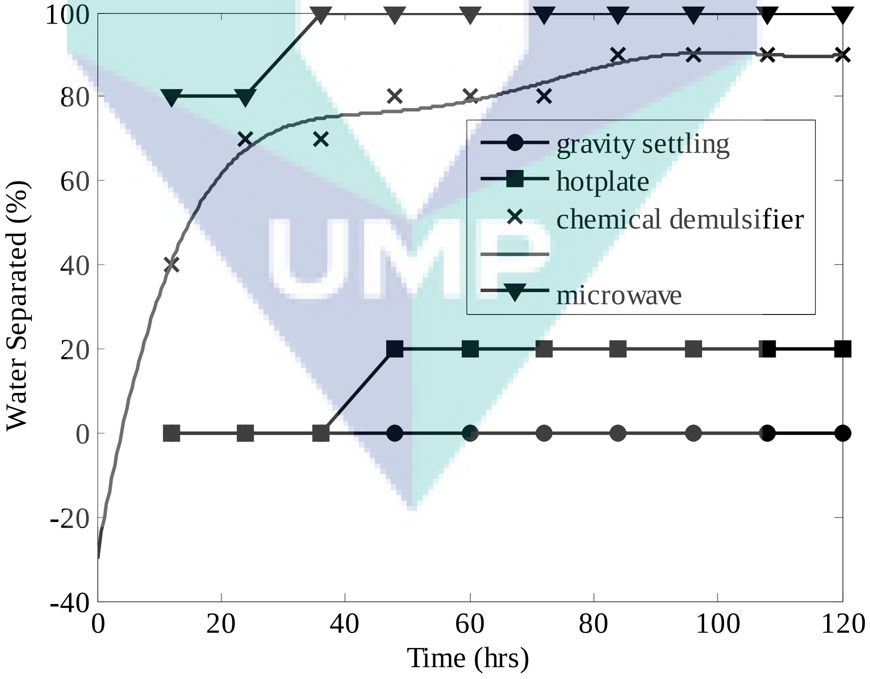
6.5.1 Comparison between Microwave Irradiation and Conventional Methods

The comparison of conventional and microwave demulsification methods were reflected in Figure 6.6 and 6.7. The figures illustrated that at crude oil B, the microwave demulsification offered rapid separation compared to conventional methods, whereas the emulsion was totally demulsified within 30 hours in microwave irradiation compared to chemical demulsifier was separated entirely in 100 hours. This was because of microwave quickly heat emulsion, huge temperature rises and reducing the viscosity of continuous phase, thus favouring the contact among water droplets and coalesce the droplets. Besides, microwave is non-destructive method on emulsion, do not required addition of chemical agents, which do not implies for further waste water treatment (Rajakovic and Skala; 2006). The percentage of water separation for both conventional and microwave method was higher at 50-50 % W/O emulsion. As mentioned in stability part, at higher phase ratio, the droplets tends to interact each other and agglomerate thus perform coalesce. However for both ratios, emulsions could not be treated by using gravity settling due to the high stability of emulsion. As expected, the demulsification efficiency for each crude oil decreases from lighter to heavy crude oil emulsions as a consequence of the higher stability of the emulsion because of the higher content of asphaltenes and resins in the crude oil, ultimately the higher viscosity.

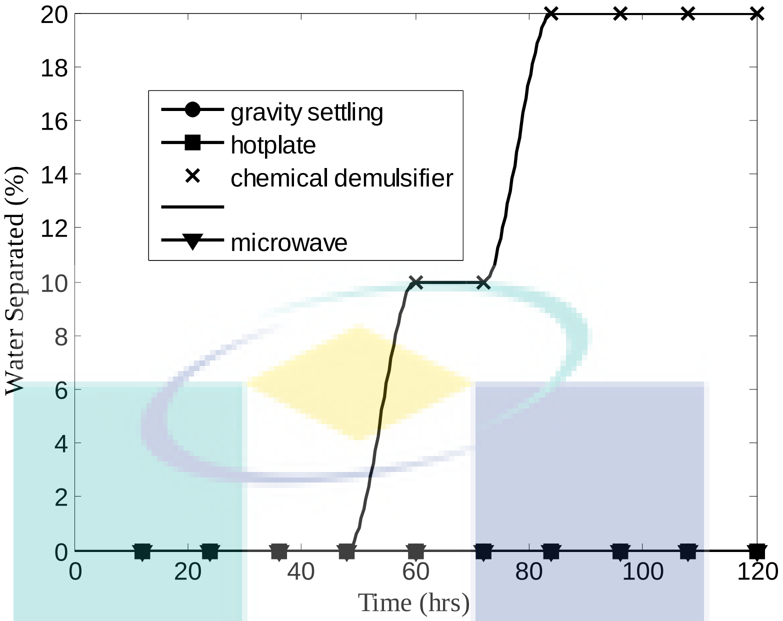
The time required for crude oil A and C for demulsification process is relatively long which within 20 to 40 hours. However, the other researches performed the chemical demulsification of W/O emulsion in a few minutes to one hour (Zhang et al., 2005; Kim et al., 1995). Most of the chemical demulsification studies described in papers have been conducted using lower asphaltenes fraction in which emulsion stability relatively lower than this study.


Water Separated (%)
60
50
40
30
20
10
0
0
20
40
60
80
100
120
Time (hrs)
gravity settling
hotplate
chemical demulsifier
microwave

(a)

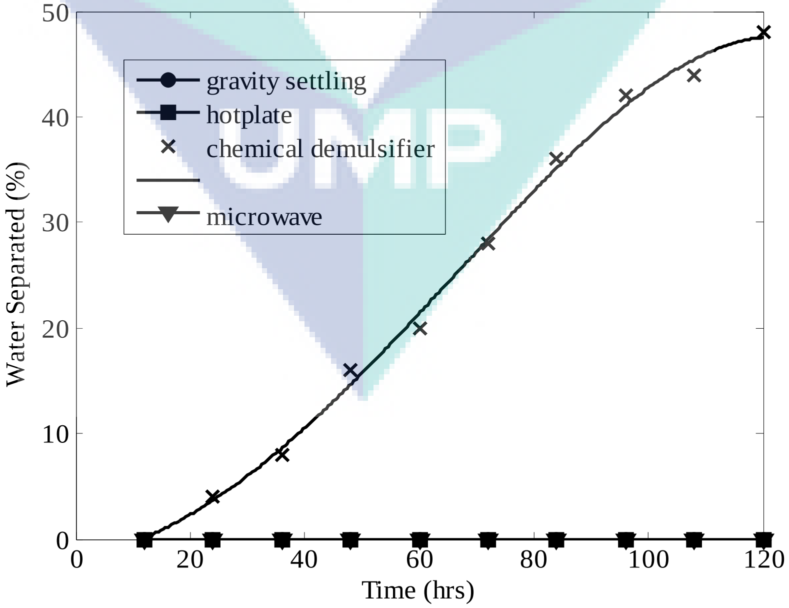

Water Separated (%)
100
80
60
40
20
0
-20
-40
0
20
40
60
80
100
120
Time (hrs)
gravity settling
hotplate
chemical demulsifier
microwave

(b)

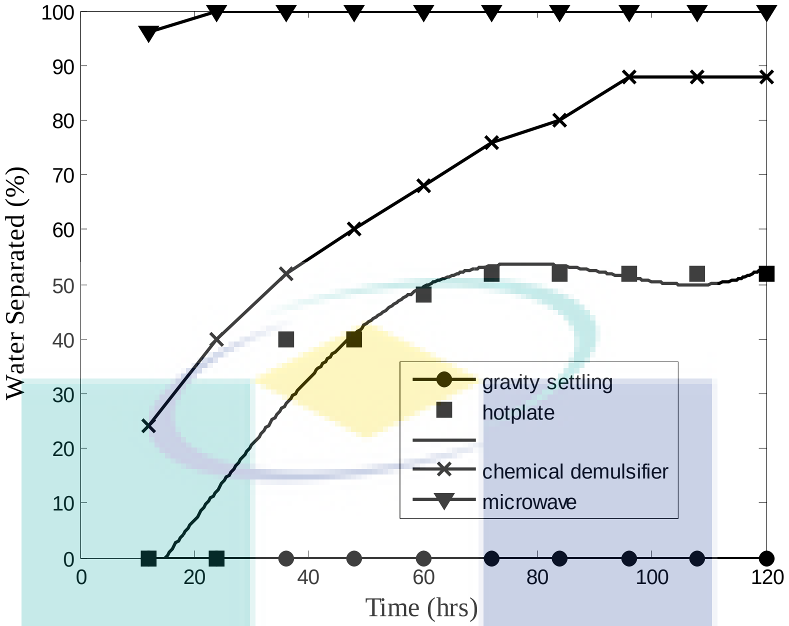


(c)

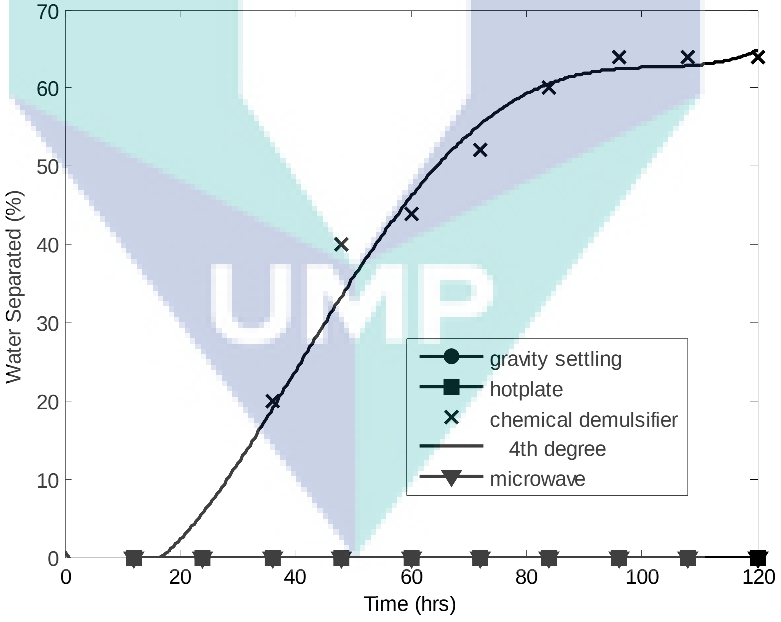
Figure 6.6: Comparison of Conventional and Microwave Methods in Demulsified W/O Emulsion for 20-80 % W/O Emulsion (a) Crude Oil A (b) Crude Oil B (c) Crude Oil C



(a)



(b)



(c)

Figure 6.7: Comparison of Conventional and Microwave Methods in Demulsified W/O Emulsion for 50-50 % W/O Emulsion (a) Crude Oil A (b) Crude Oil B (c) Crude Oil C

Yang et al. (2009) and Xia et al. (2004) have reported that microwave irradiation can accelerate the efficiency of W/O emulsion separation without use the additives. However, in this study, crude oil A and C could not be broken using microwave irradiation alone. For these emulsions, it was necessary to add a demulsifier agent before microwave irradiation. Thus, for crude oil A and C, demulsifier was added into the emulsion and results presented in Figure 6.8. As shown in figure, the demulsification efficiency increased by assisted of demulsifier under experimental conditions, having been irradiated for 3 minutes at 720 W. For both crude oil, the percentage of water separated increased within 60 minutes and crude oil A obtained higher efficiency in separation compared to crude oil C due to the lower viscosity in crude oil properties. This could be proven by observing from Figure 6.8 which, in 5 minutes crude oil A for 50-50 % W/O emulsion clearly separated about 48 %. However for 20-80 % W/O emulsion, flocculation was observed in 64 %. While within 60 minutes, the percentage of water separated increased up to 88 % and 70 % for 50-50 % W/O and 20-80 % W/O emulsion.

Figure 6.9 also demonstrates the phase separation of crude oil C for 20-80 % W/O and 50-50 % W/O emulsion. Both ratios showed the flocculation occurred after 5 minutes of crude oil being irradiated whereas emulsion do not totally separated. In Figure 6.8, crude oil C at 50-50 % W/O emulsion separated about 65 % within 60 minutes and for 20-80 % W/O emulsion, the percentage of water separated is 40 %. Crude oil A and C acquired the percentage of water separated in emulsion increased as phase ratio increases. This was due to the acceleration of demulsifier through emulsion before irradiated in microwave irradiation. Still, these results were contrasted with previous researcher (Guzmán-Lucero et al., 2010), who studied. the effect of demulsifier in microwave effect which 95% of water could be removed within 30 minutes due to the dissimilarity natural surface active presented whereas about 15 wt%, two times smaller than this study.

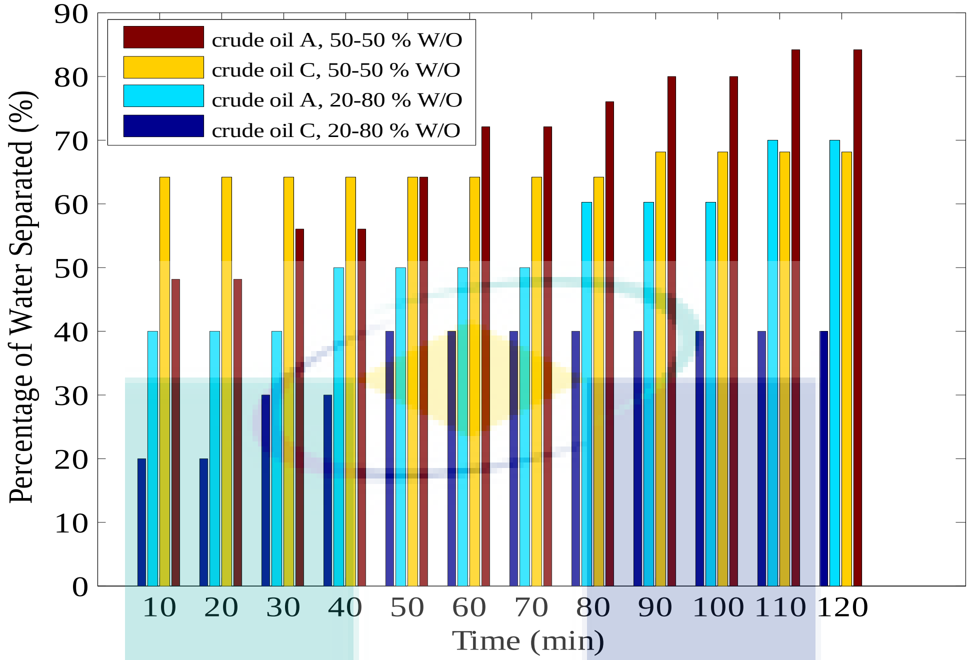


Figure 6.8: Demulsification Efficiency in Microwave Irradiation during 60 Minutes for Crude Oil A and C with addition 0.1% of Demulsifier

(a)

(b)

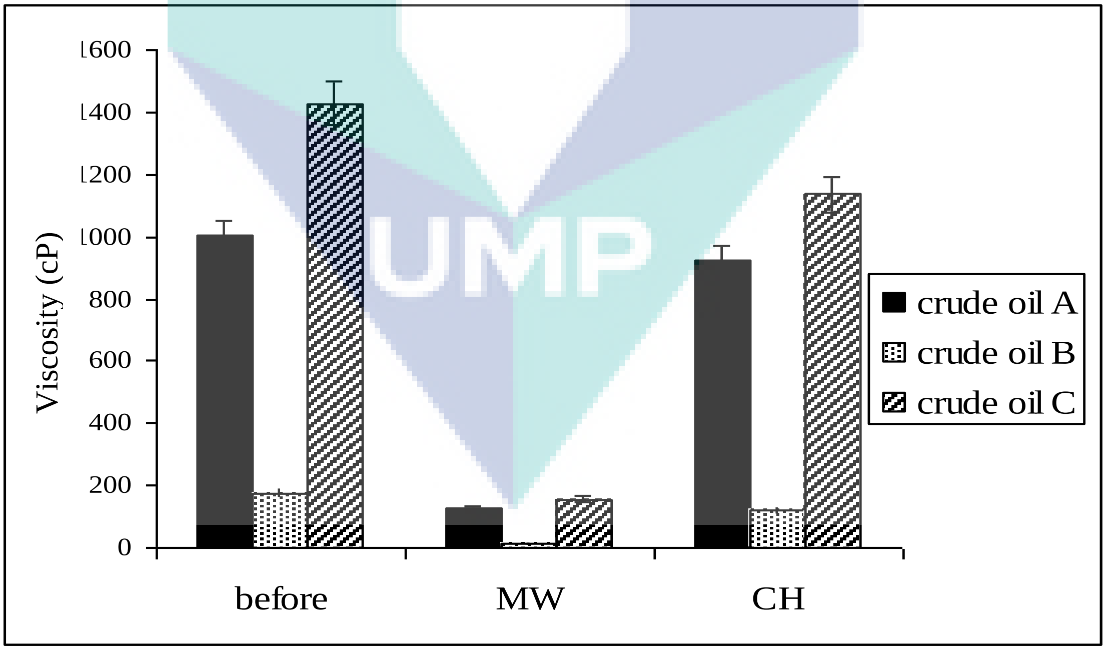
Figure 6.9: Photography of Emulsion after Irradiation in 3 minutes for Crude Oil A and C with 0.1 % Demulsifier at (a) 50-50 % W/O Emulsion (b) 20-80 % W/O Emulsion within 5 minutes Observing the Phase Separation

6.6 COMPARISON BETWEEN MICROWAVE IRRADIATION AND CONVENTIONAL HEATING

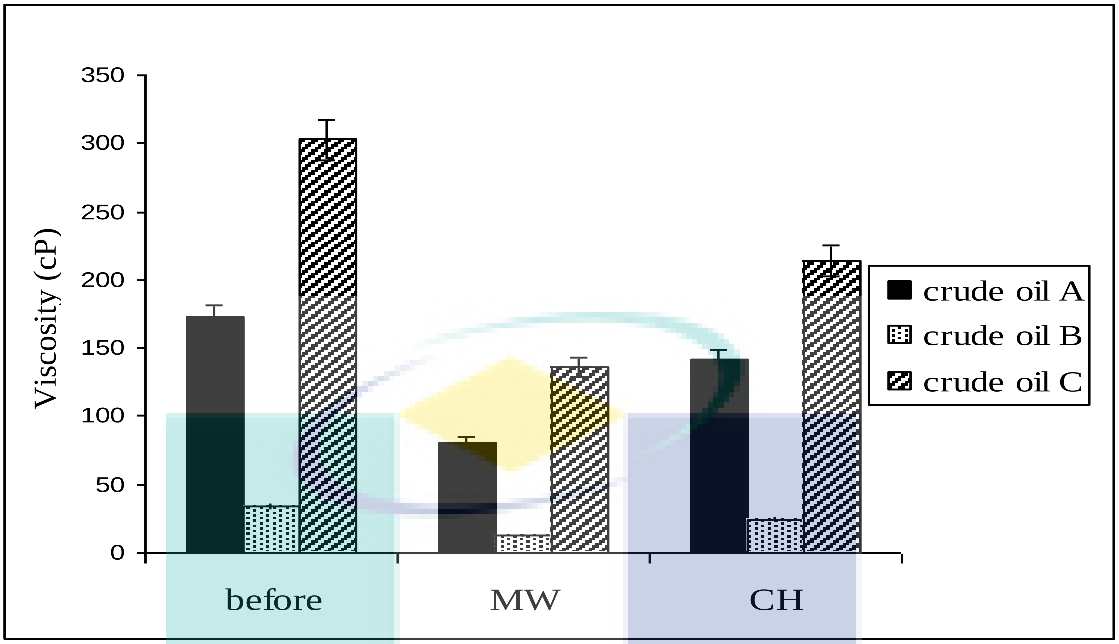
The fundamental in different method of transferring energy from the source to the sample is the main benefit of utilizing the microwave irradiation compared to conventional heating processing. The energy delivered to microwave-absorbing materials is directly penetrated into the sample. The delivering energy generates heat by collisions dipole moment molecules in the emulsion. Thus, the viscosities of microwave and conventional heating can be examined due to the heat transfer mechanisms from both methods.

The viscosities of conventional and microwave irradiation for 50-50 % W/O and 20-80 % W/O emulsion were shown in Figure 6.10. Both ratios showed the lowest viscosity obtained once the emulsion was demulsified in microwave irradiation. Indeed, the percentage of viscosity for 50-50 % W/O emulsion in both before and after demulsified in microwave irradiation were higher than conventional method for crude oils A, B and C were 87.3, 91.4 and 89 % while for conventional, the percentage decreasing viscosity in crude oil A, B and C were 7.64, 32.34 and 20.4 %. This was because of the mechanisms of heating emulsion in both methods was different. In conventional heating, heat was applied to the surface of body, stimulating the outside molecules or atoms. The kinetic energy is gradually transferred to the inside molecules or atoms until the whole body is heated. While microwave irradiation allows volumetric heating of samples by penetrated the electromagnetic wave (Mutyala et al., 2010).

The lower ratio (20-80 % W/O emulsion) also displayed the same result which, viscosity of emulsion was reduced after demulsified in microwave irradiation. However, the decreasing viscosity was lesser than higher ratio because of the content of droplets in 20-80 % W/O emulsion was lower than 50-50 % W/O emulsion. The effect of viscosity was related to temperature. At lower phase ratio, the continuous phase content was dominant thus temperature cannot distribute easily through the whole body of sample in conventional heating. In microwave irradiation, the lower phase ratio reduce the efficiency of electromagnetic to heat emulsion which water only was selected and has ability to absorb electromagnetic field.



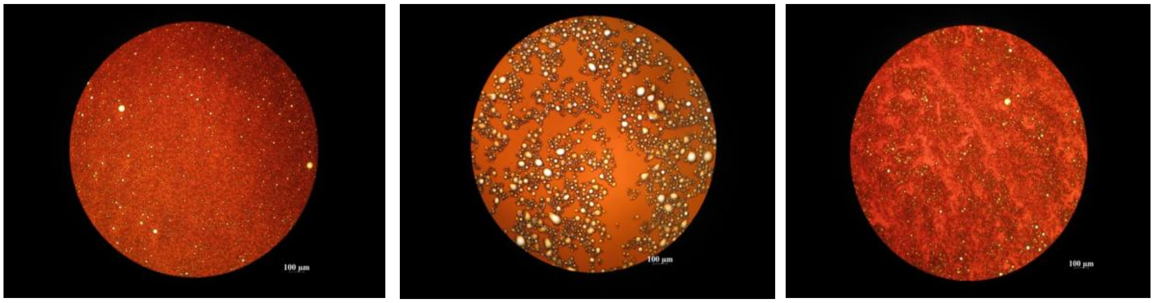
(a)



(b)

Figure 6.10: Effect of Viscosity by Comparison Microwave (MW) and Conventional Heating (CH) (a) 50-50 % W/O Emulsion (b) 20-80 % W/O Emulsion

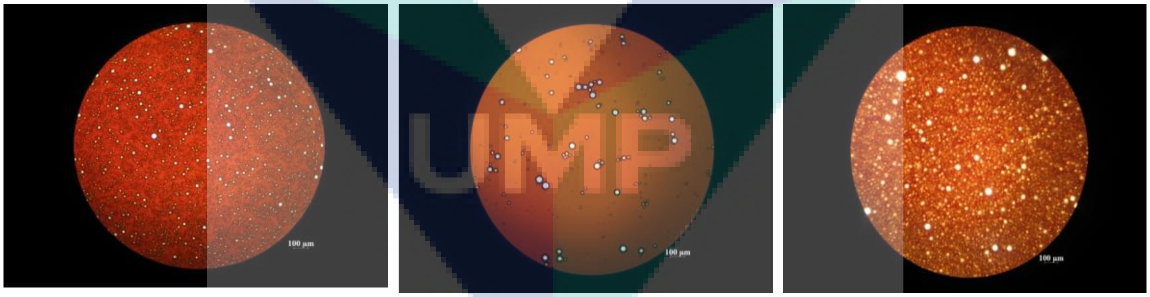
The droplets size distribution of the crude oils before and after demulsified the emulsion were illustrated in Figure 6.11 and 6.12. Figure 6.11 indicates the scatter of droplets size in crude oil B higher compared to crude oil A and C due to the lower viscosity of crude oil thus droplets can interact each other easily compared to crude oil A and C. While when compared the crude oil A and C, crude oil C illustrated non-statistical distribution due to the sedimentation and weak interaction between the droplets. This figure supported the crude oil characteristics studied and discussed in Chapter 5. The droplets size distribution can be concluded generally become much tighter as the droplets size is increased.



(a) (b) (c)

Figure 6.11: Microscope Image of an Emulsion in Crude Oil A, B and C before Demulsified in Microwave

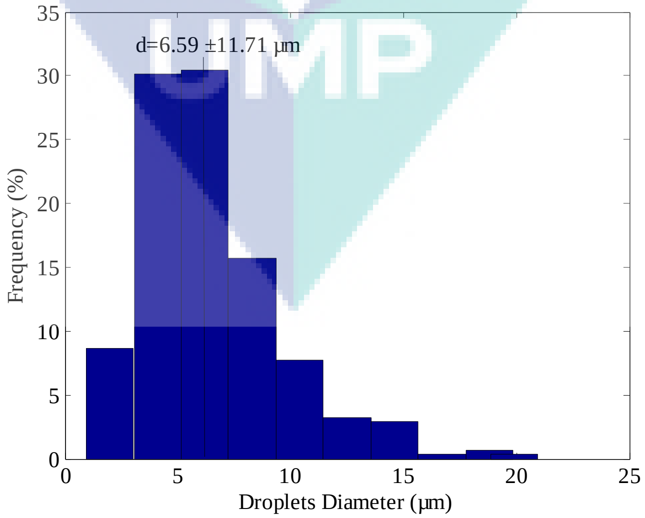
After emulsions were demulsified in microwave irradiation, the droplets literally high and scattered far away from each other and the droplet size distribution quite uniform. The quite long distance between droplets existed in crude oil B. However, the size distribution in crude oil A and C do not display high scattered of droplets because of the high viscosity of the crude oil itself and this was reason for the lower separating of emulsion even demulsified in microwave.



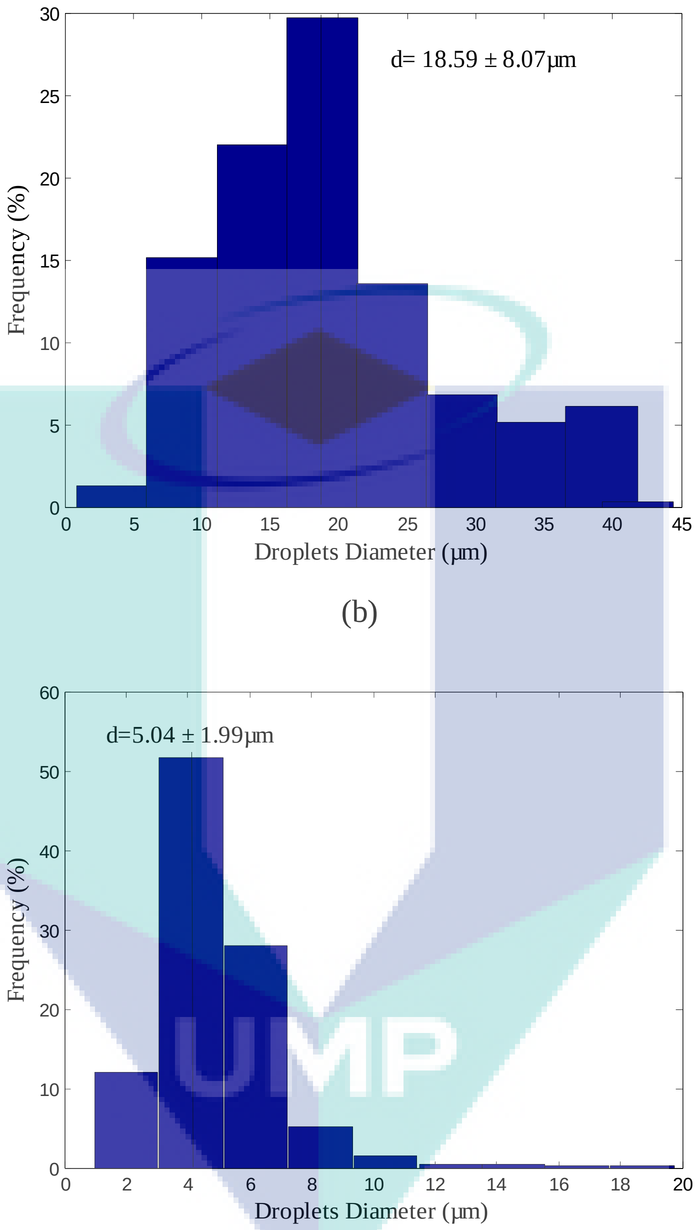
(a) (b) (c)

Figure 6.12: Microscope Image of an Emulsion in Crude Oil A, B and C after Demulsified in Microwave

The effectiveness of microwave irradiation was also determined by observing the droplets diameter of emulsion. According to Figure 6.13, the emulsion droplets were dependent on the effectiveness of demulsification process in microwave irradiation. As discussed previously, the emulsion do not separated in microwave irradiation and demulsifier was added to enhance the separation process. This happens to all emulsions except the emulsion prepared from crude oil B. Figure 6.13 showed the droplets diameter before demulsified in microwave irradiation whereas emulsion in crude oil A and C obtained 6.59 and 5.04 μm smaller than three times emulsion prepared in crude oil B (18.59 μm). The droplets diameter increases after demulsified in microwave irradiation as postulated from Holtze et al. (2006), the heating increases with droplets size diameter. The droplets diameter of emulsion increases after demulsified (Figure 6.14) in microwave heating which for crude oil A, the mean droplets increase up to 12.1 μm. While for crude oil B, the mean droplets diameter showed there was a slightly increasing about 19.5 μm due to the droplets are expected coalescence each other and only small droplets can be observed through microscope using 10x resolutions. Indeed, when studied the distribution of droplets, emulsion in crude oil B obtained a uniform distribution compared before demulsified emulsion due to the volumetric heating arises in microwave irradiation. From figure, the droplets diameter from crude oil C cannot be examined because emulsion still viscous and accumulate each other thus it was hard to measure droplets diameter. Besides, Urdahl et al. (1997) postulated that viscosity is higher when the size distribution is narrow due to the low degree of polydispersity.



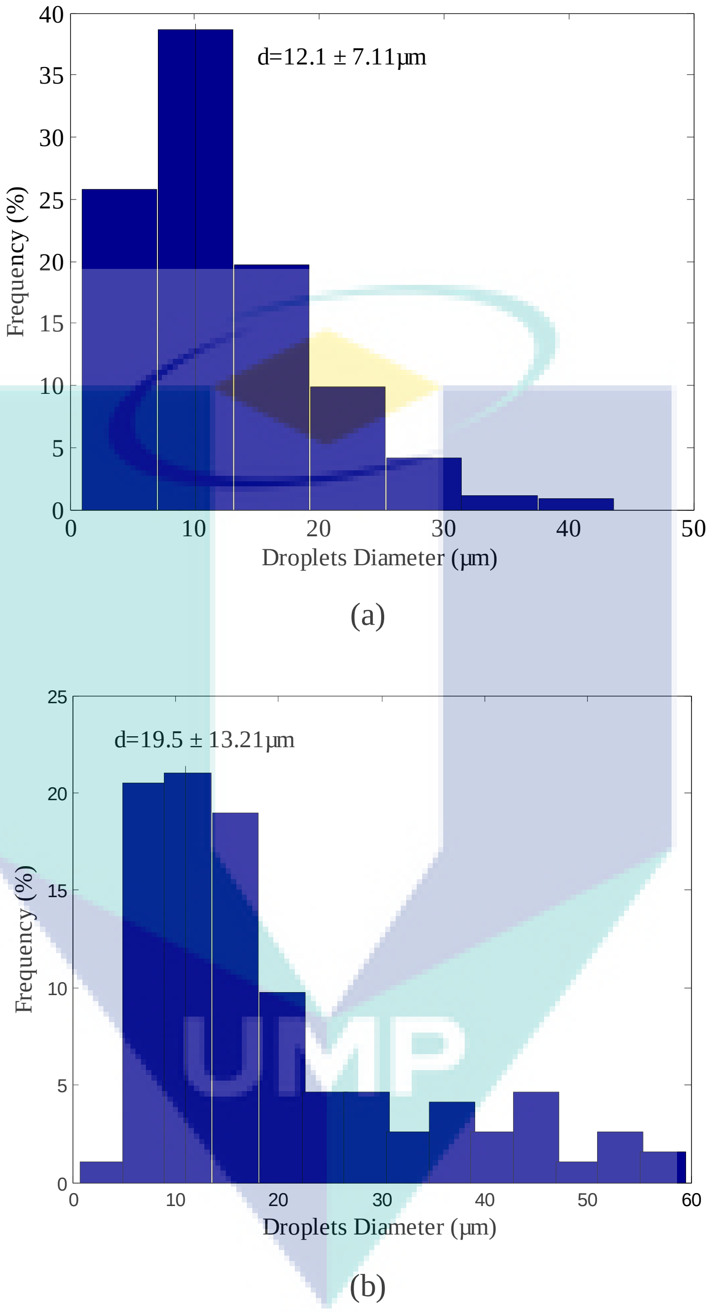
(a)



(b)

(c)

Figure 6.13: Droplets Diameter (µm) before Demulsified in Microwave Irradiation (a) Crude Oil A (b) Crude Oil B (c) Crude Oil C



(a)

(b)

Figure 6.14: Droplets Diameter (µm) before Demulsified in Microwave Irradiation (a) crude oil A (b) crude oil B

6.7 EFFECT OF VOLUME FRACTION ON DIELECTRIC CONSTANT, DIELECTRIC LOSS, WAVELENGTH AND MICROWAVE PENETRATION DEPTH

Theoretically the effect of volume fraction on dielectric properties is important to better understanding the interaction between droplets in the emulsion. Figure 6.15 shows the effect of dielectric constant at 0.0625, 0.171 and 0.32 of volume fraction. By measurements, it is observed that higher volume fraction (Φ = 0.32) obtained higher dielectric constant within radiation time. It would seem reasonable to believe that at higher volume fraction, more droplets exist thus higher interaction with the electric fields therefore increase in the dielectric constant. However, the dielectric constant for higher volume fraction (Φ = 0.32) decreases from 35.2 to 25.9 and lower volume fraction (Φ = 0.0625) shows only slightly decreases from 9.1 to 7.6 because the abrupt changing of dielectric constant at higher volume fraction compared to lower volume fraction due to the decreasing of heat generation within radiation time and the compactness of molecules in these emulsions. This results was supported the explanation from Calla et al. (2007) who studied the effect of microwave irradiation with radiation time in soil.

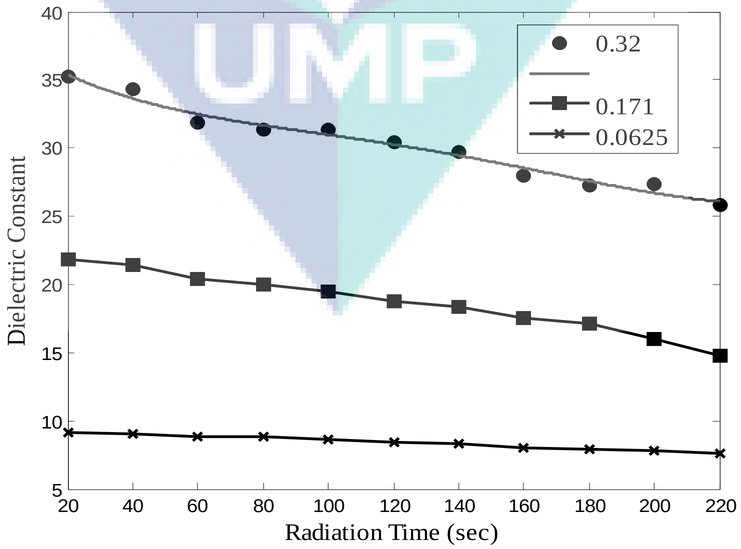


Figure 6.15: Effect of Dielectric Constant within Radiation Time

Figure 6.16 shows the effects of tangent loss with temperature in varied volume fraction. It can be seen that the tangent loss exponential decreased as increasing temperature when emulsion is heated under microwave irradiation. Volume fraction at 0.32 has a decreases tangent loss from 0.081 at 50.71^{o}C to 0.052 at 106.14^{o}C can be explained by the reduction of interaction matter with the electric field of the incident radiation. Initially, the droplets absorb more electromagnetic wave due to the polar molecules exist in the droplets. However, as radiation time increase, temperature also increase and lead the decreasing of dielectric properties due to the decreasing of heat generation.

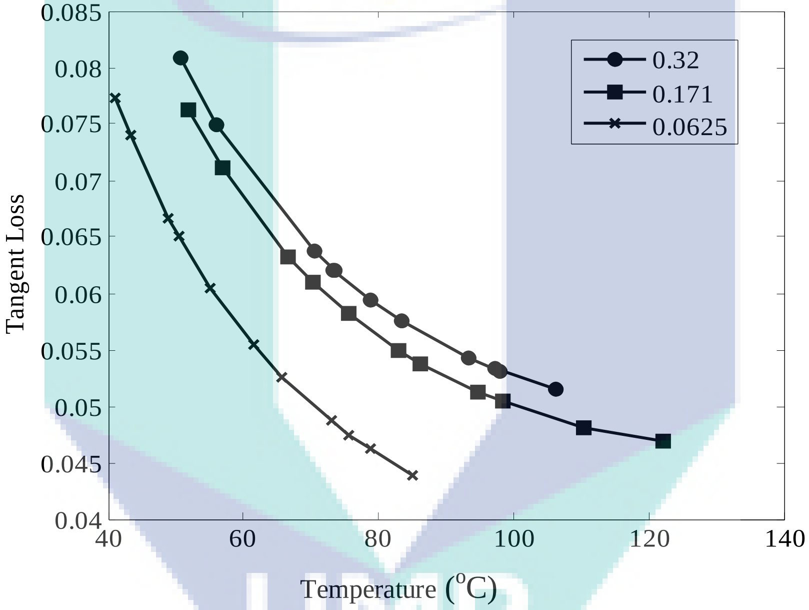


Figure 6.16: Plots of Tangent Loss (tan δ) with Temperature (^{o}C) in Varied Volume Fraction

Volume fraction has the greater influence in microwave irradiation due to the influence on dielectric properties. Figure 6.17 gives the effect of wavelength and penetration depth at various volume factions. As revealed by the figure, the wavelength and penetration depth decrease in all the range of volume fraction. As discussed in previous, the increasing volume fraction leads to the increasing of the droplets interaction thus, the propagate wave more rapidly thereafter penetration depth rapidly decreased. As mention before, penetration depth is a depth which power has been attenuated to 1/e times approximately. As electromagnetic introduced to the medium, the transmitted radiation would gets attenuated exponentially while passing through medium and acquired the higher frequency. The microwaves operate at high frequency has a short wavelength which corresponds to a smaller penetration depth (Rao et al., 1988; Rattanadecho, 2006).

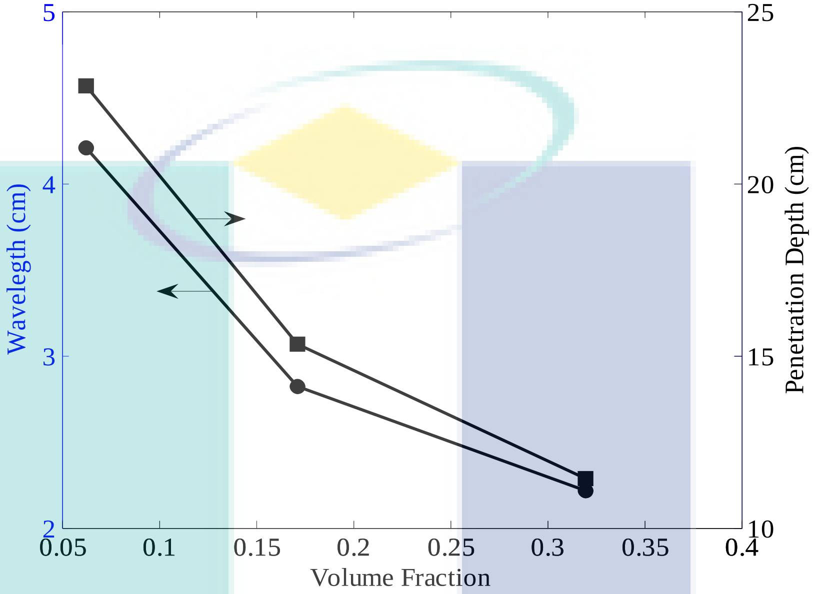


Figure 6.17: Effect of Penetration Depth, D_p and Wavelength, λ_m on Varied Volume Fraction

A convenient expression for penetration depth, D_p as a function of permittivity, ε is shown in Equation 6.2, respectively.

$$D_P = \frac{\lambda\sqrt{\varepsilon'}}{2\Pi\,\varepsilon''_{eff}} \tag{6.2}$$

6.8 OPTIMISATION

6.8.1 Optimisation for Crude Oil A

To study the optimisation of emulsion demulsification, three variables; microwave power, microwave processing time and demulsifier concentration were investigated in crude oil A. As discussed previously, emulsions of crude oil A can be separated by chemical demulsifiers before microwave irradiation introduced. The water separation yield obtained from experiments that based on the experimental design from Design of Expert was given in Table 6.1.

Table 6.1: 2^3 Factorial Design with Response

Run	Type	Factor A, power (Watt)	Factor B, time (min)	Factor C, concentration (wt %)	Response, water separated (%)
1	Fact	540	2.0	0.05	30.8
2	Fact	900	2.0	0.05	28.8
3	Fact	540	3.0	0.05	34.8
4	Fact	900	3.0	0.05	24.6
5	Fact	540	2.0	0.15	34.0
6	Fact	900	2.0	0.15	36.0
7	Fact	540	3.0	0.15	34.2
8	Fact	900	3.0	0.15	30.8
9	Axial	540	2.5	0.10	40.8
10	Axial	900	2.5	0.10	32.0
11	Axial	720	2.0	0.10	36.2
12	Axial	720	3.0	0.10	38.0
13	Axial	720	2.5	0.05	40.8
14	Axial	720	2.5	0.15	44.6
15	Center	720	2.5	0.10	40.2

16	Center	720	2.5	0.10	42.8
17	Center	720	2.5	0.10	45.0
18	Center	720	2.5	0.10	44.6
19	Center	720	2.5	0.10	44.2

The analysis of variance (ANOVA) from DOE was analysed to measure the variability of the observed response values as shown in Table 6.2. The value of R^2 is 0.94801 which the second-order model explained about 94.801% of the variability observed in the gain.

Table 6.2: Analysis of Variance (ANOVA)

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Model	617.457	9	68.6063	18.2351	<0.0001	significant
A	50.176	1	50.176	13.3364	0.0053	
B	1.156	1	1.156	0.30726	0.5929	
C	39.204	1	39.204	10.4202	0.0104	
A2	102.257	1	102.257	27.1793	0.0006	
B2	80.1946	1	80.1946	21.3152	0.0013	
C2	0.09098	1	0.09098	0.02418	0.8799	
AB	23.12	1	23.12	6.14514	0.0351	
AC	14.58	1	14.58	3.87527	0.0805	
BC	2.88	1	2.88	0.76548	0.4044	
Residual	33.8609	9	3.76232			
Lack of Fit	18.6289	5	3.72578			not significant
Pure Error	15.232	4	3.808			
Cor Total	651.318	18				
Std. Dev.	1.93967			R-Squared		0.94801
Mean	37.0105			Adj R^2		0.89602

The application of the response surface methodology (RSM) yielded the following regression equation. The empirical relationship between response and variables in coded unit are summarised in Table 6.3 and the equation was given in Equation 6.3.

Table 6.3: Regression Coefficient Values for Response Surface

Coefficients	Values
b_o	42.9856
b_1	-2.24
b_2	-0.34
b_3	1.98
b_1^2	-6.1175
b_2^2	-5.4175
b_3^2	0.18247
b_{12}	-1.7
b_{13}	1.35
b_{23}	-0.6

$$Y=42.9856–2.24X_1-0.34X_2+1.98 X_3-6.1175 X_1^2 -5.4175X_2^2+0.18247X_3^2 -1.7X_1 X_2+1.35X_1 X_3-0.6X_2X_3 \quad (6.3)$$

Each of observation values y_A is compared with predicted value, y_o as shown in Table 6.4.

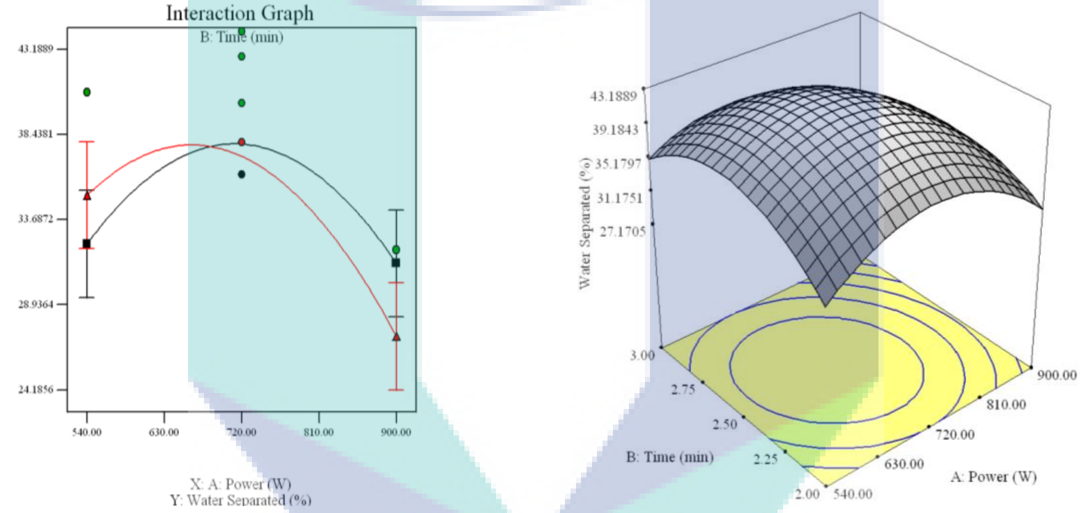
Table 6.4: Observed Response and Predicted Values

Actual value (y_A)	Predicted value (y_O)	Errors (y_A-y_O)	Squared errors
30.8	31.2830	-0.4830	0.2333
28.8	27.5030	1.2970	1.6822
34.8	35.2030	-0.4030	0.1624
24.6	24.6230	-0.0230	0.0005

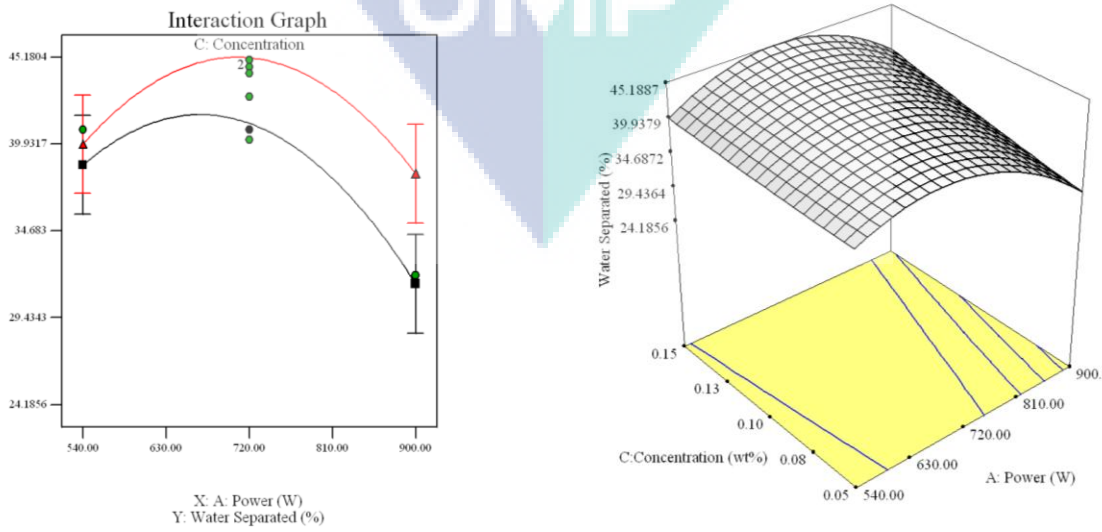
34.0	33.7430	0.2570	0.0661
36.0	35.3630	0.6370	0.4058
34.2	35.2630	-1.0630	1.1299
30.8	30.0830	0.7170	0.5141
40.8	39.1080	1.6920	2.8627
32.0	34.6280	-2.6280	6.9066
36.2	37.9080	-1.7080	2.9174
38.0	37.2280	0.7720	0.5959
40.8	41.1880	-0.3880	0.1506
44.6	45.1480	-0.5480	0.3003
40.2	42.9856	-2.7856	7.7594
42.8	42.9856	-0.1856	0.0344
45.0	42.9856	2.0144	4.0579
44.6	42.9856	1.6144	2.6064
44.2	42.9856	1.2144	1.4748

Sum of squared errors = 33.8609
Mean squared errors = 1.7822

The effects of microwave power, time processing and concentration of demulsifier on the yield of water separation percentage, as well as their interaction are shown in Figure 6.18. An increasing microwave power resulted in higher percentage of water separation while the percentage (yield) reached a maximum when both microwave power and time processing up to a certain value, with no significantly further improvement thereafter. Time processing and concentration of demulsifier in microwave irradiation had similar effect on the yield. The yield increased to a certain value with elevating time and concentration (Figure 6.18c). A different effect on the percentage of water separated was shown for concentration of demulsifier. As shown in Figure 6.18b and c, there were plateau in relation to concentration of demulsifier, indicating that the percentage of water separated increased with increasing the concentration. High percentage of water separated could only be produced at higher demulsifier concentration. Molecules presented in the emulsion could be accelerated by increasing the concentration of demulsifier. Therefore, in this model, microwave power acquired high effect on the percentage of water separated due to the fact that the wavelength and penetration depth increases along with microwave power. Thus, the ability of electromagnetic to penetrate into the emulsion could be evaluated by correlation of both penetration depth and wavelength with microwave power. The overall results obtained show that there are limitation of microwave power, time processing in microwave irradiation and also concentration of demulsifier to achieve optimum point of water separated. Based on Figure 6.18, the maximum yield of water separation predicted through this model is 45.10 % at microwave power 710 W in 2.40 min with 0.15 wt% demulsifier.



(a)



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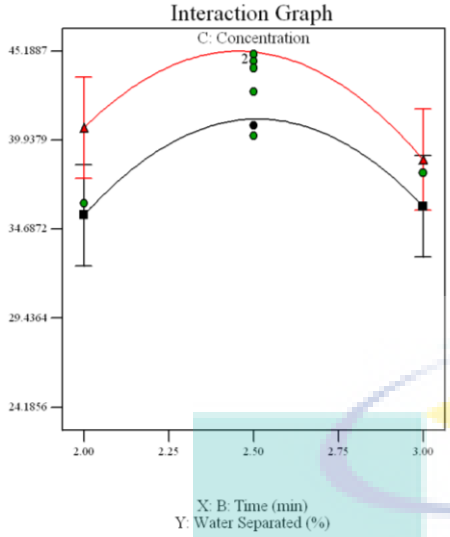
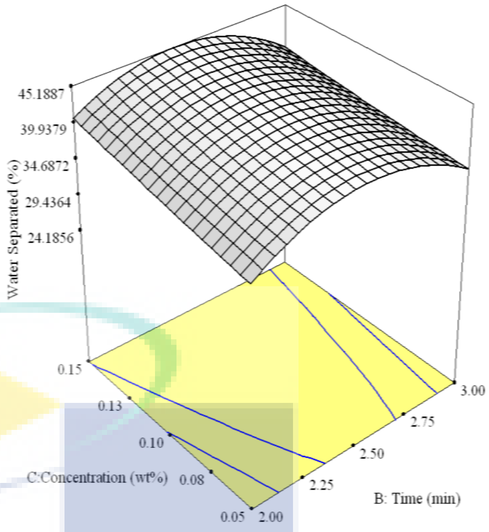

Interaction Graph
C: Concentration
45.1887
39.9379
34.6872
29.4364
24.1856
2
2.00
2.25
2.50
2.75
3.00
X: B: Time (min)
Y: Water Separated (%)


45.1887
39.9379
34.6872
29.4364
24.1856
Water Separated (%)
0.15
0.13
0.10
0.08
0.05
C:Concentration (wt%)
2.00
2.25
2.50
2.75
3.00
B: Time (min)

(c)

Figure 6.18: Response Surface of Predicted Water Separated in Microwave Irradiation by Interaction (a) Power-Time (b) Power-Concentration and (c) Time-Concentration

6.8.2 Optimisation for Crude Oil B

The variables in optimisation of crude oil B involved microwave power and time processing in microwave. The percentage of water separated in crude oil B obtained from the experiments based on the experimental design are given in Table 6.5. The model was considered as a second-order model for the transistor gain data. The combination of variables can be treated as 2^2 factorial design using Yates' Method (Lazić, 2004) to calculate response from main and interactive effects from the factorials.

Table 6.5: 2^2 Factorial Design with Response

Run	Type	Factor A, power (Watt)	Factor B, time (min)	Response, water separated (%)
1	Fact	540	2.0	54.4
2	Fact	900	2.0	52.6
3	Fact	540	3.0	57.0
4	Fact	900	3.0	49.0
5	Axial	540	2.5	56.6
6	Axial	900	2.5	50.2

7	Axial	720	2.0	60.0
8	Axial	720	3.0	62.0
9	Center	720	2.5	65.8
10	Center	720	2.5	64.2
11	Center	720	2.5	63.6
12	Center	720	2.5	64.8
13	Center	720	2.5	63.0

Subsequently, the significance interaction of each factors were showed in an analysis of variance (ANOVA) from Table 6.6. The factors can be declared as significant when the Prob > F is less than 0.05, thus A and A2 are significantly model terms. The "Lack of Fit F-value" of 2.73 implies the *Lack of Fit* is not significant relative to the pure error. By analysis of variance, the R^2 value of this model was determined to be 0.96451, which showed that the regression model defined well the true behaviour of the system.

Table 6.6: Analysis of Variance (ANOVA)

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Model	388.011	5	77.6023	38.0462	<0.0001	significant
A	43.74	1	43.74	21.4445	0.0024	
B	0.16667	1	0.16667	0.08171	0.7833	
A2	242.433	1	242.433	118.858	<0.0001	
B2	8.64266	1	8.64266	4.23725	0.0785	
AB	9.61	1	9.61	4.7115	0.0666	

Residual	14.2778	7	2.03969			
Lack of Fit	9.58982	3	3.19661	2.72748	0.1784	not significant
Pure Error	4.688	4	1.172			
Cor Total	402.289	12				
Std. Dev.	1.42818			R^2		0.96451
Mean	58.7077			Adj. R^2		0.93916

The application of the response surface methodology (RSM) yielded the following regression equation. The empirical relationship between response and variables in coded unit are summarised in Table 6.7. While the mathematical model representing the yield of water separation percentage as a function of the independent variables within the region under this study was expressed from Equation 6.4.

Table 6.7: Regression Coefficient Values for Response Surface

Coefficients	**Values**
b_o	63.8483
b_1	-2.7
b_2	0.16667
b_1^2	-9.369
b_2^2	-1.769
$b_1 b_2$	-1.55

$$Y= 63.8483-2.7\ X_1+0.16667\ X_2-9.369X_1^2-1.769X_2^2-1.55\ X_1X_2 \tag{6.4}$$

The yield or response expression to be optimised was the water separated in percent (%). Table 6.8 listed the actual and predicted of responses from model. The differential values between actual and predicted are ranging between -1.9 and 1.9. The comparison of the error and squared error indicates that none of the individual error exceeds twice of the squared root of the errors. Due to this smaller differential, the regression model indicates in good adequacy.

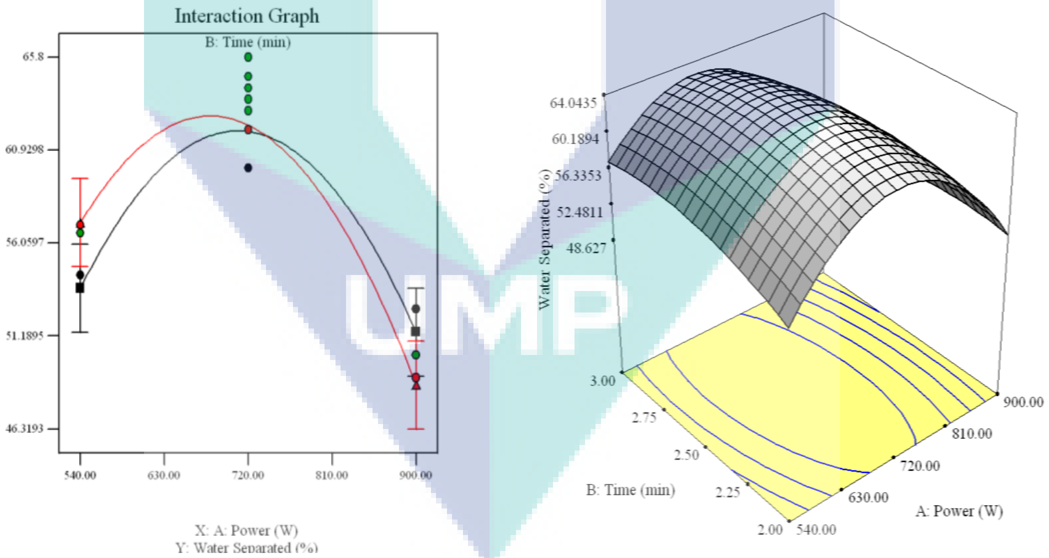
Table 6.8: Observed Response and Predicted Values

Actual value (y_A)	**Predicted value (y_O)**	**Errors (y_A-y_O)**	**Squared errors**
54.4	53.69368	0.706322	0.498891
52.6	51.39368	1.206322	1.455212
57	57.12701	-0.12701	0.016132
49	48.62701	0.372989	0.13912
56.6	57.17931	-0.57931	0.3356
50.2	51.77931	-1.57931	2.494221
60	61.91264	-1.91264	3.658206
62	62.24598	-0.24598	0.060505
65.8	63.84828	1.951724	3.809227
64.2	63.84828	0.351724	0.12371
63.6	63.84828	-0.24828	0.061641
64.8	63.84828	0.951724	0.905779
63	63.84828	-0.84828	0.719572

Sum of squared errors = 14.2778

Mean squared errors = 1.09829

The interaction and 3D graphs of optimisation in crude oil B arises between two variables are identified and explained in Figure 6.19. Both variables obtain quadratic trend of graphs however, microwave power has significant factor compared to time of microwave processing. The reason for this result due to the characteristics of crude oil B which crude oil B acquired a light type of crude oil. Thereby, the thermal heating occurred could be avoided when demulsified under microwave irradiation. The thermal heating was correlated to the higher temperature. In crude oil B, the light crude oil might have lower interaction of molecules compared to heavy crude oil. Thus, as increasing time, only slightly temperature increased arises in this type of crude oil. The maximum yield of water separation predicted from the response surface under microwave irradiation illustrates in Figure 6.19b. The response surface plot in figure shows this model is quadratic. The maximum yield of water separation predicted through this model is 64.0661 % at microwave power 692 W in 2.56 min.



(a) (b)

Figure 6.19: Response Surface of Predicted Water Separated by Interaction Power (X_1) and Time (X_2) in Microwave Irradiation (a) Interaction (b) 3D Graph

6.8.3 Optimisation for Crude Oil C

This crude oil also selected same variables (microwave power, time of microwave processing and concentration of demulsifier) with factorial design 2^3 factorial design. The water separation yield obtained from experiments that based on the experimental design is given in Table 6.9.

Table 6.9: 2^3 Factorial Design with Response

Run	Type	Factor A, power (Watt)	Factor B, time (min)	Factor C, concentration (wt %)	Response, water separated (%)
1	Fact	540	2.0	0.05	28.6
2	Fact	900	2.0	0.05	30
3	Fact	540	3.0	0.05	26.2
4	Fact	900	3.0	0.05	30.2
5	Fact	540	2.0	0.15	32.4
6	Fact	900	2.0	0.15	30.4
7	Fact	540	3.0	0.15	28.8
8	Fact	900	3.0	0.15	32.4
9	Axial	540	2.5	0.10	32.4
10	Axial	900	2.5	0.10	36.2
11	Axial	720	2.0	0.10	36.0
12	Axial	720	3.0	0.10	32.2
13	Axial	720	2.5	0.05	38.0
14	Axial	720	2.5	0.15	38.0
15	Center	720	2.5	0.10	36.8
16	Center	720	2.5	0.10	36.0
17	Center	720	2.5	0.10	38.0
18	Center	720	2.5	0.10	38.0
19	Center	720	2.5	0.10	36.2

The analysis of variance (ANOVA) from DOE was analysed to measure the variability of the observed response values as shown in Table 6.10. The value of R-squared from regression coefficient table is 0.94389. That is, the second-order model explained about 94.389 % of the variability observed in the gain. The adjusted R^2 for this model is 0.88777 which considered as good fit for the observed response values. The Prob>F values of the model were 0.0001 which indicated that the model fitness was significant. The values of Prob> F less than 0.05 indicate model terms are not significant, and in this crude oil, A, A2, B2 and AB display the significant model terms. The 'Lack of Fit F-Value' of 2.33 implies the Lack of Fit is not significant relative pure error. Thus model was acceptable to fit.

Table 6.10: Analysis of Variance (ANOVA)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	242.036	9	26.8929	16.8208	0.0001	significant
A	11.664	1	11.664	3.61273	0.0244	
B	5.776	1	5.776	5.06633	0.0898	
C	8.1	1	8.1	22.6082	0.0509	
A2	36.1457	1	36.1457	25.1629	0.0010	
B2	40.2302	1	40.2302	0.00676	0.0007	
C2	0.01081	1	0.01081	5.2571	0.9363	
AB	8.405	1	8.405	1.12898	0.0476	
AC	1.805	1	1.805	0.02815	0.3157	
BC	0.045	1	0.045		0.8705	

Residual	14.3891	9	1.59879			
Lack of Fit	10.7091	5	2.14182	2.32807	0.2166	not significant
Pure Error	3.68	4	0.92			
Cor Total	256.425	18				
Std. Dev.	1.26443			R^2	0.94389	
Mean	33.5158			Adj. R^2	0.88777	

The application of the response surface methodology (RSM) yielded the following regression equation. The empirical relationship between response and variables in coded unit are summarised in Table 6.10 and the equation was given in Equation 6.5.

Table 6.11: Regression Coefficient Values for Response Surface

Coefficients	**Values**
b_o	37.4165
b_1	1.08
b_2	-0.76
b_3	0.9
b_1^2	-3.63711
b_2^2	-3.83711
b_3^2	0.06289
b_{12}	1.025
b_{13}	-0.475
b_{23}	0.075

$$Y=37.4165+1.08\,X_1-0.76X_1+0.9X_3-3.63711\,X_1^2-3.83711X_2^2+0.06289X_3^2 \\ +1.025X_1\,X_2-0.475X_1\,X_3+0.075X_2X_3 \qquad (6.5)$$

where Y is the response of water separated and X_1, X_2 and X_3 are the coded variables for microwave power, time of processing and concentration of demulsifier, respectively.

Table 6.12 listed the actual and predicted of responses from model. The differential values between actual and predicted are ranging between -1.41 and 1.66. The agreement between actual and predicted value of percentage water separation yield confirmed the significance of model. Thus, due to this smaller differential, the regression model indicates in good adequacy.

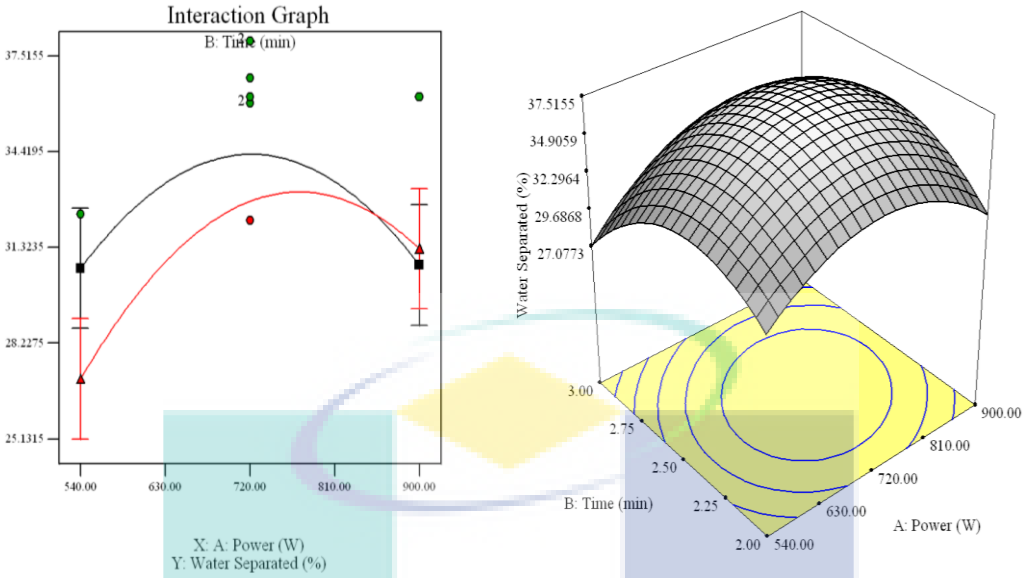
Table 6.12: Observed Response and Predicted Values

Actual value (y_A)	**Predicted value (y_O)**	**Errors (y_A-y_O)**	**Squared errors**
28.6	29.41015	-0.81015	0.656351
30.0	30.47015	-0.47015	0.221045
26.2	25.69015	0.509845	0.259942
30.2	30.85015	-0.65015	0.422701
32.4	32.01015	0.389845	0.151979
30.4	31.17015	-0.77015	0.593138
28.8	28.59015	0.209845	0.044035
32.4	31.85015	0.549845	0.30233
32.4	32.69938	-0.29938	0.089629
36.2	34.85938	1.340619	1.797258

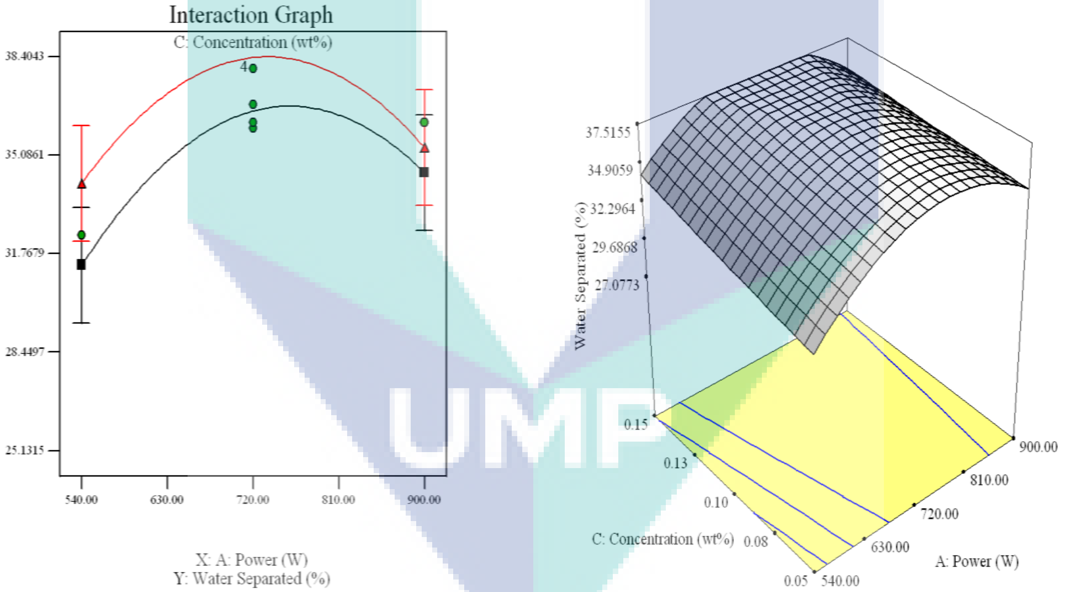
36.0	34.33938	1.660619	2.757654
32.2	32.81938	-0.61938	0.383633
38.0	36.57938	1.420619	2.018157
38.0	38.37938	-0.37938	0.14393
36.8	37.41649	-0.61649	0.380066
36.0	37.41649	-1.41649	2.006458
38.0	37.41649	0.583505	0.340478
38.0	37.41649	0.583505	0.340478
36.2	37.41649	-1.21649	1.47986

Sum of squared errors = 14.3891
Mean squared errors = 0.75732

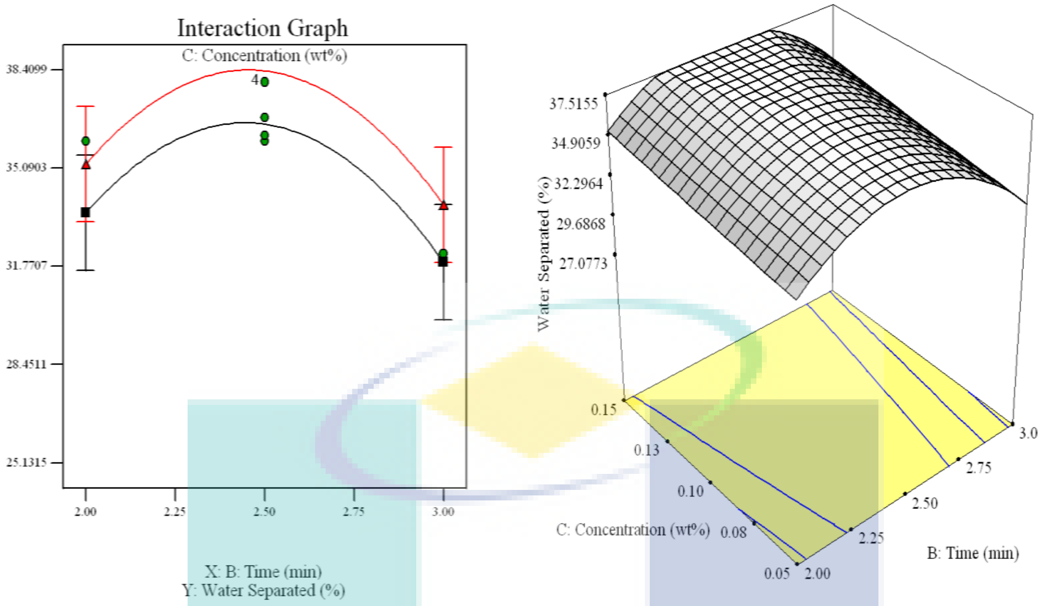
As shown in Figure 6.20a, there was an optimal value for microwave power and time processing in microwave to obtain the highest percentage of water separated. Indeed, microwave power and time processing arises a maximum point in the experimental region. However both Figure 6.20b and c display there were plateau in relation to concentration of demulsifier, which also as same in crude oil A that indicating that the concentration do not affected in this microwave-assisted chemical system. This is due to the higher asphaltenes presented in this crude oil. The content of asphaltenes in crude oil can be an indicator in determining the viscosity of crude oil. Crude oil C had higher viscosity thus as increasing the demulsifier concentration in the microwave-assisted system conveyed thermal heating in microwave system. Thus, the concentration of demulsifier was allowed of 0.14wt% at 767 W in 2.50 min.


Interaction Graph
B: Time (min)
37.5155
34.4195
31.3235
28.2275
25.1315
540.00
630.00
720.00
810.00
900.00
X: A: Power (W)
Y: Water Separated (%)
Water Separated (%)
37.5155
34.9059
32.2964
29.6868
27.0773
3.00
2.75
2.50
2.25
2.00
B: Time (min)
540.00
630.00
720.00
810.00
900.00
A: Power (W)

(a)


Interaction Graph
C: Concentration (wt%)
38.4043
35.0861
31.7679
28.4497
25.1315
540.00
630.00
720.00
810.00
900.00
X: A: Power (W)
Y: Water Separated (%)
Water Separated (%)
37.5155
34.9059
32.2964
29.6868
27.0773
0.15
0.13
0.10
0.08
0.05
C: Concentration (wt%)
540.00
630.00
720.00
810.00
900.00
A: Power (W)

(b)



(c)

Figure 6.20: Response Surface of Predicted Water Separated by Interaction Microwave Power (X_1), Time Processing (X_2) and Concentration of Demulsifier (X_3) in Microwave Irradiation

6.9 VALIDATION OF MODEL PREDICTION

Optimum variables gained by Design of Expert (DOE) will be used in order to validate this predicted model. However, the microwave power obtained through this model cannot be followed exactly due to the drawback of microwave power used. Table 6.13 indicates the optimum variables for each crude oil.

Table 6.13: Model Prediction Variables

Crude oil	Microwave power (Watt)	Time (min)	Concentration (wt %)
A	710	2.40	0.15
B	692	2.56	-
C	767	2.50	0.14

Crude oil A was pursued the variables listed from Table 6.13. In contrast, the microwave power in crude oil B and C were operated at 690 W and 770 W. The results obtained in this validation model are shown in Figure 6.21. It seems that each crude oil excellently break after 5 minutes as followed by response of prediction model. This results proved that the W/O emulsion for each crude oil is better separation in both real and prediction model. In this results, within 5 minutes, crude oil A obtained 44.0 % of water separated, which is 1.1.0% lower than prediction model. While crude oil B shows that 60.0 % of water can be separated and 38.0% for crude oil C. The percentage of water separated in crude oil B lower 4.0 % than predicted model. This is might be obtained due to the microwave power operated was lower than predicted model. However, still W/O emulsion can be separated in microwave irradiation and microwave-assisted chemical for heavy crude oil.

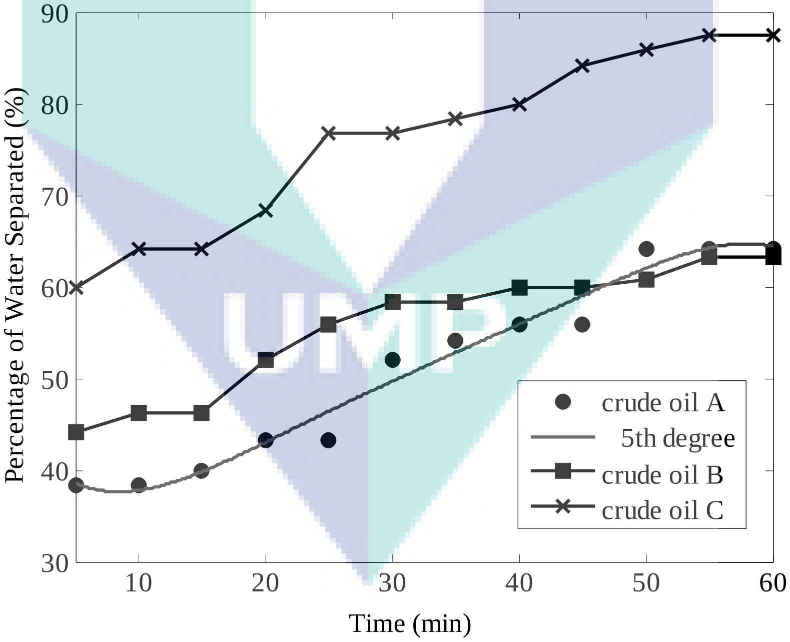


Figure 6.21: W/O Emulsion Demulsified Using Optimum Variables

6.9 SUMMARY

By comparing the effectiveness methods of microwave irradiation and conventional methods in demulsification, microwave irradiation indicates the highest percentage of water separation for lighter crude oil. However, for heavy crude oil which in this study, crude oils A and C were treated in chemical demulsifier to accelerate the droplets in emulsion before enhanced in microwave irradiation.

In optimisation part, crude oil A and C used 2^3 factorial design in modelling experiments using design expert. In contrast, 2^2 factorial design was selected in crude oil B due to the properties of crude oil and only this type of crude oil can be separated while using microwave irradiation.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSION

The behaviour of water-in-oil emulsion was investigated by studying the formation, stabilisation and demulsification of emulsions by various methods (chemical demulsifications and microwave irradiation). The principal objective of this study work was to develop a better fundamental understanding of the mechanisms of emulsion stabilisation, mechanisms of coalescence demulsification (emulsion breaking), as well as microwave method for emulsion demulsification.

This chapter presents the main results discussed in chapter 5 and 6. In this study, three types of crude oils were used namely; crude oil A, B and C. results showed crude oil C is the heaviest and followed by crude oil A and B, respectively. Based on the results of this study, it can be concluded that:-

7.1.1 Characterisation of Crude Oil and Stability of W/O Emulsion

According to the characterisation results of crude oil A, B, C and W/O emulsion prepared from these crude oils, the following conclusion can be made:-

i. The physical properties of three types of crude oil showed that the range of viscosity was between 24.6 to 207.8 cP; the API density obtained ranged from 26.481 to 29.226; pour point acquired value ranged from -12.0 to -20.4^{o}C; wax appearance temperature within range -1.18 to 4.44°C and for surface tension analysis, the range within 13.046 to 13.659 m/Nm. While for chemical properties, crude oil C obtained the highest asphaltenes content 14.7 wt%, followed by crude oil A (11.0 wt%) and 5.94 wt% in crude oil B. Therefore, the presents of solid particles in crude oil C was highest (15.27 wt %) followed by crude oil A (14.20 wt %) and 9.77wt% for crude oil B. The analysis of the properties shows that there are correlations between some physical and chemical properties of crude oil. For instance, crude oil C whereas the heaviest crude oil indicated the higher asphaltenes content and viscosity. In contrast, higher resin content performed the instability of crude oil as following crude oil B>crude oil A>crude oil C. Besides, asphaltenes and resins analysed by FTIR showed that they have functional groups of hydrocarbon and aromatic.

ii. The analysis of the factor affected the stability of emulsion were demonstrated that the emulsion prepared in crude oil C acquired the highest viscosity as comparing the stirring intensity and temperature. Besides, phase inversion of W/O to O/W emulsion investigated closely which caused at higher temperature and ratio. Crude oil B showed that the W/O emulsion inversed to O/W at higher temperature (90°C) and at 60-40 % W/O emulsion for all crude oil types, emulsions were inversed to O/W. In addition the emulsion also varied with the ratio of water-oil to analyse the rheology of emulsion. The behaviour of emulsion observed through plotting graph shear stress versus shear rate and viscosity versus shear rate. Higher ratio (50-50 % w/o emulsion) indicated emulsion behave as non-Newtonian for crude oil B and C only. However, for crude oil A, the emulsion showed non-Newtonian behaviour at higher ratio (55-45 % W/O emulsion) due to the content of wax in crude oil.

7.1.2 Demulsification

Analysis of demulsification was conducted by comparing microwave irradiation with conventional methods such as chemical demulsification, thermal heating (hotplate) and settling gravity. In optimisation, the optimum conditions in microwave irradiation of percentage water separated were arises. The following of analysis in demulsification were concluded below:-

i. There were no separation observed in emulsion prepared from crude oil A and C compared to crude oil B after demulsified in microwave irradiation and conventional methods. Thus, chemical demulsifier was added into emulsions from crude oil A and C to accelerate the droplets in emulsion before enhanced using microwave irradiation.

ii. The correlation of volume fraction of emulsion and microwave power with dielectric properties, wavelength and penetration depth also discussed in demulsification part. Volume fraction increased with increasing the dielectric properties and has reversed correlation with wavelength and penetration depth due to the efficiency of microwave absorption high. While, microwave power has directly correlation with penetration depth and wavelength because of more electromagnetic intense inside the water molecules.

iii. In optimisation part, the analysis of demulsification in microwave irradiation using response surface methodology, two types of factorial designs selected which 2^2 factorial design for crude oil B and 2^3 factorial design for crude oil A and C. From factorial design analysis, it was found that the optimum variables and yield (percentage of water separation) in crude oil A which are 710 W in 2.40 min with 0.15 wt% of demulsifier and maximum yield of water separation predicted was 45.10 %. While in crude oil B, the maximum yield of water separation predicted through this model is 64.07 % at microwave power 692 W in 2.56 min. The last sample analysis was crude oil C whereas based on the model; the maximum yield of water separation predicted through this model is 38.03 % at microwave power 767 W in 2.50 min with 0.14 wt% demulsifier.

7.2 RECOMMENDATIONS

Based on this study, some additional experiments in characterisation of crude oil are suggested before demulsification is a`cquired. Therefore, some further studies are still required as follows:-

i. For heavy crude oil, viscosity reduction is necessary to obtain the optimum viscosity point by dilution of heavy crude oil with light crude oil.
ii. Instead of using bottle test to asses the emulsion stability, this study suggests water concentration profile (hold-up) and coalescing interface behaviour as future investigation or emulsion stability.

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APPENDIX A

FTIR ANALYSIS FOR CRUDE OIL

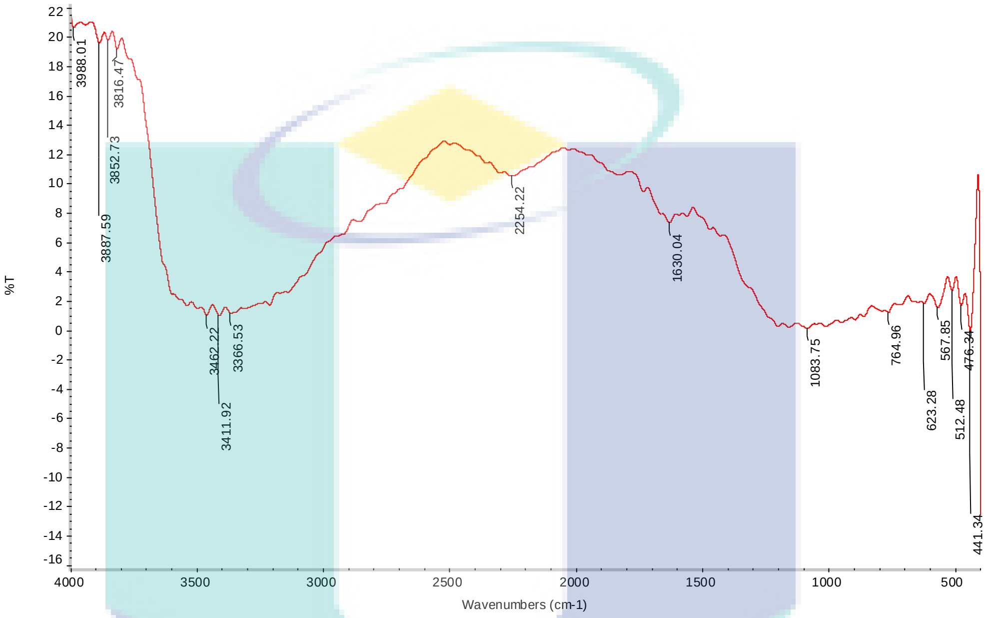


Figure A1: FTIR Analysis of Crude Oil A

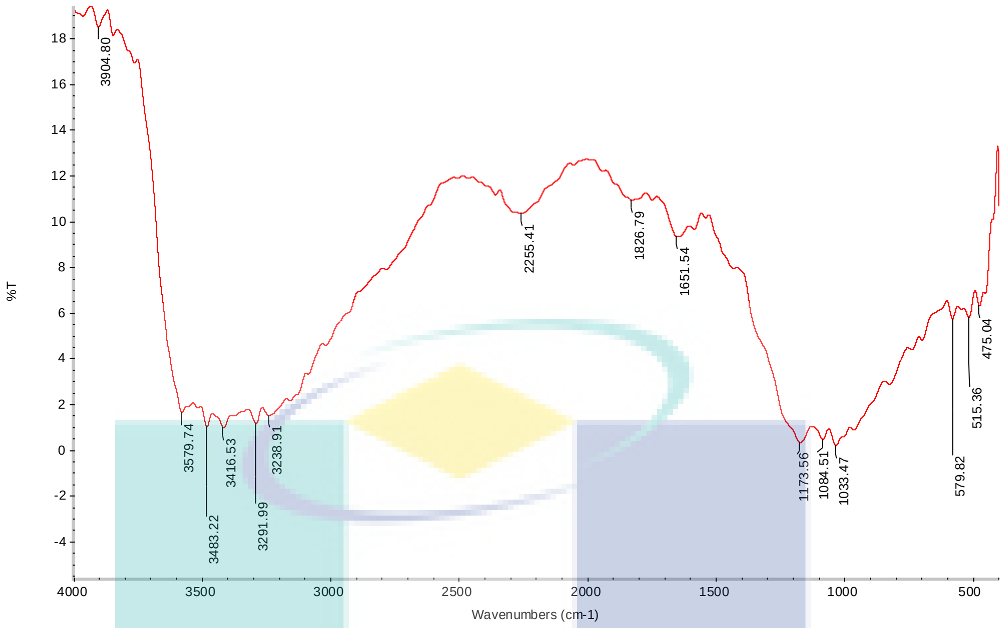


Figure A2 FTIR Analysis of Crude Oil B

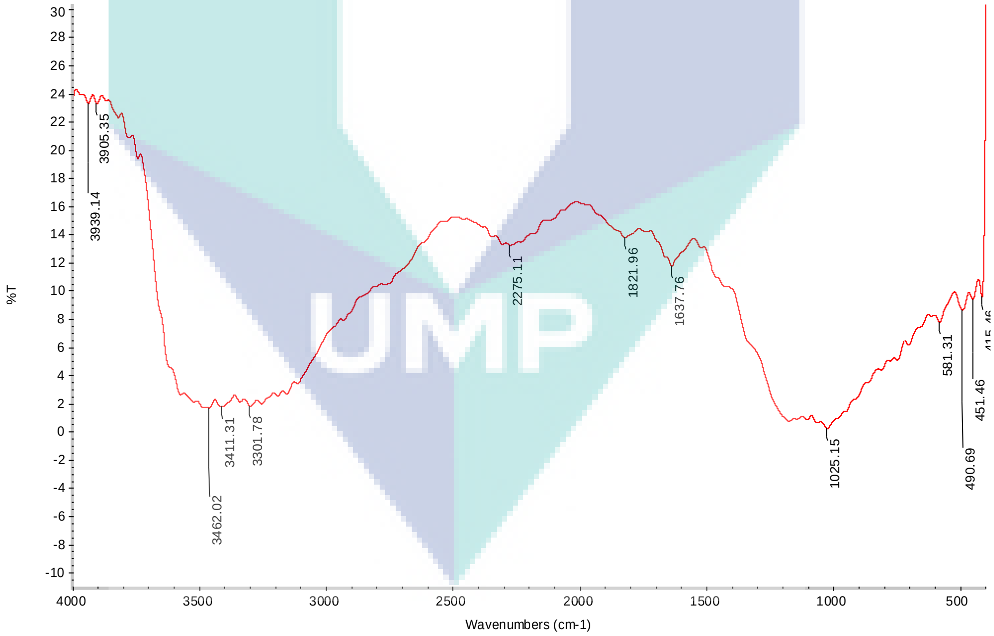


Figure A3 FTIR Analysis of Crude Oil C

APPENDIX B

ANALYSIS OF DIFFERENTIAL SCANNING CALORIMETRY (DSC)

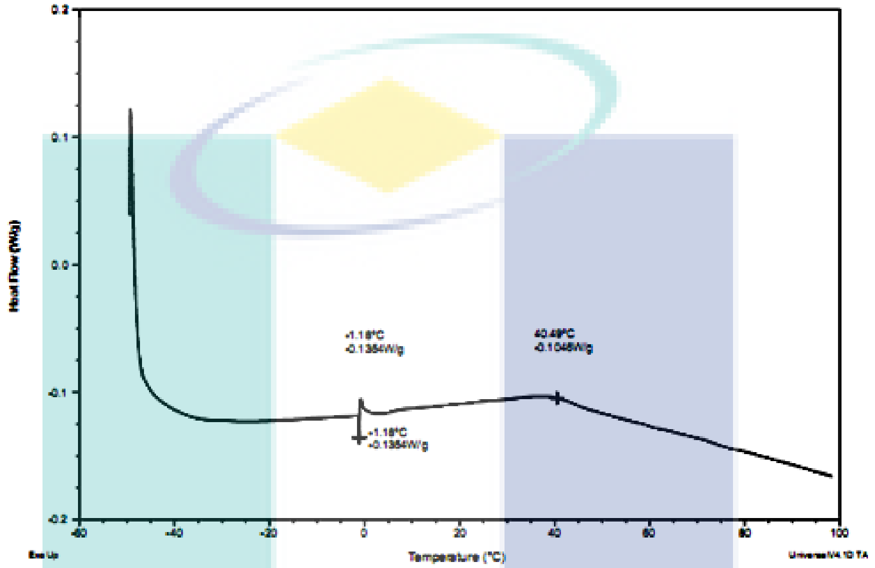


Figure B1: DSC Analysis of Crude Oil A

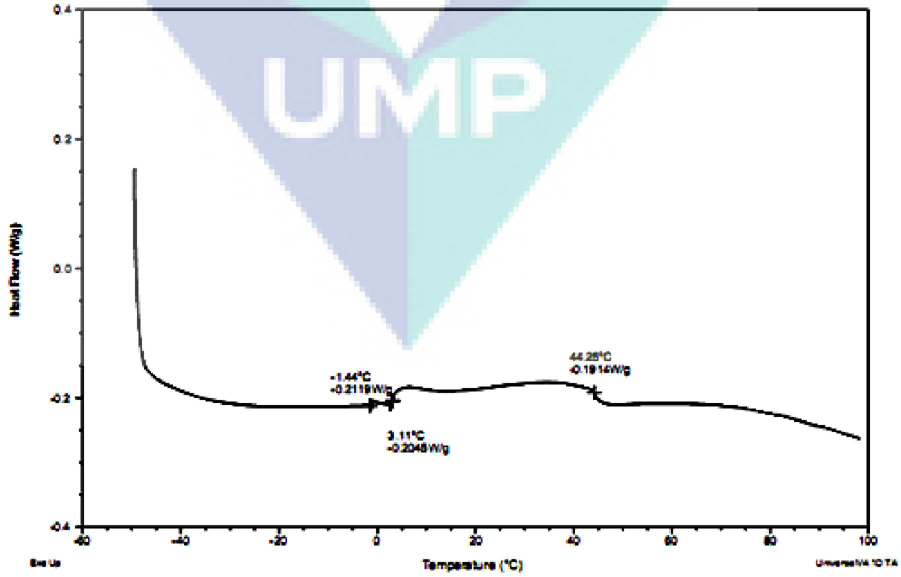


Figure B2: DSC Analysis of Crude Oil B

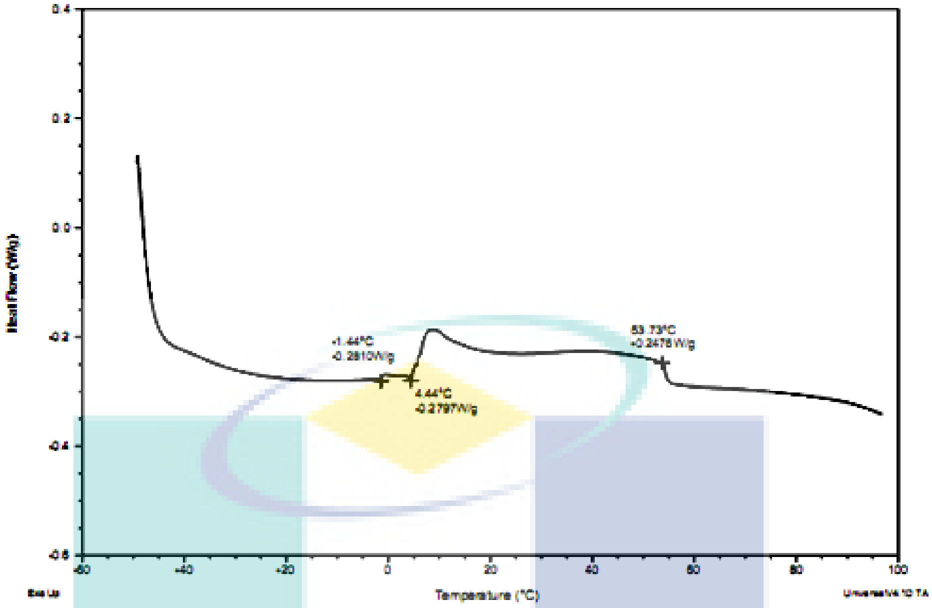
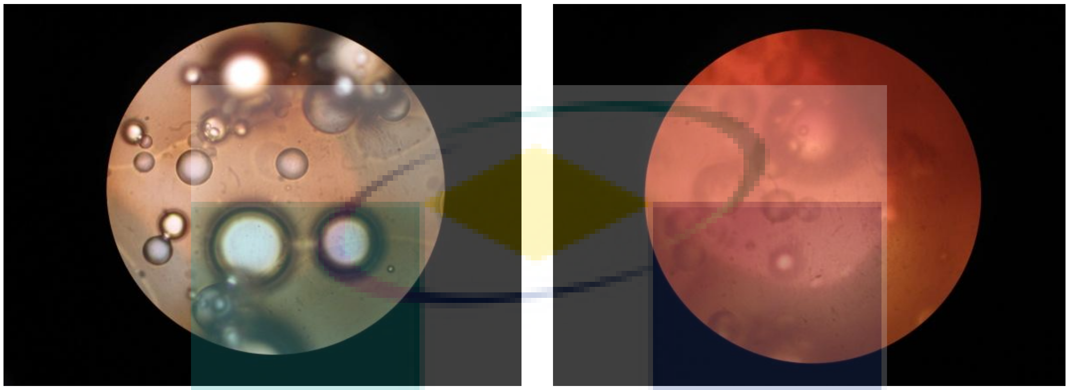


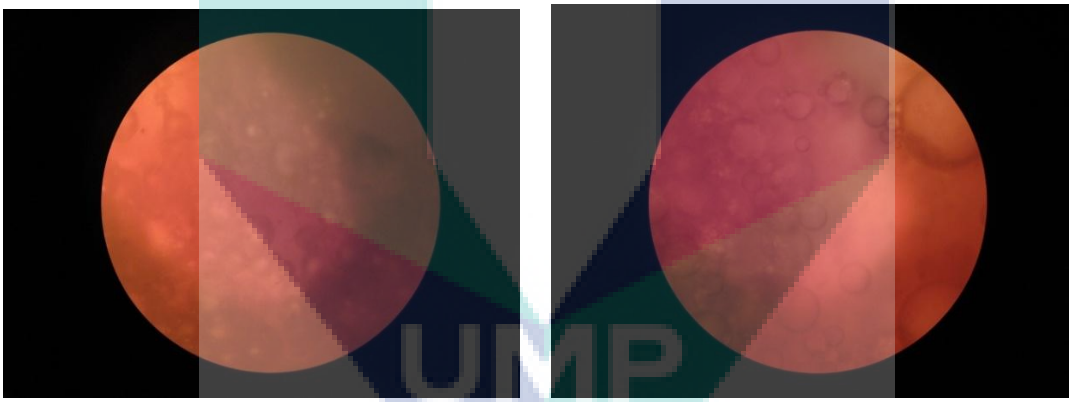
Figure B3: DSC Analysis of Crude Oil C

APPENDIX C

EFFECT OF DROPLETS SIZE ON STIRRING INTENSITY



(a) 500 rpm (b)1000 rpm

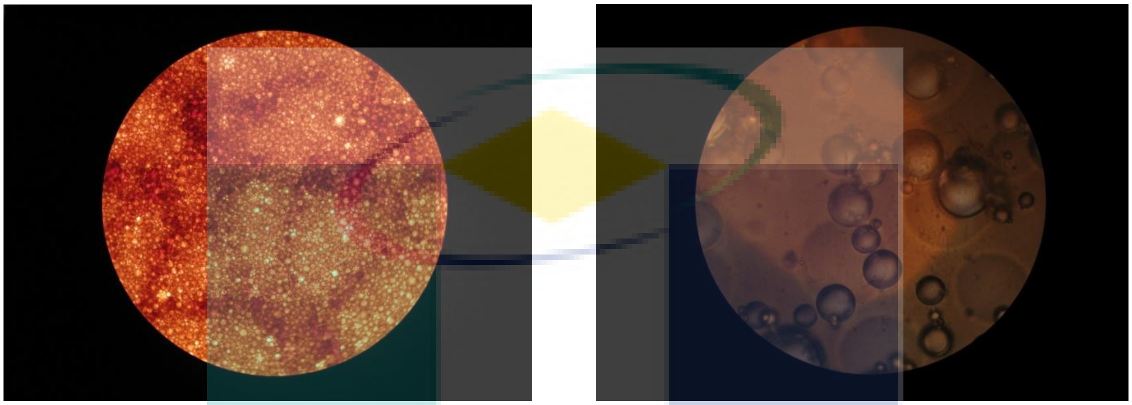


(c) 1500 rpm (d)2000 rpm

Figure C1: Droplet Size Affect at Varied Stirring Intensity

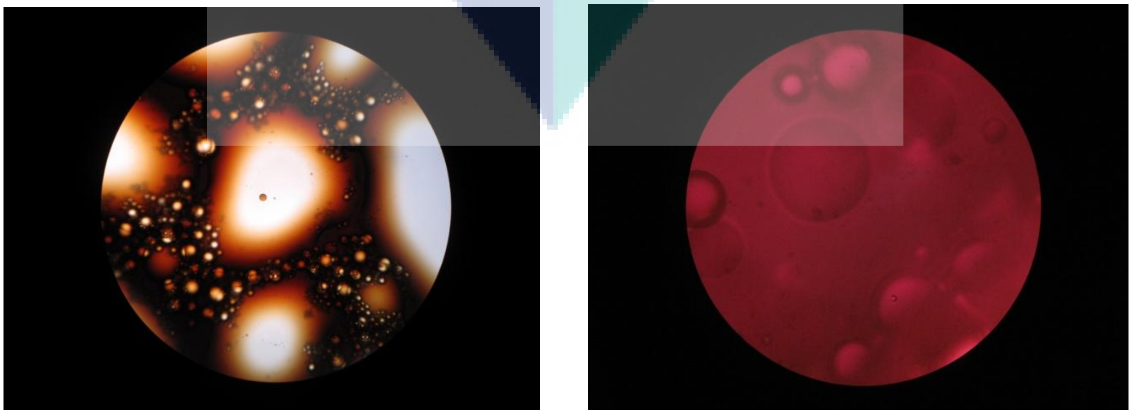
APPENDIX D

EFFECT OF TEMPERATURE ON EMULSION STABILITY

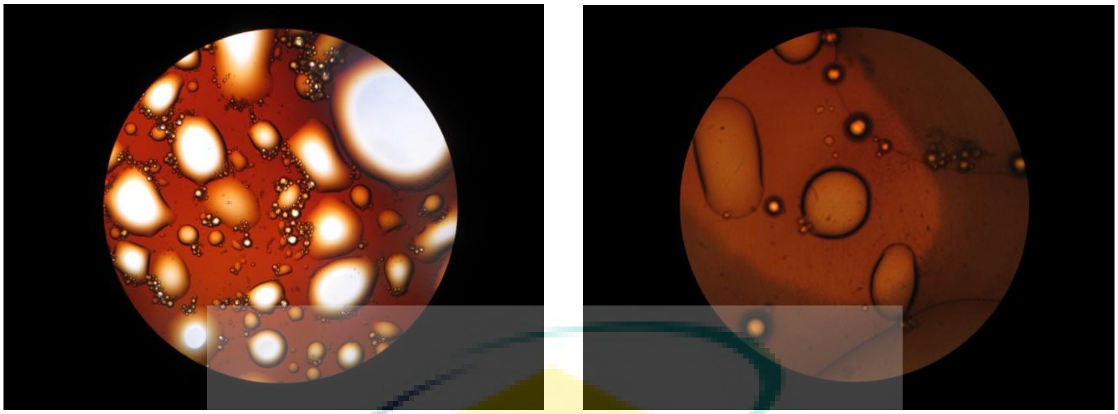


Ambient temperature

Temperature 50°C

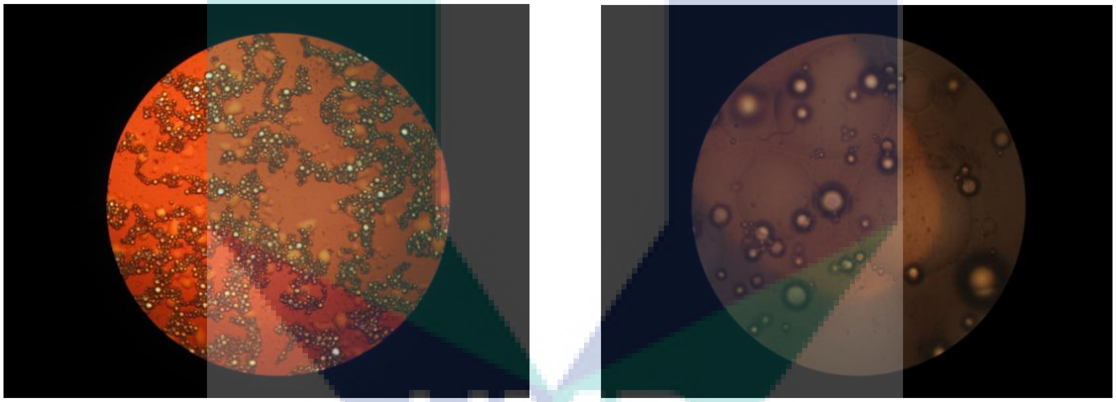


Temperature 70°C

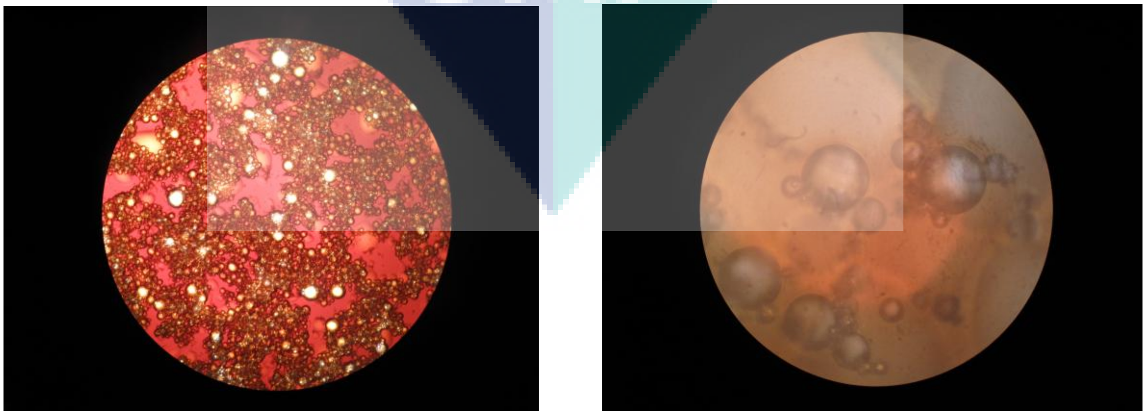


Temperature 90°C

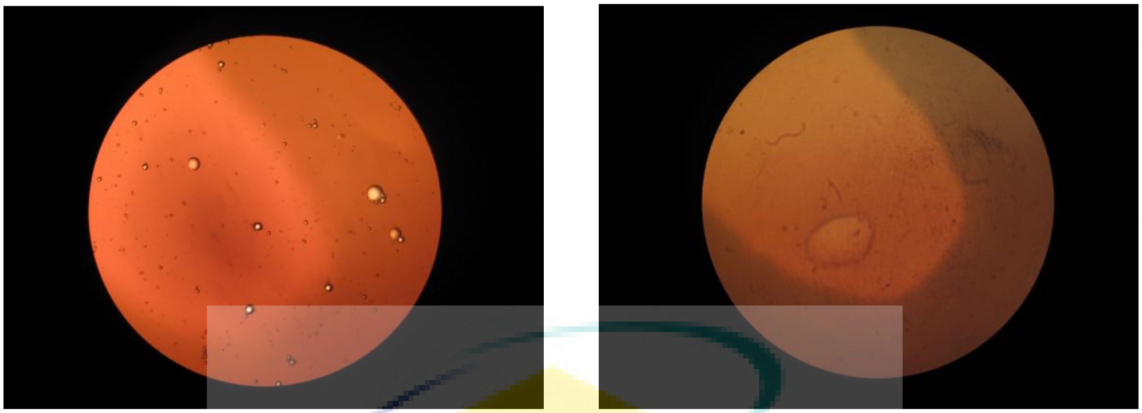
Figure D1 50-50 % W/O Emulsion (Left at 10x resolution; Right at 100x resolution)



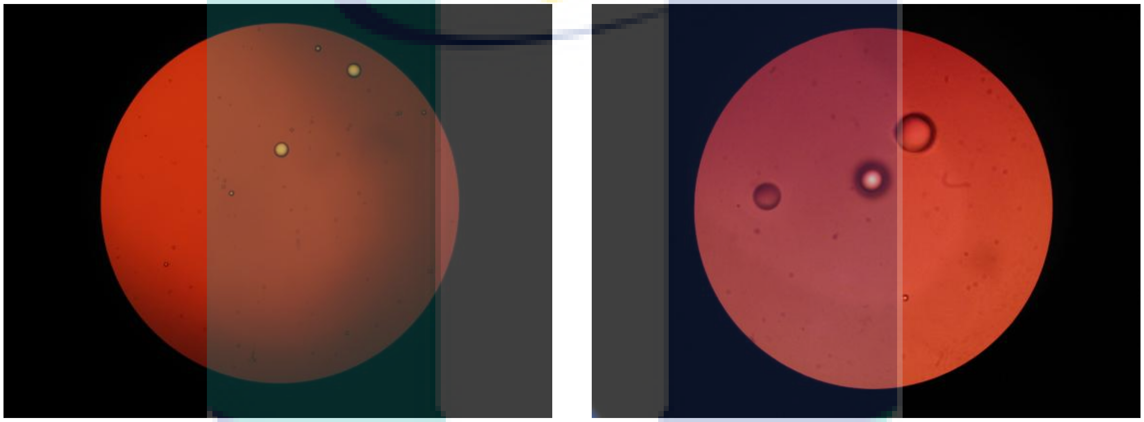
Ambient temperature



Temperature 50°C

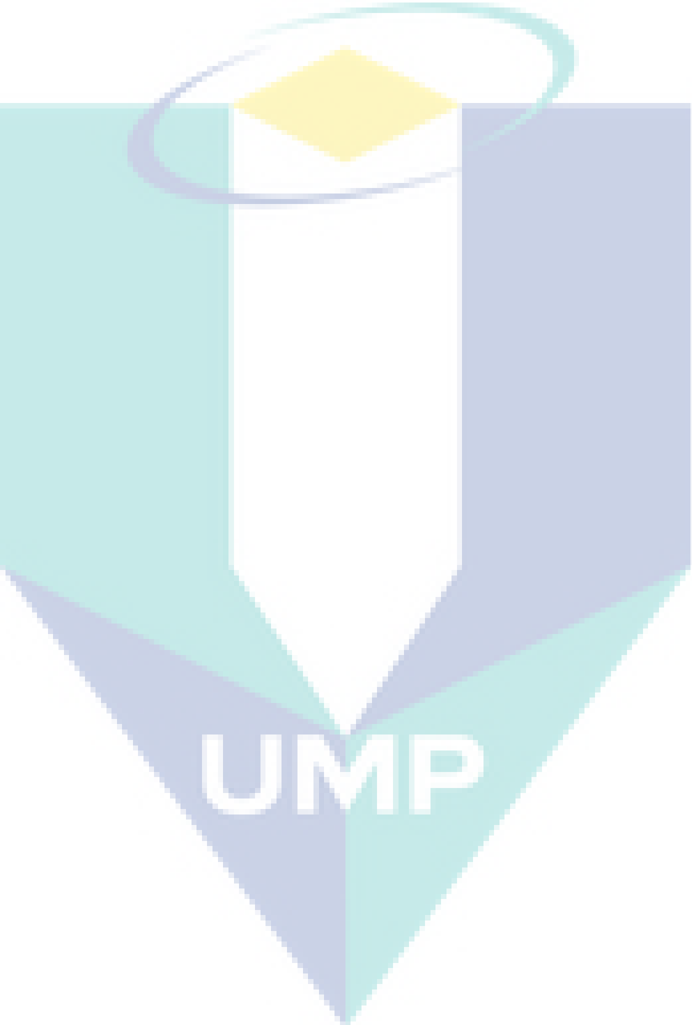


Temperature 70°C



Temperature 90°C

Figure D2 20-80 % W/O Emulsion (Left at 10x resolution; Right at 100x resolution)



APPENDIX E

W/O EMULSION HEATED BY MICROWAVE RADIATION IN VARIED MICROWAVE POWER

Table E1: Experimental Results of 900 W

time (sec)	**Temperature average (^{o}C)**	**heating rate ,dT/dt (^{o}C/s)**	**volume rate of heat generation, q_{mv} (cal/s.cm^{3})**	**ε'r (water)**	**ε'r (oil)**	**dielectric constant, ε'r**	**ε''r (water)**	**ε''r (oil)**	**dielectric loss, ε''r**	**tan δ**
20	50.3333	1.1330	2.4834	68.31156	2.203408	35.25748	5.7356	0.0000023	2.8678	0.081338
40	63.8033	0.9033	1.9328	63.78793	2.193615	32.99077	4.4960	0.0000010	2.2480	0.068141
60	71.4533	0.7297	1.5614	61.21883	2.188053	31.70344	4.0025	0.0000007	2.0013	0.063124
80	79.3067	0.6454	1.3811	58.58144	2.182344	30.38189	3.5961	0.0000005	1.7980	0.059182
100	87.9033	0.6023	1.2888	55.69442	2.176094	28.93526	3.2355	0.0000003	1.6177	0.055909
120	93.3267	0.5471	1.1707	53.87311	2.172152	28.02263	3.0426	0.0000003	1.5213	0.054288
140	90.7100	0.4503	0.9635	54.75186	2.174054	28.46296	3.1327	0.0000003	1.5664	0.055032
160	106.8233	0.4947	1.0586	49.34052	2.162339	25.75143	2.6485	0.0000002	1.3243	0.051425
180	96.1133	0.3802	0.8136	52.93726	2.170126	27.55369	2.9520	0.0000002	1.4760	0.053569
200	98.8333	0.3558	0.7614	52.0238	2.168148	27.09597	2.8686	0.0000002	1.4343	0.052935
220	97.0533	0.3154	0.6748	52.62158	2.169442	27.39551	2.9227	0.0000002	1.4613	0.053342
AVERAGE		0.5961	1.2756			29.41373			1.7560	0.059701

Table E2: Experimental Results of 720 W

time (sec)	Temperature average (^{o}C)	heating rate ,dT/dt (^{o}C/s)	volume rate of heat generation, q_{mv} (cal/s.cm^3)	ε'r (water)	ε'r (oil)	dielectric constant, ε'r	ε''r (water)	ε''r (oil)	dielectric loss, ε''r	tan δ
20	50.7067	0.9657	2.1166	68.18618	2.203136	35.19466	5.6922	0.0000022	2.8461	0.080868
40	56.0567	0.6166	1.3194	66.38949	2.199247	34.29437	5.1351	0.0000016	2.5676	0.074868
60	70.4933	0.6517	1.3945	61.54122	2.188751	31.86499	4.0585	0.0000007	2.0292	0.063682
80	73.4967	0.5263	1.1262	60.53261	2.186568	31.35959	3.8883	0.0000006	1.9441	0.061995
100	73.3933	0.4200	0.8987	60.56732	2.186643	31.37698	3.8939	0.0000006	1.9470	0.06205
120	78.8800	0.3957	0.8468	58.72473	2.182654	30.45369	3.6161	0.0000005	1.8080	0.05937
140	83.3367	0.3710	0.7939	57.22805	2.179414	29.70373	3.4176	0.0000004	1.7088	0.057529
160	93.3933	0.3875	0.8292	53.85072	2.172103	28.01141	3.0403	0.0000003	1.5202	0.05427
180	97.9133	0.3696	0.7908	52.33277	2.168817	27.25079	2.8963	0.0000002	1.4482	0.053142
200	97.2900	0.3295	0.7050	52.5421	2.16927	27.35568	2.9154	0.0000002	1.4577	0.053286
220	106.1433	0.3398	0.7271	49.56888	2.162834	25.86586	2.6660	0.0000002	1.3330	0.051535
AVERAGE		0.4885	1.0453			30.24834			1.8736	0.061941

Table E3: Experimental Results of 540 W

time (sec)	Temperature average (^{o}C)	heating rate ,dT/dt (^{o}C/s)	volume rate of heat generation, q_{mv} (cal/s.cm^{3})	ε'r (water)	ε'r (oil)	dielectric constant, ε'r	ε''r (water)	ε''r (oil)	dielectric loss, ε''r	tan δ
20	47.1667	0.8115	1.7787	69.37502	2.20571	35.790364	6.1313	0.0000028	3.0657	0.085656
40	50.7300	0.4948	1.0589	68.17834	2.203119	35.190732	5.6895	0.0000022	2.8448	0.080838
60	62.6300	0.5282	1.1303	64.18197	2.194468	33.188218	4.5825	0.0000011	2.2913	0.069039
80	68.7933	0.4732	1.0126	62.11213	2.189987	32.151061	4.1615	0.0000008	2.0807	0.064718
100	69.2900	0.3835	0.8207	61.94534	2.189626	32.067483	4.1309	0.0000008	2.0654	0.064409
120	80.7667	0.4152	0.8886	58.09113	2.181283	30.136206	3.5294	0.0000004	1.7647	0.058557
140	77.0700	0.3295	0.7051	59.33258	2.18397	30.758276	3.7033	0.0000005	1.8516	0.0602
160	83.0833	0.3259	0.6974	57.31312	2.179598	29.746361	3.4284	0.0000004	1.7142	0.057626
180	84.5467	0.2978	0.6373	56.82169	2.178535	29.500114	3.3674	0.0000004	1.6837	0.057075
200	82.4833	0.2577	0.5515	57.51462	2.180035	29.847328	3.4540	0.0000004	1.7270	0.05786
220	85.7933	0.2493	0.5336	56.40302	2.177628	29.290327	3.3172	0.0000003	1.6586	0.056626
AVERAGE		0.4152	0.8884			31.606043			2.0680	0.06543

Table E4: Experimental Results of 360 W

time (sec)	**Temperature average (^oC)**	**heating rate ,dT/dt ($^oC/s$)**	**volume rate of heat generation, q_{mv} (cal/s.cm^3)**	**ε'r (water)**	**ε'r (oil)**	**dielectric constant, ε'r**	**ε''r (water)**	**ε''r (oil)**	**dielectric loss, ε''r**	**tan δ**
20	30.0133	0.0507	0.1111	75.13562	2.21818	38.6769	9.7529	0.0000122	4.8765	0.126082
40	35.2167	0.1554	0.3326	73.38819	2.214397	37.80129	8.2764	0.0000074	4.1382	0.109472
60	44.8200	0.2637	0.5642	70.1631	2.207416	36.18526	6.4612	0.0000034	3.2306	0.089279
80	55.4100	0.3301	0.7064	66.60666	2.199717	34.40319	5.1967	0.0000016	2.5983	0.075526
100	47.5000	0.1850	0.3959	69.26308	2.205468	35.73427	6.0871	0.0000028	3.0436	0.085172
120	57.7133	0.2393	0.5120	65.83313	2.198042	34.01559	4.9838	0.0000014	2.4919	0.073258
140	61.8733	0.2348	0.5025	64.43608	2.195018	33.31555	4.6401	0.0000011	2.3200	0.069639
160	76.7533	0.2985	0.6387	59.43893	2.1842	30.81156	3.7190	0.0000005	1.8595	0.06035
180	82.1533	0.2953	0.6319	57.62545	2.180275	29.90286	3.4682	0.0000004	1.7341	0.057991
200	75.4067	0.2320	0.4965	59.89118	2.185179	31.03818	3.7872	0.0000006	1.8936	0.061009
220	64.8433	0.1629	0.3486	63.43866	2.192859	32.81576	4.4220	0.0000009	2.2110	0.067376
AVERAGE		0.2225	0.4761			34.06367			2.7634	0.081124

APPENDIX F

W/O EMULSION HEATED BY MICROWAVE RADIATION IN VARIED VOLUME FRACTION

Table F1: Experimental Results of 50-50 % Water-in-oil (W/O) Emulsion Heated by Microwave Radiation

time (sec)	**Temperature average (^{o}C)**	**heating rate ,dT/dt (^{o}C/s)**	**volume rate of heat generation, q_{mv} (cal/s.cm^{3})**	**ε'r (water)**	**ε'r (oil)**	**dielectric constant, ε'r**	**ε''r (water)**	**ε''r (oil)**	**dielectric loss, ε''r**	**tan δ**
20	50.7067	0.9657	2.0543	68.18618	2.203136	35.19466	5.6922	0.0000022	2.8461	0.080868
40	56.0567	0.6166	1.3117	66.38949	2.199247	34.29437	5.1351	0.0000016	2.5676	0.074868
60	70.4933	0.6517	1.3863	61.54122	2.188751	31.86499	4.0585	0.0000007	2.0292	0.063682
80	73.4967	0.5263	1.1196	60.53261	2.186568	31.35959	3.8883	0.0000006	1.9441	0.061995
100	73.3933	0.4200	0.8935	60.56732	2.186643	31.37698	3.8939	0.0000006	1.9470	0.062050
120	78.8800	0.3957	0.8418	58.72473	2.182654	30.45369	3.6161	0.0000005	1.8080	0.059370
140	83.3367	0.3710	0.7893	57.22805	2.179414	29.70373	3.4176	0.0000004	1.7088	0.057529
160	93.3933	0.3875	0.8243	53.85072	2.172103	28.01141	3.0403	0.0000003	1.5202	0.054270
180	97.9133	0.3696	0.7862	52.33277	2.168817	27.25079	2.8963	0.0000002	1.4482	0.053142
200	97.2900	0.3295	0.7009	52.5421	2.169270	27.35568	2.9154	0.0000002	1.4577	0.053286
220	106.1433	0.3398	0.7228	49.56888	2.162834	25.86586	2.6660	0.0000002	1.3330	0.051535
AVERAGE		0.4885	1.0391			30.24834			1.8736	0.061941

Table F2: Experimental Results of 30-70 % Water-in-oil (W/O) Emulsion Heated by Microwave Radiation

time (sec)	**Temperature average (^{o}C)**	**heating rate ,dT/dt (^{o}C/s)**	**volume rate of heat generation, q_{mv} (cal/s.cm^{3})**	**ε'r (water)**	**ε'r (oil)**	**dielectric constant, ε'r**	**ε''r (water)**	**ε''r (oil)**	**dielectric loss, ε''r**	**tan δ**
20	51.9333	1.0270	2.1054	67.77423	2.202244	21.87384	5.5542	0.0000021	1.6663	0.076176
40	56.8267	0.6358	1.3035	66.13090	2.198687	21.37835	5.0637	0.0000015	1.5191	0.071058
60	66.7000	0.5884	1.2063	62.81514	2.191509	20.37860	4.2957	0.0000009	1.2887	0.063238
80	70.3667	0.4872	0.9987	61.58376	2.188843	20.00732	4.0660	0.0000007	1.2198	0.060967
100	75.5733	0.4418	0.9057	59.83521	2.185058	19.48010	3.7786	0.0000005	1.1336	0.058192
120	82.9067	0.4293	0.8800	57.37245	2.179727	18.73755	3.4359	0.0000004	1.0308	0.055010
140	86.2433	0.3918	0.8032	56.25190	2.177301	18.39968	3.2994	0.0000003	0.9898	0.053796
160	94.7233	0.3958	0.8114	53.40406	2.171136	17.54101	2.9965	0.0000002	0.8990	0.051249
180	98.3900	0.3722	0.7630	52.17269	2.168470	17.16974	2.8819	0.0000002	0.8646	0.050354
200	110.4067	0.3951	0.8099	48.13713	2.159734	15.95295	2.5603	0.0000001	0.7681	0.048148
220	122.1300	0.4124	0.8455	44.20008	2.151211	14.76587	2.3083	0.0000001	0.6925	0.046898
AVERAGE		0.5070	1.0393			18.69864			1.0975	0.058692

Table F3: Experimental Results of 10-90 % Water-in-oil (W/O) Emulsion Heated by Microwave Radiation

time (sec)	**Temperature average (^oC)**	**heating rate ,dT/dt ($^oC/s$)**	**volume rate of heat generation, q_{mv} ($cal/s.cm^3$)**	**ε'r (water)**	**ε'r (oil)**	**dielectric constant, ε'r**	**ε''r (water)**	**ε''r (oil)**	**dielectric loss, ε''r**	**tan δ**
20	41.1267	0.4867	1.1105	71.40343	2.210101	9.129434	7.0576	0.0000045	0.7058	0.077307
40	43.2733	0.2970	0.6777	70.68252	2.20854	9.055938	6.6984	0.0000038	0.6698	0.073967
60	48.8867	0.2916	0.6653	68.79739	2.204459	8.863753	5.9099	0.0000025	0.5910	0.066675
80	50.3867	0.2374	0.5418	68.29365	2.203369	8.812397	5.7293	0.0000023	0.5729	0.065015
100	55.0500	0.2366	0.5398	66.72756	2.199979	8.652737	5.2316	0.0000017	0.5232	0.060462
120	61.4467	0.2504	0.5715	64.57937	2.195328	8.433732	4.6732	0.0000011	0.4673	0.055411
140	65.7067	0.2451	0.5593	63.14873	2.192231	8.287881	4.3624	0.0000009	0.4362	0.052635
160	73.0967	0.2606	0.5948	60.66695	2.186859	8.034867	3.9101	0.0000006	0.3910	0.048665
180	75.5533	0.2453	0.5598	59.84192	2.185073	7.950758	3.7796	0.0000006	0.3780	0.047538
200	78.7500	0.2368	0.5403	58.76839	2.182749	7.841313	3.6222	0.0000005	0.3622	0.046194
220	85.1067	0.2442	0.5571	56.63363	2.178127	7.623678	3.3447	0.0000004	0.3345	0.043872
AVERAGE		0.2756	0.6289			8.426044			0.4938	0.058605

APPENDIX G

LIST OF PUBLICATIONS

1. A.N. Ilia Anisa, Abdurahman H.Nour and Azhary H.Nour. Catastrophic and Transitional Phase Inversion of Water-in-Crude Oil (W/O) Emulsion. (Published in Journal Applied of Science 10 (23): 3076-3083, 2010)
2. A.N. Ilia Anisa and Abdurahman H.Nour (2010). Affect of Viscosity and Droplet Diameter on Water-in-Oil (W/O) Emulsions: An Experimental Study. Proceedings in International Conference of Chemical Engineering 2010 Issue 62, February 2010,128: 691-694
3. A.N. Ilia Anisa and Abdurahman H.Nour (2009). Demulsification of Water-in-Crude Oil Emulsion via Microwave Heating Technology and Conventional Method. Proceedings in Regional Conference on Environmental and Earth Resources (RCER 2009). Pahang, Malaysia, December 7-8, 2009.
4. A.N. Ilia Anisa and Abdurahman H.Nour (2009). Emulsion Separation Rate Enhancement via Microwave Heating Technology (ISBN 978-967-5080-81-4) National Conference on Postgraduate Research (NCON-PGR 2009). 018, pp. 79. Pahang, Malaysia, October 1st, 2009.