SEPARATION OF CRUDE OIL EMULSIONS VIA MICROWAVE HEATING TECHNOLOGY

CHANG SER ER

DEGREE OF BACHELOR OF CHEMICAL ENGINEERING (CHEMICAL) UNIVERSITI MALAYSIA PAHANG

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BORANG PENGESAHAN STATUS TESIS

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

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Special Dedication to my supervisor, my family members, my friends, my fellow colleague and all faculty members for all your care, support and believe in me.

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ABSTRACT

Enhancement of separation process involving liquid-liquid or solid-liquid can be achieved using microwave irradiation technology. The traditional ways of breaking emulsions include heating and chemical are disadvantageous both from economic and environmental perspectives. In this thesis, the microwave potentials in demulsification of water-in-crude oil emulsions are investigated. The study began with some characterization of w/o emulsions such as formation, formulation, stabilization and breaking of emulsions to provide fundamental understanding of crude oil emulsions. The aim was to obtain optimized operating conditions as well as fundamental understanding of water-in-oil emulsions, upon which further developments on demulsification processes can be developed. The stability studies were carried out by analyzing operating condition such as stirring time, surfactant concentration, (50-50%) temperature, water-oil ratios and 20-80%) and agitation speed (500rpm,1000rpm and 1500rpm). Four emulsifiers namely: Span 80, Span 83, Cocamide MEA and Triton X-100 were used for w/o stabilizations. It was found that they exist a correlations between these factors and emulsion stability. For microwave power applied (720 watts, 540 watts and 360 watts), it conclude that the microwave power was proportional to the volume rate of heat generation and rate of temperature increase. Results show that microwave radiation can enhance the demulsification rate by order of magnitude. The result obtained in this study has exposed the capability of microwave technology in demulsification of water-in-oil emulsions. Further work is nevertheless required to provide deeper understanding of the mechanisms involved to facilitate the development of optimum system applicable to the industries.

ABSTRAK

Peningkatan pretasi proses pemisahan yang melibatkan cecair-cecair atau pepejal-cecair boleh dicapai dengan menggunakan teknologi penyinaran gelombang mikro. Cara-cara tradisional yang digunakan untuk memecahkan emulsi termasuk pemanasan dan penggunaan bahan kimia adalah kurang memuaskan dari segi ekonomi dan alam sekitar. Dalam kajian ini, potensi gelombang mikro pemisahan air dalam minyak mentah emulsi disiasat. Kajian ini bermula dengan pencirian beberapa emulsi air dalam minyak mentah seperti pembentukan, penggubalan, penstabilan, dan pembukaan emulsi untuk memberi kefahaman asas emulsi minyak mentah. Tujuannya adalah untuk mendapatkan keadaan operasi optimum serta memahami asas emulsi air dalam minyak, di mana perkembangan lanjut mengenai proses demulsification boleh dimajukan. Kajian kestabilan telah dijalankan dengan menganalisis keadaan operasi seperti kacau masa, kepekatan pengemulsi, suhu, nisbah air-minyak (50-50% dan 20-80%) dan kelajuan pergolakan (500rpm, 1000rpm dan 1500rpm). Empat pengemulsi iaitu: SPAN 80, SPAN 83, Cocamide MEA dan Triton X-100 telah digunakan untuk penyediaan emulsi stabil. Adalah didapati bahawa pembolehubah ini saling bergantung antara faktor-faktor ini dan kestabilan emulsi. Untuk penggunaan kuasa gelombang mikro (720 watt, 540 watt dan 360 watt), ia menyimpulkan bahawa kuasa gelombang mikro adalah berkadar dengan kadar jumlah penjanaan haba dan kadar kenaikan suhu. Keputusan menunjukkan bahawa radiasi gelombang mikro boleh meningkatkan kadar demulsification melalui perintah magnitud. Keputusan yang diperolehi dalam kajian ini telah mendedahkan keupayaan teknologi gelombang mikro dalam pemisahan air dari emulsi air dalam minyak. Kerja selanjutnya namun diperlukan untuk memberi kefahaman yang lebih mendalam tentang mekanisme yang terlibat bagi memudahkan pembangunan and penyelidikan sistem yang optimum yang diperlukankan oleh industri.

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LIST OF SYMBOLS

А	Sample's container surface area
D	Diameter of water droplets
C_p	Heat capacity
\mathbf{D}_{p}	Penetration depth
Pz	Microwave power transmitted
Po	Microwave power flux
m	Mass of sample
q_{MW}	Rate of heat generation
tan δ	Loss tangent
$V_{\rm W}$	Velocity of water
$\alpha_{\rm E}$	Attenuation factor
ε _r '	Dielectric constant
8 r"	Dielectric Loss
λ_{w}	Wavelength
ρ_{m}	Density of emulsions
ρ_{o}	Density of oil
ρ_{w}	Density of water
μ _o	Viscosity of oil

LIST OF ABBREVIATIONS

O/W	Oil-in-water emulsion
W/O	Water-in-oil emulsion
W/O/W	Water-in-oil-in-water emulsion
PIT	Phase Inversion Temperature
Cocamide MEA	Cocamide monoethanolamine
Span 80	Sorbitan (Z)-mono-9-octadecenoate
Span 83	Sodium dodecyl sulphates
Triton X-100	Octylphenolpoly (ethyleneglycolether)x

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Oil is world's major source of primary energy. It is used for a wide diversity of purposes ranging from fueling car to running machinery. When petroleum products are burned to produce energy, they may be used to propel a vehicle, as would be the case with gasoline, jet fuel, or diesel fuel; to heat a building, as with heating oil or residual fuel oil; or to produce electric power by spinning a turbine directly or by creating steam to spin a turbine. In addition, of course, oil products may be used as a raw material (a "feedstock") to create petrochemicals and products, such as plastics, polyurethane, solvents, and hundreds of other intermediate and end-user goods (U.S Energy Information Administration, Independent Statistics and analysis).

However, the amount of crude oil has decreased since last few decades due to high demand, large consumption and inefficient separation of crude oil. According to Saudi Arabic Marketing Informations Resource and Directory (SAMIRAD) the total consumption of crude oil has increased to 84.1 Million Barrel per Day on 2009, compared to 79.4 Million Barrel per Day on 2003. Scientists in Kuwait carried out a study in American Chemical Society (ACS) Energy & Fuels predicted that world conventional crude oil production will peak in 2014 -- almost a decade earlier than some other predictions. Ibrahim Nashawi and colleagues point out that rapid growth in global oil consumption has sparked a growing interest in predicting "peak oil" -- the point where oil production reaches a maximum and then declines. Those cycles can be heavily influenced by technology changes, politics, and other factors. Therefore, the increasing demand of crude oil requires a higher and effective technology to extract and produce large amount of quality crude oil in shorter time.

The crude oil occurs naturally in the form of emulsions, which will cause problems during transportation, processing and storage (Kokal, 2006). According to Lixin et. al. (2003), about eighty percent of exploited crude oils exist in an emulsion state, all over the world. Water and often fine sand and silt are held in various crude oils in permanent emulsions (Leslie & Donald, 1987). Emulsions are two immiscible liquid, whereby one of liquid will become a collection of droplets and dispersed in another liquid phase (Schramm, 1992). Water present as a droplet dispersed in the continuous phase of oil that make crude oil an emulsion, which is difficult to separate. Therefore, various methods have been used to separate the crude oil emulsion to reduce the cost of production and increase the quality of crude oil emulsions.

Separation of oil and water from emulsified solutions, in the process termed demulsification, indicates breakage of the emulsified film surrounding oil or water droplets to allow coalescence or gravitational settling of the oil (Schramm, 1992). Conventionally, demulsification has been achieved by heating and addition of chemicals. Several alternative methods of demulsification have been proposed; these include chemical destabilization with dissolved air flotation (Al-Shamrani et al., 2002), membrane-associated processes (Benito et al., 2001), freezing and thawing (Chen and He, 2003) and (Rajakovic and Skala, 2006), electrical systems (Eow et al, 2001), ultrasonication (Ye, 2008), and microwave irradiation (Chan and Chen, 2002). Among these methods, microwave irradiation is considered effective in demulsification owing to the rapid heating caused by molecular friction and rotation.

1.2 Problem statement

This natural occurring water in oil emulsions have been identified as largely responsible for the stability of these emulsions (Lixin et al., 2003). The water in crude oil (w/o) emulsions is often very stable due to the presence of an interfacial network surrounding the water droplets (Lawrence & Killner, 1948; Blakey & Lawrence, 1954). Nevertheless, stable w/o emulsions have been generally found to exhibit high interfacial viscosity and elasticity modulus (Christophe et al., 2006). The increase in the viscosity of the emulsion will cause problem in transportation and decrease the production rate. Lower viscosity of crude oil with good stability is intended for economic pipeline transportation over large distance.

Other than that, crude oil emulsions also caused some other problem during transportation and processing. The presence of water droplets in the oil will cause corrosion to the pipeline during transportation of the crude oil. It also caused deposition of impurities along the pipeline along transportation. For economic and operational purposes, it is necessary to separate the water completely from the crude oils before transporting or refining them. Minimizing the water levels in the oils can reduce pipeline corrosion and maximize pipeline usage (Harris, 1996; Taylor, 1992).

However, conventional heating methods such as hot plate heating to separate crude oil emulsion needs excessive heating, chemical addition and high residence time (Lemos. R. C. B. et. al., 2010). These increase the cost of production and also will pollute the oil without proper chemical selections.

1.3 Research Objectives

1. To study the stabilization and destabilization of water-in-oil emulsions (w/o) via Microwave Heating Technology.

1.4 Research Questions

- 1. What are the characteristics in terms of physical properties and chemical properties and stability of crude oil with different w/o ratio?
- 2. How to separate water-in-crude oil (w/o) emulsion via microwave heating effectively with different microwave penetrating power?
- 3. Among the conventional methods and microwave heating, which is the most effective way to separate water- in-crude oil (w/o) emulsion?

1.5 Scope of studies

The main objective of this research is to separate water-in-oil in crude oil emulsion. The final product will have two phases which consist of water and oil. In order to obtain the result, we have limited our research within a scope which consists of:

- 1. Characterization of emulsions in terms of physical and chemical properties.
- 2. Examination of demulsification of emulsions by conventional methods, which is gravitational separation.
- 3. Examination of demulsification of emulsions by microwave heating technology.
- 4. Investigation on the effect of temperature distribution at different locations of irradiated emulsions.
- Investigation on the effect of varying microwave power generation (360 watts, 540 watts, and 720 watts) on demulsification of emulsions.

1.6 Significance of studies

Separation of water-in-crude oil emulsion via microwave heating is a new concept compared to the conventional method of separation. Microwave heating is a more effective separation whereby previous studies show that this method is able to separate w/o emulsion more effectively and in shorter time. In this research, we are also to investigate the effect of varying microwave power generation on the characteristics and temperature distribution of the irradiated emulsions.

Therefore, a study in this will able to increase the production rate of crude oil. Other than that, effective separation of crude oil able to decrease the corrosion in pipeline and also deposition of impurities in the pipeline along the crude oil transportation. Microwave heating is also an environmentally friendly method whereby no chemical used during the separation. Therefore, no hazardous waste produced along the separation and the oil produced is safe for usage.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

A review of the literature was performed to identify the previous studies performed and identify the studies related to topic. The main sources used are Encyclopedia of Chemical Technology, Emulsions in the petroleum Industry by Schramm, Emulsions and Oil Treating Equipment by Steward & Arnold, Petroleum Engineering Handbook edited by Lake, et al. and some journals of previous research related to this field. The literature will be divided into four main themes: Crude Oil Emulsions; Stability of Crude Oil Emulsions; Separation of Crude oil Emulsions; and Microwave Heating Technology.

2.2 Crude Oil Emulsions

In oil production, oil and water are two mutually immiscible liquid. When oil and water are produced from a well, some organic and inorganic materials also present as contaminants in the fluid stream. These contaminants are absorbed on the interfaces between oil and water phases and form a layer of film that impedes the coalescence of water droplets. Along the way to well bore, up the tubing and through surfaces chokes, agitation occurred, which is sufficient to disperse on liquid as fine droplets and thus make a very good condition of forming a crude oil emulsions (Stewart. & Arnold, 2009).

Emulsions are two immiscible liquids which are brought to contact with each other in a container with sufficient mixing (Kokal, 2006) and one of the two phases will become a collection of droplets that dispersed in the continuous phase of the other liquid (Calderon et al., 2007). Examples of emulsions which we can see in our daily life are milk, mayonnaise, creams and lotions. There are two types of emulsions, which are:

- i. Oil-in-water (o/w) Oil droplets dispersed in continuous phase of water
- ii. Water-in-oil (w/o) water droplets dispersed in continuous phase of oil

During crude oil production, there are several sources of mixing or amount of shear such as flow through reservoir rock, flow through flow lines, fittings and valves which are difficult to avoid (Kokal, 2006). Most of the emulsions present in the form of water-in-oil (w/o) emulsions. Water droplets are dispersed in continuous phase of oil. Water present as the dispersed phase (internal phase) whiles the oil present as the continuous phase (external phase) (Stewart & Arnold, 2009). However, in some cases, crude oil emulsions also present in the form of oil-in-water (o/w).

2.3 Stability of Crude Oil Emulsions

According to Stewart & Arnold, K. (2009), a stable emulsion formed when the water droplets will not settle out of oil phase. As a consequence of small droplet size and presence of an interfacial film on the droplets, a stable dispersion of emulsions

formed (Schramm, 1992). The thin film prevents the suspended water droplets from flocculate and coalesces.

2.3.1 Factor Affecting Stability of Crude Oil Emulsions

2.3.1.1 Difference in density between the water and oil phases

Density difference between oil and water phases is one of the factors that determine the rate of which water droplets settle through the continuous oil phase. The greater the difference in density, the more quickly water droplets will settle through the oil phase. Thus, the greater the difference in density between the oil and water phases, the easier the water droplets will settle.

2.3.1.2 Temperature

Temperature affects the physical properties of oil, water, interfacial films and surfactants solubility in oil and water phases will directly affect the stability of emulsions (Kokal, 2006). The most significant effect of temperature is on the viscosity of emulsions because viscosity decreases with increase in temperature.

Temperature will also affect the solubility of surfactant. During phase inversion temperature (PIT), the surfactant loses its solubility in the water and oil phases and thus affected hydrophile-lipophile balance (HLB). Thus, the emulsions tend to invert from water-in-oil to oil-in-water when temperature increases.

2.3.1.3 Size of Water Droplets

The size of the dispersed water droplets affects the rate at which water droplets move through the oil phase. The larger the water droplet, the easier flocculation and coalescence take place. Thus, the water droplets will settle out of oil phase faster. Smaller average size distributions of dispersed water droplets represent tighter emulsions and require longer residence time to separate (Kokal, 2006). The droplet size in an emulsion is highly dependent on the degree of agitation of the emulsions.

2.3.1.4 Viscosity

Viscosity of emulsions is usually higher than that of water and oil because emulsions show non-Newtonian behavior (viscosity is a function of shear rate). Viscosity of emulsions are affected by viscosities of water and oil, volume fraction of water dispersed, droplet size distributions, temperature, shear rate and amount of solids present (Kokal, 2006). However, viscosity is significantly affected by temperature. When temperature increases, viscosity of the emulsions decreases. According to Stoke's Law, when velocity of water droplets increases (due to increase in temperature), viscosity decreases more significantly than the difference in density and thus allow droplet sizes of water increases, indicating coalescence of smaller water droplets forming larger water droplets (Nour, et al., 2010).

2.3.1.5 Interfacial tension

Interfacial tension is the force that holds the surfaces of the water and oil phases together. When the emulsifying agent is not present in two the immiscible liquid, the interfacial tension between water and oil is low. As a result, there is a high probability of coalescence of water droplets and emulsions are said to be unstable.

2.3.1.6 Degree of Agitation

The types and severity of agitation applied to oil-water mixtures determine the size of water droplets. The higher the degree of agitation, the smaller the size of water droplets and thus, added to the stability of emulsions.

2.3.2 Emulsifiers

According to Stewart & Arnold (2009), emulsifiers, also known as emulsifying agent or stabilizer is a material, which has surface active behavior. Some elements in emulsifiers have a preference to the oil, whilst some elements to the water. An emulsifier tends to be insoluble in one of the liquid in emulsion, thus it concentrates at the interface. Paraffins, resins, organic acids, metallic salts, colloidal sites and clays, and asphaltenes are common, naturally occurring surface active material.

Emulsifiers will form a viscous coating on the droplets. This thin film prevents the water droplets to coalescence into larger droplets when they collide. The presence of this film makes the small water droplets take a longer time to settle out from the oil phase-stability added. Emulsifiers may be polar molecules that align themselves around the water droplets. This alignments cause an electrical charge on the surface of the water droplets and since like electrical charges repel, water droplets must collide with sufficient force to overcome the repulsion before coalescence.

2.3.2.1 Surface Active Agent

Surface-active agents (surfactants) are compounds that partially soluble in both phases (water and oil). Surfactants have two parts, hydrophobic part that has affinity to oil phase and a hydrophilic part that has affinity for water (Kokal, 2006). Thus, surfactants have high tendency to concentrate at water/oil interface, and form a thin layer of interfacial film that encapsulates and prevent the water droplets to coalescence. Thus, the water droplets are dispersed in the continuous phase of oil and promote the stability of the emulsions.

2.3.2.2 Finely Divided Solids

Other than surfactants, finely divided solids can act as mechanical stabilizer. The fine solids which are much smaller than dispersed droplets (usually submicron) are collected at the interface of water and oil and are wetted by both water and oil. The very fine solids block the movement of water droplets and prevent them from coagulate and coalescence. However, the effectiveness of the solids highly dependent on particle sizes, interparticle interactions and wettability of the particles (Kokal, 2006).

2.4 Separation of Crude oil Emulsions

Crude oil present as emulsions naturally, even in the crude oil well. However the presence of these emulsions (water-in-oil or oil-in-water) caused the quality of the oil deplete. Therefore, separation needed to separate the emulsion into their respective phase. Three processes are considered in separation: creaming (sedimentation), aggregation, and coalescence (Schramm, 1992). When the emulsion starts to separate, we can observe the oil layer on the top of water with our naked eyes.

2.4.1 Mechanism of Separation

There are there mechanisms involved in separation of emulsions: aggregation, coalescence an sedimentation of creaming. Aggregation is a phenomenon where two droplets become attached to each other at a certain point but are still separated by a thin layer and virtually no change in total surface area or lose their identity. This is also sometimes known as coagulation or flocculation (Schramm, 1992; Kokal, 2006). When more droplets are attached to each other, the individual cluster together and the thin film is retained between them. The thin liquid film will eventually destabilized, burst and form a large single droplet, which known as coalescence (Jacqueline, 1994). The droplet has a size that recognized by naked eyes as a separate phase. Creaming is the opposite of sedimentation and is result from a density difference between two liquid phases.

2.4.1.1 Aggregation or Flocculation

Aggregation or flocculation is a phenomena where droplets clump together, forming aggregates or "flocs". The droplets are close to each other and touch at certain points but there is a film that surrounds the droplets and prevents the droplets to coalescence. When temperature increases, the thermal energy in the water droplets increase and cause the frequency of collisions between water droplets increase thus promote flocculation (Kokal, 2006).

2.4.1.2 Coalescence

Coalescence occurred when small water droplets fused and from bigger droplets. The coalescence rate increases when the frequency of collision increases which can be induced by increasing temperature (Kokal, 2006). Coalescence is a irreversible process

and number of water droplets will decrease due to formation of big water droplets from few small water droplets.

2.4.1.3 Sedimentation

Sedimentation or creaming is a phenomenon occurred due to the density difference between two phases. Sedimentation occurred when the water droplets in emulsions settle due to its higher density (Kokal, 2006). Creaming, reverse of sedimentation is used to describe the oil phase, which has lower density rise to the surface of the sample (Schramm, 1992).

2.4.2 Methods of Separation

However, as consequences of small droplet size and presence of interfacial film on the droplet, the emulsion exerts a stable dispersion and it does not settle out by itself and coalesce quickly. Therefore various separation methods are introduced to effectively separate the crude oil emulsions: chemical destabilization with dissolved air flotation (Al-Shamrani et al., 2001), membrane associated process (Benito et al., 2006), freezing and thawing (Chen & He, 2003), electrical system (Eow et al., 2001), ultrasonic (Ye, 2008), microwave irradiation (Chan & Chen, 2002) and other methods or combinations. The conventional method possesses excessive heating, chemical addition and high residence time (Eow & Ghadiri, 2002). Improvement of existing technologies and development of new appropriate method are important to ensure high productivity in crude oil processing.

2.5 Microwave Heating Method

Microwave radiation has been successfully used in many fields of chemistry, including organic synthesis (Cravotto & Cintas, 2007), sample digestion and drying processes (Maichin, 2000). Taking into account the fast energy transfer to irradiated medium, microwaves could be used to perform the demulsification of heavy crude oil emulsions (and, consequently, reducing interferences in further analysis) in a faster way than conventional methods. The microwave demulsification process allows for the destabilization of emulsions, first, by increasing the temperature (it causes a reduction of the continuous phase viscosity and breaks the outer film of drops allowing for the coalescence) and, second, by rearranging the electrical charge distribution of water molecules while rotating them and moving ions around the drops. These two combined effects could result in emulsion breaking without the addition of any chemical agent (Chan & Chen, 2002).

The concept of microwave heating to separate w/o emulsions is first used by Klaila (1983) and shown a positive result. Microwave heating is a different method from other conventional heating method because it make use of electromagnetic waves that penetrate into the molecule and the mechanism of heat transfer took place while other conventional heating transfer heat to the surface of the material. By penetrating heat energy direct into the water molecule, the interfacial thin film in between the small water droplet become destabilized, break and therefore coalescence to form a bigger water molecule. The big water droplet is then separated, where form two layers (oil on top and water at bottom), as the density of oil is much lower than that of water.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This chapter covers the materials, equipments and methods used to solve the problems stated in Chapter 1. Generally, the study is divided into three parts, namely Phase 1: Preparation and formulation of crude oil emulsions; Phase 2: Characterization of the prepared and formulated emulsions in terms of physical and chemical properties; Phase 3: Demulsification of crude oil emulsions via Microwave Heating Technology. Phase 1 is treated as the fundamental phase for undergoing Phase 2 and 3. Phase 1 covers preparation and stabilization of crude oil emulsions using agent-in-oil method with different types of emulsifier and agitation speeds. Phase 2 is the characterization of emulsion formulated whether it is water-in-oil (w/o) or oil-in-water (o/w) from its physical and chemical properties. Phase 3 is a separation of crude oil emulsions formulated using Microwave Heating Technology at different microwave power generation.



Figure 3.1: Flow Chart of Methodology on Microwave Heating Technology in Separating Water-in-oil Emulsions

3.2 Materials

3.2.1 Raw Material

- i. Crude Oil (collected from Petronas Refinery at Melaka)
- ii. Distilled water

3.2.2 Emulsifiers (Emulsifying Agent/ Stabilizer)

- i. Triton X-100
- ii. Span 80
- iii. Span 83
- iv. Cocoamide MEA

3.3 Equipments

- i. Propeller
- ii. Pico-TC-08 Data Logger
- iii. Brookfield Device
- iv. Digital Tensiometer
- v. Microscope
- vi. Elba domestic microwave oven model: EMO 808SS

3.4 Methods of Research

3.4.1 Crude Oil

The crude oil used in this research is 50-50% blended crude oil obtained from Petronas Refinery at Melaka.

3.4.2 Phase 1: Preparation and formulation of crude oil emulsions

In laboratory, water-in-oil emulsions of 20-80% and 50-50% were prepared. Emulsions were prepared in a 200ml clear graduated glass beaker, which ranges by volume of water and oil phase using different types of emulsifiers and thus agitated at different speeds using a propeller.

The agent-in-oil method is implemented to prepare the w/o emulsions (adapted from Nour.et al., 2010). Distilled water is used in preparing the emulsions. The emulsifying agents, Triton X-100, Span 80, Span 83 and Cocoamide MEA were used as manufactured without dilution and dissolved in the continuous oil phase at a concentration of 0.50 v/v%. Then, distilled water is added gradually into the mixture. The emulsions are then agitated vigorously using a standard three blade propeller at a speed of 500rpm, 1000rpm and 1500rpm and a temperature of 28 $^{\circ}$ C for 7 minutes on different samples. 40ml of the sample is poured into 50ml measuring cylinder and allow standing for 2 days. The observation on the separation is recorded to calculate the separation efficiency of the emulsions.

The percentage of water separation is calculated as separation efficiency (e) from the volume of water observed at the bottom of the beaker (Abdurahman & Rosli,

2006). All emulsions investigated must be water-in-oil emulsions (oil as continuous phase).

Separation efficiency (e) =
$$\frac{Vol.of water layer(ml)}{Original amount of water(ml)} \times 100\%$$
 (3.1)

3.5 Phase 2: Characterization of the prepared and formulated emulsions in terms of physical and chemical properties

The stability of emulsions prepared was tested in laboratory by determining its physical and chemical properties. The torque, shear rate, shear stress, viscosity based on the spindle rotation speed (rpm) and temperature of emulsions was determined using Brookfield device. The diameter of water droplets present in the emulsions is observed under microscope. The size of water droplets present is measured using Axio Vision Rel. 4.8 software.

3.5.1 Shear rate

Shear rate, Υ is the gradient in velocity of a flowing fluid perpendicular to the velocity. The measurement of overall velocity over the cross section of a channel with which molten or fluid layers are gliding along each other, or along the wall, in laminar flow gives Shear rate, Υ . It is expressed in reciprocal seconds (sec⁻¹)

3.5.2 Shear Stress

A shear stress, denoted τ (tau), is the stress which is applied parallel or tangential to a face of a material, as opposed to a normal stress which is applied perpendicularly. By plotting a graph of Shear Stress, τ against Shear rate, Υ the type of fluid (Newtonian or non-Newtonian) can be determined.

3.5.3 Viscosity

Viscosity is the internal resistance of a fluid to motion. The higher the viscosity, the more internal resistance present in the fluid. A viscous fluid is slow to flow and viscosity also known as "fluidity" (Cengel & Cimbala, 2006). Viscosity plays a primary role in the stability of emulsions. When viscosity of oil increases, the migration of emulsifiers to the water droplets in the water-oil interface is retarded. Thus, large droplets of water suspended in the oil and form less stable emulsions. Therefore, when the viscosity increases, more agitation speed needed to shear the large molecules of water droplets to form stable emulsions. (Stewart. & Arnold, 2009)

3.5.4 Temperature

The stability testing is carried out in a range of temperature in Brookfield device to study the effect of temperature on viscosity of emulsions. Temperature can be changed by manipulating the temperature of the water bath at the Brookfield device.

3.5.5 Rotational per minute (rpm)

Rotational per minutes refers to the rotating speed of spindles on the Brookfield per minute. The effect of spindle's rotational speed per minute on stability of emulsions is studied.

3.5.6 Surface Tension

Surface Tension, σ_s is the magnitude of the tension pulling the surface of a liquid per unit length. The pulling force acts parallel to the surface and is due to the attractive forces between molecules of the liquid. This tension cause the surface of a liquid acts like a stretch elastic membrane.

3.5.7 Interfacial Tension

Interfacial Tension is the force that holds together the surfaces of the water and oil phases. When emulsifiers are added in an emulsion, the interfacial tension increases and obstruct the coalescence of water droplets and thus form stable emulsions (Stewart & Arnold, 2009).

3.5.8 Particle Diameter, D_p

Particle diameter, D_p refers to the size of water droplets. The stability of emulsions is highly influenced by particle diameter. The larger the droplet, the faster it will settles out from the oil phase (Stewart & Arnold, 2009). Agitation speed of emulsions during preparation highly influences the particle diameter, D_p .
3.6 Phase 3: Demulsification of crude oil emulsions via Microwave Heating Technology

In this study, Elba domestic microwave oven model: EMO 808SS with output power 900 watts and operation frequency of 2450 MHz. A 500mL graduated cylinder with diameter 8.7cm and height 11.8cm was used as sample container. Three thermocouples type (K-IEC- 584-3) which connected to Pico-TC-08 data logging with PicoLog R5.08.03 software. The three thermocouples are inserted into the emulsions sample at three different locations: top, middle, and bottom to measure the temperature of the emulsions and determine the temperature distributions at all different locations of irradiated emulsions.

3.6.1 Preparation of Samples

From the result obtained in Phase 1: Preparation and formulation of crude oil emulsion, the most stable set of water-in-oil emulsions sample is prepared for demulsification. It was known that 50-50% w/o emulsions prepared using Span 80 under agitation speed of 1000rpm is the most stable emulsions. This set of emulsions was prepared at volume of 200mL in a 500mL graduated cylinder. The container of emulsion sample was placed at the centre of the Elba EMO 808SS microwave oven and three thermocouples connected to Pico-TC-08 were placed at three locations of the sample: top, middle and bottom as shown in Figure 3.2.



Figure 3.2: Elba EMO 808SS Microwave Oven

3.6.2 Microwave Heating

Microwave heating has been widely used in various industries such as food industries and chemical industries for heating, melting and sintering of ceramics due to its volumetric heating effects that provides faster processing rate with uniform distribution of heat. Microwave heating has a high penetrating power, which able to penetrate energy, not on the surface of the materials but into the molecules of the substance. The penetrating energy in microwave heating technology overcomes many surface limiting characteristics than normal heating (Abdurahman & Rosli, 2006). Therefore, microwave heating provides a better heating and separation of water.

The separation of w/o emulsions consists of two main stages: flocculation and coalescence. When w/o emulsions are being heated in the microwave, the temperature will increase and causes the reduction in viscosity of the liquid and coalescence. According to Stoke's Law, if the oil is the continuous phase, the settling velocity of water will be given as:

$$v_w = \frac{(\rho_w - \rho_0)gD^2}{18\mu_0}$$
(3.2)

where, D is the diameter of the droplets. The viscosity which is sensitive to temperature will decrease more significantly than the density difference ($\rho_w - \rho_o$), and thus the droplet size, D increases. This explains the phenomenon of flocculation. The microwave heating also increase the velocity of the water, v_w as energy is transferred to the water and accelerates the separation.

The microwave is first set to its highest power setting. Sets of sample emulsions is heated under microwave under different penetrating power (350 watts, 540 watts and 720 watts) for 5 minutes, 3 minutes and 2 minutes respectively to investigate the effect of varying the microwave power generation on w/o emulsion separation.

3.6.3 Microwave Power Generation

In the study of demulsification via microwave heating, the main focus are rate of heat generation, q_{MW} , temperature distributions, rate of temperature increase, penetration depth, D_p , wavelength, λ_w and separation efficiency of the emulsion samples.

The rate of heat generation, q_{MW} from microwave heating is dependent on physical and dielectric properties. There are three dielectric properties involves in microwave heating: dielectric constant (\mathcal{E}_r '), dielectric loss (\mathcal{E}_r '') and loss tangent (tan δ).

Dielectric constant (\mathcal{E}_r) and dielectric loss (\mathcal{E}_r) of water used in this study given by Wolf (1986) are expressed as following (Nour et.al., 2010; Fang & Lai, 1994):

$$\mathcal{E}'_r = 85.215 - 0.33583 \, T \tag{3.3}$$

$$\mathcal{E}_{r}^{"} = 320.658 \, T^{-1.0268} \tag{3.4}$$

Dielectric properties of various petroleum oils were proposed by von Hippel (1954). The dielectric constant (\mathcal{E}_r ") and loss tangent (tan δ) of crude oil in this study is based on these equations.

$$\mathcal{E}'_{r,o} = 2.24 - 0.000727 \, T \tag{3.5}$$

$$\tan \delta_o = (0.527 \, T + 4.82) \, x \, 10^{-4} \tag{3.6}$$

According to Nour et.al., (2010) & Fang & Lai (1994), Microwave power flux for a sample in cylinder container was calculated as:

$$P_o = \frac{453.2 + 59.8 \ln(m)}{A} \tag{3.7}$$

Where,

- m = mass of the sample
- A = sample's container surface area

The attenuation factor of the electric field can be calculated from the electromagnetic field theory:

$$\alpha_E = \frac{2\Pi f}{c} \left[\frac{\varepsilon_r'}{2} \left(\sqrt{1 + \tan^2 \delta} - 1 \right) \right]^{1/2}$$
(3.8)

Microwave power transmitted, P_z is given by Beer-Lambert's equation, expressed as:

$$P_z = P_o e^{2\alpha z} \tag{3.9}$$

Where,

 $P_{\rm o}$ is the microwave power flux

 α is the attenuation power expressed in Equation 3.8

The rate of heat generation, q_{MW} by microwave heating is calculated using:

$$q_{MW} = \frac{2\alpha_E}{4.184} P_z \tag{3.10}$$

If the dielectric properties are assumed to be independent of temperature at frequency 2450 MHz, the penetration depth, D_p and wavelength, λ_w within a sample for the radiation of the frequency are related to dielectric constant (\mathcal{E}_r) and dielectric loss (\mathcal{E}_r) using the equations as follow:

$$D_{p} = \frac{c}{2\Pi f} \left[\frac{\mathcal{E}_{r}^{\prime} \left(\sqrt{1 + \left(\frac{\mathcal{E}_{r}^{\prime \prime}}{\mathcal{E}_{r}^{\prime \prime}}\right)^{2}} - 1 \right)}{2} \right]^{1/2}$$
(3.11)

and

$$\lambda_m = \frac{c}{f} \left[\frac{\mathcal{E}'_r \left(\sqrt{1 + \left(\frac{\mathcal{E}_r''}{\mathcal{E}_r'}\right)^2 + 1} \right)}{2} \right]^{-1/2}$$
(3.12)

Since microwave heating heats materials volumetrically, the volume rate of microwave heat generation can be calculated using energy balance equation by taking into consideration of convective heat transfer, radiative heat due to microwave and conductive heat transfer as expressed in Equation 3.13.

$$g_{MW} = \frac{hA}{V}(T_m - T_a) + \frac{\epsilon A\sigma}{V}[(T_m + 273.15)^4 - (T_a + 273.15)^4] + \rho C_p\left(\frac{dT}{dt}\right)$$
(3.13)

Equation 3.13 assumes the rate of heat transfer from the water droplets to continuous phase of oil is very rapid, thus water and oil possessed the same temperature.

For the calculation of volume rate of microwave heat generation in Equation 3.13, the density, ρ and heat capacity, Cp of the emulsions can be calculated using mixing rules:

$$\rho_{\rm m} = \rho_{\rm w} \phi + \rho_0 (1 - \phi) \tag{3.14}$$

$$C_{pm} = C_{p,w}\phi + C_{p,0}(1-\phi)$$
 (3.15)

The separation efficiency of the demulsified emulsions are determined using Equation 3.1. The data obtained are presented in Chapter 4.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Overview

This chapter presents all the results of the research carried out based on the methodology discussed in Chapter 3 and critically discusses the results obtained. This chapter was presented in two sections:

- i. Study the emulsification and stabilization of w/o emulsions; and
- ii. Study the demulsification of crude oil emulsions via microwave heating technology.

In order to achieve the objectives of this research, a screening process was carried out to identify the most effective emulsifiers without considering the price of the emulsifiers. The main objectives of this research is to identify the most effective emulsifiers which can be used to prepare a stable emulsions, and to study on the heating mechanism and penetration power of microwave heating technology. The raw data for all tests are shown in Appendix.

4.2 Emulsification

Emulsions were prepared using Agent in Oil method. Four types of emulsifiers were chosen to conduct the comparative studies: Span 80, Span 83, Triton X-100 and Cocamide MEA. Table 4.1 shows the properties of the emulsifiers used.

Emulsifier	HLB	Solubility
Span 80	4.3	Non ionic; oil soluble
Span 83	3.7	Non-ionic; oil soluble
Triton X-100	13.7	Non-ionic; water soluble
Cocamide MEA	13.5	Non-ionic; water soluble

Table 4.1: Properties of Emulsifiers

Emulsions of ratio 20-80% and 50-50% were prepared using different agitation speeds (500rpm, 1000rpm and 1500rpm) to identify the threshold agitation speed in preparing stable emulsions. The concentrations of emulsifiers were kept constant at 0.5v/v%.

The performance of the emulsifiers was evaluated using Bottle Test for two days (Schramm, 2005). The chemical and physiochemical properties were investigated to access the stability of each emulsion: viscosity, shear rate, and shear stress. The droplets sizes of the emulsions were observed under microscope and measured using Axio Vision Rel. 4.8.

The most stable emulsions prepared were used in phase 2 of this experiment, demulsification of crude oil emulsions via microwave heating technology to investigate the effect of microwave heating power on separation efficiency of water from emulsions.

4.3 Bottle test (Gravitational Settling)

The prepared emulsions were allowed to stand and settle for 2 days and the percentage of water separation which is the amount of water separated from the total amount of water were determined using Equation 4.1.

Separation Efficiency (e) =
$$\frac{\text{Volume of water layer (mL)}}{\text{Original Amount of water (mL)}} X 100\%$$
 (4.1)

Percentage of water separated determined the stability of the emulsions and thus classifies the emulsifiers. Comparisons of percentage of water separation between samples were based on the w/o ratio and agitation speed used to prepare the emulsions. The percentage of water separation of the four emulsifoers used (Span 80, Span 83, Triton X-100 and Cocamide MEA) to prepare samples of 20-80% and 50-50% w/o emulsions with 500rpm, 1000rpm and 1500rpm agitation speed were shown in Figures below.



Figure 4.1: Percentage of water separation for 20-80% w/o emulsions at 500rpm



Figure 4.2: Percentage of water separation for 20-80% w/o emulsions at 1000rpm



Figure 4.3: Percentage of water separation for 20-80% w/o emulsions at 1500rpm



Figure 4.4: Percentage of water separation for 50-50% w/o emulsions at 500rpm



Figure 4.5: Percentage of water separation for 50-50% w/o emulsions at 1000rpm



Figure 4.6: Percentage of water separation for 50-50% w/o emulsions at 1500rpm

From the Figures shown above, it was found that the percentage of water separation for emulsions prepared using Triton X-100 were the highest, indicating the

Triton X-100 was not an effective emulsifiers compared to the other three. The emulsions prepared were unstable and easily separated from the emulsions to form two phases, water and oil.

Cocamide MEA is an emulsifier present in the form of solid. Thus it was not readily mixed or dispersed in the continuous oil phase during sample preparation. Thus, the solid was grounded to $360\mu m$ in size so that it can be distributed evenly in the water and oil interface and thus enables the formation of emulsions.

From the experiment, it was found that the emulsions prepared using Cocamide MEA has very high viscosity, which will add the stability of the emulsions. However, the water starts to separate at time 120s from the emulsions although it possessed a high viscosity. This may due to improper dissolved and not uniform distribution of Cocamide MEA in the oil phase during sample preparation. Absence of emulsiers in some area in the continuous oil phase allowed coalescence of water droplets occur easily.

Other than that, instability of the emulsions formed may also caused by wettability of Cocamide MEA as a mechanical stabilizer. Cocamide MEA may not be able to wet by oil and water completely and cause instability of emulsions formed. This phenomenon is confirmed by the small droplet size of the emulsions formed, ranged from 0.377μ m to 0.91μ m. Due to this relatively small water droplets, the Cocamide MEA, which is water soluble is unable to dissolve completely in the water to perform as an effective emulsifier.

Span 83 and Span 80 were effective emulsifiers because 0% of water separated from the emulsions for both 20-80% and 50-50% w/o emulsions. However, Span 80 emerges as a more effective emulsifier because the percentage of oil separation for emulsions prepared using Span 80 is lower.

As a conclusion, the classification of emulsifiers in terms of decreasing stability of emulsion is therefore as following:

Span 80 > Span 83 > Cocamide MEA > Triton X-100

Decreasing stability

Based on the % water separation, it was found that for (i) 50-50% w/o emulsions, Span 80 at 1000rpm produced the most stable emulsions while for (ii) 20-80% w/o emulsions, Span 80 at 1500rpm produced the most stable emulsions.

4.4 Emulsification of Crude Oil Emulsions

4.4.1 Span 80, 50-50% w/o emulsions at 1000rpm

The separation of 50-50% w/o emulsions formed using 0.5v/v% Span-80 emulsifiers under agitation speed of 1000rpms is shown in Figure 4.7. The emulsions prepared were stable and no water is separated from the emulsions on standing after 2 days.



Figure 4.7: Separation of Crude Oil Emulsions (Span 80, 50-50%, 1000rpm)



Figure 4.8: Effect of temperature on the viscosity

From Figure 4.8, viscosity decreased as the temperature increased at varied stirring speed. The trend followed Stoke's Law Equation (Equation 4.2).

$$v_{\rm w} = \frac{(\rho_0 - \rho_{\rm w}) D^2 g}{18\mu_0}$$
(4.2)

Viscosity is a function of temperature. Viscosity of the emulsions decreases with the increase in temperature. When the temperature increased, the solubility of emulsifiers in the emulsions changed. The water droplets possessed higher energy and tend to move more vigorously and the possibility of water droplets to collide increased. These will affect the interfacial film surrounding the water droplets and disturb the interfacial tension. The flow of molecules through the interfaces will be increased and causes the reduction of viscosity that implies the decrease of emulsion stability.



Figure 4.9: Photomicrograph of water droplet distributions

4.4.2 Span 80, 20-80% w/o emulsions at 1500rpm

The separation of 20-80% w/o emulsions formed using 0.5 v/v% Span-80 emulsifiers under agitation speed of 1500rpms is shown in Figure 4.10. No water is separated from the emulsions proves that the emulsions prepared are very stable. From Figure 4.10, the oil starts to separate out from the emulsions at time 120s and only 14ml of oil separated from the emulsions after 2 days shows the stability of the emulsions.



Figure 4.10: Separation of Crude Oil Emulsions (Span 80, 20-80%, 1500rpm)



Figure 4.11: Effect of temperature on the viscosity

The viscosity of the emulsions decreased with increased temperature shows the stability of emulsion is affected with increase temperature as discussed in Section 4.4 above.



Figure 4.12: Photomicrograph of droplet size distributions

4.5 Brookfield Analysis

The characteristics of the emulsions were tested using Brookfield Device to determine the viscosity with ranges of temperature (30°C, 50°C, 70°C and 90°C) and different spindle rotational speed (50rpm, 100rpm, 150rpm and 200rpm).

4.5.1 Viscosity versus Temperature

The effects of temperature on the viscosity of the emulsions are shown in figures below.



Figure 4.13: Viscosity versus temperature at 150rpm Brookfield stirring speed

Figure 4.13 shows how the viscosity of emulsions varies with the increase of temperature. According to Stoke's Law, viscosity is affected by the changes in temperature. Viscosity is inversely proportional to temperature, thus viscosity will decrease when temperature increased. Change of temperature will affect the stability of the emulsions.

Energy is transferred from the heat energy to kinetic energy in the water droplets. The motions of water droplets increased due to the kinetic energy and allow more frequent collisions between water droplets. These will affect the interfacial film surrounding the water droplets and weaken the interfacial film surrounding the water droplets that prevent it from coalescence and form bigger droplets and eventually settles due to gravitational force. The flow of molecules through the interfaces will be increased when energy is absorbed and causes the reduction of viscosity that implies the decrease of emulsion stability.

From the figure above, the viscosity of emulsion prepared using Cocamide MEA shows a sudden increase in viscosity with increase of temperature at 70 °C. This turning point indicated the phase inversion temperature (PIT) at which the w/o emulsions inverted to o/w emulsions. When temperature increased, the hydrophilic and lipophilic tendencies were balanced. Phase inversion occurred due to the change in the characteristics of the emulsifiers during the increase of temperature.



Figure 4.14: Viscosity versus temperature (Span 83, 50-50%, 500rpm)

Figure 4.14 shows the viscosity versus temperature graph for emulsions prepared using Span 83, 50-50% at 500rpm. The strange phenomenon occurred in the experiment is when multiemulsions (w/o/w) occurred when the temperature increases. The viscosity of multiemulsions will produce a polynomial curve with variations of temperature as shown in Figure 4.14. As temperature increases, the phases in the emulsions changes from water in oil to water-in-oil-in-water (w/o/w). These occurred

highly due to improper dispersion of emulsifiers among the oil phase during emulsions preparation and cause the water droplets are not properly dispersed in the continuous phase of oil. The interfacial film formed surrounding water droplets are weak in certain area of the emulsions and cause water coalescence and form bigger water droplets when energy introduced into the sample by increasing the temperature.

4.5.2 Shear stress versus shear rate



i. 20-80% w/o emulsions at 500rpm

Figure 4.15: Shear Stress versus Shear Rate at 30°C

For Newtonion fluid, shear stress is directly proportional to shear rate and the curve of shear stress versus shear rate will pass through the origin. However, Figure 4.15 shows the deviation of behavior of the fluids from Newtonion fluid. Thus, the emulsions prepared were non Newtonion fluid.

4.6 Demulsification via Microwave Heating Technology

Microwave heating technology was used to examine water, oil and emulsions sample (50-50% w/o emulsions). Three different microwave powers were used to investigate on the effect of varying microwave penetration power on the crude oil emulsions separation:

- i. 360 watts for 5minutes
- ii. 540 watts for 3 minutes
- iii. 720 watts for 2 minutes

Transient temperature profiles of water-in-oil (w/o) emulsions inside a cylindrical glass beaker during batch microwave heating were measured. Figure 4.16 shows temperature variations of the emulsions sample with heating time.



Figure 4.16: Transient Temperature Profile (middle of sample)

The experiment results showed that microwave heating is effective in separation of w/o emulsions. Volumetric heating effects of microwave heating technology heated the emulsions sample in bulk, rather than just in its surface causes faster processing rate. This is proved by transient temperature profile at the middle of the sample which increased rapidly in short time. Conventional heating which transfers the heat from point to point via conduction and convection has lower rate of temperature increase.

The rate of temperature increase was calculated from temperature increase over radiation time as showed in Table 4.2 to Table 4.8. The average rates of temperature increase of 50-50% w/o emulsions at 360 watts, 540 watts and 720 watts are 0.297, 0.953 and 1.029 °C s⁻¹ respectively. From Figure 4.17, it is observed that the rates of temperature increase (dT/dt) were decreased at elevated temperature (Δ T). This was the expected results since the dielectric loss of water is small.

Dielectric constant, dielectric loss, loss tangent were calculated using Equation 3.3 to 3.6. Emulsions density (ρ_m) and heat capacity (Cp_m) were calculated using mixtures rules in Equation 3.14 and 3.15. From the results, it is observed that dielectric properties of emulsions were function of temperature. Dielectric constant and dielectric loss decreased when temperature increased.

Volume rate of heat generation, q_{MW} were calculated using Energy Balance (Equation 3.13). The Energy Balance takes into considerations of convective, radiations (due to microwave) and conductive heat transfer in the emulsions sample. However from the calculations, the heat transfer from radiations and convective heat transfer were very small. The heat loss by the glass cylinder is assumed to be negligible due to small dielectric loss. The rates heat of generation for water, crude oil and 50-50% w/o emulsions at various microwave power were shown in Table below.

Radiation time (s)	ΔT (°C) T ₀ =28.9°C	Rate of Temperature, dT/dt (°C/s)	Rate of heat generation, q_{MW} (cal/s.cm ³)
10	2.15	0.21	0.0054
20	8.70	0.43	0.0062
30	10.32	0.34	0.0064
40	0.88	0.25	0.0064
50	15.08	0.30	0.0070
60	18.30	0.31	0.0074
70	17.83	0.25	0.0073
80	21.17	0.26	0.0077
90	26.17	0.29	0.0082
100	25.62	0.26	0.0082
110	27.93	0.25	0.0084
120	33.56	0.28	0.0090
130	32.91	0.25	0.0089
140	33.56	0.24	0.0090
150	40.24	0.27	0.0097
160	39.86	0.25	0.0096
170	39.14	0.23	0.0096
180	45.01	0.25	0.0101
190	46.40	0.24	0.0102
200	44.94	0.22	0.0101
210	48.11	0.23	0.0104
220	52.07	0.24	0.0108
230	50.49	0.22	0.0106
240	51.31	0.21	0.0107
250	56.69	0.23	0.0112
260	55.82	0.21	0.0111
270	55.27	0.20	0.0110
280	60.31	0.22	0.0115
290	61.11	0.21	0.0115
300	60.03	0.20	0.0114

 Table 4.2: Experimental Results of Continuous Microwave Heating (Crude Oil) (Microwave power: 360 watts)

Radiation time (s)	ΔT (°C) T ₀ =28.9°C	Rate of Temperature, dT/dt (°C/s)	Rate of heat generation, q_{MW} (cal/s.cm ³)
10	12.87	1.29	0.0067
20	21.70	1.09	0.0077
30	19.67	0.66	0.0075
40	18.63	0.47	0.0074
50	28.41	0.57	0.0085
60	26.31	0.44	0.0082
70	22.44	0.32	0.0078
80	31.33	0.39	0.0088
90	32.06	0.36	0.0088
100	26.37	0.26	0.0082
110	30.57	0.28	0.0087
120	36.21	0.30	0.0093
130	28.99	0.22	0.0085
140	27.43	0.20	0.0084
150	35.26	0.24	0.0092
160	30.60	0.19	0.0087
170	27.11	0.16	0.0083
180	33.26	0.18	0.0090
190	31.82	0.17	0.0088
200	27.39	0.14	0.0083
210	29.66	0.14	0.0086
220	30.56	0.14	0.0087
230	26.55	0.12	0.0083
240	26.66	0.11	0.0083
250	33.12	0.13	0.0089
260	30.13	0.12	0.0086
270	28.00	0.10	0.0084
280	35.33	0.13	0.0092
290	32.65	0.11	0.0089
300	28.76	0.10	0.0085

 Table 4.3: Experimental Results of Continuous Microwave Heating (Water) (Microwave power: 360 watts)

Radiation time (s)	ΔT (°C) T ₀ =28.9°C	Rate of Temperature, dT/dt (°C/s)	Rate of heat generation, q_{MW} (cal/s.cm ³)
10	5.93	0.59	0.0059
10	21.85	1.09	0.0077
20	33.03	1.10	0.0089
30 40	25.28	0.63	0.0081
40 50	38.01	0.76	0.0094
50	49.76	0.83	0.0106
00 70	36.89	0.53	0.0093
70	39.93	0.50	0.0096
80	54.65	0.61	0.0110
90	46.90	0.47	0.0103
100	39.85	0.36	0.0096
110	53.50	0.45	0.0109
120	51.75	0.40	0.0107
130	40.00	0.29	0.0096
140	49 50	0.33	0.0105
150	56.04	0.35	0.0111
160	30.67	0.33	0.0006
170	J7.02 12.96	0.23	0.0090
180	43.80	0.24	0.0100

Table 4.4: Experimental Results of Continuous Microwave Heating (Crude Oil)
(Microwave power: 540 watts)

Radiation time (s)	ΔT (°C) T ₀ =28.9°C	Rate of Temperature, dT/dt (°C/s)	Rate of heat generation, q_{MW} (cal/s.cm ³)
10	4.11	0.41	0.00568
20	26.25	1.31	0.00823
30	38.83	1.29	0.00952
0	26.03	0.65	0.00820
50	36.99	0.74	0.00934
60	51.61	0.86	0.01072
70	39.23	0.56	0.00956
80	37.78	0.47	0.00942
90	54.58	0.61	0.01098
100	50.85	0.51	0.01066
110	38.18	0.35	0.00946
120	47.00	0.40	0.01037
130	59.44	0.46	0.01140
140	41.75	0.30	0.00981
150	44.79	0.30	0.01010
160	57.31	0.36	0.01122
170	47.56	0.28	0.01036
180	41.57	0.23	0.00979

 Table 4.5: Experimental Results of Continuous Microwave Heating (Water) (Microwave power: 540 watts)

Radiation time (s)	ΔT (°C) T ₀ =28.9°C	Rate of Temperature, dT/dt (°C/s)	Rate of heat generation, q_{MW} (cal/s.cm ³)
10	8.16	0.82	0.0062
20	15.76	0.79	0.0071
30	13.07	0.44	0.0068
40	16.08	0.40	0.0071
50	24.81	0.50	0.0081
60	23.18	0.39	0.0079
70	21.30	0.30	0.0077
80	29.38	0.37	0.0086
90	32.48	0.36	0.0089
100	27.99	0.28	0.0084
110	30.70	0.28	0.0087
120	37.38	0.31	0.0094
130	33.36	0.26	0.0090
140	32.96	0.24	0.0089
150	41.02	0.27	0.0097
160	38.49	0.24	0.0095
170	35.30	0.21	0.0092
180	43.01	0.24	0.0099
190	43.55	0.23	0.0100
200	38.52	0.19	0.0095
210	41.82	0.20	0.0098
220	48.10	0.22	0.0104
230	42.67	0.19	0.0099
240	38.75	0.16	0.0095
250	47.50	0.19	0.0104
260	46.36	0.18	0.0102
270	41.20	0.15	0.0098
280	48.34	0.17	0.0104
290	53.60	0.18	0.0109
300	46.87	0.16	0.0103

Table 4.6: Experimental Results of Continuous Microwave Heating (50-50% w	N/O
emulsions) (Microwave power: 360 watts)	

Radiation time (s)	ΔT (°C) T ₀ =28.9°C	Rate of Temperature, dT/dt (°C/s)	Rate of heat generation, q_{MW} (cal/s.cm ³)
10	17.09	1.71	0.0072
20	55.99	2.80	0.0111
30	60.52	2.02	0.0115
40	49.27	1.23	0.0105
50	68.72	1.37	0.0121
60	80.61	1.34	0.0130
70	63.56	0.91	0.0117
80	71.80	0.90	0.0124
90	84.30	0.94	0.0132
100	71.52	0.72	0.0123
110	71.68	0.65	0.0123
120	76.71	0.64	0.0127
130	72.10	0.55	0.0124
140	65.16	0.47	0.0119
150	75.73	0.50	0.0126
160	79.31	0.50	0.0129
170	72.01	0.42	0.0124
180	88.72	0.49	0.0135
190	93.52	0.49	0.0137
200	83.05	0.42	0.0131

Table 4.7: Experimental Results of Continuous Microwave Heating (50-50% w/oemulsions) (Microwave power: 540 watts)

Radiation time (s)	ΔT (°C) T ₀ =28.9°C	Rate of Temperature, dT/dt (°C/s)	Rate of heat generation, q_{MW} (cal/s.cm ³)
10	10.70	1.07	0.0065
20	41.74	2.09	0.0098
30	54.45	.81	0.0110
40	46.22	1.16	0.0102
50	59.15	1.18	0.0114
60	67.80	1.13	0.0121
70	59.13	0.84	0.0114
80	62.09	0.78	0.0116
90	72.57	0.81	0.0124
100	70.43	0.70	0.0123
110	66.53	0.60	0.0120
120	75.35	0.63	0.0126
130	74.88	0.58	0.0126

Table 4.8: Experimental Results of Continuous Microwave Heating (50-50% w/oemulsions) (Microwave power: 720 watts)



Figure 4.17: Rates of Temperature Increase for Water and Crude Oil (Microwave Power: 360 watts)



Figure 4.18: Rates of Temperature Increase for Water and Crude Oil (Microwave Power: 540 watts)



Figure 4.19: Rates of Temperature Increase for 50-50% w/o emulsions at various Microwave Powers



Figure 4.20: Heating Rate vs. Radiation Time for 50-50% w/o emulsions

Microwave heating with volumetric heating effects heated the emulsions sample at high rate. Heat is transferred uniformly into the 50-50% w/o emulsions sample (Nour, A.H. et.al., 2010). When the temperature increased, viscosity decreased and allowed coalescence of water droplets, resulting in separation of water without chemical additions (Fang et.al., 1989). According to Stoke's Law, when temperature increased, viscosity which is temperature sensitive decreased rapidly than the density difference $(\rho_w-\rho_o)$ and caused droplet size increased. When heating effect took place, the water droplets also possessed kinetic energy and increased it velocity. Increased in temperature and velocity of water droplets as well as decreased in viscosity made coagulations easier and accelerated separation of water. The separation efficiency of water is presented in Figure 4.21.



Figure 4.21: Water Separation Efficiency vs. time

Microwave heating has unique penetrating power that distributed the energy uniformly with the bulk of most materials. The relatively long wavelength of microwave penetrates deeply into the emulsions sample, overcomes surface limiting characteristics of conventional heating. Temperature within the emulsions samples increased at high rate reduced the viscosity and increased velocity of water, which are able to accelerate the demulsification process.

Table 4.9 shows penetration depth (D_p) and wavelength (λ_m) at different penetration power.

Penetration Power	Penetration Depth, D _p (cm)	Wavelength, λ_m (cm)
360	6.87	1.53
540	9.72	1.70
720	8.82	1.64

Table 4.9: Penetration depth (D_p) and wavelength (λ_m)

Experiment results showed microwave heating effectively separates water-in-oil emulsions without chemical additions. Based on the results, the orders of efficiency of Microwave Power are:

540 watts > 720 watts > 360 watts

Decreasing efficiency

This phenomenon is confirmed by the larger penetration depth, D_p and longer wavelength of microwave power 540 watts. Penetration depth is deduced to have relationship with the viscosity of the emulsions. When the viscosity of emulsion increased, the hindrance of electromagnetic wave also increased. Thus, the penetration depth will then decrease. The phenomenon where the penetration depth of 720 watts is shorter can be explained based on these. As the crude oil, characteristics of the emulsions and experiment preparation time are difficult to control, the emulsions used to investigation the separation efficiency using 720 watts may face some aging and caused the viscosity increase, indirectly affected the penetration depth of microwave. **CHAPTER 5**

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

5.1.1 Emulsion Stability

Stability of emulsions was investigated by studying viscosity of the emulsions and separation efficiency of water by gravitational settling. Temperature has significant effect of emulsion viscosity. Emulsion viscosity decreases when temperature is increased. Decreased in viscosity implies the stability deficiency of an emulsion.

Based on results of the experiment, it was found that Span 80 and Span 83 formed more stable emulsion for both emulsions (20-80% and 50-50%) over the changes in temperature. No water separated from the emulsions after two days proved Span 80 and Span 83 are stable emulsifiers.
Emulsions formed using Cocamide MEA has high viscosity but it is not stable. Separation of water occurred after 2 hours indicated instability of the emulsion. Cocamide MEA naturally occurred in solid form which does not dissolve in oil or water. Thus, it was grinded to very fine particles ($< 360\mu$ m). These fine particles were collected at the water and oil interfaces and hindered coalescence of water droplets. This is known as mechanical stabilizer (Kokal, S.L., 2006). The high viscosity is deducted to be contributed by the fine solid collected at the oil and water interphase. The effectiveness of mechanical stabilizer depends on particle size, interparticle interactions and also the wettability of the particles. Irregular distribution of particles in both phases and unwettability of the particles allowed water separation rate increased.

Triton X-100 showed the highest percentage of water separation indicating that Triton X-100 is the least stable emulsifiers. Emulsions prepared using Triton X-100 also possess low viscosity. Thus the efficiency of emulsifiers is classified as following:

Span 80 > Span 83 > Cocamide MEA > Triton X-100

Decreasing stability

From the study, it was found that viscosity of the emulsions decreased with increased stirring speed of spindle. This phenomenon can be explained by the friction force presents between the emulsions and wall of spindle. Heat will be dissipated when there is frictional force and thus increased the temperature in the emulsion samples. Temperature increased again will cause the decrease in viscosity. The turbulent flow induced as the stirring speed increased also contributed in the decrease in viscosity. Turbulent flow will exhibit a drag reduction and this drag reduction lower the viscosity of the emulsion kinetically.

Significant findings in this study were found in Figure 4.13 where phase inversion of emulsions took place, where w/o emulsions is inverted to o/w emulsions.

Viscosity is no longer function of temperature and it increased with the rising of temperature. The temperature where viscosity deviates from its trend is known as Phase Inversion Temperature (PIT). At this temperature, the hydrophilic and lipophilic tendencies were balanced. Phase inversion thus occurred due to the change in the properties and characteristics of the emulsifiers when the temperature increased.

It was also found the phenomenon of formation of multiemulsions (w/o/w) when temperature increased as shown in Figure 4.14. This phenomenon can be explained by improper dispersions of emulsifiers in the continuous phase of oil during emulsion preparation due to low agitation speed. Thus, the emulsifiers were unevenly distributed in both phase. Some water droplets are encapsulated by the thin interfacial films formed by the emulsifiers while some were not. These allowed formation of multiemulsions where temperature is introduced in the emulsions sample.

Curve line of the graph Shear stress versus shear rate in Figure 4.15 shows all the emulsion formed are non-Newtonion fluid. As a conclusion, the emulsifiers are classified as follow:

Span 80 > Span 83 > Cocamide MEA > Triton X-100

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Decreasing stability

From all the samples, it was found that for (i) 50-50% w/o emulsions, Span 80 at 1000rpm will produce the most stable emulsions while for (ii) 20-80% w/o emulsions, Span 80 at 1500rpm will produce the most stable emulsions.

5.1.2 Demulsification via Microwave Heating Technology

The microwave heating process was examined for water, oil and 50-50% w/o emulsions using different microwave power generation (360 watts. 540 watts and 720 watts). Results showed that microwave heating is a dielectric heating technique that possesses fast energy transfer, volumetric and effective bulk heating.

From the transient temperature profile of irradiated emulsion (Figure 4.16), it shows water-in-oil emulsion has been heated rapidly and uniformly by microwave compared to conventional heating. Microwave which has relatively longer wavelength penetrates deeply and distributes energy within the materials in bulk, rather than just on its surface.

Microwave irradiation significantly increased the temperature of the sample at faster rate and causes reduction of viscosity of emulsions and breaks the interfacial film of the emulsions, allowing coalescence of water droplets. Microwave also rearranges the electrical charge distribution of water molecules while rotating them and moving ions around the drops. This two combined effect could result in emulsion breaking without addition of any chemical agent.

From the study which varied the microwave power generation, it was found the separation efficiency of water-in-oil emulsions follows the following trend:

540watts > 720 watts > 360 watts

Decreased efficiency

However from the previous similar studies by Nour, A.H et. al. (2009 & 2010) and Fang, C.S. et. al. (1994), high separation efficiency of water can be obtained using microwave irradiation power of 900 watts. Thus, it can be conclude that, the separation efficiency of water is directly proportional with the increase with microwave penetration power.

5.2 **Recommendations**

- i. During preparation of emulsions using Agent in oil method, emulsifiers are agitated vigorously with maximum required speed before addition of water to make sure that the emulsifiers are evenly disperses in the continuous phase of oil.
- ii. Cocamide MEA are grinded to a finer particles to study the efficiency of Cocamide MEA is preparation of a stable emulsion.
- iii. Investigation of emulsions stability by varying the concentration of emulsifiers and study the effect of varying concentration of emulsifiers on the stability of emulsions.
- iv. Separation efficiency of water also depends on the type of crude oil. For heavier crude oil, it is proposed to increase the microwave irradiation time to study the demulsification efficiency and obtain the maximum irradiation time to separate the emulsions effectively.

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APPENDIX A1

RESEARCH PLANNING

Table 6.1: Research Planning

(A) EMU	LSIFICATION	No. of samples
(i)	Ratio a. 50-50% b. 20-80%	2
(ii)	Agitation Speed a. 500rpm b. 1000rpm c. 1500rpm	2 x 3
(iii)	Concentration of emulsifier a. 0.5 v/v%	2 x 3 x1
(iv)	Emulsifier a. Span 80 b. Span 83 c. Triton X-100 d. Cocamide MEA	2 x 3 x 1 x 4
TOTAL NO	OF SAMPLES	24 samples
(B) DEM	ULSIFICATION	
(i) R a. b.	atio 50-50% 20-80%	2
(ii) M a. b. c.	licrowave Power Generation 360 watts 540 watts 720 watts	2 x 3
TOTAL NO	OF SAMPLES	6 samples

Total Crude Oil required = $(24 \times 100 \text{mL}) + (6 \times 100 \text{mL})$

= 3.0 L

APPENDIX B1

BROOKFIELD ANALYSIS



Figure 6.1: Viscosity vs Temperature (Span 80,50-50%,1000rpm)



Figure 6.2: Viscosity vs Temperature (Span 80,50-50%,500rpm)



Figure 6.3: Viscosity vs Temperature (Span 80,50-50%,1500rpm)



Figure 6.4: Viscosity vs Temperature (Span 80, 20-80%, 500rpm)



Figure 6.5: Viscosity vs Temperature (Span 80, 20-80%, 1000rpm)



Figure 6.6: Viscosity vs Temperature (Span 80,20-80%,1500rpm)



Figure 6.7: Viscosity vs Temperature (Span 83, 50-50%, 1000rpm)



Figure 6.8: Viscosity vs Temperature (Span 83, 50-50%, 500rpm)



Figure 6.9: Viscosity vs Temperature (Span 83, 50-50%, 1500rpm)



Figure 6.10: Viscosity vs Temperature (Span 83, 20-80%, 500rpm)



Figure 6.11: Viscosity vs Temperature (Span 83, 20-80%, 1000rpm)



Figure 6.12: Viscosity vs Temperature (Span 83, 20-80%, 1500rpm)



Figure 6.13: Viscosity vs Temperature (Triton X-100, 50-50%, 500rpm)



Figure 6.14: Viscosity vs Temperature (Triton X-100, 50-50%, 1000rpm)



Figure 6.15: Viscosity vs Temperature (Triton X- 100, 50-50%, 1500rpm)



Figure 6.16: Viscosity vs Temperature (Triton X-100, 20-80%, 500rpm)



Figure 6.17: Viscosity vs Temperature (Triton X-100, 20-80%, 1000rpm)



Figure 6.18: Viscosity vs Temperature (Triton X-100, 20-80%, 1500rpm)



Figure 6.19: Viscosity vs Temperature (Cocamide MEA, 50-50%, 1000rpm)



Figure 6.20: Viscosity vs Temperature (Cocamide MEA, 50-50%, 1500rpm)



Figure 6.21: Viscosity vs Temperature (Cocamide MEA, 20-80%, 500rpm)



Figure 6.22: Viscosity vs Temperature (Cocamide MEA, 20-80%, 1000rpm)



Figure 6.23: Viscosity vs Temperature (Cocamide MEA, 20-80%, 1500rpm)

APPENDIX C1

MICROWAVE IRRADIATION CALCULCATIONS

Radiation time (s)	ΔΤ	Rate of temperature increase, dT/dt	ε' _{r, w}	ε' r, o	tan δ (ε'/ε'')	٤" _{r, w}	ε" r, o	rate of heat generation, q (cal/cm3.s)	Penetration Depth, Dp (cm)	Wavelength, λw (cm)
10.00	4.11	0.41	74.13	2.22	0.0022	8.84	997.38	0.0057	3.80	1.42
20.00	26.25	1.31	66.69	2.20	0.0034	5.22	649.27	0.0082	6.10	1.50
30.00	38.83	1.29	62.47	2.19	0.0041	4.23	540.72	0.0095	7.29	1.55
40.00	26.03	0.65	66.77	2.20	0.0034	5.24	651.49	0.0082	6.08	1.50
50.00	36.99	0.74	63.09	2.19	0.0040	4.35	554.37	0.0093	7.12	1.54
60.00	51.61	0.86	58. <u>1</u> 8	2.18	0.0047	3.54	461.69	0.0107	8.40	1.60
70.00	39.23	0.56	62.34	2.19	0.0041	4.20	537.89	0.0096	7.32	1.55
80.00	37.78	0.47	62.82	2.19	0.0040	4.30	548.43	0.0094	7.19	1.54
90.00	54.58	0.61	57.18	2.18	0.0049	3.41	446.45	0.0110	8.64	1.62
100.00	50.85	0.51	58.43	2.18	0.0047	3.58	465.79	0.0107	8.34	1.60
110.00	38.18	0.35	62.69	2.19	0.0040	4.27	545.47	0.0095	7.23	1.55
120.00	47.70	0.40	59.49	2.18	0.0045	3.73	483.36	0.0104	8.07	1.59
130.00	59.44	0.46	55.55	2.18	0.0051	3.22	423.52	0.0114	9.03	1.64
140.00	41.75	0.30	61.49	2.19	0.0042	4.05	520.48	0.0098	7.55	1.56
150.00	44.79	0.30	60.47	2.19	0.0044	3.88	500.86	0.0101	7.82	1.57
160.00	57.31	0.36	56.26	2.18	0.0050	3.30	433.26	0.0112	8.86	1.63
170.00	47.56	0.28	59.54	2.18	0.0045	3.73	484.21	0.0104	8.06	1.59
180.00	41.57	0.23	61.55	2.19	0.0042	4.06	521.63	0.0098	7.54	1.56

Table 6.2: Experimental Results for Microwave Irradiation for water (540watts)

Radiation time (s)	ΔΤ	Rate of temperature increase, dT/dt	ε' _{r, w}	ε' _{r, o}	tan δ (ε'/ε'')	ε" _{r, w}	٤", ο	rate of heat generation, q (cal/cm3.s)	Penetration Depth, Dp (cm)	Wavelength, λw (cm)
10	2.15	0.21	74.79	2.22	0.0021	9.42	1046.87	0.0054	3.58	1.41
20	8.70	0.43	72.59	2.21	0.0025	7.74	898.19	0.0062	4.30	1.44
30	10.32	0.34	72.05	2.21	0.0025	7.41	867.70	0.0064	4.47	1.44
40	9.88	0.25	72.19	2.21	0.0025	7.50	875.76	0.0064	4.42	1.44
50	15.08	0.30	70.45	2.21	0.0028	6.59	788.68	0.0070	4.97	1.46
60	18.30	0.31	69.36	2.21	0.0030	6.13	742.74	0.0074	5.30	1.47
70	17.83	0.25	69.52	2.21	0.0029	6.19	749.13	0.0073	5.25	1.47
80	21.17	0.26	68.40	2.20	0.0031	5.77	706.09	0.0077	5.59	1.48
90	26.17	0.29	66.72	2.20	0.0034	5.23	650.08	0.0082	6.09	1.50
100	25.62	0.26	66.91	2.20	0.0034	5.28	655.82	0.0082	6.04	1.50
110	27.93	0.25	66.13	2.20	0.0035	5.06	632.37	0.0084	6.26	1.50
120	33.56	0.28	64.24	2.19	0.0038	4.60	581.54	0.0090	6.80	1.53
130	32.91	0.25	64.46	2.20	0.0037	4.65	587.02	0.0089	6.74	1.52
140	33.56	0.24	64.24	2.19	0.0038	4.60	581.56	0.0090	6.80	1.53
150	40.24	0.27	62.00	2.19	0.0041	4.14	530.74	0.0097	7.42	1.55
160	39.86	0.25	62.12	2.19	0.0041	4.16	533.41	0.0096	7.38	1.55
170	39.14	0.23	62.37	2.19	0.0041	4.21	538.54	0.0096	7.32	1.55
180	45.01	0.25	60.39	2.19	0.0044	3.87	499.46	0.0101	7.84	1.57
190	46.40	0.24	59.93	2.19	0.0045	3.79	491.03	0.0102	7.96	1.58

Table 6.3: Experimental Results for Microwave Irradiation for water (360 watts)

200	44.94	0.22	60.42	2.19	0.0044	3.87	499.90	0.0101	7.83	1.57
210	48.11	0.23	59.35	2.18	0.0045	3.71	481.04	0.0104	8.10	1.59
220	52.07	0.24	58.02	2.18	0.0047	3.52	459.29	0.0108	8.44	1.61
230	50.49	0.22	58.56	2.18	0.0047	3.59	467.74	0.0106	8.31	1.60
240	51.31	0.21	58.28	2.18	0.0047	3.55	463.28	0.0107	8.37	1.60
250	56.69	0.23	56.47	2.18	0.0050	3.33	436.21	0.0112	8.81	1.63
260	55.82	0.21	56.77	2.18	0.0049	3.36	440.40	0.0111	8.74	1.62
270	55.27	0.20	56.95	2.18	0.0049	3.38	443.04	0.0110	8.70	1.62
280	60.31	0.22	55.25	2.18	0.0052	3.19	419.62	0.0115	9.09	1.65
290	61.11	0.21	54.99	2.17	0.0052	3.16	416.14	0.0115	9.16	1.65
300	60.03	0.20	55.35	2.18	0.0052	3.20	420.89	0.0114	9.07	1.65

Radiation time (s)	ΔΤ	Rate of temperature increase, dT/dt	٤' _{r, w}	ε' _{r, o}	tan δ (ε'/ε'')	ε" _{r, w}	٤ " _{r, o}	rate of heat generation, q (cal/cm3.s)	Penetration Depth, Dp (cm)	Wavelength, λw (cm)
10	5.93	0.59	73.52	2.21	0.0023	8.37	955.72	0.0059	4.00	1.43
20	21.85	1.09	68.17	2.20	0.0032	5.69	698.01	0.0077	5.66	1.48
30	33.03	1.10	64.42	2.19	0.0037	4.64	586.04	0.0089	6.75	1.52
40	25.28	0.63	67.02	2.20	0.0033	5.32	659.38	0.0081	6.00	1.49
50	38.01	0.76	62.74	2.19	0.0040	4.28	546.71	0.0094	7.21	1.54
60	49.76	0.83	58.80	2.18	0.0046	3.63	471.71	0.0106	8.24	1.60
70	36.89	0.53	63.12	2.19	0.0039	4.36	555.14	0.0093	7.11	1.54
80	39.93	0.50	62.10	2.19	0.0041	4.16	532.91	0.0096	7.39	1.55
90	54.65	0.61	57.16	2.18	0.0049	3.41	446.11	0.0110	8.65	1.62
100	46.90	0.47	59.76	2.18	0.0045	3.77	488.07	0.0103	8.00	1.58
110	39.85	0.36	62.13	2.19	0.0041	4.16	533.48	0.0096	7.38	1.55
120	53.55	0.45	57.53	2.18	0.0048	3.46	451.64	0.0109	8.56	1.61
130	51.75	0.40	58.13	2.18	0.0047	3.53	460.96	0.0107	8.41	1.61
140	40.00	0.29	62.08	2.19	0.0041	4.15	532.44	0.0096	7.39	1.55
150	49.50	0.33	58.89	2.18	0.0046	3.64	473.16	0.0105	8.22	1.59
160	56.04	0.35	56.69	2.18	0.0050	3.35	439.32	0.0111	8.76	1.63
170	39.62	0.23	62.20	2.19	0.0041	4.18	535.10	0.0096	7.36	1.55
180	43.86	0.24	60.78	2.19	0.0043	3.93	506.72	0.0100	7.74	1.57
190	53.82	0.28	57.44	2.18	0.0048	3.44	450.27	0.0109	8.58	1.61

Table 6.4: Experimental Results for Microwave Irradiation for Oil (540 watts)

Radiation time (s)	ΔΤ	Rate of temperature increase, dT/dt	ε' _{r, w}	ε' r, o	tan δ (ε'/ε'')	٤" _{r, w}	٤ " _{r, o}	rate of heat generation, q (cal/cm3.s)	Penetration Depth, Dp (cm)	Wavelength, λw (cm)
10.00	12.87	1.29	71.19	2.21	0.0027	6.95	823.47	0.0067	4.74	1.45
20.00	21.70	1.09	68.22	2.20	0.0031	5.70	699.74	0.0077	5.65	1.48
30.00	19.67	0.66	68.90	2.20	0.0030	5.95	724.85	0.0075	5.44	1.47
40.00	18.63	0.47	69.25	2.21	0.0030	6.08	738.36	0.0074	5.34	1.47
50.00	28.41	0.57	65.97	2.20	0.0035	5.02	627.69	0.0085	6.31	1.51
60.00	26.31	0.44	66.67	2.20	0.0034	5.22	648.64	0.0082	6.11	1.50
70.00	22.44	0.32	67.97	2.20	0.0032	5.62	691.00	0.0078	5.72	1.48
80.00	31.33	0.39	64.99	2.20	0.0037	4.77	600.66	0.0088	6.59	1.52
90.00	32.06	0.36	64.74	2.20	0.0037	4.71	594.30	0.0088	6.66	1.52
100.00	26.37	0.26	66.66	2.20	0.0034	5.21	648.05	0.0082	6.11	1.50
110.00	30.57	0.28	65.24	2.20	0.0036	4.83	607.47	0.0087	6.52	1.51
120.00	36.21	0.30	63.35	2.19	0.0039	4.40	560.28	0.0093	7.05	1.54
130.00	28.99	0.22	65.77	2.20	0.0035	4.97	622.16	0.0085	6.37	1.51
140.00	27.43	0.20	66.30	2.20	0.0035	5.11	637.34	0.0084	6.21	1.50
150.00	35.26	0.24	63.67	2.19	0.0039	4.47	567.78	0.0092	6.96	1.53
160.00	30.60	0.19	65.23	2.20	0.0036	4.83	607.27	0.0087	6.52	1.52
170.00	27.11	0.16	66.41	2.20	0.0034	5.14	640.54	0.0083	6.18	1.50
180.00	33.26	0.18	64.34	2.19	0.0038	4.62	584.05	0.0090	6.77	1.53
190.00	31.82	0.17	64.82	2.20	0.0037	4.73	596.35	0.0088	6.64	1.52
200.00	27.39	0.14	66.31	2.20	0.0034	5.11	637.70	0.0083	6.21	1.50

 Table 6.5: Experimental Results for Microwave Irradiation for Oil (360 watts)

210.00	29.66	0.14	65.55	2.20	0.0036	4.91	615.85	0.0086	6.43	1.51
220.00	30.56	0.14	65.25	2.20	0.0036	4.83	607.59	0.0087	6.52	1.51
230.00	26.55	0.12	66.59	2.20	0.0034	5.19	646.21	0.0083	6.13	1.50
240.00	26.66	0.11	66.56	2.20	0.0034	5.18	645.03	0.0083	6.14	1.50
250.00	33.12	0.13	64.39	2.19	0.0038	4.63	585.24	0.0089	6.76	1.53
260.00	30.13	0.12	65.39	2.20	0.0036	4.87	611.52	0.0086	6.48	1.51
270.00	28.00	0.10	66.11	2.20	0.0035	5.06	631.70	0.0084	6.27	1.50
280.00	35.33	0.13	63.64	2.19	0.0039	4.47	567.17	0.0092	6.97	1.53
290.00	32.65	0.11	64.54	2.20	0.0037	4.66	589.19	0.0089	6.72	1.52
300.00	28.76	0.10	65.85	2.20	0.0035	4.99	624.31	0.0085	6.34	1.51

Radiation time (s)	ΔΤ	Rate of temperature increase, dT/dt	ε' _{r, w}	ε' _{r, o}	tan δ (ε'/ε'')	٤" _{r, w}	ε" _{r,o}	rate of heat generation, q (cal/cm3.s)	Penetration Depth, Dp (cm)	Wavelength, λw (cm)
10	8.16	0.82	72.77	2.21	0.00	7.85	908.78	0.01	4.24	1.43
10	15.76	0.79	70.22	2.21	0.00	6.48	778.51	0.01	5.04	1.46
10	13.07	0.44	71.12	2.21	0.00	6.91	820.29	0.01	4.76	1.45
10	16.08	0.40	70.11	2.21	0.00	6.44	773.89	0.01	5.07	1.46
10	24.81	0.50	67.18	2.20	0.00	5.37	664.39	0.01	5.96	1.49
10	23.18	0.39	67.73	2.20	0.00	5.54	682.53	0.01	5.80	1.49
10	21.30	0.30	68.36	2.20	0.00	5.75	704.54	0.01	5.61	1.48
10	29.38	0.37	65.64	2.20	0.00	4.93	618.49	0.01	6.40	1.51
10	32.48	0.36	64.60	2.20	0.00	4.68	590.72	0.01	6.70	1.52
10	27.99	0.28	66.11	2.20	0.00	5.06	631.79	0.01	6.27	1.50
10	30.70	0.28	65.20	2.20	0.00	4.82	606.33	0.01	6.53	1.52
10	37.38	0.31	62.96	2.19	0.00	4.32	551.44	0.01	7.16	1.54
10	33.36	0.26	64.31	2.19	0.00	4.61	583.26	0.01	6.78	1.53
10	32.96	0.24	64.44	2.20	0.00	4.64	586.61	0.01	6.74	1.52
10	41.02	0.27	61.74	2.19	0.00	4.09	525.42	0.01	7.49	1.56
10	38.49	0.24	62.58	2.19	0.00	4.25	543.22	0.01	7.26	1.55
10	35.30	0.21	63.66	2.19	0.00	4.47	567.47	0.01	6.96	1.53

Table 6.6: Experimental Results for Microwave Irradiation for 50-50% w/o emulsions (360 watts)

10	43.01	0.24	61.07	2.19	0.00	3.98	512.17	0.01	7.66	1.57
10	43.55	0.23	60.89	2.19	0.00	3.95	508.70	0.01	7.71	1.57
10	38.52	0.19	62.57	2.19	0.00	4.25	542.99	0.01	7.26	1.55
10	41.82	0.20	61.47	2.19	0.00	4.05	520.01	0.01	7.56	1.56
10	48.10	0.22	59.36	2.18	0.00	3.71	481.10	0.01	8.10	1.59
10	42.67	0.19	61.18	2.19	0.00	4.00	514.39	0.01	7.63	1.56
10	38.75	0.16	62.50	2.19	0.00	4.23	541.31	0.01	7.28	1.55
10	47.50	0.19	59.56	2.18	0.00	3.74	484.52	0.01	8.05	1.59
10	46.36	0.18	59.94	2.19	0.00	3.79	491.29	0.01	7.95	1.58
10	41.20	0.15	61.67	2.19	0.00	4.08	524.17	0.01	7.50	1.56
10	48.34	0.17	59.28	2.18	0.00	3.69	479.69	0.01	8.12	1.59
10	53.60	0.18	57.51	2.18	0.00	3.45	451.36	0.01	8.56	1.61
10	46.87	0.16	59.77	2.18	0.00	3.77	488.25	0.01	8.00	1.58

Radiation time (s)	ΔΤ	Rate of temperature increase, dT/dt	ε' _{r, w}	ε ¹ r, o	tan δ (ε'/ε'')	٤" _{r, w}	٤ " _{r, o}	rate of heat generation, q (cal/cm3.s)	Penetration Depth, Dp (cm)	Wavelength, λw (cm)
10	17.09	1.71	69.77	2.21	0.0029	6.29	759.46	0.0072	5.18	1.46
20	55.99	2.80	56.71	2.18	0.0050	3.35	439.57	0.0111	8.75	1.63
30	60.52	2.02	55.19	2.17	0.0052	3.18	418.72	0.0115	9.11	1.65
40	49.27	1.23	58.96	2.18	0.0046	3.65	474.45	0.0105	8.20	1.59
50	68.72	1.37	52.43	2.17	0.0056	2.91	385.52	0.0121	9.72	1.69
60	80.61	1.34	48.44	2.16	0.0063	2.58	345.50	0.0130	10.51	1.76
70	63.56	0.91	54.17	2.17	0.0054	3.07	405.79	0.0117	9.34	1.66
80	71.80	0.90	51.40	2.17	0.0058	2.81	374.32	0.0124	9.93	1.71
90	84.30	0.94	47.20	2.16	0.0064	2.50	334.65	0.0132	10.73	1.78
100	71.52	0.72	51.49	2.17	0.0058	2.82	375.30	0.0123	9.91	1.71
110	71.68	0.65	51.44	2.17	0.0058	2.82	374.72	0.0123	9.92	1.71
120	76.71	0.64	49.75	2.16	0.0060	2.68	357.70	0.0127	10.26	1.74
130	72.10	0.55	51.30	2.17	0.0058	2.81	373.24	0.0124	9.95	1.71
140	65.16	0.47	53.63	2.17	0.0054	3.02	399.27	0.0119	9.46	1.67
150	75.73	0.50	50.08	2.16	0.0060	2.71	360.91	0.0126	10.20	1.73
160	79.31	0.50	48.88	2.16	0.0062	2.61	349.48	0.0129	10.43	1.75
170	72.01	0.42	51.33	2.17	0.0058	2.81	373.58	0.0124	9.95	1.71
180	88.72	0.49	45.71	2.15	0.0067	2.40	322.49	0.0135	10.99	1.81
190	93.52	0.49	44.10	2.15	0.0069	2.30	310.22	0.0137	11.24	1.84
200	83.05	0.42	47.62	2.16	0.0064	2.52	338.25	0.0131	10.66	1.77

Table 6.7: Experimental Results for Microwave Irradiation for 50-50% w/o emulsions (540 watts)

Radiation time (s)	ΔΤ	Rate of temperature increase, dT/dt	٤' _{r, w}	ε' r, o	tan δ (ε'/ε'')	ε" _{r, w}	٤" _{r, o}	rate of heat generation, q (cal/cm3.s)	Penetration Depth, Dp (cm)	Wavelength, λw (cm)
10	10.70	1.07	71.92	2.21	0.0026	7.34	860.72	0.0065	4.51	1.44
20	41.74	2.09	61.49	2.19	0.0042	4.05	520.53	0.0098	7.55	1.56
30	54.45	1.81	57.22	2.18	0.0049	3.42	447.12	0.0110	8.63	1.62
40	46.22	1.16	59.99	2.19	0.0044	3.80	492.09	0.0102	7.94	1.58
50	59.15	1.18	55.65	2.18	0.0051	3.23	424.82	0.0114	9.00	1.64
60	67.80	1.13	52.74	2.17	0.0056	2.93	388.95	0.0121	9.65	1.69
70	59.13	0.84	55.65	2.18	0.0051	3.23	424.89	0.0114	9.00	1.64
80	62.09	0.78	54.66	2.17	0.0053	3.12	411.94	0.0116	9.23	1.66
90	72.57	0.81	51.14	2.17	0.0058	2.79	371.60	0.0124	9.98	1.71
100	70.43	0.70	51.86	2.17	0.0057	2.85	379.19	0.0123	9.84	1.70
110	66.53	0.60	53.17	2.17	0.0055	2.97	393.84	0.0120	9.56	1.68
120	75.35	0.63	50.21	2.16	0.0060	2.72	362.16	0.0126	10.17	1.73
130	74.88	0.58	50.36	2.16	0.0060	2.73	363.72	0.0126	10.14	1.72

Table 6.8: Experimental Results for Microwave Irradiation for 50-50% w/o emulsions (720 watts)