DEMULSIFICATION OF WATER-IN-CRUDE OIL EMULSIONS VIA MICROWAVE HEATING TECHNOLOGY

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DEMULSIFICATION OF WATER-IN-CRUDE OIL EMULSIONS VIA MICROWAVE HEATING TECHNOLOGY

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A thesis submitted to the Faculty of Chemical and Natural Resources Engineering
in Partial Fulfillment of the Requirement for the
Degree of Bachelor Engineering in Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

APRIL 2010

I declare that this thesis entitled “*Demulsification of water-in-crude oil via microwave heating technology*” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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To my beloved father and mother

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ABSTRACT

The traditional ways of breaking emulsions using heat and chemicals are disadvantageous from both economic and environmental perspectives. In this study, an alternative and cost effective technology for high frequency energy separation of oil emulsions has developed. The potentials of microwave technology in demulsification of water-in-crude oil emulsions are investigated. After exposing the emulsion to the microwave electromagnetic (EM) field, molecular rotation, and ionic conduction due to the penetration of EM into the emulsion are responsible for the internal heating. In this study, microwave demulsification was applied in a 50-50 %, 30-70 % and 10-90 % water-in-oil emulsions with microwave exposure time varied from 20-200 sec. The temperature rise at a given location was almost horizontal (linear). The average rates of temperature increase of 50-50 %, 30-70 % and 10-90 % water-in-oil emulsion are 1.042, 0.582 and 0.218 ^{o}C/sec, respectively. The rate of temperature increase of emulsions decreased at higher temperature due to decreasing dielectric loss of water. Viscosity increases with amount of surfactant used, whereas, viscosity and shear stress decreases as temperature and rpm increased.

ABSTRAK

Kaedah-kaedah tradisional yang biasa digunakan dalam pemisahan air daripada emulsi air dalam minyah mentah seperti pemanasan dan penggunaan bahan kimia memdatangkan masalah dari segi ekonomi dan alam sekitar. Dalam kajian ini, cara alternatif dan teknologi yang murah untuk pemisahan emulsi dari segi tenaga berfrekuensi tinggi dikaji. Keupayaan teknologi gelombang mikro dalam pemisahan emulsi air dalam minyak tanah. Setelah mendedahkan emulsi kepada medan electromagnet gelombang mikro, putaran molekul dan ion konduksi berlaku kerana penetrasi gelombang mikro ke dalam emulsi bertanggungjawab atas pemanasan dalaman. Dalam kajian ini, pemisahan emulsi dengan penggunaan gelombang mikro digunakan ke atas emulsi pada kadar 50-50%, 30-70% dan 10-90% dengan pendedahan gelombang mikro pada variasi masa dari 20 hingga 200 saat. Peningkatan suhu pada lokasi berlainan dalam emulsi adalah lebih kurang sama (linear). Peringkat rata-rata kenaikan suhu untuk emulsi pada kadar 50-50%, 30-70% dan 10-90% adalah 0.886, 0.526 dan 0.395 ^{o}C/sec masing-masing untuk radiasi 540W, manakala 1.042, 0.582 dan 0.218 ^{o}C/sec untuk radiasi720W. Pada suhu tinggi, kadar peningkatan suhu emulsi berkurang kerana kehilangan dielektrik air berkurang. Kelikatan emulsi meningkat dengan jumlah surfaktan yang digunakan, manakala, kelikatan dan tegangan ricih emulsi menurun apabila suhu dan rpm bertambah.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION

mw : microwave
o/w : oil-in-water emulsion
w/o : water-in-oil emulsion
rpm : rotations per minute
SDDS : Sodium Dodecyl Sulfate
LSWR : Low Sulfur Wax Residue
MESB : Mechanical Emulsion Breaker
R/A : Resin to Asphaltene ratio
EM : Electromagnetic
SARA : Saturated Asphaltene, Resin and Aromatic

LIST OF SYMBOLS

V_w : Settling velocity (cm/sec)

ρ_w : Density of dispersed phase (g/cm^3)

ρ_o : Density of continuous phase (g/cm^3)

g : Gravity

D : Droplet diameter (cm)

Po : Microwave surface power (W)

A : Sample container area (cm^2)

m : Mass of sample (g)

P_z : Microwave power transmitted (W)

α_E : Electromagnetic attenuation factor (cm^{-1})

f : Frequency of incident microwaves

δ : Loss tangent

q_{MW} : Volume rate of heat generation (W/cm^3)

λ_m : Wavelength (cm)

D_m : Penetration depth (cm)

ε’’r : Dielectric loss

ε’r : Dielectric constant

c : Speed of light (cm/sec)

h : Convective heat transfer coefficient (cal/s cm^2 ^{o}C)

v : Volume of water separated (cm^3)

T_m : Temperature of emulsion ^{o}C

T_a : Temperature of ambient ^{o}C

σ : Stefan-Boltzmann constant

φ : Volume fraction of emulsified water

ε : Emissivity of surface

Cp_m : Heat capacity of emulsion (cal/g^oC)

ρ_m : Density of emulsion (g/cm^3)

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The complex nature of the emulsions of water in crude oil is one of the main drawbacks to the development of techniques suitable for demulsification and phase separation in the oil industry. In spite of the huge recent efforts for developing dependable and efficient demulsification techniques, most emulsions of water in crude oil cannot be broken in reduced times. Actually the demulsification operation is a key process for removing water from crude oil in refineries (Coutinho *et al.*, 2007). Specifically, in order to remove water from crude oil up to acceptable levels, there is a need of demulsification (dehydration) stages in the desalting plants generally encountered in environmental technology, painting, coating and petroleum refineries.

One of the most widely used methods in treating water-in-oil emulsions is chemical destabilization, which involves the use of chemical additives to accelerate the emulsion breaking process. For economic and operational reasons, it is necessary to separate the water completely from the crude oil before transporting or refining. There are many methods for the demulsification process, such as gravity separation, electrostatic coalescence, centrifugal and filtration methods.

In this Research Project, the microwave heating technology as an alternative demulsification process will be used. Electromagnetic radiation in the frequency range 300MHz to 300 GHz are known as microwaves, microwave energy is non-iodizing radiations that cause molecular motion by migration of ions and dipole rotations, but does not cause changes in molecular structure and wavelengths ranging from a few centimeters to a few millimeters (Abdurahman *et al.,* 2007). Microwave heating offers a faster processing rate because of its volumetric heating effects. In conventional thermal processing, energy is transferred to the material through convection; conduction and radiation of heat the surfaces of the material. In contrast, microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field. In heat transfer, energy is transferred due to thermal gradients, but microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion, rather than heat transfer. This difference in the way energy is delivered can result in many potential advantages to using microwaves for processing of materials. The transfer of energy does not rely on diffusion of heat from the surfaces and it is possible to achieve rapid and uniform heating of thick materials (Abdurahman *et al.,* 2007).

Below follows a list of abbreviations and concepts that needs to be defined and clarified. These concepts will be used throughout the paper and therefore it is important to explain how they will be used to prevent misinterpretations as well as increase the understanding of the paper.

a) **Separation** is done to separate two or more things which are in a mixture form.

b) **Crude oil** is defined as a type of oil in a nature state that has not yet been treated. Geologists generally agree that crude oil was formed over millions of years from the remains of tiny aquatic plants and animals that lived in ancient seas. There may be bits of brontosaurus thrown in for good measure, but the petroleum owes its existence largely to one-celled marine organisms. It is the particular crude oil’s geological history that is most important in determining its characteristics, which is why crude oils formed in similar marine deposits at different continents can resemble each other. Regions characterized by different marine deposits, pressures and temperatures may however produce crude oil with a great variety in appearance, from honey-colored, greenish to black, light or heavy, waxy or not (A. Hannisda, 2005).

c) **Emulsion** is a mixture of two immiscible (unblendable) liquids. One liquid (the dispersed phase) is dispersed in the other (the continuous phase). Many emulsions are oil/water emulsions, with dietary fats being one common type of oil encountered in everyday life. Emulsions tend to have a cloudy appearance, because the many phase interfaces (the boundary between the phases is called the interface) scatter light that passes through the emulsion. Emulsions are unstable and thus do not form spontaneously. Over time, emulsions tend to revert to the stable state of the phases comprising the emulsion. Surface active substances (surfactants) can increase the kinetic stability of emulsions greatly so that, once formed, the emulsion does not change significantly over years of storage.

d) **Microwave** is a very short electromagnetic wave used for sending information by radio or radar.

1.2 Problem Statement

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, which are usually referred to as oil field emulsions (Abdurahman *et al.*, 2007). 90% to 95% of the world crude oil is produced in the form of emulsion. The presence of water in oil creates a lot of problems, due to economic reasons and pipeline corrosion; it is required to separate water completely from the oil before sending oil for processing. The conventional methods for this process are usage of chemicals and high heat to separate water from oil and then send the oil to the refinery and water to the treatment plant processes, but these methods are expensive. So, microwave has been discovered as an alternative way to solve this problem to save energy and time.

1.3 Objective

The objectives of this research is focus on the stability of crude oil emulsions and understand the mechanisms of the demulsification of crude oils using microwave heating technology.

1.4 Scope of Research

To accomplish the objective of this study, the scope of this research focuses on:

a) Characterization of emulsions in terms of chemical and physical properties such as shear stress, shear rate, viscosity, rotations per minute (rpm), temperature, surface tension and interfacial tension.
b) To examine the demulsification of water in crude oil emulsions by microwave heating using batch processes system.
c) To determine the temperature distributions at different locations (top, middle and bottom) for irradiated emulsions.
d) To study the effect of varying the microwave power generation at 720 and 540 watts.
e) Analyzing the overall potential of microwave demulsification as an alternative energy generation for water in crude oil emulsion demulsification.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The formation of water-in-oil emulsions during production and transport of crude oils is a great problem challenging the petroleum industry. Tremendous research works are directed to understanding the mechanism of formation, stabilization, and controlling of oil field emulsions (Al-Sahhaf *et al.*, 2008). Microwave method used in demulsification process need to be done to remove water-in-crude oil emulsions, which cause corrosion in pipelines. There are many types of methods used such as heating (conventional method), usage of chemicals, membrane separation and microwave heating technology. Many parameters had been considered in the previous researches. This study enhances microwave heating technology by varying the power generation and usage of different emulsifier and demulsifiers.

2.2 Stability of Crude Oil

2.2.1 Mechanisms of Stabilization of Water-In-Crude Oil Emulsions

In this research, the mechanisms of stabilization of water-in-crude oil emulsions have been investigated by changing the solvent−solute interactions in crude oil. Diluting the original crude oil with varying amounts of heptane, which is a poor solvent for asphaltenes, changes the solvent−solute interactions, leading to flocculation of asphaltenes and thus changing the emulsion stability. The interactions between the water droplets in an emulsion system have been quantified by measuring the radial distribution function and thereby the pair potential using the digitized optical imaging technique. It has been observed that the force of interaction between water droplets is oscillatory. This shows that non-DLVO forces, such as attractive depletion and repulsive structural forces exist between the droplets. The interaction between the water droplets has been modeled by studying the properties of a thin liquid film sandwiched between the water droplets. Because of the film confinement effect, asphaltene−resin particles form a layered structure inside the thin liquid film. Also, the role of hydrodynamic interactions has been studied by using the film rheometer to measure the dynamic film tension and film elasticity. It has been found that, because of the adsorption of asphaltene at the film interfaces, the film elasticity plays a significant role in stabilizing these emulsions (Kumar *et al.,* 2001).

2.2.2 Water-In-Crude Oil Emulsions: Its Stabilization and Demulsification

Traditional ways of breaking emulsions using heat and chemicals are disadvantageous from both economic and environmental perspectives. In this research, the potential of microwave technology in demulsification of water-in-crude oil emulsions were investigated. The study produces some characterization studies to provide understandings of fundamental issues such as formulation, formation and breaking of emulsions by both chemical and microwave approaches. The goal of this research was to obtain optimized operating conditions as well as fundamental understanding of water-in-oil emulsion stability upon which further developments on demulsification processes could be developed. Experimental results found that microwave radiation method can enhance the demulsification of water-in-oil emulsions in a very short time compared to the conventional heating methods. The results obtained in this study have exposed that the capability of microwave technology in demulsification of water-in-oil emulsions (Abdurahman *et al.,* 2007).

In this research, it was found that emulsion stability was related to some parameters such as, the surfactant concentration, water content, temperature and agitation speed. Here, I will enhance this microwave heating technology by varying the power generation and usage of different emulsifier and demulsifiers.

Since water-in-crude oil emulsion creates many problem, especially foaming and corrosion in pipeline, many researches done to overcome this problem. From all the above researches, we can see that most of the researches were using complicated methods. Few researches used chemicals to demulsify water-in-crude oil emulsions, which may require additional cost and sometimes affect the chemical properties of the crude oil itself. So, to demulsify water-in-crude oil emulsions, it is required an easy, applicable, safe, cost effective method. So, I will be using microwave method in demulsification process to remove water-in-crude oil emulsions, which cause corrosion in pipelines.

2.2.3 Stability Investigation of Water-in-Crude Oil Emulsion

An experimental study was done by Abdurahman *et al.* (2006) to investigate the stability of water-in-crude oil emulsions in both creaming and coalescence states were measured as a function of sodium chloride concentration. The parameters measured in this research are salt concentration, mixing speed, water concentration and temperature.

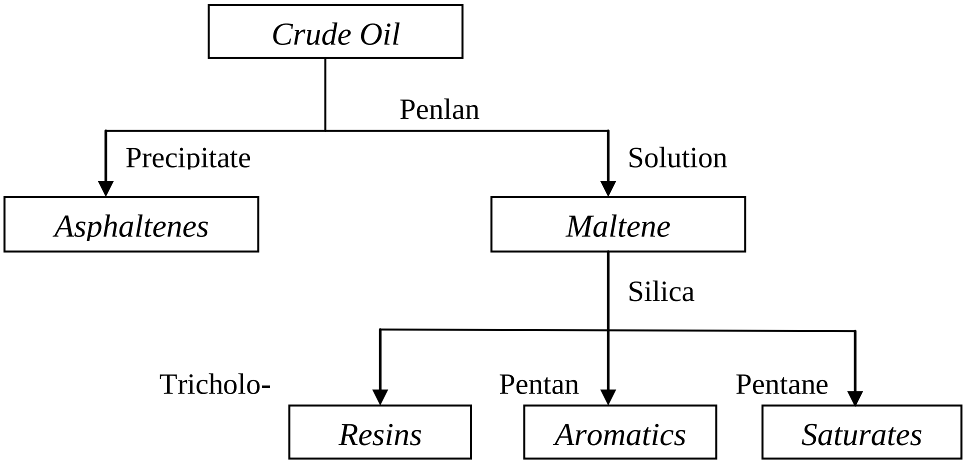


Fig 2.1 : Separation of crude oil fractions

Separation of water layer was used as a measure of physical instability for water-in-oil emulsions. Separated water was increased for emulsions having high salt concentrations. A long duration was necessary for separation of w/o emulsions with no heat and salt is remarkable for sedimentation experiments. However, an unstable emulsion could be eventually destroyed leading to complete separation of two phases.

From the interfacial tension measured in this research, it was discovered that the interfacial tension falls to low values at higher sodium chloride concentration. Other than that, density difference increases with salt concentration increase and consequently the interfacial tension decreases. Furthermore, with increasing of salinity of sodium chloride percentage, the chance for the molecules to collide with each other increases. It was discovered that as the volume fraction decreases, the separation time for water to separate from the emulsion decreased. Viscosity of the emulsion increases as surfactant concentration increases.

Viscosity of emulsion increases greatly as internal volume fraction increases, the result leads to emulsion stability. A surprising situation occurs where emulsion converted from w/o to o/w when the volume fraction reached certain level. In this study, when surface active agents added to the emulsions, the interfacially active agents were adsorbed or deposited at the interface of the o/w system. Other than that, in evaluation of temperature, emulsions were more stable when the temperature is near the point of minimum solubility of emulsifying agents. Emulsion stability decreases when temperature was increased.

In this stability investigation, the researchers focus on salt concentration, mixing speed, water concentration and temperature. In my research, I will be enhancing on more parameters but the similar parameter is the temperature and mixing speed (rpm).

2.3 Chemical Demulsification

2.3.1 Chemical Demulsification of Water-In-Crude Oil Emulsions

Chemical demulsification is the most widely applied method of treating water-in-crude oil emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The effect of chemical demulsification operations on the stability and properties of water-in-crude oil emulsions was assessed experimentally. Furthermore, influences of chemical demulsifiers on the destabilization of emulsions were studied in this research. Few chemicals such as Amine groups, Polyhydric Alcohol, Acid and Polymeric demulsifiers were used in this research as demulsifiers. Low sulfur Wax Residue (LWSR) and Triton X-100 were used to form emulsion in this study. These emulsifiers were not diluted before being used. Stability of the emulsions was determined at 30°C as a function of time.

From this study, it was discovered that effect of amine group demulsifiers on crude oil emulsion stability (percentage water separation) increase with time. Decyl-amine has highest stability at the end of analysis and followed by Octyl-amine, Hexyl-amine, Pentyl-amine, Dioctyl-amine, Trioctyl-amine and Propyl-amine. Same data obtained for effect of amine group demulsifiers on crude oil emulsion stability (percentage oil separation). However, percentage oil separations for all amine group demulsifiers are higher compared to percentage of water separation. This was due to high molecular weight factor of amine which acts as flocculants in adsorption and interaction activities.

Data on the influence of polyhydric alcohols group on crude oil emulsion stability (percentage of water separation) shows that Polyethylene glycol (PEG) 1000 shows highest stability, whereas Ethylene glycol, PEG 600 and PEG shows stability in decreasing order. Emulsion stability of these alcohols on percentage of water separation is higher than percentage of water separation. This is because of low molecular weight alcohols are water soluble such as methanol and ethanol.

The researchers found out that influence of acid demulsifiers group on emulsion stability is higher for percentages of oil separation. In comparison, percentage of water separation in this category is lower for formic acid, butanoic acid and octanoic acid. Whereas, pentanoic acid, heptanoic acid and hexanoic acid shows very much lower than percentage of oil separation.

At the end of this research, the researchers discovered that all acid demulsifiers permit oil separation. Maximum percentage of separation occurs at 1340 mins compared to polyhydric demulsifiers group, acid demulsifiers were lower in both water and oil separations. It was also discovered that there is a strong correlation between good performance and the demulsifiers. Furthermore, the amine group demulsifiers promoted as the best coalescence of droplets at the end of the study. In contrast, polymeric demulsifiers group is the least in water separation (Abdurahman *et al.*, 2007).

This method takes very long time duration to complete demulsification of water in crude oil emulsions. So, I decided to choose faster and more effective method to separate water from crude oil emulsions, which is microwave heating technology.

2.3.2 Characterization and Demulsification of Water-in-Crude Oil Emulsions

The effect of chemical demulsifiers in demulsification of water-in-oil emulsions were assessed experimentally by Abdurahman *et al.* (2007). The relative rates of water separation were characterized via graduated beakers.

Four groups of demulsifier with different functional groups were used in this research work namely amines, polyhydric alcohol, sulphonate and polymer. The effect of alcohol addition on demulsification performance was also studied in this research study.

Water-in-oil emulsions were prepared by dispersing distilled water in crude oil at room temperature with a three blade propeller at speed of 1600rpm. Triton X-100 was used beside asphaltenes and resins originally present in crude oil to stabilize the emulsions. As stated earlier, four different groups of demulsifiers were used in this study.

Rate or speed at which the separation took place and the amount of water left in the crude oil after separation were the two most important aspects in this study. The researcher discovered that coalescences need to be minimized to obtain any useful rheological information. In addition, shear rate is inversely proportional with viscosity.

It was also discovered that low pH (acidic) generally produce w/o emulsions, whereas high pH (basic) produces o/w emulsion. The optimum pH demulsification is found at 10 without demulsifiers. Addition of a demulsifiers enhances demulsification after 5 hours and the maximum water separation (95% v/v) was achieved after 15 hours.

From the experimental work done, it was discovered that the higher the interfacial pressure, the higher the instability of emulsion and vice versa. The interfacial pressure of various demulsifiers related to the percentage of water and oil separation.

The researchers categorized the demulsifiers into three groups. The first group consists of the demulsifiers such as amine group, sulphonate and polyhydric alcohols group which have interfacial pressure values ranging from 4.1 to 7.5 which can destabilize the emulsion. The amount of water can be separated from the emulsion was up to 80%.

The second group comprises Polyethylene Glycol (PEG) 600, Polyethylene Glycol (PEG) 1000, AOT, propylamine which have interfacial pressure values ranging from 2 to 6 and can partly break the emulsion. The amount of water separated from this group was in the intera of 25 to 67%.

The third group consist of poly PO terminated, polyethylene block PEG, polyethylene oxide (PEO) 100000, trioctylamine, Propylene glycol (PG), ethylene glycol (EG) and NaDBS which have interfacial pressure values ranging from -8 to 2.8 and could not destabilize the emulsion. The percentage of water separation was less than 15%.

Effect of alcohol addition on demulsification performance of oil soluble demulsifiers studied as well. Three oil soluble demulsifiers used in this study; they are dioctylamine, igepal and aerosol T (AOT). This experiment's results showed that using butanol alone there were no emulsion destabilization 24 hours, these percentages of separation are smaller than other demulsifiers. It means that butanol did not effect the destabilization if used alone as destabilizer, but they can enhance the destabilization process when used together with a demulsifier.

2.4 Multiple Stage Demulsification Process

2.4.1 Systematic Crude Oil Dewatering

Crude oil dewatering is one of the most common processes done in petrochemical industries to improve quality of the crude oil. MAHLE Industriefiltration Company in Hamburg is doing three stages separation process to separate water from crude oil. This separation system is being done under fully automatic without usage of chemicals.

At the first stage, which is the Multi-Phase Separation (MPS) separates oil, water and solids. During this process, oil is pumped through the MPS profiles and as it passes through the inlet the oil is swirled on to the MPS profiles, the small water droplets merge to form larger drops. These are bound by the gravitational and adhesion forces of the profiles and directed down into the water collecting area. The solids slide down the profiles into the sludge holding tank.

The next stage is Mechanical Emulsion Breaker (MESB). At this stage, the fine water droplets are separated and the oil flows through a micro-fibre bed where small water droplets merge to form larger drops which flow down into the water collecting area.

Final stage of this process is called Membrane Filtration, where the oil flows through a water-repellent membrane which dependably retains the last remaining water droplets.

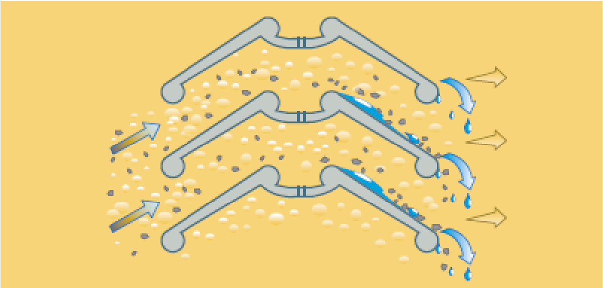


Fig 2.2: Multi-Phase Separation (MPS) Process

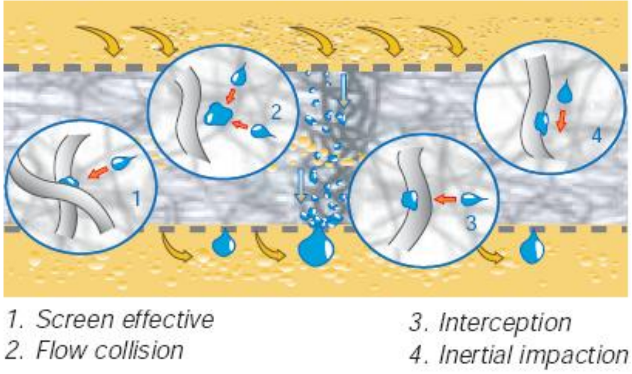


Fig 2.3: Mechanical Emulsion Breaker (MESB) Process

Although this process has good energy balance and fully automated, this can be considered as a complicated process which requires many types of equipment. This may cause high installation and maintenance cost. So, it is advisable to produce an easier equipment model which simplifies the dewatering process (www.mahle-industrialfiltration.com).

2.5 Microwave Heating Technology

Microwave irradiation is being used as a tool of demulsification due to the fact that microwave irradiation offers a clean, cheap and convenient heating process and most of times results into better yields and shorter reaction times. In comparison with chemical demulsification method, microwave heating technology is cheaper. Furthermore, chemical additives used in chemical demulsification process will be carried into the wastewater streams or follow the hydrocarbon into the refining process.

Microwave heating was 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. The two main dielectric heating mechanisms are dipole rotation and ionic conduction.

2.5.1 Study on Demulsification of Water-in-Oil Emulsions via Microwave Heating Technology

A batch microwave heating process of 2450 MHz was examined on crude oil emulsions. The mechanism of microwave heating was essentially that of dielectric heating. In this study, microwave demulsification method was applied on a 50-50 and 20-80% water-in-oil emulsions with microwave exposure time varied from 20 to 180 seconds. Transient temperature profiles of water-in-oil emulsions inside a cylindrical container (top, middle and bottom) were measured.

From the result obtained in this research, it was found that the rate of temperature increase of emulsions decreased at higher temperature due to decreasing dielectric loss of water. Furthermore, from temperature distribution profiles of irradiated emulsions, it appears water-in-oil emulsion had been heated quickly and uniformly by microwaves rather than conventional heating. Therefore, Abdurahman *et. al.*, 2006 discovered that microwave radiation is a dielectric heating technique with unique characteristics of fast, volumetric and selective heating is appropriate and has the potential to be used as an alternative way in the demulsification process.

This research is almost similar to the experimental work that I'm going to conduct for undergraduate research project. The factors that I'm going to enhance are the usage of different emulsifying agent and different power generation of the microwave. At the end of my project, I will be doing demulsification process using two chemical. This is to compare the results obtained from microwave heating methods and chemical demulsification method. The motive here is to prove that microwave heating method is more feasible.

2.5.2 A Continuous Microwave Heating of Water-in-Oil Emulsions: An experimental Study

Water-in-oil emulsions were demulsified using continuous microwave heating technology in this research. The power output used was 900 watts and operation frequency was 2450 MHz. The crude oil samples were prepared in 50-50% and 20-80% w/o emulsions. Three blade propeller used at speed of 1800 rpm to agitate the emulsion for 8 minutes at temperature 30^{o}C. The surfactants used in this research were Triton X-100 and low sulfur wax residue (LSWR).

The amount of water separation in percent was calculated as separation efficiency. Microwave distributes energy within the bulk of most materials, rather than just on it surface. Any heat produced at the surface will be conducted or convicted into the material. Microwave, because the wave length is relatively long and the method of interaction so mild, can penetrate deeply into substance.

The researchers, Abdurahman *et al.* (2006) found that increase of temperature causes reduction viscosity and coalescence. It resulted in separation of water without chemical addition. When viscosity decreases, the droplet size increases. Therefore, microwave heating increases the velocity of water and accelerates the separation of emulsion. It was found that Triton X-100 and the LSWR stabilize w/o emulsions, while in the absence of Triton X-100 and LSWR, emulsions were not stable. It was observed that, the rate of temperature increase (dT/dt) was inversely proportional to the increase in temperature ΔT; this was expected result since the dielectric loss water is small.

The shear rate, shear stress and viscosity of the emulsion samples were measured with Brookfield (DV-III) Rheometers. The viscosity of an emulsion diminishes when the volume fraction of the dispersed phase was induced. It was noticed that, when temperature increased, the viscosity decreased very fast. Increases in the internal phase volume fraction lead to an increase in both the viscosity and the degree of shear thinning. Its clear that the shear rate increases as shear stress increases and emulsions behaves as non-Newtonian.

2.5.3 Method for the Microwave Treatment of Water-in-Oil Emulsions

In this research paper, Coutinho *et al*., (2007) determined optimum conditions of w/o emulsion for water content, salt content, pH value of the aqueous phase, initial temperature, microwave application power, final temperature and drop size distribution to be adjusted in the industrial plant, as a function of the features of the tested crude oil such as viscosity, density, asphaltene content, total acidity, such conditions being those required for obtaining at least 90% separation efficiency of the emulsion in the presence of microwave radiation. The researchers utilized the information obtained for the initial adjustment of application conditions of the method to phase separation units in refineries and production units. Furthermore, these research group also performed on line tests of the variables of the process response in the streams effluent from separation units, being the response the water content and salt content tests, so as to feedback the information to the best adjustment of the process conditions for microwave application. Finally, they utilized the on line or laboratory tests of the effect of the method as a tool for monitoring the efficiency of the breaking of the w/o emulsion.

During the microwave heating of a material, radiation penetrates the material so that heat transfer occurs from within the material up to the surface of it. This kind of transfer causes the global warming of the material and a quick increase of its temperature. This kind of heating is quite different from conventional heating which depends on the thermal conductivity of the material, on temperature gradients created throughout the material and no convention currents. Conventional heating is characterized by low rates in temperature increase. Besides the quick heating of the materials, other advantages can be attributed to dielectric heating relative to conventional heating such as selective heating, miniaturization of equipment, Low electrical power consumption cost and reduced environmental pollution. Microwaves quickly heat emulsions, reducing the viscosity of the continuous phase (water-in-oil emulsions), thus favoring the contact among water drops. The temperature increase can cause reduction in the viscosity of the rigid film formed by natural surface agents in the water-oil interface, making easier the coalescence between said dispersed drops. The microwave-induced molecular rotation neutralizes the zeta potential of the dispersed drops, thus reducing the stabilization offered by the ionic surface agents. The preferred absorption of microwaves by water drops in water-in-oil emulsions causes intense internal pressure in these drops, resulting in the expansion of the dispersed phase and in the reduction of the thickness of the interfacial film.

The researcher reached a conclusion that the addition of low concentrations of electrolytes and acids raises the demulsification rate of the mixtures. The addition of high electrolyte concentrations can limit the dipole rotation of the water molecules and reduce the efficiency of the phase separation. Furthermore, the research team found that the demulsification rate rises with the dispersed phase drop size.

According to the inventive method, a series of demulsification runs were carried out in the batch mode in order to evaluate the final residual water content of emulsion samples after exposition to microwaves. Tests were run at distinct heating temperatures using water-in-heavy crude oil emulsion samples containing different contents of salt, water and pH value. Precise heating and final temperature programs were set so as to monitor the amount of energy applied to the emulsion and consequently the viscosity of the oleaginous phase. The viscosity reduction caused by the temperature effect for each of the oils is determined by rheological tests of this fluid at the chosen temperatures. The influence of temperature on the viscosity was described with the aid of decreasing exponential functions.

A patent was developed by the agents Nixon & Vanderhye, PC after this research. It is important to stress that higher salinity contributes to emulsion stability. This effect, combined to the lower applied energy result in reduced microwave demulsification efficiency with the increase in the aqueous phase salinity. Thus, according to the invention the microwave desalter will be more efficient when the emulsion fed to it has a minimum salt concentration, which is an easily attainable condition via dilution-operation. In this case the water addition doubly favors the microwave demulsification process, through salinity reduction via dilution as well as by increase in water content.

From this research, it was discovered that pH 12.0 tests provided a highly efficient demulsification. This was explained by the reduced stability of water-in-oil emulsions with increased pH, the microwave effects being apparently independent. Anyways, according to the invention, it was considered that the ideal pH range is between 7.0 and 9.5 in which high efficiencies can be obtained with or without salt.

Since, most of the information provided in this journal was according to the developed patent, it was quite hard to imagine the process and to extract information.

2.6 Comparative Studies

2.6.1 A Comparative Study on Emulsion Demulsification by Microwave Radiation and Conventional Heating

A heavy crude oil has been increasingly important sources of hydrocarbons in many parts of the world, in which transportation of this heavy crude oil to refinery can be a problem. During the lifting, transportation and processing of oil, frequently emulsions either water-in-oil or oil-in-water are created. Formation of these emulsions during oil production is a costly problem, both in terms of chemicals used and due to production losses. The traditional methods of eliminating these emulsions, utilize high heat and chemicals, which forces the emulsion to separate into water, hydrocarbon and solids. This study investigates comparatively on emulsion demulsification between the conventional and microwave heating. Two types of different crude oils were used as samples for the study. The oils are denoted as A and B. crude oils were synthesized in the laboratory. The water to oil ratio was varied from 30-50: 70-50. In company the two heating methods, the heating duration was varied from 5 to 60 min for conventional heating method, while for microwave heating, the duration was varied from 30 sec to 4 min. Microwave demulsification is primarily due to heating. However, the comparisons between the microwave heating and conventional heating shows that these methods are different. (Abdurahman, H. N. & Rosli, M. Y., 2006).

2.7 Latest Discoveries

2.7.1 Development of New Demulsifiers for Oil Production

In this study, the researchers discovered that heavy crude oils which contain high asphaltene and resins possess the tendency to form stable water-in-crude oil emulsions. Stable water-in-oil emulsions can occur at many stages during the production and processing of crude oil. The formation of these emulsions is generally caused by the presence of resins an asphlatenes which play the role of 'natural emulsifiers' and also by wax and solids. All these components can organize and form rigid films at the oil and water interface. Effective separation of oil and water is essential in ensuring the crude oil quality and low cost of the oil production. Chemical demulsifiers forms the most important steps in breaking of water-in-crude oil emulsions. Commercial demulsifiers are generally polymeric surfactants such as copolymers of polyoxyethylene and polypropylene. Due to increase of severity of environmental constraints, there is now a strong need in the oil production to restrict the use of chemicals and to utilize safer formulations, less toxic, but at least efficient as classical demulsifiers. Therefore the researchers developed a methodology in order to screen the main chemicals that could be used as demulsifiers. The objective was to find a chemical family that could be the base of new demulsifiers formulations for oil production. As a conclusion, a large screening of different chemicals that could be used as demulsifiers for oil production was performed by classical bottle tests. Other than that, silicone derivatives were found effective in breaking two types of emulsions made from an asphaltenic and paraffinic crude oil (Abdurahman *et al.,* 2008).

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

For this research the type of method that is used is experimental method. In this research, crude oil samples from two different locations collected. They are from Saudi Arabia and Kuwait.

In this study, microwave heating concept will be used to separate water in crude oil emulsion. The concept of microwave is very recent in breaking the emulsion of crude oil, which was started in the year 1989. Microwave method is considered as a cost effective method in the laboratory and all the feed and the raw materials proves that the microwave is the best equipment in terms of applicability. Crude oil industry can benefit from this concept, since this can be considered as one of the easiest and cheapest process.

3.2 Materials

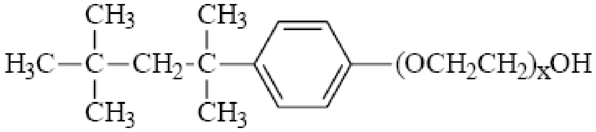
3.2.1 Emulsifying agent

An emulsifier (also known as an emulgent) is a substance which stabilizes an emulsion, frequently a surfactant.

3.2.1.1 Triton X-100

Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$) is a nonionic surfactant which has a hydrophilic polyethylene oxide group (on average it has 9.5 ethylene oxide units) and a hydrocarbon lipophilic or hydrophobic group. The hydrocarbon group is a 4-(1,1,3,3-tetramethylbutyl)-phenyl group. It is related to the Pluronic range of detergents. The pluronics are triblock copolymers of ethylene oxide and propylene oxide. The part formed from ethylene oxide is more hydrophilic than the part from propylene oxide. It is very viscous at room temperature and is thus easiest to use after being gently warmed. Properties of Triton X-100 are as in the table below:

Table 3.1: Properties of Triton X-100

Other names	polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether, octyl phenol ethoxylate, polyoxyethylene octyl phenyl ether, 4-octylphenol polyethoxylate, Mono 30, TX-100, t-octylphenoxypolyethoxyethanol, Octoxynol-9
Molecular Structure	
CAS number	[9002-93-1]
Molecular formula	$C_{14}H_{22}O(C_2H_4O)_n$ (n = 9-10)
Appearance	viscous colourless liquid
Density	1.07 g/cm^3
Melting point	6 °C
Boiling point	> 200 °C
Solubility in water	Soluble
Vapor pressure	< 1 mmHg (130 Pa) at 20 °C
Flash point	251 °C

3.2.1.2 SDDS

Sodium dodecyl sulfate (SDDS) is an anionic surfactant used in many cleaning and hygiene products. The molecule has a tail of 12 carbon atoms, attached to a sulfate group, giving the molecule the amphiphilic properties required of a detergent.

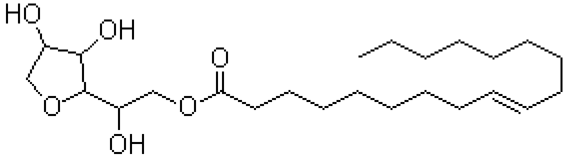
Table 3.2: Properties of SDDS

Other names	Sodium monododecyl sulfate; Sodium lauryl sulfate; Sodium monolauryl sulfate; Sodium dodecanesulfate; dodecyl alcohol, hydrogen sulfate, sodium salt; n-dodecyl sulfate sodium; Sulfuric acid monododecyl ester sodium salt;
CAS number	[151-21-3]
Molecular formula	$NaC_{12}H_{25}SO_4$
Molar mass	288.38 g mol^{-1}
Density	1.01 g/cm^3
Melting point	206 °C

3.2.1.3 Span 80

Span 80 is a Sorbitan Ester widely used in food products and oral pharmaceuticals. This is amber viscous oily liquid with acid value of 8.0 maximum. Properties of Span 80 are as in the table below:

Table 3.3: Properties of Span 80

Other names	Sorbitan oleate; Sorbitan (Z)-mono-9-octadecenoate
Molecular Structure	
Molecular Formula	$C_{24}H_{44}O_6$
Molecular Weight	428.61
CAS Registry Number	1338-43-8
Density	0.986
Refractive index	1.48
Flash point	>110 ºC

3.2.2 Demulsifiers

Demulsifiers are a class of chemicals used to aid the separation of emulsions (w/o). They are commonly used in the processing of crude oil, which is typically produced along with significant quantities of saline water.

3.2.2.1 Octyl-amine

Octyl Amine is used for the synthesis of organic chemicals and surfactants used as a corrosion inhibitor, detergent, ore floating agent, fabric softener, antistatic agent, germicide, insecticide, emulsifier, dispersant, anticaking agent, lubricant and water treatment agent. This is a flammable and reactive chemical.

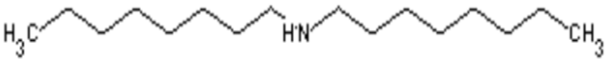
Table 3.4: Properties of Octyl-amine

Other names	1-Aminooctane; 1-Octanamine; Monoctylamine; n-Octylamine
Molecular Structure	
Molecular Formula	$C_8H_{19}N$
Molecular Weight	129.24
CAS Registry Number	111-86-4
Density	0.782
Melting point	-1 ºC
Boiling point	179 ºC
Refractive index	1.428-1.43
Flash point	60 ºC
Water solubility	0.2 g/L (25 ºC)

3.2.2.2 Dioctyl-amine

Dioctyl-amine is an immiscible liquid used to demulsify w/o emulsions. This is a flammable and reactive chemical too.

Table 3.5: Properties of Dioctyl-amine

Other names	Dioctylamine N-octyloctan-1-amine
Molecular Structure	
Molecular Formula	$C_{16}H_{35}N$
Molecular Weight	241.461 g/mol
CAS Registry Number	1120-48-5
Density	0.79 g/cm^3
Melting point	14-15 ºC
Boiling point	297-298 ºC

3.3 Equipments

3.3.1 Microwave

In this research, Elba domestic microwave oven model: EMO 808SS, its rated power output is 800, 600 and 540 watts and its operation frequency is 2450 MHz will be used in heating water-in-oil emulsion samples. A 900 mL graduated cylindrical glass will be used as sample container. The diameter and height of emulsion sample in the container are 11.5 and 11cm respectively.

3.3.2 Thermocouples

A thermoelectric device used to measure temperatures accurately, especially one consisting of two dissimilar metals joined so that a potential difference generated between the points of contact is a measure of the temperature difference between the points.

A variety of thermocouples are available for different measuring applications. They are usually selected based on the temperature range and sensitivity needed. Thermocouples with low sensitivities (B, R, and S types) have correspondingly lower resolutions. Other selection criteria include the inertness of the thermocouple material, and whether or not it is magnetic. The thermocouple types are listed below with the positive electrode first, followed by the negative electrode.

In my research study, i will be using thermocouples type K. Three thermocouples type (K-IEC-584-3) will be connected to Pico-TC-08 data logging and then connected to microwave oven as shown in Fig 3.1. The thermocouples will be inserted to different locations top, middle and bottom of the emulsion sample to measure local temperatures.

3.3.3 Data Logger

A data logger is an electronic device that is used to record measurements over time. Pico data loggers require no power supply and simply plug into a parallel, serial or USB port on your PC. By connecting suitable sensors, Pico data acquisition products can be used to measure temperature, pressure, relative humidity, light, resistance, current, power, speed, vibration... in fact, anything that you need to measure. In my research study, the data logger is connected to PC; the Pico Log R5.08.3 software.

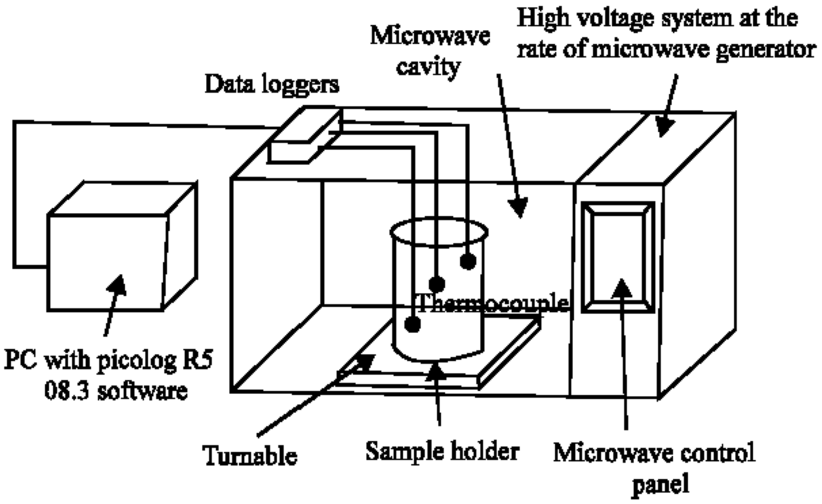


Fig 3.1: Elba microwave oven

3.4 Method of Research

3.4.1 Sample Preparation and Procedures

Emulsions of water and crude oil at 50-50, 30-70 and 10-90 ratios need to be prepared using the same volumes of oil and water. Emulsions will be prepared in 900 mL graduated beakers, with ranges by volume of the water and oil phase. The microwave radiation will be set to its highest power setting. The water phase is tab water. The emulsions need to be agitated vigorously using a standard three blade propeller at speed of 1600 rpm and temperature

28^{o}C for 7 minutes. The container of emulsion sample will be placed in the center of Elba domestic microwave oven model: EMO 808SS. Three thermocouples should be inserted in the emulsion sample at different locations, top, middle and bottom. The emulsion samples will be heated with microwave radiation for 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 sec. Temperature profiles of emulsions inside a cylindrical container during batch microwave heating at 2450 MHz will be recorded by Pico-TC-08 data logging. The surfactants that will be used in this study are commercially available as Triton X-100, SDDS and Span 80. In order to prepare water-in-oil emulsions, the agent-in-oil method will be followed; that is; in this study, the emulsifying agent (Triton X-100, SDDS and Span 80) should be dissolved in the continuous phase (oil), then water will be added gradually to the mixture. The volume of water settled to the bottom will be read from the scale on the beaker with different times. The amount of water separation in percent was calculated as **separation efficiency** from volume of water observed in the beaker as follows:

$$(\%\ of\ water\ separation, e)\ \frac{(Volume\ of\ water\ layer, mL)}{(Original\ amount\ of\ water, mL)} \times 100\% \qquad (Eq. 1)$$

3.4.2 Stability Testing

Stability testing will be done on the emulsions prepared. This test should be done before demulsification process to test how stable are the emulsions prepared. There will be few parameters tested to determine the stability of the emulsions. They are:

3.4.2.1 Shear stress

A shear stress, denoted τ(tau), is defined as a stress which is applied parallel or tangential to a face of a material, as opposed to a normal stress which is applied perpendicularly.

3.4.2.2 Shear rate

Shear rate is the rate at which a shear is applied. For the simple shear case, it is just a gradient of velocity in a flowing material. The SI unit of measurement for shear rate is sec^{-1}, expressed as "reciprocal seconds" or "inverse seconds.

3.4.2.3 Viscosity

Viscosity is a measure of a fluid's resistance to flow. It describes the internal friction of a moving fluid. A fluid with large viscosity resists motion because its molecular makeup gives it a lot of internal friction. A fluid with low viscosity flows easily because its molecular makeup results in very little friction when it is in motion.

3.4.2.4 Rpm

Revolutions per minute (abbreviated '*rpm*', RPM, r/min, or r·min^{-1}) is a unit of frequency: the number of full rotations completed in one minute around a fixed axis. It is most commonly used as a measure of rotational speed or angular velocity of some mechanical component.

3.4.2.5 Temperature

Temperature is a physical property of a system that underlies the common notions of hot and cold; something that feels hotter generally has the higher temperature. Temperature is one of the principal parameters of thermodynamics. If no heat flow occurs between two objects, the objects have the same temperature; otherwise heat flows from the hotter object to the colder object. This is the content of the zeroth law of thermodynamics. On the microscopic scale, temperature can be defined as the average energy in each degree of freedom in the particles in a system.

3.4.2.6 Surface tension

Surface tension is a property of the surface of a liquid. It is what causes the surface portion of liquid to be attracted to another surface, such as that of another portion of liquid (as in connecting bits of water or as in a drop of mercury that forms a cohesive ball).

3.4.2.7 Interfacial tension

Interfacial tension is somewhat similar to surface tension in that cohesive forces are also involved. However the main forces involved in interfacial tension are adhesive forces (tension) between the liquid phase of one substance and either a solid, liquid or gas phase of another substance. The interaction occurs at the surfaces of the substances involved, that is at their interfaces.

3.4.3 Microwave Radiation

A number of studies were carried out on Microwave Heating (MW) of oil and water systems. Microwave heating because of its volumetric heating effects, offers a faster processing rate. The separation of emulsified water from crude oil has several stages, due to gravity settling, water droplet/droplet flocculation takes place as water droplets approach each other. The purpose of heating water-in-oil emulsions with microwave radiation is to separate water from oil. When water-in-oil emulsion is heated with microwave radiation, two phenomena will occur; the first one is the increase of temperature, which causes reduction of viscosity and coalescence. The result is separation of water without addition of chemicals. According to Stoke’s law, if oil is the continuous phase, the **settling velocity of water droplet** is given by:

$$v_w = \frac{(\rho_w - \rho_o) g D^2}{18\mu_o} \qquad (Eq. 2)$$

Where, D is the diameter of the droplets. The viscosity of oil very sensitive to temperature, as temperature increases, viscosity decreases much faster than the density difference, $(\rho_w - \rho_o)$ does, the result when viscosity decreases, the droplets size increases. Therefore, microwave heating increases the velocity of water (V_w) and accelerates the separation of emulsion. The second phenomenon is coagulation. The higher temperature and lower viscosity make the coagulation process easier. The results are larger particle diameter D and rapid separation.

3.4.4 Microwave Power Generation

Using microwaves as a source of heat in the processing (heating, melting, drying and thawing) of materials is one of the advantageous because it results in faster, more uniform heating than conventional heating does. This study, focus on generation of microwaves in the oven, temperature distribution, microwave power absorption as well as separation of emulsified water from crude oil. The variables affecting microwave power absorption by an element are dielectric constant and dielectric loss, location and microwave power incident at the load. For a sample in cylinder container, **the local microwave power flux** will be calculated as:

$$P_o = \frac{453.2+59.8ln\,(m)}{A} \qquad (Eq.3)$$

Where, m is mass (g) of the sample, A is sample's container area. The microwave power absorption density at any location within the sample is one of the interesting terms, in this regards, the electric field attenuates (decay) exponentially in x and y directions within the sample due to dissipation as heat and can be expressed as:

$$P_{\aleph} = P_o e^{-2\alpha\aleph} \qquad (Eq.4)$$

where, $P_{\aleph}$ is **microwave power transmitted**. The **attenuation factor** can be calculated from the electromagnetic field theory given by Von Hippel (1954) as:

$$\propto_E = \frac{2\pi f}{c}\left[\frac{\varepsilon'_r}{2}\sqrt{1+tan^2\delta-1}\right] \qquad (Eq.5)$$

The above equation will be used for calculation of the volume rate of heat generation by microwave radiation as:

$$q_{MWz} = \frac{2\propto_E}{4.184}P_z \qquad (Eq.6)$$

If the dielectric properties are assumed to be independent of temperature at Frequency 2450 MHz, the **wavelength λ_m** and **penetration depth D_p** within a sample for a radiation of the above frequency (2450 MHz) are related to dielectric constant ε''r as follows:

$$\lambda_m = \frac{c}{f}\left[\frac{\varepsilon'_r\left(\sqrt{1+\left(\frac{\varepsilon''_r}{\varepsilon'_r}\right)^2}+1\right)}{2}\right]^{-1/2} \qquad (Eq. 7)$$

and

$$D_p = \frac{c}{2\pi f}\left[\frac{\varepsilon'_r\left(\sqrt{1+\left(\frac{\varepsilon''_r}{\varepsilon'_r}\right)^2}-1\right)}{2}\right]^{-1/2} \qquad (Eq. 8)$$

Since microwave heats materials volumetrically, it is possible to calculate the **volume rate of microwave heat generation** from energy balance equation as:

$$q_{MW} = \frac{hA}{V}(T_m - T_a) + \frac{\varepsilon A\sigma}{V}\left[(T_m + 273.15)^4 - (T_a + 273.15)^4\right] + \rho C_p\left(\frac{dT}{dt}\right) \qquad (Eq. 9)$$

The above equation assumes that the rate of heat transfer from emulsified water droplets to the continuous phase (oil) is very rapid; therefore, water and oil practically have the same temperature. The right hand side of equation above comprises of three terms, convective heat transfer, and radiative heat due to microwave and conductive heat in the sample respectively. From results of this study, the effect of radiative term is very small as well as convective term. Since the sample container (glass) has low dielectric constant, therefore, its heat generated assumed to be negligible. For calculation of volume rate of heat generation in Equation 9, the density (ρ) and (Cp) of the emulsions calculated from mixing rules as:

$$\rho_m = \rho_w\varphi + \rho_o(1-\varphi) \qquad \text{(Eq.10)}$$

$$C_{pm} = C_{pw}\varphi + C_p(1-\varphi) \qquad \text{(Eq.11)}$$

3.4.5 Comparative Studies

3.4.5.1 Demulsification Using Chemical Demulsifiers

Emulsions of water and crude oil at 50-50, 30-70 and 10-90 ratios need to be prepared using the same volumes of oil and water. Emulsions will be prepared in 900 mL graduated beakers, with ranges by volume of the water and oil phase. The microwave radiation will be set to its highest power setting. The water phase is tab water. In order to prepare water-in-oil emulsions, the agent-in-oil method will be followed; that is; in this study, the emulsifying agent (Triton X-100, SDDS and Span 80) should be dissolved in the continuous phase (oil), then water will be added gradually to the mixture. The emulsions need to be agitated vigorously using a standard three blade propeller at speed of 1600 rpm and temperature 28^{o}C for 7 mins. After that, demulsifiers (Octyl-amine and Dioctyl-amine) will be added to the emulsions. The emulsions will be placed on a flat surface to allow separation of water and crude oil. Then, the separation efficiency will be calculated and the results will be compared with the results obtained from microwave heating technology demulsification.

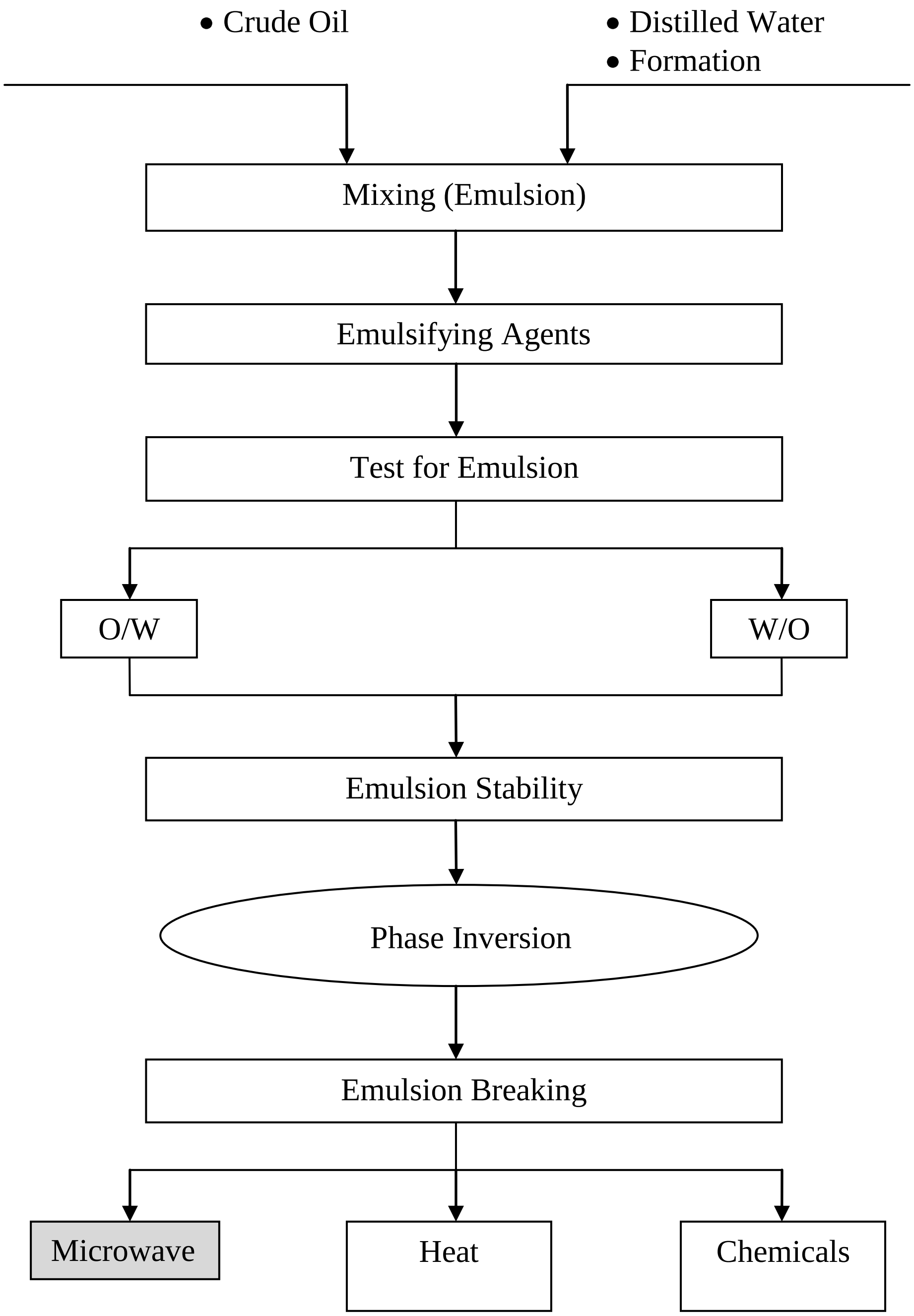


Fig 3.2: Flow Chart of Research Methodology

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The result of this study is discussed in three major parts; which are water separation, stability and microwave heating. At the water separation and stability part, Kuwait and Saudi Arabia crude oil samples were used. Since both the crude oils were heavy crude oil, the separation by gravity does not occur. If both crude oil samples used for microwave demulsification, there will be no difference between the separation and the properties will be almost similar. So, for demulsification part, Kuwait sample remained and Saudi Arabia sample replaced with PETRONAS refinery. This was because, PETRONAS crude oils are light crude oil and will be easier to be compared with heavy crude oil sample from Kuwait in terms of demulsification. Since, his crude oil sample was not available in the laboratory; result for demulsification of PETRONAS sample was taken from the journal written by Abdurahman (2010).

In this research three stabilizing agents (emulsifiers) known Triton x-100, SDDS and Span 80 used. Emulsifiers used to produce stable emulsion and to compare between these three emulsifiers. An emulsion is a dispersion of two immiscible liquids, normally referred to as oil and water. Without any stabilizing agent such dispersions are not stable however with the presence of emulsifying agent and aggressive agitation, the droplets after sometime, will coalesce and the coalescing process normally starts immediately after agitation stopped. In order to enhance the dispersion process and stabilize the emulsion, emulsifying agents are added and the effect on the stability of emulsion will be observed.

4.2 Water Separation (By Gravity Settling)

4.2.1 Kuwait Sample

All the three ratios of water-in-crude oil emulsions (50-50%, 30-70% and 10-90% w/o emulsions) had no separation until 24hours of analysis period. Although the analysis was varied between three different emulsifiers, namely Triton X-100, SDDS and Span 80 at three different concentrations, there were no changes in the emulsions.

4.2.2 Saudi Arabia Sample

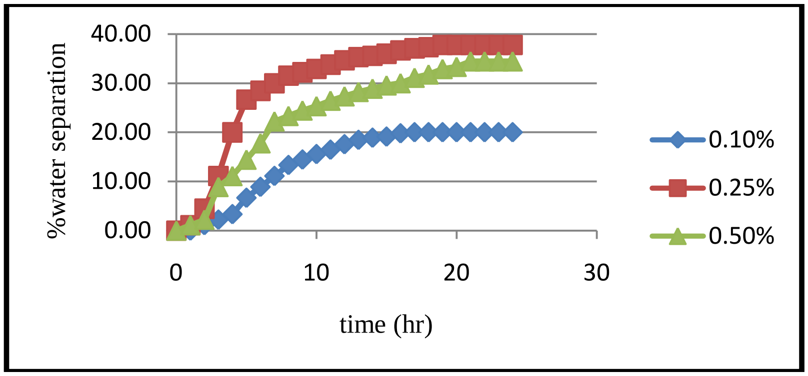


Fig 4.1: % water separation vs. time for 50-50% w/o

30-70% and 10-90% ratios of water-in-crude oil emulsions had no separation until 24hours of analysis with variation on the concentration of emulsifier; Triton X-100. Emulsions which prepared with SDDS and Span 80 sample onto Saudi Arabia samples did not separate although the emulsions were prepared in 50-50%, 30-70% and 10-90% w/o ratios with variation in concentration of emulsifiers.

Both crude oil samples show very limited separation because the emulsion was prepared with very high agitation speed which is 1600 rpm. This cause the emulsion is very stable and hard to be separated. Other than that, the crude oils used in this research were heavy crude oils. The small amount of sample prepared could be another reason for the separation to be too small, where there is limited space for the molecules to move and separate.

The presence of asphaltene and resin in crude oil can stabilize the emulsion. Asphaltene and resin act as an emulsifying agent, which reduce the interfacial tension and to induce repulsive forces between the droplets. Therefore, the resin/asphaltene ratio (R/A) is an important parameter to predict the emulsion stability. Resins increase the solubility of asphaltene in the crude oil and minimize the asphaltene interaction with water droplets. The resin/asphaltene ratio (R/A) may be expected to provide valuable information on tight emulsion formation. Since the emulsion prepared in this research is hard to break, it can be concluded that R/A ratio is small. High resin concentration keeps more of the asphaltene dissolved in the oil phase (Abdurahman *et. al.*, 2006).

4.3 Stability

Table 4.1: Density, surface tension and interfacial tension of crude oils

	SAUDI			KUWAIT		
	50-50% w/o	30-70% w/o	10-90% w/o	50-50% w/o	30-70% w/o	10-90% w/o
Density (kg/m3)	0.9643	0.9508	0.9373	0.9442	0.9227	0.9012
Surface Tension (mN/m)	11.7187	9.7992	9.2303	9.8877	9.2724	9.2189
Interfacial Tension (mN/m)	1.8386	2.2595	2.2757	1.1593	1.8526	2.2695

Determination of interfacial tension: Since oil is lighter than water, the aqueous solution (water) was first placed in the sample vessel and the ring was immersed therein. The oil on top of the water solution then oil was poured to form two-layer system (emulsion). Contact between the oil and the ring was avoided during the operation. After following sufficient time, for the interfacial tension to come to its equilibrium value, measurements were taken.

Interfacial tension is an important factor in emulsion stability. It arises because the intermolecular forces in the interior of a liquid equal in all directions. The interfacial tension falls to low values at higher sodium chloride (NaCl%) concentration (Abdurahman, H. N. & Rosli, M. Y., 2006). From Table 6, we can see that the interfacial tension decreases as the density of the emulsion increases. Surface tension of the emulsions was seemed to decrease with density decrease.

4.3.1 Effect of temperature towards rpm

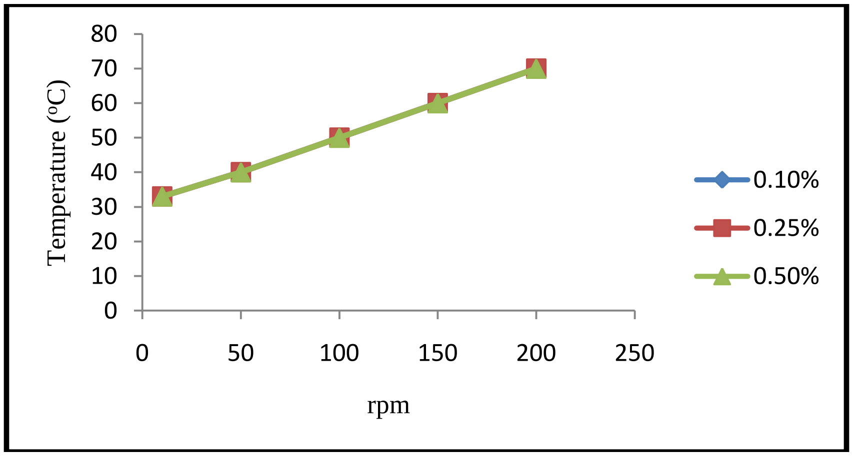


Fig 4.2: Temperature vs. rpm

Trend of the Fig 4.2 of temperature against rpm are similar for all the ratios of water-in-crude oil emulsions, which are 50-50%, 30-70% and 10-90% with variation of three different emulsifiers at three different concentrations of emulsifiers. When the rpm of the spindle attached to the viscometer increases, temperature of the emulsion increases. This may cause because when spindle rotates, the friction between spindle and the emulsion increases. This causes increase in temperature of the emulsion.

4.3.2 Effect of temperature towards shear rate

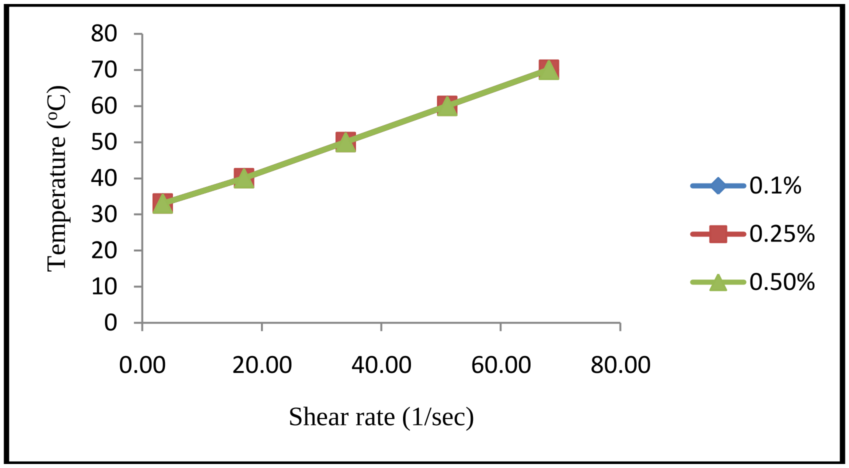


Fig 4.3: Temperature vs. shear rate

From the results obtained from experimental work, it had been proven that temperature increases with shear rate. The shearing effects decreased as the temperature increased; that is, the emulsion became more Newtonian in the higher temperature region. Shear rate of all the emulsion were constant for each rpm regardless of w/o ratio, emulsifier used and amount of emulsifier used. Trend of the graphs of temperature versus shear rate is similar to Fig 4.3 regardless of w/o ratio, emulsifier used and amount of emulsifier used.

4.3.3 Effect of viscosity towards shear rate

From the results obtained from experimental work, viscosity of emulsions decreases as the shear rate increases. The rate of viscosity decrease increases with shear rate, which may cause by the intermolecular forces become low at high shear rate. Some results for viscosity of emulsion (50-50% w/o of Kuwait sample using Span 80 and 50-50% w/o of Saudi Arabia sample using Span 80) could be obtained because the emulsion turns out to be very viscous and the viscometer was unable to read the viscosity. Viscosity values for other ratios of w/o emulsions were obtained from the viscometer panel and the trend of the graph is the same where viscosity decreases with increasing shear rate. Higher viscosity of emulsion shows that the stability of the emulsion is higher. When the shear rate increases, viscosity of the emulsion decreases and it causes stability of the emulsion decreases. Increase in concentration of emulsifier, increases viscosity of the emulsion, whereas effect of w/o ratio is inversely proportional towards viscosity of the emulsion.

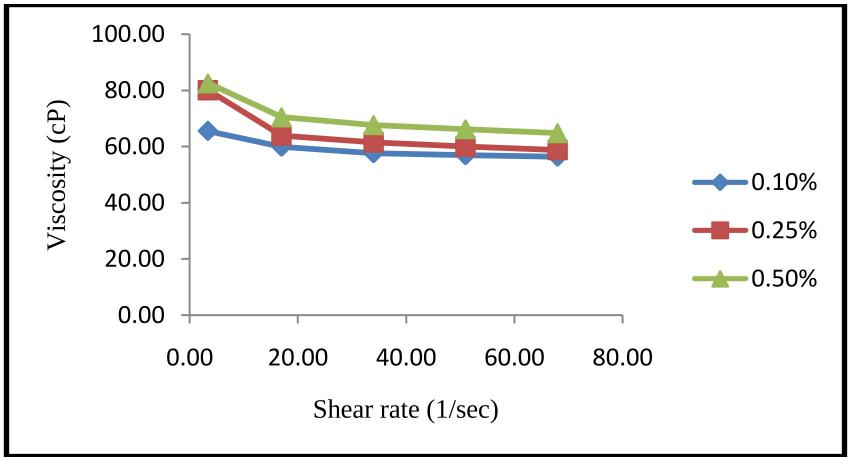


Fig 4.4: Viscosity vs. shear rate

4.3.4 Effect of viscosity towards temperature

The viscosities of the emulsions proved to be nearly independent of the kind of the resins. It is remarkably, emulsion is very sensitive to temperature, as temperature increases, the viscosity decreases fast. This phenomenon occurs when the temperature increases, the kinetic energy of molecules within the emulsion increases. When this situation happens there will be more rapid molecules interchange occurs and cause viscosity of the emulsion decreases. As the temperature increases, the molecules being transferred will obtain sufficient energy to escape the system. So, the rate of viscosity difference decreases with increase of temperature. Stability of emulsion increases due to increase in viscosity. From Fig 4.5 it is clear that emulsion with highest emulsifier concentration has highest stability compared to smaller amount of emulsifiers.

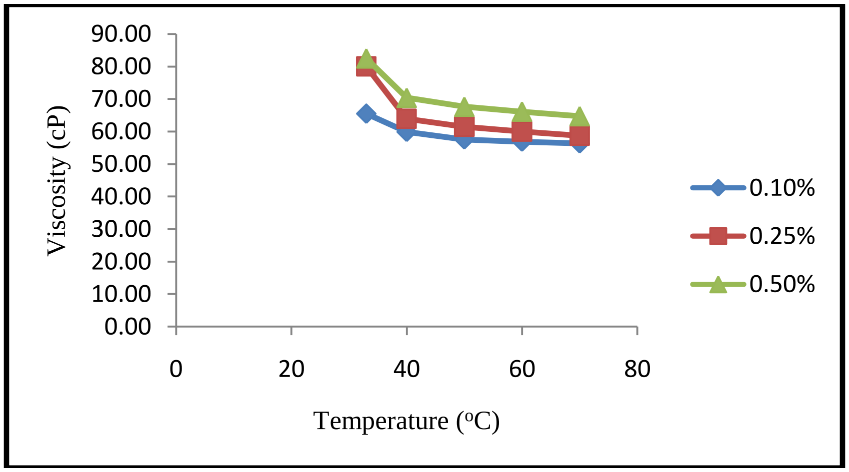


Fig 4.5: Viscosity vs. temperature

4.3.5 Effect of shear stress towards shear rate

Basically relationship between shear stress and shear rate is directly proportional. From Fig 4.6 it is clear that at few conditions (50-50% and 30-70% w/o ratios) the correlation between shear stress and shear rate are linearly proportional. A fluid whose stress at each point is linearly proportional to its strain rate at that point is called Newtonian fluid. Newtonian fluid is any kind of fluid continues to flow, regardless of the forces acting on it.

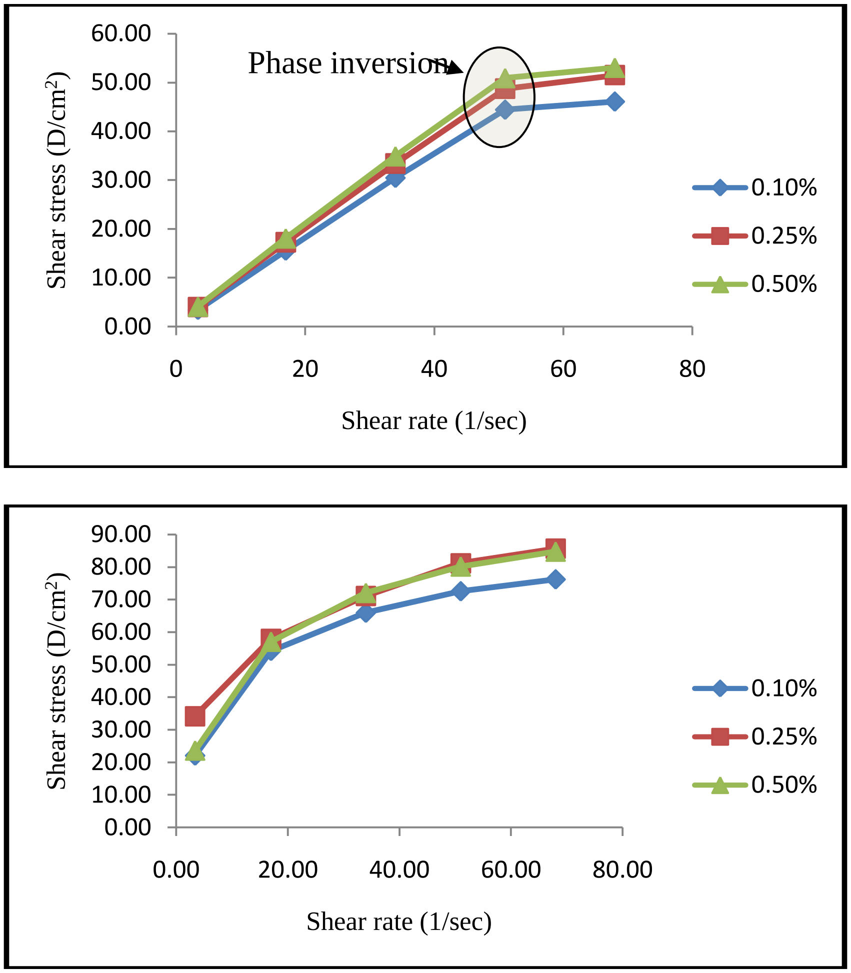


Fig 4.6 and 4.7: Shear stress vs. shear rate

From Fig 4.7 it can be observed that the graph is nonlinear. This is because the emulsions (10-90% w/o emulsions) are non-Newtonian, so called pseudoplastic behavior. When a linear line in a graph starts to form a curve, it can be concluded that phase inversion occur from w/o to o/w. This situation occurs because, as the emulsion's shear rate increase, temperature of the emulsion increase which cause the intermolecular forces between molecules increase. Consequently, the phase of the emulsion converts from w/o to o/w.

4.3.6 Effect of different concentration of emulsifiers

The effect of surfactant concentration and volume fraction on emulsion stability is studied by three ratios of water-in-oil emulsions that; 50-50%, 30-70% and 10-90% w/o emulsions. It found that as the volume fraction (φ) decreases, the separation time for water to separate from the emulsion increased. In this regards, the volume fraction (φ) of water for 50-50% w/o is 0.459, 30-70% w/o is 0.267 and 10-90% is 0.086. The concentration of surfactant mainly affects the viscosity of emulsion. Fig 4.5 shows that the viscosity of emulsion increases as surfactant concentration increases. The concentration of surfactant mainly affects the viscosity of emulsion.

All emulsifying agents adsorbed onto the oil-water interface to provide a protective barrier around the dispersed droplets. In addition to this protective barrier, emulsifiers stabilize the emulsion by reducing the interfacial tension of the system. Therefore high concentration of emulsifiers means high amount of surfactant molecules to provide a coated film around the water droplets and bind it with oil to produce a stable emulsions. As the amount of surfactant molecules increased, the efficiency of producing barrier to separate w/o droplets and to prevent coalescence will increase.

4.3.7 Effect of water-in-crude oil ratio

According to the results obtained, by decreasing the phase ratio from 50-50% to 30-70% and 10-90%, the stability of emulsions increased as in Fig

4.5. Higher viscosity of emulsions indicates higher stability. When the volume of dispersed phase reached to 50-50% the emulsion behavior completely has changed as shown in Fig 4.6. The emulsion changed from w/o to o/w, from these measurements and observations, it can be deduced that the phase inversion point should be in the range of % water. As the volume of the dispersed phase increases, the continuous phase must spread out further to cover all of the droplets, this cause the likelihood of impacts to increase, thus decreasing the stability of the emulsion. This means that, the emulsion might not break as increase the volume of the dispersed phase. In fact this increment caused an emulsion to invert from one phase (w/o) to another (o/w).

4.4 Microwave Demulsification

The microwave heating process was examined for emulsion samples. Transient temperature profiles of water-in-crude oil emulsions inside a cylindrical container during batch microwave heating were measured. Three temperature readings were placed at the top, middle and bottom of the sample container.

Table 4.2: Experimental results of batch microwave heating on Kuwait samples (Microwave power is: 540 W)

Radiation time(sec)	C	C/s	q_{MW}	ϵ' r	ϵ" r
50-50 % w/o					
20	16.23	0.812	1.665	69.374	6.131
40	19.79	0.495	1.015	68.178	5.690
60	31.69	0.528	1.084	64.182	4.583
80	37.85	0.473	0.971	62.113	4.162
100	38.35	0.384	0.787	61.945	4.131
120	49.83	0.415	0.852	58.090	3.529
140	46.13	0.330	0.676	59.333	3.703
160	52.14	0.326	0.669	57.314	3.428
180	53.61	0.298	0.611	56.821	3.367
200	51.54	0.258	0.529	57.516	3.454
30-70 % w/o					
20	14.54	0.727	0.985	69.841	6.322
40	16.5	0.413	0.559	69.182	6.056
60	26.45	0.441	0.597	65.841	4.986
80	32.53	0.407	0.551	63.799	4.498
100	33.04	0.330	0.448	63.628	4.462
120	44.45	0.370	0.502	59.796	3.773
140	42.95	0.307	0.416	60.300	3.851
160	48.18	0.301	0.408	58.543	3.591
180	55.03	0.306	0.414	56.243	3.298
200	56.66	0.283	0.384	55.696	3.236
10-90 % w/o					
20	33.24	1.662	1.204	63.258	4.385
40	26.08	0.652	0.472	65.663	4.939
60	36.48	0.608	0.440	62.170	4.172
80	43.88	0.549	0.397	59.685	3.756
100	33.3	0.333	0.241	63.238	4.381
120	51.75	0.431	0.312	57.042	3.395
140	45.38	0.324	0.235	59.181	3.681
160	47.61	0.298	0.216	58.433	3.576
180	54.88	0.305	0.221	55.991	3.269
200	58.34	0.292	0.211	54.829	3.141

Table 4.3: Experimental results of batch microwave heating on Kuwait samples (Microwave power is: 720 W)

Radiation time(sec)	C	C/s	q_{MW}	ϵ' r	ϵ" r
50-50 % w/o					
20	19.32	0.966	1.982	68.185	5.692
40	24.67	0.617	1.266	66.388	5.135
60	39.1	0.652	1.337	61.542	4.059
80	42.11	0.526	1.080	60.531	3.888
100	42	0.420	0.862	60.568	3.894
120	47.49	0.396	0.812	58.725	3.616
140	51.95	0.371	0.761	57.227	3.418
160	62	0.388	0.795	53.852	3.040
180	66.52	0.370	0.758	52.334	2.896
200	74.3	0.372	0.762	49.721	2.678
30-70 % w/o					
20	14.6	0.730	0.989	67.775	5.555
40	19.5	0.488	0.660	66.130	5.063
60	29.37	0.490	0.663	62.815	4.296
80	33.04	0.413	0.559	61.583	4.066
100	38.24	0.382	0.518	59.836	3.779
120	45.58	0.380	0.515	57.371	3.436
140	48.91	0.349	0.473	56.253	3.300
160	57.39	0.359	0.486	53.405	2.997
180	61.06	0.339	0.460	52.173	2.882
200	73.08	0.365	0.495	48.136	2.560
10-90 % w/o					
20	10.89	0.545	0.394	71.402	7.057
40	13.03	0.326	0.236	70.684	6.699
60	18.65	0.311	0.225	68.796	5.910
80	20.15	0.252	0.182	68.293	5.729
100	24.81	0.248	0.180	66.728	5.232
120	31.21	0.260	0.188	64.578	4.673
140	35.47	0.253	0.184	63.148	4.362
160	42.86	0.268	0.194	60.666	3.910
180	45.31	0.252	0.182	59.843	3.780
200	60.24	0.301	0.218	54.829	3.141

From Fig 4.8 and Fig 4.9, it is clear that temperature of emulsions increase with radiation time. This is due to continuous supply of heat in the form of radiation. In Fig 4.8 line of 10-90% w/o is above 30-70% and 50-50% w/o because the initial temperature of the emulsion of 10-90% w/o emulsion is higher than the other two emulsions but by comparison temperature increase of 50-50% emulsions is higher than 30-70% and 10-90% w/o emulsions due to small dielectric loss of water. Higher amount of water in 50-50% w/o emulsion cause less dielectric loss in the emulsion and higher temperature increase in the emulsion, whereas higher dielectric loss in 30-70% and 10-90% w/o emulsions.

The temperature increasing rates of irradiated samples and their volume rates of heat generation were shown in table 4.2 and 4.3, respectively. These samples comprise 50-50%, 30-70% and 10-90% water-in-crude oil emulsions. The temperatures of emulsions were obtained from the average value of three location temperature readings. The rate of temperature increase was calculated from temperature increase divided by radiation time. The average rates of temperature increase of 50-50%, 30-70% and 10-90% water-in-crude oil emulsions were 0.886, 0.526 and 0.395 C/sec for 540W power generation, whereas 1.042, 0.582 and 0.218 C/sec, respectively for 720W power generation.

The rate of temperature increase of emulsions decreases as radiation time increase due to decreasing dielectric loss of water. Decrease in rate of temperature increase of 10-90% w/o emulsion is higher than 30-70% and 50-50% w/o emulsion according to Fig 4.10 and Fig 4.12. In Fig 4.11 and Fig 4.13, line of 10-90% and 30-70% w/o emulsion seems to be below 50-50% w/o emulsion because the initial temperatures of these three emulsions are different, but if we analyze the graphs thoroughly, the difference in rate of temperature increase is fastest for 10-90% w/o followed by 30-70% and 50-50% w/o ratio. This situation occurs because 10-90% w/o emulsion content least amount of water compared to the other two ratios which cause temperature of these emulsion increase very fast and achieve its maximum temperature.

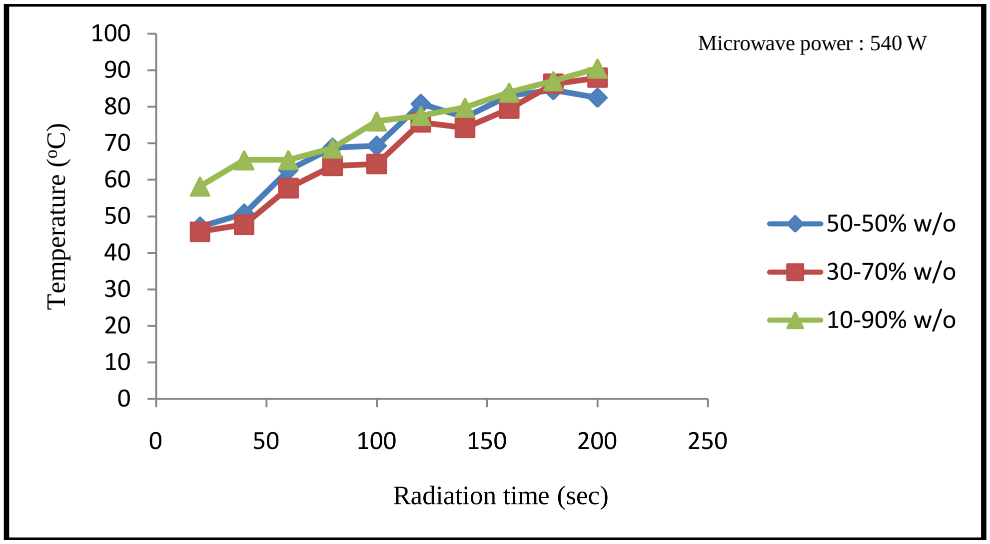


Fig 4.8: Temperature vs. radiation time (540W)

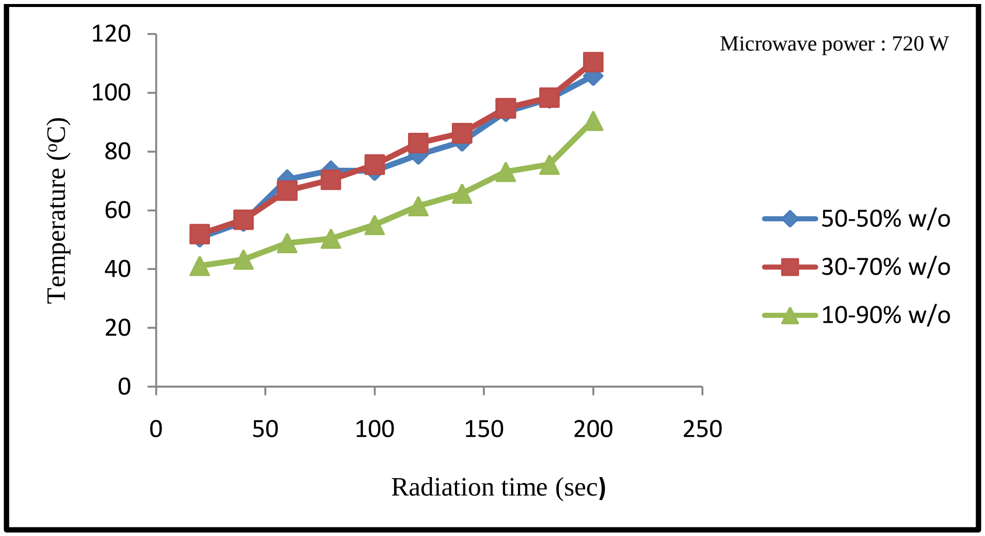


Fig 4.9: Temperature vs. radiation time (720W)

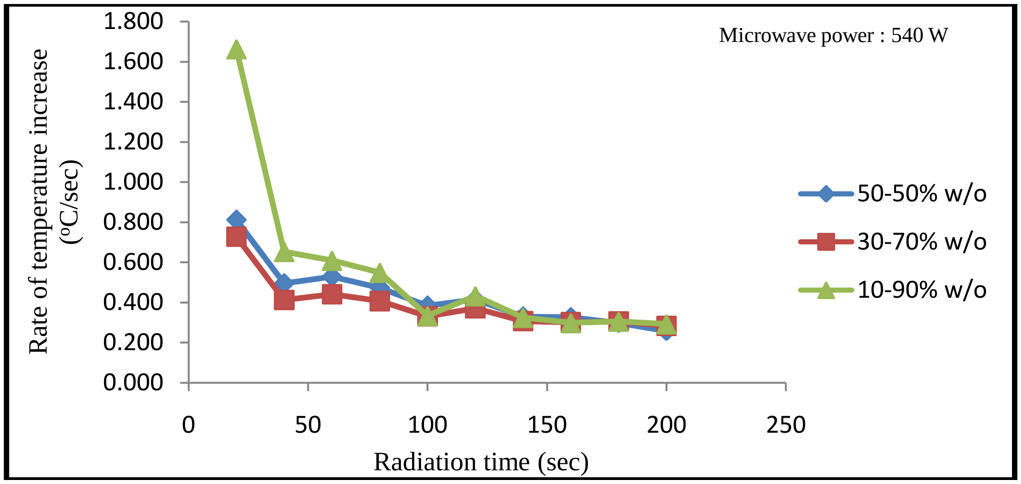


Fig 4.10: Rate of temperature increase vs. radiation time (540W)

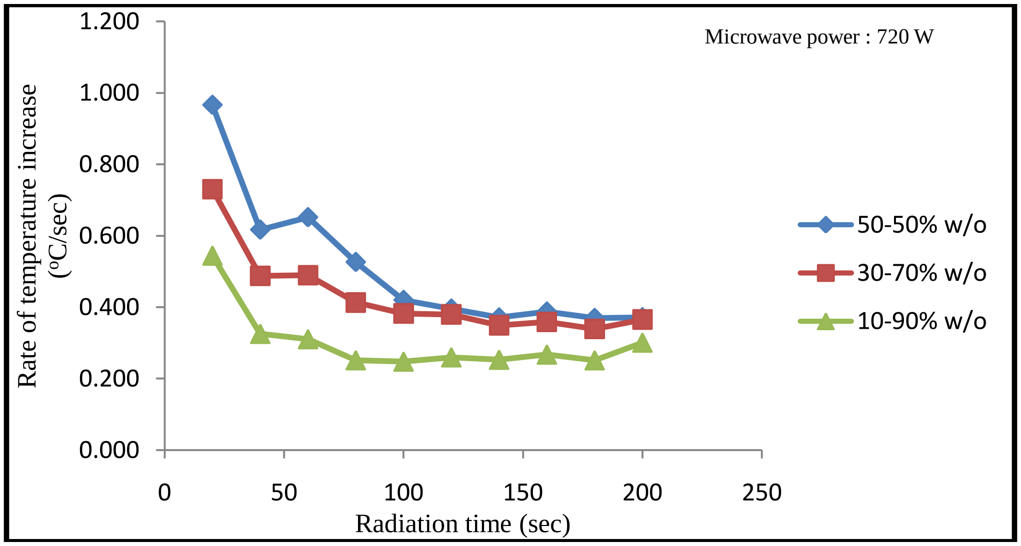


Fig 4.11: Rate of temperature increase vs. radiation time (720W)

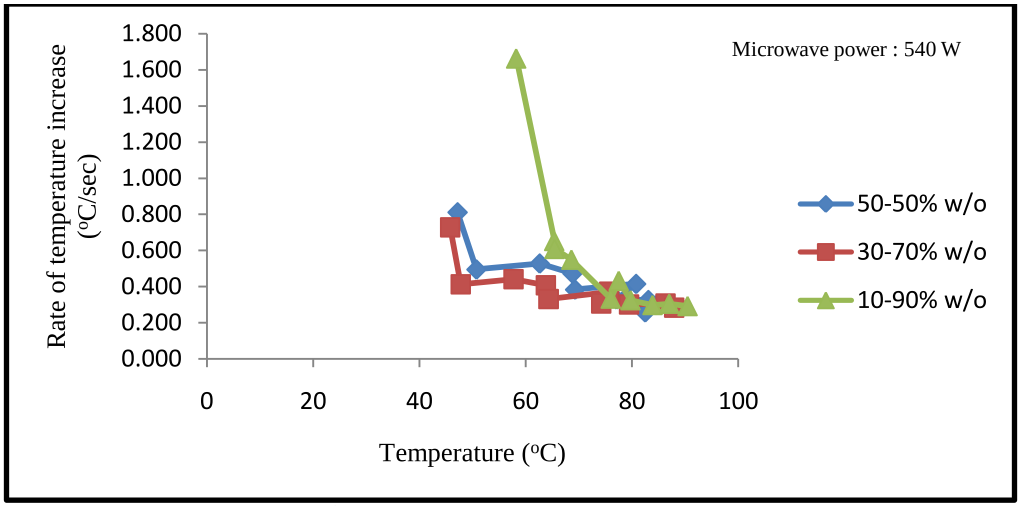


Fig 4.12: Rate of temperature increase vs. temperature (540W)

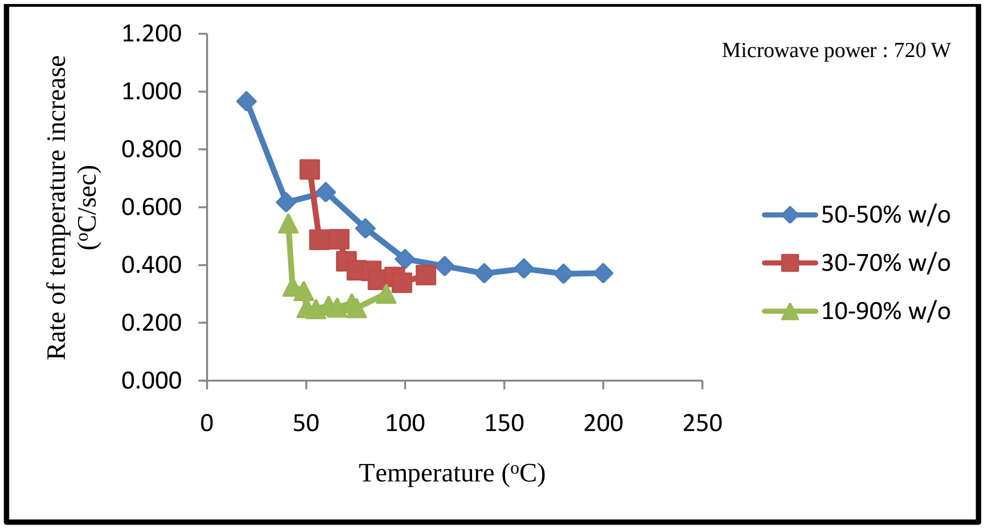


Fig 4.13: Rate of temperature increase vs. temperature (720W)

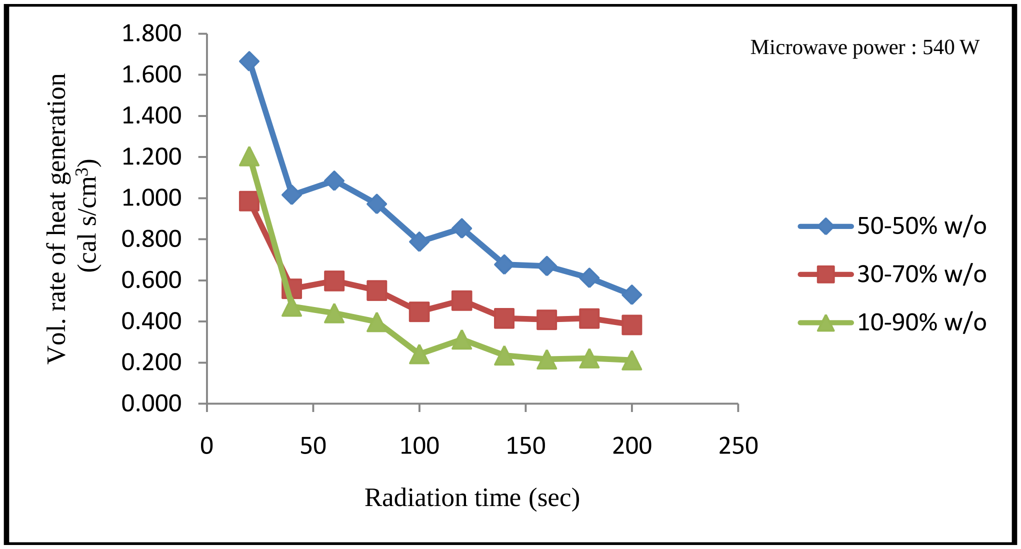


Fig 4.14: Volume rate of heat generation vs. radiation time (540W)

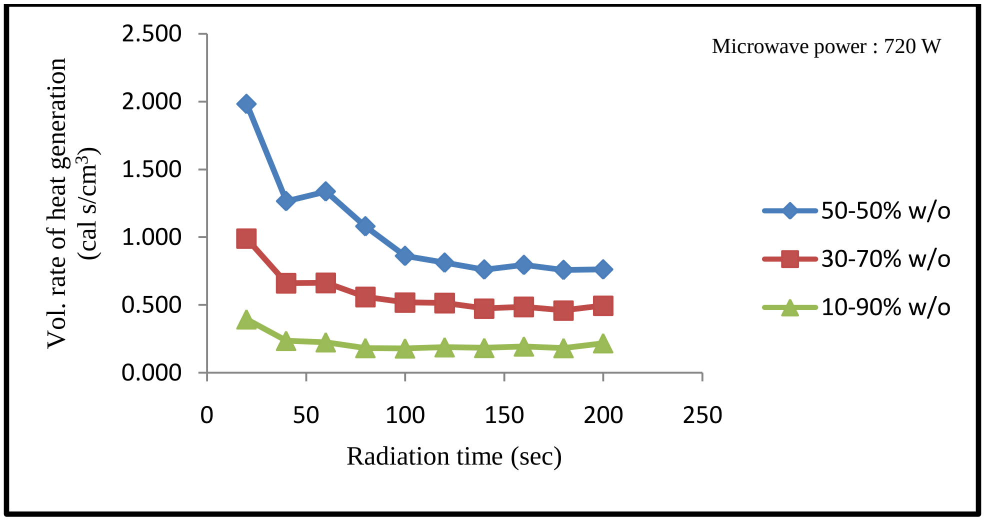


Fig 4.15: Volume rate of heat generation vs. radiation time (720W)

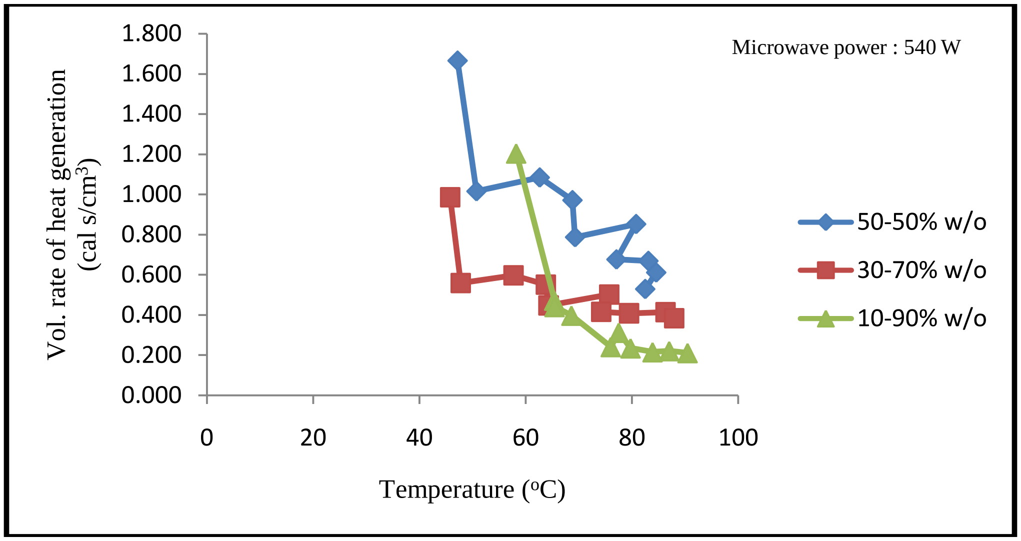


Fig 4.16: Volume rate of heat generation vs. temperature (540W)

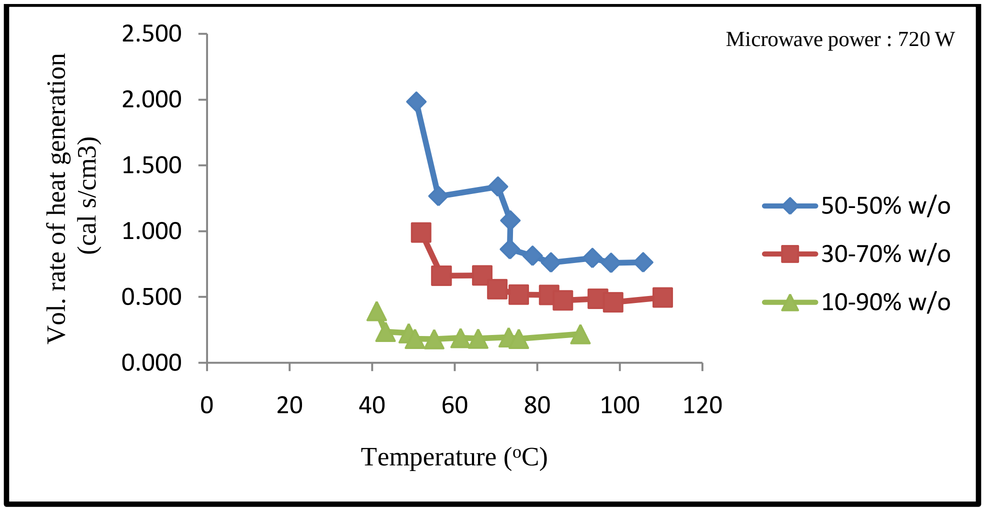


Fig 4.17: Volume rate of heat generation vs. temperature (720W)

The volume rate of heat generation of emulsions decreases with temperature and time increase, respectively. The mechanism of microwave heating is essentially that of dielectric heating. After exposing the emulsion to the microwave electromagnetic (EM) field, molecular rotation, and ionic conduction due to the penetration of EM into the emulsion are responsible for the internal heating (Chan et al., 2002). In this situation, the temperature distribution will occur to equalize temperature at three different locations in the emulsion. This heat transfer phenomenon occurs where heat from higher temperature region flows towards lower temperature region.

The energy balance Equation 9 used to calculate the volume rate of heat generation. This equation 9 included three terms, convective heat transfer, irradiative heat transfer due to microwave and conduction heat transfer respectively. From calculations of this study, the contributions of convective and irradiation terms are very small. Since, the sample container is a glass cylinder (transparent to microwave and has very low dielectric constant), its heat loss assumed to be zero. The volume rates of microwave heat generation of water-in-crude oil emulsions shown in Table 4.2 and 4.3. In application of equation of Equation 9 for determination of volume rates of heat generation, the emulsion density (ρ_m) and heat capacity (C_{pm}) calculated from Equation 10 and 11, respectively.

From Fig 4.8 through Fig 4.17, it is observed that when the microwave power generation increased from 540W to 720W, temperature of all emulsions increase faster with radiation time. This is due to higher amount of radiation supplied to the emulsions converts into heat and increases temperature of the emulsions. This situation cause rate of temperature increase and volume rate of heat generation of emulsion supplied with 720W is higher than 540W.

There was no separation of water from water-in-crude oil emulsion although microwave radiation supplied to the emulsion. This was because the crude oil was very heavy and stable. The crude oil sample may contain a large amount of natural stabilizers which is saturated asphaltene, resin and aromatic (SARA). These natural stabilizers comes with the crude oil during drilling process which make the crude oil very stale and even high radiation unable to remove water from it. Chemical demulsification was done towards this sample as well and there was no separation was observed.

To prove that microwave heating technology is efficient, results from microwave demulsification for light crude oil samples used as comparison. The sample used was crude oil from PETRONAS refinery. These results were taken from journal written by Abdurahman (2010). From the results obtained by the researcher it is clear that this sample is light crude oil.

Table 4.4: Experimental results of continuous microwave heating on PETRONAS samples (Microwave power is: 900 W)

Radiation time(sec)	ΔT	$\frac{dT}{dt}$	q_{MW}	ϵ' r	ϵ" r
50-50% w/o					
20	11.1	0.555	0.231	72.890	7.933
40	14.8	0.370	0.214	71.647	7.188
60	23.8	0.397	0.229	68.625	5.847
80	26.6	0.333	0.192	67.685	5.525
100	34.5	0.345	0.199	65.032	4.781
120	37.1	0.309	0.179	64.158	4.577
140	40.2	0.287	0.166	63.117	4.356
160	46.7	0.292	0.169	60.934	3.954
180	49.1	0.273	0.158	60.128	3.824
20-80% w/o					
20	15.9	0.795	0.460	71.278	6.992
40	19.5	0.488	0.282	70.069	6.420
60	29.8	0.497	0.287	66.610	5.198
80	33.2	0.415	0.240	65.468	4.889
100	41.1	0.411	0.238	62.815	4.296
120	43.6	0.363	0.210	61.976	4.136
140	46.2	0.330	0.191	61.102	3.983
160	51.4	0.321	0.186	59.356	3.707
180	55.7	0.309	0.179	57.912	3.506

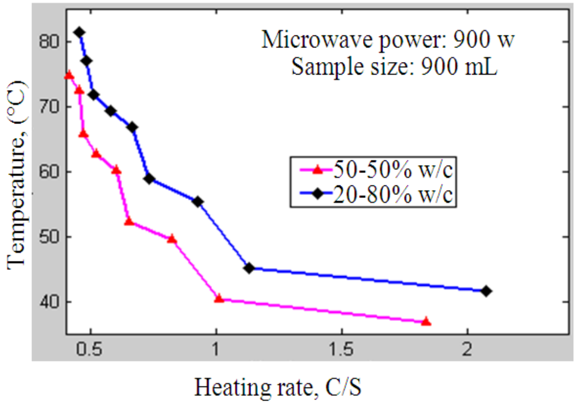


Fig 4.18: Rates of temperature increase for 50-50 and 20-80% w/o

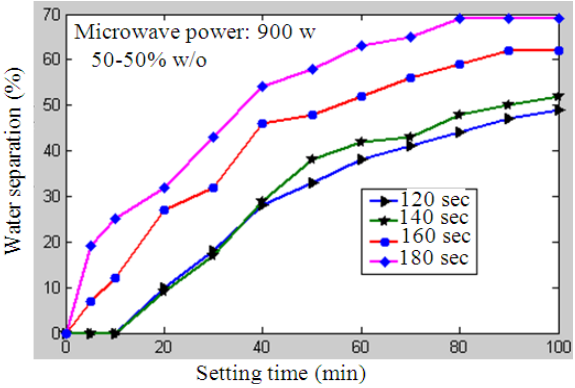


Fig 4.19: Separation of water from 50-50% w/o

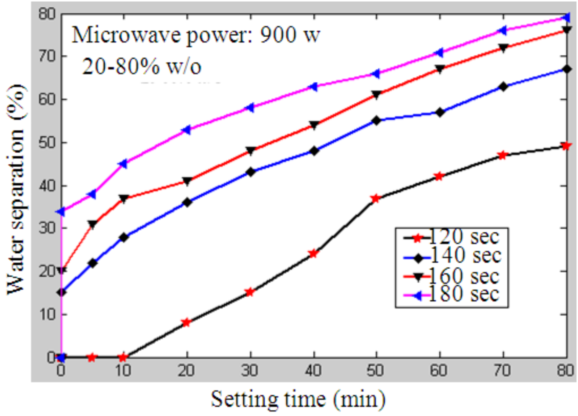


Fig 4.20: Separation of water from 20-80% w/o emulsions

Results from this research clearly show that separation of water-in-crude oil is available for light crude oil via microwave heating. Since the purpose of heating water-in-crude oil emulsions with microwave is to separate water from oil, therefore, the separation efficiency of 50-50 and 20-80%

water-in-oil emulsions calculated by using Eq. 1. In this research, rate of temperature increase increases with heating rate due to low dielectric loss of water. This sample shows separation because the sample used is 900ml, but in my research I used only 400ml. So, limited space for the molecules to move causes no separation in the emulsion. Further comparison could not be made due to lack of crude oil sample.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The behaviors of water-in-crude oil emulsions investigated by studying stability and demulsification of emulsion by batch microwave. Stability studies carried out by analyzing on emulsions which varied by the type of emulsifier, water-in-oil ratio, amount of emulsifier and settling time. Correlation between these factors and stability were observed. Emulsions are, by nature, physically unstable, that is they tend to separate into two distinct phases or layers over time.

In this research, emulsion characterized by type of emulsion (water-in-oil or oil-in-water), nature of emulsifying agents present, different concentration of emulsifying agent and w/o ratio and its viscosity, temperature, shear rate, shear stress, surface tension and interfacial tension. Stability of emulsion increases as concentration of emulsifier increases. Moreover, viscosity of the emulsion increase and consequently interfacial tension between oil and water decrease.

The batch microwave heating process was examined for emulsion samples. Results of this study showed that, microwave radiation is a dielectric heating technique with the unique characteristics of fast, volumetric and effective heating is feasible and has the potential to be used an alternative way in the demulsification of water-in-oil emulsions. From temperature distribution profiles of irradiated emulsion, it appears water-in-oil emulsion has been heated quickly and uniformly by microwave rather than by conventional heating. This new technology does not require chemical addition.

Higher power generation could have been used for efficient separation of water-in-crude oil. Some modification could be made towards the process to be able to separate water from heavy crude oil emulsions. Batch microwave heating had been done, so, continuous heating could be tried out either in laboratory or pilot scale.

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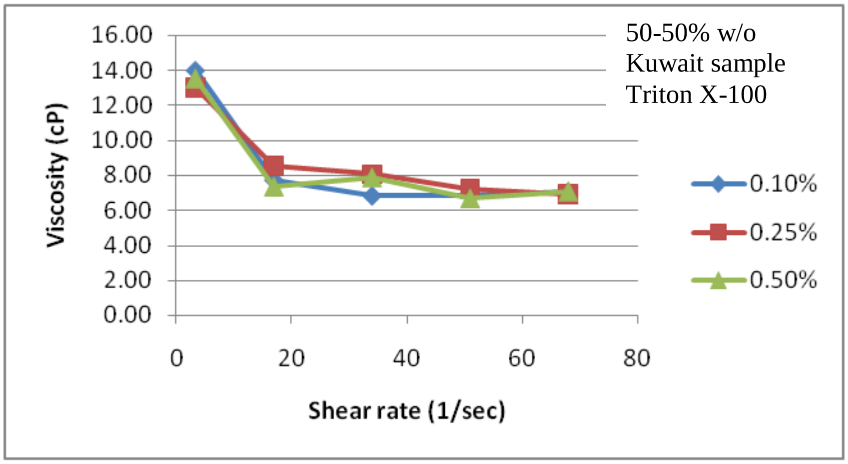
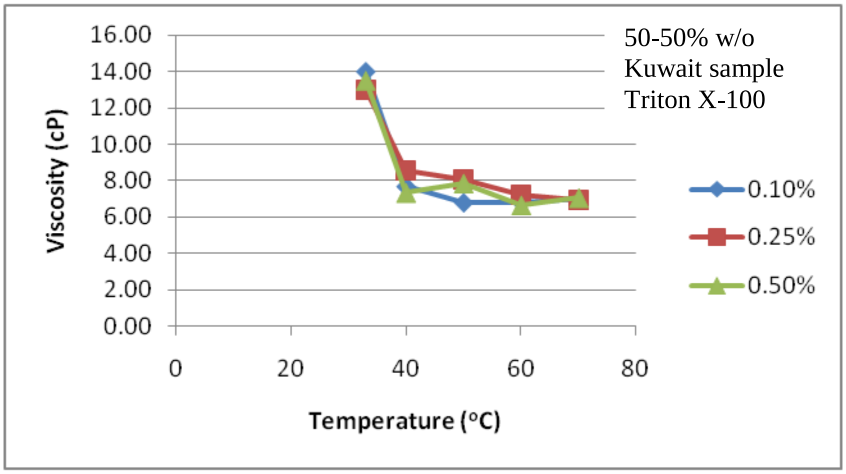
APPENDIX A

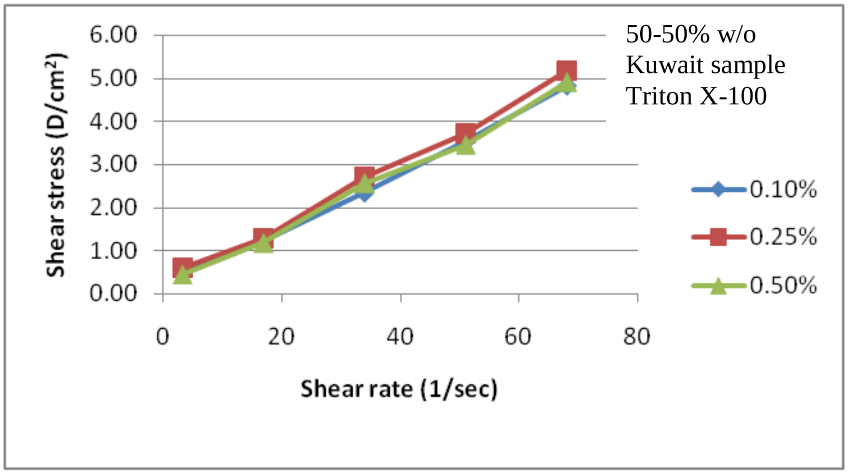
STABILITY TESTING RESULTS



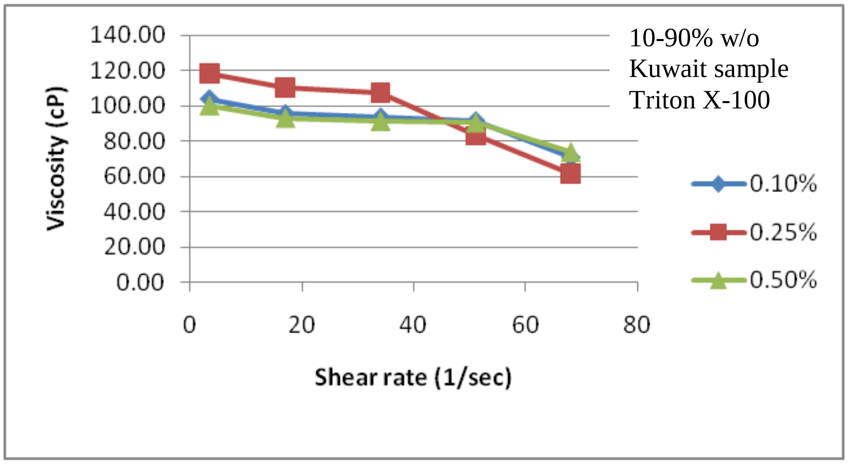
Appendix A1: Viscosity vs. shear rate



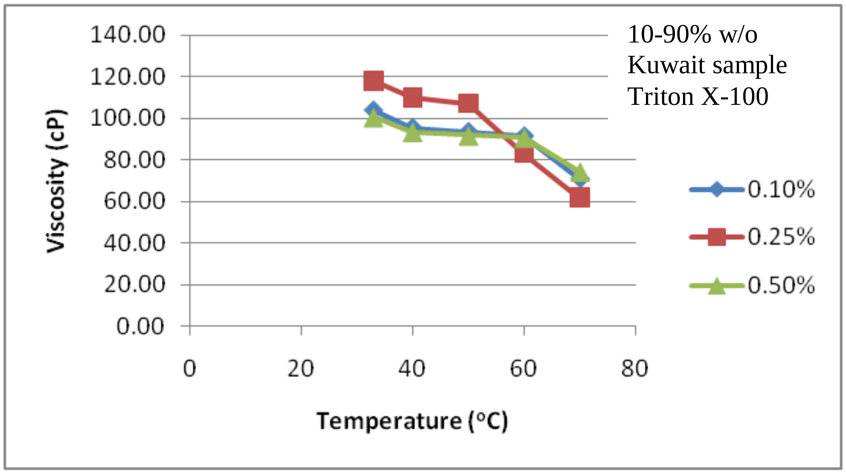
Appendix A2: Viscosity vs. temperature



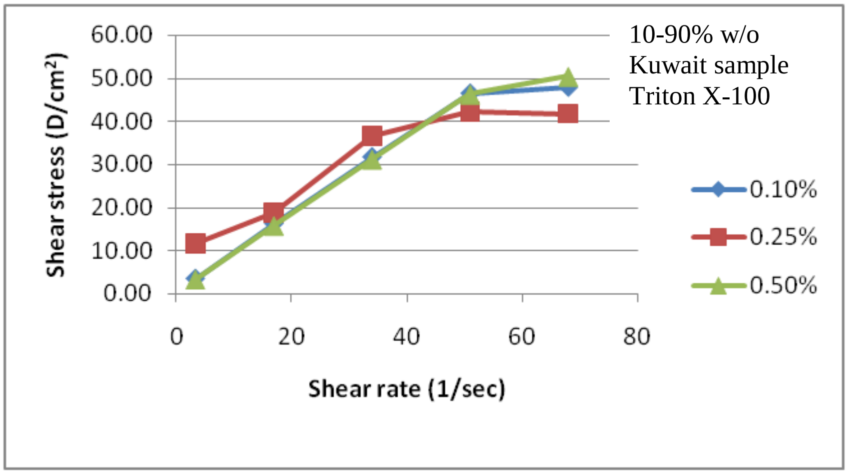
Appendix A3: Shear stress vs. shear rate



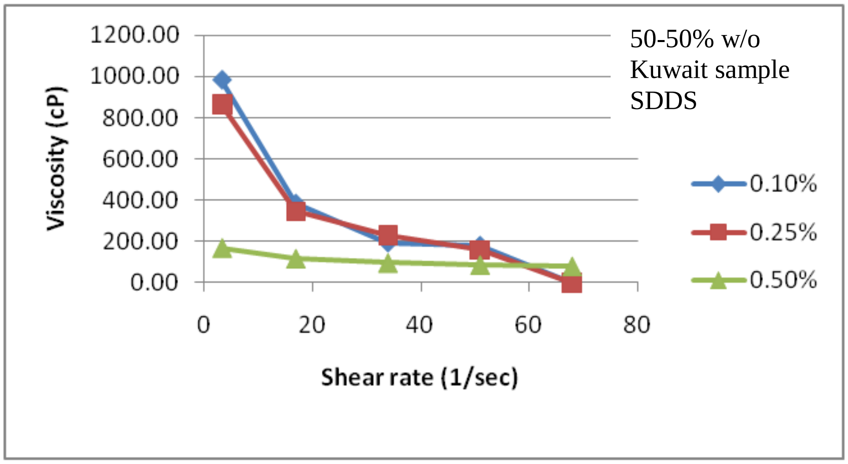
Appendix A4: Viscosity vs. shear rate



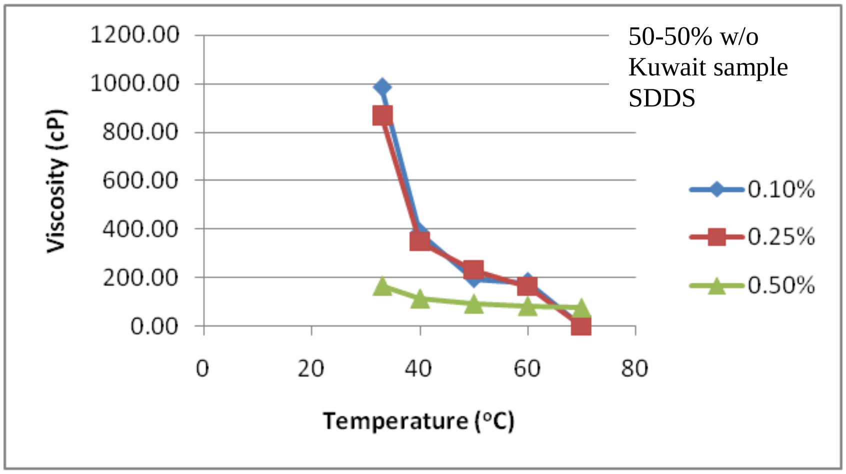
Appendix A5: Viscosity vs. temperature



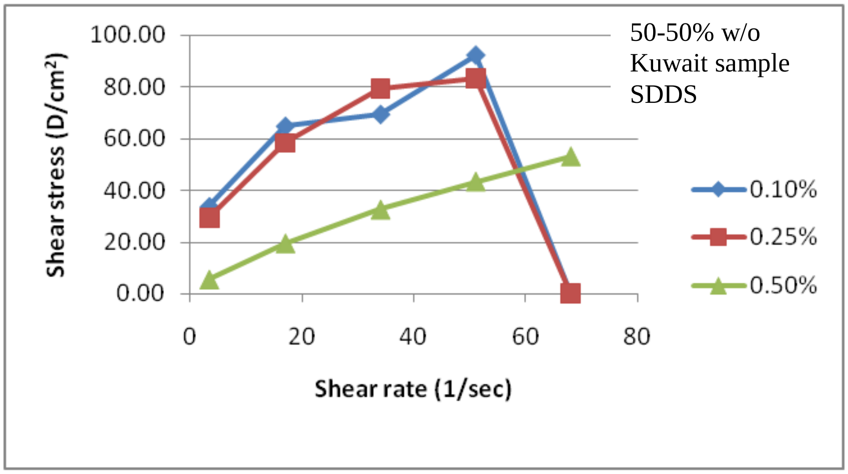
Appendix A6: Shear stress vs. shear rate



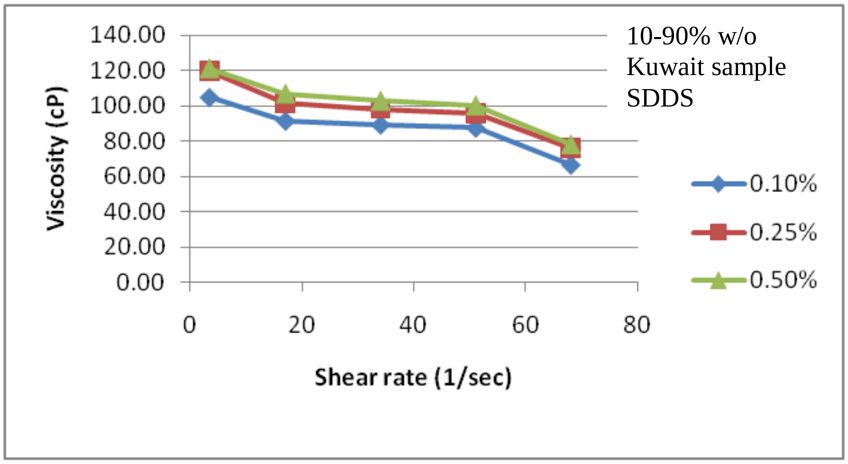
Appendix A7: Viscosity vs. shear rate



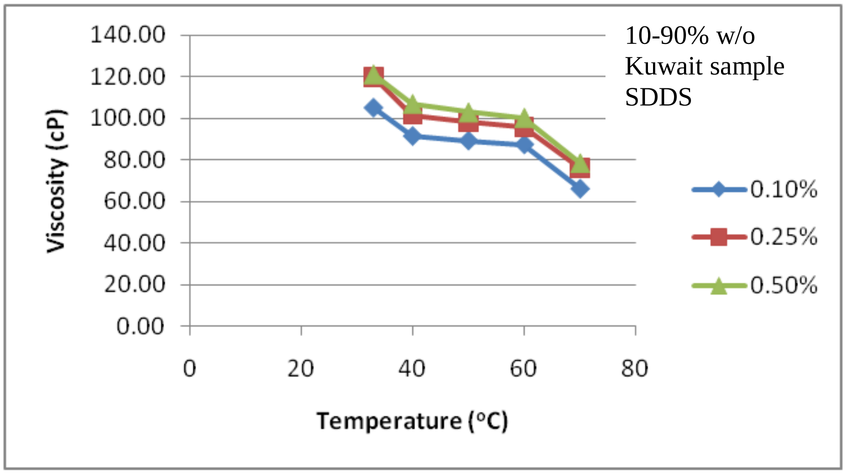
Appendix A8: Viscosity vs. temperature



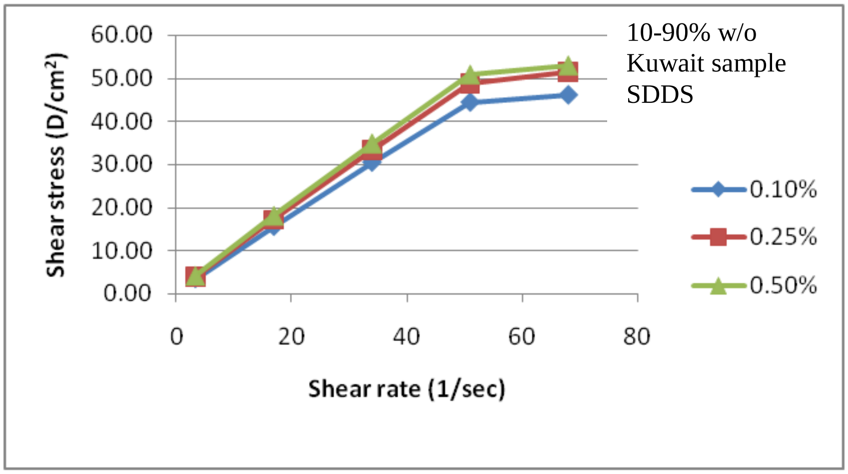
Appendix A9: Shear stress vs. shear rate



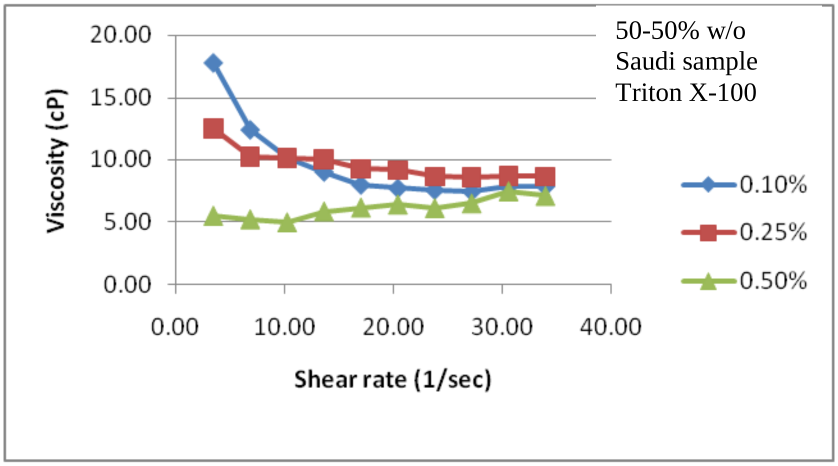
Appendix A10: Viscosity vs. shear rate



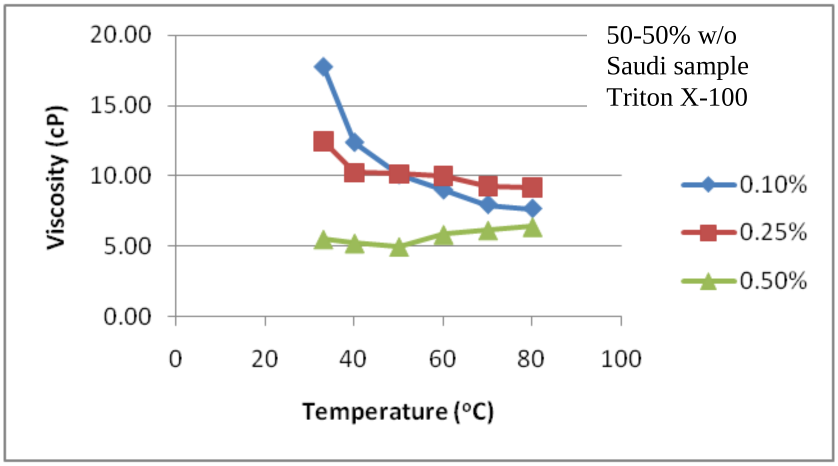
Appendix A11: Viscosity vs. Temperature



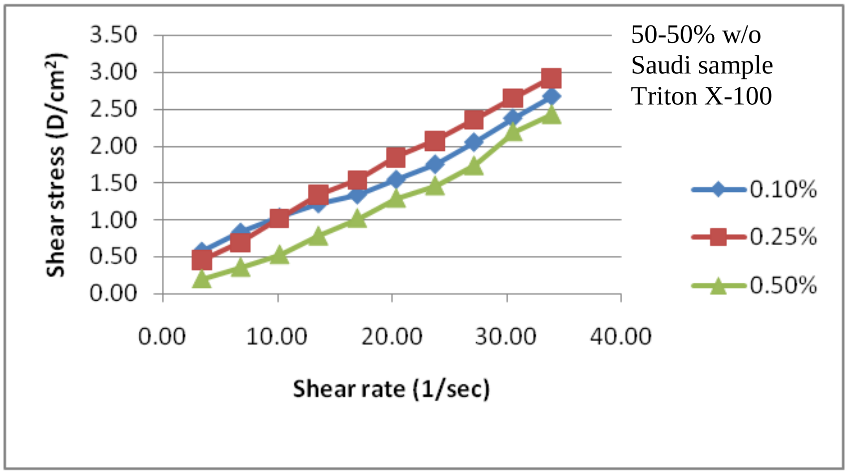
Appendix A12: Shear stress vs. shear rate



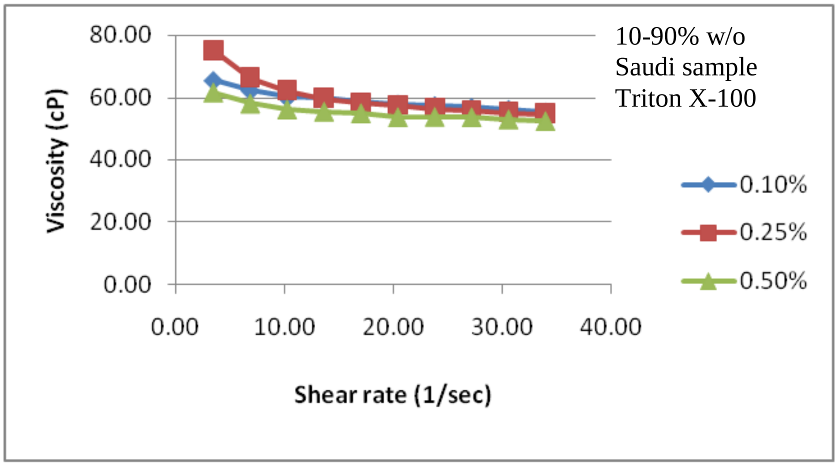
Appendix A13: Viscosity vs. shear rate



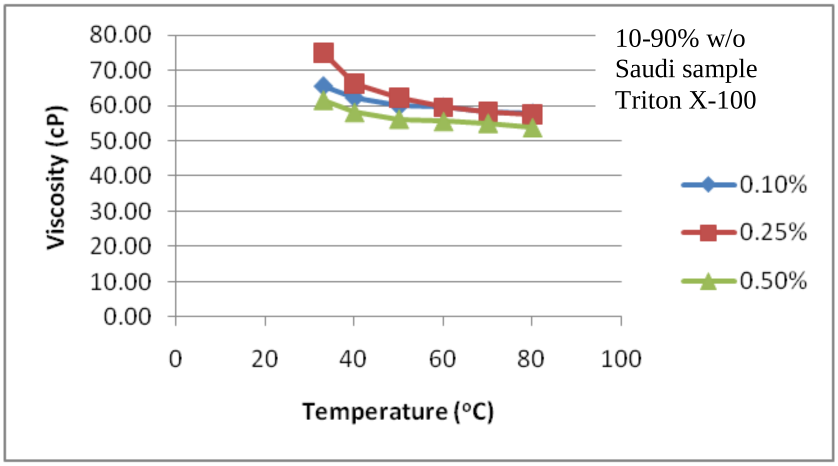
Appendix A14: Viscosity vs. temperature



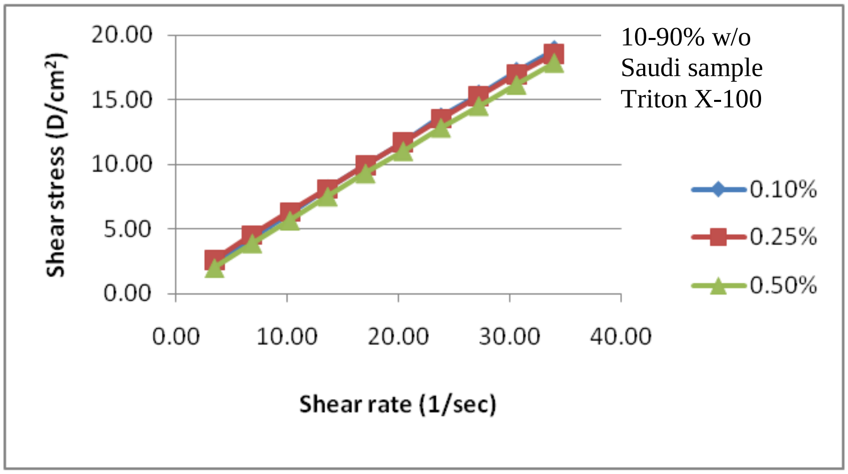
Appendix A15: Shear stress vs. shear rate



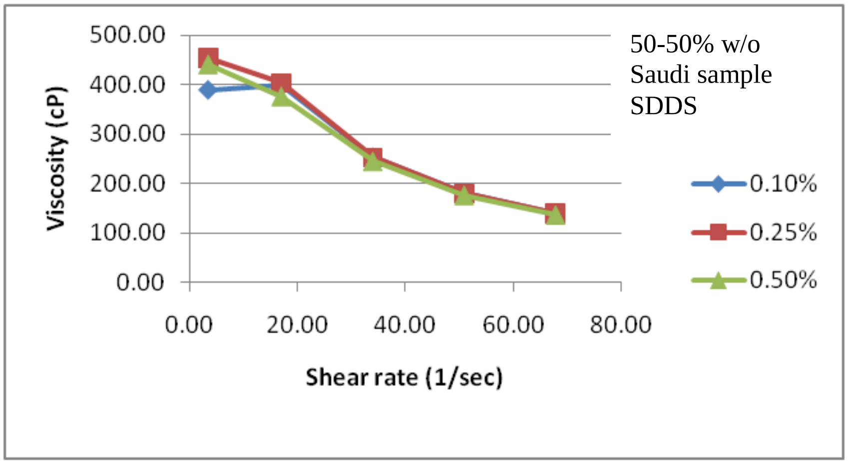
Appendix A16: Viscosity vs. shear rate



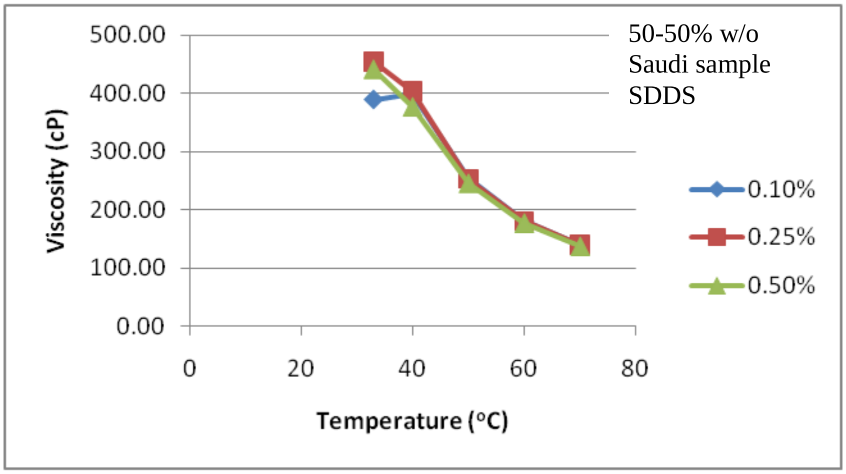
Appendix A17: Viscosity vs. temperature



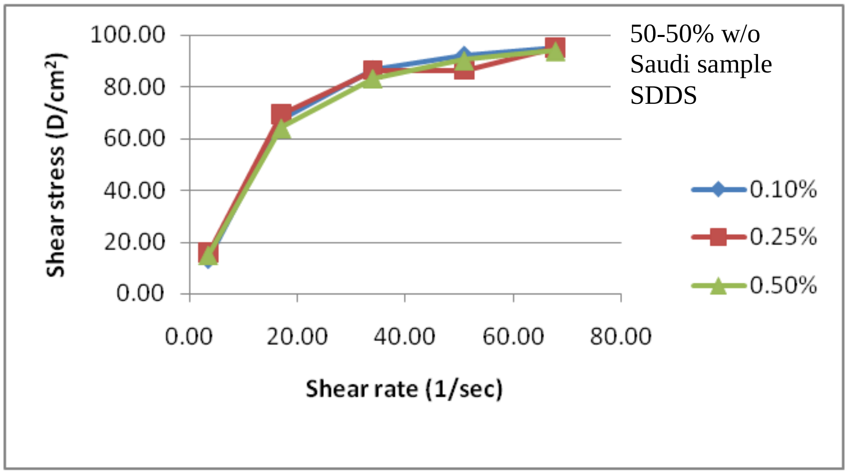
Appendix A18: Shear stress vs. shear rate



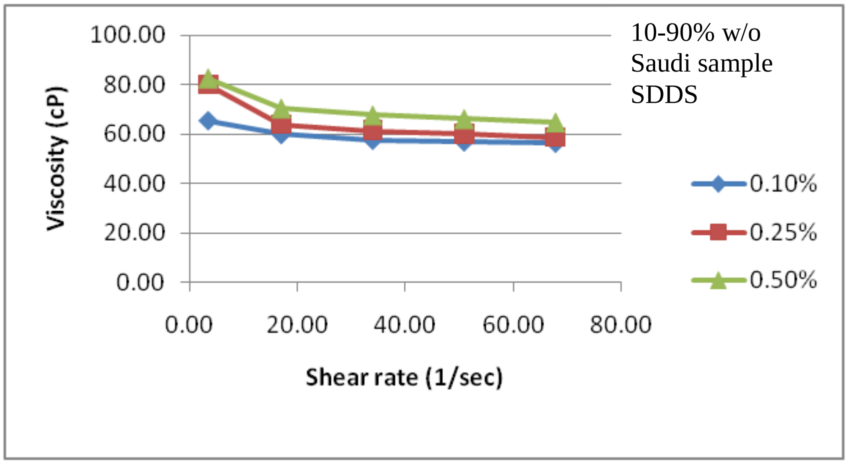
Appendix A19: Viscosity vs. shear rate



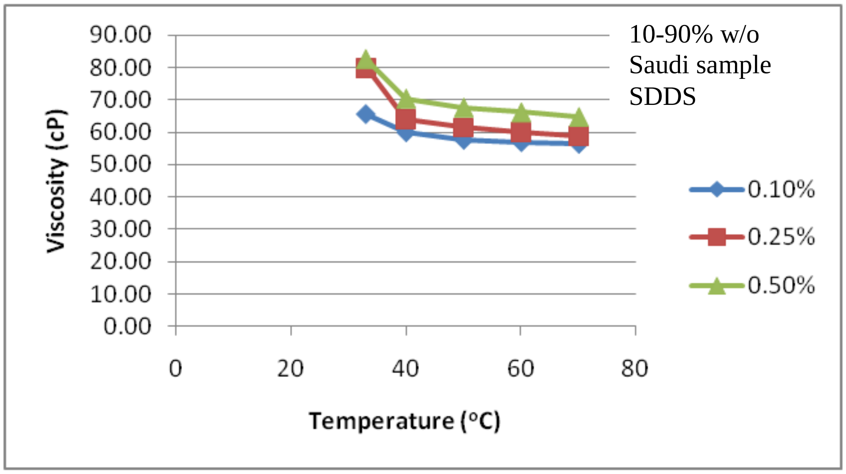
Appendix A20: Viscosity vs. temperature



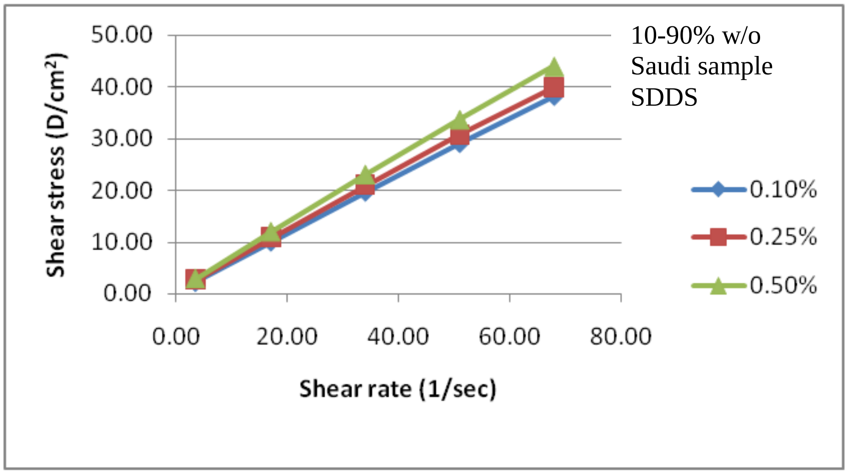
Appendix A21: Shear stress vs. shear rate



Appendix A22: Viscosity vs. shear rate



Appendix A23: Viscosity vs. temperature



Appendix A24: Shear stress vs. shear rate