APPLICATION OF MICROWAVE AND ULTRASONIC DEMULSIFICATION TECHNIQUES ON PETROLEUM BASED EMULSIONS

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

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Dedicated to my parents and siblings

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ABSTRACT

Although emulsions are very useful and desired products in cosmetic, food and soft drink industries, yet they are considered as troublesome and undesired product in petroleum industries wherein; they eventually need to be broken into pure oil and water. The current demulsification techniques that consist of mainly chemicals together with mechanical, heating and electrical methods are not very good, since chemical for instance are costly and harmful to the environment, mechanical techniques such as gravity settling tank, hydrocyclone vessel, centrifugal separators, and steam stripping are large requiring more space and cost, electrical techniques almost always work in a very high voltage that can easily cause fire via short circuit, the objective of this project is to assess the effectiveness of some other integrated techniques that have not being fully developed, namely microwave and ultrasonic techniques integrated with chemicals for the purpose of reducing or eliminating the chemical demusifiers, another objective of the current project is also to formulate a stable emulsion that resemble the natural emulsion, this in turn generated another interesting objective of decolorizing the crude oil for microscopic droplet size analysis of heavy oil. A massive screening was carried out to fix the optimal parameters in making a stable w/o emulsios these including stirring intensity, emulsifiers' types and concentration and water volume fraction, the results showed that the optimal parameters to produce w/o emulsions were 0.25% (v/v) emulsifiers concentration (Span 80) with mixing speed of 1600 rpm for 7 minutes. From the demulsification process it was observed that when chemical assisted microwave was used a demulsifiers' concentration of 0.1% with two minutes irradiation time gave the best separation efficiency for 50-50% w/o emulsions, while for 20-80 % w/o emulsions; 0.05% demulsifiers concentration and 3.5 minutes irradiation time gave the best water separation of 60%. Chemical assisted ultrasonic also was found to be very effective, when emulsions were sonicated with 0.7% (v/v) of demulsifiers. Hence ultrasonic-chemical integrated system gave the highest separation rate for water-in-crude oil emulsions which reached 97% at power level of 3, compare to microwave-chemical integrated system which gave maximum separation efficiency of 87% at the aforementioned concentration of 0.1%. However when the demulsifiers were increased to 0.7% microwave had given a maximum separation of 96%, Microwave also was tested in some other real industrial emulsions namely Slop oil emulsion and waste coolant emulsion and gave very high separation as expected. Fundamentally the basic mechanism behind the effectiveness of microwave demulsification is that the electromagnetic wave that induce the water molecules to move as trying to rearrange themselves with the wave in two distinct mechanisms known as ionic conduction and dipole rotation that would eventually convert the wave energy into heat generated within the water molecules, while for ultrasonic demulsification it is normally governed by the pressure exerted by the sound wave on the droplets as they travel through the emulsion medium, hence the compression refraction form of the wave motion would make the suspended water droplet to aggregate on the nodes and coalesce.

ABSTRAK

Walaupun emulsi adalah sangat berguna dan merupakan produk yang dikehendaki dalam kebanyakan industri seperti kosmetik, makanan dan minuman ringan; namun emulsi dilihat menjadi masalah dan merupakan produk yang tidak dikehendaki dalam industri petroleum dimana akhirnya ia perlu dipisahkan kepada minyak tulen dan air. Teknik terkini yang paling utama dalam pemisahan emulsi adalah terdiri daripada kaedah secara kimia beserta mekanikal, dan pemanasan beserta elektrikal. Namun begitu, teknik-teknik ini adalah tidak baik sebagai contoh kaedah menggunakan kimia yang boleh memberi bahaya kepada alam sekitar disamping kosnya yang tinggi, manakala kaedah mekanikal yang menggunakan peralatan seperti tanki pengenapan graviti, saluran hydrocyclone, pengasing sentrifugal, and strippings pengewap adalah memerlukan ruang yang besar dan kos yang tinggi. Manakala teknik pemisahan yang menggunakan elektrik selalunya memelukan voltan yang tinggi menghadapi masalah litar pintas yang boleh mengakibatkan kebakaran. Oleh itu, tujuan projek ini dijalankan adalah untuk menguji keberkesanan teknik-teknik bersepadu yang lain yang masih belum sepenuhnya dibangunkan iaitu kaedah menggunakan gelombang mikro dan ultrasonic yang disepadukan dengan kaedah secara kimia bagi tujuan pengurangan dan penyingkiran bahan kimia pemisah emulsi, objektif lainnya pula adalah untuk menghasilkan emulsi yang lebih stabil menyerupai emulsi semulajadi bagi tujuan menyahwarnakan minyak mentah likat untuk analisis saiz titisan mikro. Bagi tujuan penghasilan emulsi yang lebih stabil, penyaringan besar-besaran dilakukan untuk menentukan nilai optimum bagi parameter- parameter seperti keamatan adukan, jenis-jenis dan kepekatan emulsi, dan nisbah isipadu air. Keputusan menunjukkan bahawa nilai optimum untuk menghasilkan w/o emulsi bagi parameter-parameter ini adalah: 0.25% (v/v) kepekatan emulsi (Span 80) dengan 1600 rpm kelajuan adukan bagi tempoh 7 minit. Selepas proses pemisahan emulsi dijalankan menggunkan kaedah gelombang mikro bantuan kimia, diperhatikan bahawa 50-50% w/o emulsi dengan mengunakan kepekatan bahan pemisah emulsi sebanyak 0.1% bagi tempoh 2 minit pendedahan sinaran gelombang mikro menunjukkan keberkesanan yang terbaik dalam pemisahan emulsi, manakala 20-80% w/o emulsi dengan 0.05% kepekatan bahan pemisah emulsi bagi tempoh 3.5 minit pula adalah yang terbaik bagi 60% pemisahan air. Kaedah Ultrasonik bantuan kimia pula didapati sangat berkesan apabila emulsi yang telah disonofikasi dengan 0.7% (v/v) bahan pemisah emulsi; menunjukan pemisahan yang tinggi. Oleh itu, sistem yang menyepadukan ultrasonic dan kimia menunjukkan kadar pemisahan bagi w/o emulsi mencapai 97% pada aras kuasa 3, dibandingkan dengan system yang menyepadukan gelombang mikro dan kimia yang hanya menunjukkan keberkesanan pemisahan sebanyak 87% pada nilai 0.1% seperti yang telah dinyatakan di atas; akan tetapi apabila nilai bahan pemisah emulsi ditingkatkan sebanyak 0.7%, keberkesanan pemisahan meningkat kepada 96%. Selain itu, gelombang mikro juga diuji keatas emulsi sebenar dari industri seperti emulsi minyak Slop dan emulsi sisa penyejuk dimana kelihatan pemisahan adalah tinggi sebagaimana yang dijangkakan. Secara dasarnya, mekanisma asas kepada keberkesanan dalam pemisahan menggunakan gelombang mikro adalah disebabkan oleh gelombang elektromagnetik yang mengaruhkan dan menyusun molekul-molekul air melalui konsep konduksi ion dan putaran kutub yang seterusnya menjanakan gelombang tenaga kepada haba antara molekul-molekul air. Sementara itu, pemisahan menggunakan ultrasonik dilihat menggunakan tekanan yang dihasilkan melalui gelombang bunyi keatas titisan-titisan emulsi dimana gerakan gelombang dilihat mampu menguraikan titisan-titisan air dan minyak yang bersatu.

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A	sample container area
c	Speed of light
D	droplet diameter
f	Frequency of incident microwaves
G	gravity
h	Convective heat transfer coefficient
m	Mass of sample
V	Volume of water separated
α_E	Electromagnetic attenuation factor
ε'	Dielectric constant
ε''	Dielectric loss
λ_m	Wave length
ρ_O	Density of emulsion (mixture)
ρ_W	Density of emulsion (mixture)
ρ_m	Density of emulsion (mixture)
ϕ	Volume fraction of emulsified water
δ	stafan-boltzman constant
cp_m	Heat capacity of emulsion (mixture).
D_P	Penetration depth
P_0	Microwave surface power
P_z	Microwave power transmitted
q_{MW}	Volume rate of heat generation
T_a	Temperature of ambient
T_m	Temperature of emulsion (mixture)
v_0	settling velocity of oil droplets

v_w	Settling velocity of water droplets

LIST OF ABBREVIATIONS

EMT	Emulsification temperature
EO	Ethylene Oxide
HLB	Hydrophiliv Lipophilic Balance
HLB	Hydrophiliv Lipophilic Balance
IF	Interfacial Tension
LSWR	Low Sulphur Wax Residue
O/W	oil-in-water emulsion
PIT	phase inversion temperature
PO	Propylene Oxide
SDDS	Sodium dodecyl Sulfate
Span 80	Sorbutan Monoleate
Triton X-100	Iso-octylphenoxy polyethoxy ethanol
w/o	water-in-oil emulsion

CHAPTER 1

INTRODUCTION

1.1 Background

A significant portion of the world crude oil is produced in the form of a water-in-oil emulsion stabilized by natural surfactants that must be treated (demulsified) before they can be processed. Approximately three-quarter of all domestic crude oil must be treated. The percentage of crude oil requiring treatment increases as the oil fields become older and hence more water is produced (Strassner. 1968). Emulsions of crude oil and water can be encountered at many stages during drilling, producing, transporting and processing of crude oils and in many locations such as in hydrocarbon reservoirs, well bores, surface facilities, transportation system and refineries. A good knowledge of petroleum emulsions is necessary for controlling and improving processes at all stage.

Many studies have been carried out in the last 40 years and have lead to a better understanding of these complex systems. However there are still many unsolved questions related to the peculiar behavior of these emulsions. The complexity comes mostly from the oil composition, in particular from the surface-active molecules contained in the crude. These molecules cover a large range of chemical structures, molecular weights, and HLB (Hydrophilic-Lypophilic Balance) values; they can interact between themselves and/or reorganize at the water/oil interface.

1.2 Emulsions

An emulsion is defined as a colloidal suspension of a liquid within another liquid (with droplet sizes typically less than 20 micron) (Wassan. 2000). A colloidal suspension is a concentration of particles or droplets homogeneously dispersed through the carrier liquid (Water). This means the oil droplets are reduced in size to such a degree that the oil normal electrical repulsion of the water molecule is overcome due to it is minute size. Often this colloidal suspension is complex because the dispersed phase is partially solidified or because the continuous phase contains crystalline material like in ice-cream. All emulsions have in common that they are (thermodynamically) unstable (Shinoda 1986).

When oil and water are mixed, a temporary emulsion may form, but because of high interfacial tension, the two phases will separate fairly quickly unless an emulsifying agent or combination of agents is used to stabilize the system (Becher., 1965, Sherman., 1968). Anklam defined emulsion as a heterogeneous system containing two immiscible liquids with one dispersed as droplets in the other. One phase is droplet or discontinuous phase and the other is the external or continuous phase. Additives in the form of surfactant or finely divided solids may provide kinetic stability to this otherwise emulsion thermodynamically unstable system (Anklam., 1997).

The formation of drops requires energy which for a two phase systems, increase with interfacial area and normally that energy is supplied by mechanical device that could be used to mix the sample vigorously and lead to breaking the droplet phase into small drops therefore dispersing one liquid into another will minimize its free energy by reducing the total interfacial area through droplet coalescence. Small droplet will contact each other and coalesce to form larger droplets which will coalesce with other to form even larger droplets. The viscosity of the continuous phase also plays a minor role in increasing the total coalescence time (Friberg., 1992), but emulsion stability is dictated by the colloidal interactions between drops.

1.2.1 Emulsion Compositions

Emulsions have phases, namely, internal/discontinuous or dispersed phase, external/continuous phase and emulsifying agent. Emulsion can be in the forms of liquids or semisolids. Investigators tend to divide emulsions into 1 of the 3 categories:

i) Macro-emulsion, these are opaque emulsions with particles > 400 nm in diameter, particles which are clearly visible under a light microscope.
ii) Micro-emulsions, transparent dispersions with particles < 100nm
iii) Mini-emulsions (a term rarely used) which is intermediate in sizes.

Macro-emulsions are divided into two types, based on the nature of the dispersion. It is a dispersion of droplets of one type within another. That means there is a continuous phase and dispersed phase. If the continuous phase is water and the dispersed phase is oil, then this emulsion is called oil in water, designated O/W. If the continuous phase is the oil, it is called water in oil, designated W/O. Most emulsions are of the some kind of organic liquid or mixture of organic compounds with water. The water immiscible phase is referred to as the oil phase, whether it is really oil or not (Ali et al., 2000).

1.3 Emulsion Types

Emulsions can be classified into main two types based on the dispersed phase and based on the size of liquid droplets.

1.3.1 Based on Dispersed Phase

Oil in water (O/W): Oil droplets dispersed in water

Water in oil (W/O): water droplets dispersed in oil

1.3.2 Based on Size of Liquid Droplets

0.2-50 μm Macro-emulsion (kinetically stable), 0.01-0.2 μm Micro-emulsions (thermodynamically stable), in the oil field, the two basic types of emulsion are water-in-oil (w/o) and oil-in-water (o/w). More than 95% of the crude oil emulsion formed in the field is of the water-in-oil (w/o) type (Ali et al., 2000). An emulsion may be tight (difficult to break) or loose (easy to break).whether an emulsion is tight or loosed depends on a number of factors (Kruse. 1974), four of which are;

i) The properties of the oil and the water
ii) The amount of agitation, or shear, it undergoes
iii) The type and amounts of emulsifying agents present
iv) The percentage of oil and water found in the emulsion.

Emulsifying agents commonly found in crude emulsions include asphaltenes, resinous substances, oil-soluble organic acids, and other finely divided materials that are more soluble, wet table, or dispensable in oil than water, for example, iron, zinc, and aluminum sulfate, calcium carbonate, silica, and iron sulfide (Algam., 2000). Each of these emulsifiers usually occurs as film on the surface of the dispersed droplets. These emulsions cause multiple problems to operating units, accumulate in the refinery tanks, and increase costs of production, transportation, equipment failures, plugged pipelines and decrease throughput.

1.4 Emulsions are created in Two Ways

Beside oil, water and emulsifiers the formation of an emulsion takes energy and occurs at far from equilibrium conditions (Torry., 1984). The droplets are disrupted by shear forces or by local pressure difference, i.e. by initial forces. Lowering of the surface tension by emulsifiers makes it easier to produce an emulsion. The kinetics of adsorption of these emulsifiers at the oil/water interface is related to the droplet size distribution; there are two ways for emulsion formation, namely mechanical and chemical emulsions.

1.4.1 Mechanical Emulsions

In mechanical emulsions, a common method of creating the emulsion is by violent mixing of the shearing of the oil droplet in the water stream with a high shear transfer pump, vigorous mixture, pressure washer or other device that might disperse the oil droplet into minute droplets.

1.4.2 Chemical Emulsions

Chemical emulsions are created when a surface-active chemicals or chemicals are used, such as alkaline cleaners containing surfactants, soap and detergents having ionic or non-ionic characteristics. These chemicals interfere with the natural coalescing of the oil droplet and generally create a permanently stabilized emulsion with little chance of breaking by it self.

1.5 Emulsion Stability

The instability mechanisms of most interest for emulsion system or the process of breaking down an emulsion are Ostwald ripening, creaming (sedimentation), aggregation (flocculation), coalescence, and partial coalescence (Shinoda., 1997). As mentioned above there are two ways in which the process of breakdown of an emulsion can be influenced (chemical and mechanical).

1.6 Problem Statement

Water-in-crude oil emulsions are produced in the oil field; and stable water-in-oil emulsion can be produced during oil lifting and transportation. Formation of emulsion during oil production is a costly problem both in term of chemical used and production loss. Also these created emulsions can cause problems both upstream and downstream of petroleum industries. The traditional methods of eliminating these emulsions include intensive utilization of chemical compound; which force the emulsion to separate into water, hydrocarbon and solids. Usually, these methods are expensive and high dosage of chemical are used to overcome the difficulty, it leads to secondary pollutant, since the separated water may contain too much chemicals to be discharged to public water.

A most recent technology which has received lots of attention from researchers is the application of microwave field in the demulsification (emulsion breaking) process. Microwave offer a fast heating treatment with uniform temperature distribution to the subjected sample, beside that ultrasonic also claimed to induce some mechanical energy that will induces the water molecules to overcome the trapping barrier increasing the aggregation rate which could eventually leads to complete separation.

This study is aimed to investigate the effect of microwave radiation, chemical addition as well as ultrasonic application in the breaking of the emulsion and separation of water from crude oil comparatively.

1.7 Objectives

The objectives of this study are as follow;

- Performance of microwave to break w/o emulsion
- The performence chemical demulsifiers to break wlo emulsions
- The performance of ultrasonic demulsification techniques to break w/o mulsions

1.8 Scopes of the Study

- To investigate the stability mechanisms of the emulsion by preparing several experimental emulsions and investigate their properties such as viscosity, shear rate, shear stress and gravitational settling.

- To decolorize the crude oil.
- To investigate the microscopic behavior of emulsion.
- To examine the demulsification of emulsions by microwave heating using batch process system
- To study the microwave-chemical assisted demulsification of stable water-in-crude oil emulsion.
- To study the ultrasonic chemical assisted demulsification of stable water-in-crude oil emulsion.
- To study the microwave-chemical assisted demulsification of slop oil.
- To study the microwave chemical assisted dmulsification of waste coolant.
- To study the effect of microwave power generation in demulsifying the w/o emulsions
- To analyze the overall potential of microwave and ultrasonic demulsification method as alternative to the conventional chemical demulsification method in demulsifying water-in-crude oil emulsions.

1.9 Layout of the Thesis

In this part the construction of chapters is outlined, research work to investigate the applications and performance of microwave heating technology on crude oil emulsions breaking as well as using conventional heating methods (hotplate), this work investigates the fundamental aspects of emulsion formation, stabilization, and demulsification. Chapter 2 review the related theories of emulsion aspects such as physical-chemistries of emulsion systems, adsorption of surfactant at the liquid-liquid interface, factors that affect the emulsion stabilization, mechanism of emulsification, role of surfactant in emulsion formation, followed by the demulsification techniques such as The theory of microwave and ultrasonic demulsification and mechanisms with which they are affecting and inducing the droplets to be aggregated and separated, also fundamentals theory as well as the previous research works related to microwave energy, electromagnetic radiation, mathematical equations used for calculation of microwave heat generation, dielectric constant, dielectric loss, loss tangent, and heat transfer, Then followed by the basic fundamental and mechanisms of sound wave energy and its interaction with emulsion particles as well as the literature and previous research on the ultrasonic treatement of the water-in-crude oil emulsion demulsificstion.

Chapter 3 which concern only on the methodology used to achieve the objectives of this research which describes the experimental set-up starting from emulsification, stabilization, microwave-chemical demulsification and ultrasonic- chemical demulsification techeniques.

Chapter 4 concern with experimental results of the project and its discussion, hence the result segmented into two parts.

The first part discuses the different ways or methods used in the production of relatively stable emulsion that can be used in further investigation, knowing this process of getting a good emulsion that similar to the natural emulsion requires certain combination of water, crude oil and emulsifying agent, add to that the agitation speed and preparation time as discussed in methodology chapter.

Stability studies is most probably the first cornerstone for any types of emulsion and emulsification study in various industrial as well as real life application such as crude oil spillage, pipeline transportation, oil production from reservoir, enhanced oil recovery, in addition the wide spread food and cleaning and pharmaceutical application (Mamdouh T. Gannam., 2005). Hence the stability was studied comprehensively in chapter 4 and the optimal combination was identified.

The second part discusses the demulsification (emulsion breaking) results carried out to meet the objectives of the current research, hence this chapter consists of Two main parts, that are Microwave-chemical assisted demulisification, and Ultrasonic-chemical assisted demulsification that would be iteratively applied to several petroleum based emulsions from different production regions of the world then a qualitative comparison between the aforementioned techniques was carried out.

Chapter 5 is the last chapter and reveals the conclusions and observations obtained from the current research beside that references are also listed separaetely.

CHAPTER 2

LITERATURE REVIW

2.1 Introduction

This chapter would content the related literature of the previous studies on the subject on interest which is water-in-crude oil referred to now onward as (w/o) emulsion and its stability then followed by destabilization and the current prominent techniques.

2.1.1 Emulsion Formation and Stability

Basically all types of emulsion consists two immiscible liquids one of which dispersed as droplets (called internal phase or droplet phase) into the other normally called continuous phase then these two phase are also normally stabilized by a third phase called emulsifying agent (also known as surfactants, surface active agent, or emulsifiers) in water-in-crude emulsions, the dispersed water droplets (internal phase) are encapsulated by an oil matrix (external or continuous phase).

As stated earlier w/o emulsions made of the individual pure components of only oil and water phases are not stable and would quickly split back into their original phases (water and oil), and that is due to the thin oil film at the interface of neighboring water droplets will shrink and rupture leading the droplets to coalesce and merge together and eventually separate to two distict phases (water and oil), therefore a surface active is needed to stabilize the interfacial film and eventually the whole system. Naturally occurring petroleum crude oil emulsions are normally stabilized by the indigenous surfactants, namely asphaltenes and resins which are partially soluble in both systems and have a strong tendency to migrate and sediment at the interface of the water droplet and the oil phase forming what so called interfacial barrier (Tove Storm-kristiansen et al., 1995)

Stable Water-in-crude Emulsions are generated during crude oil mining because water and oil are produced and pumped out of the ground indeed the existence of the indigenous surfactants as such asphaltenes and resins, heavy metals, fatty acids and clays would strongly lower the interfacial tension between the oil and water and lead to the formation of stable barrier between the water-oil interface that prevent coalescence of water droplets and eventually produce stable water-in-crude oil emulsions (Inge Harald Auflem et al, 2001, Delphine Daniel-David et al.,2005,).

Beside the carbon and hydrogen, Minor quantities of others gases such as nitrogen, oxygen, together with heavy mainly sulfur, and trace amount of other common metals (mainly, iron, vanadium, and nickel) are the major components in the crude oils, these element would facilitate the formation of hydrogen bonding as well as polar interactions among the asphaltene components and that would give the interfacial film its elastic behavior and strength (Nael N. Zaki et al., 2003).

Plenty of researches have been done on the emulsion preparation and stabilization process in the field crude oil emulsion and so many composition and combinations as well as preparation conditions have been reported, since emulsions are multiphase systems of mainly Oil, water and emulsifying agent that brought together by the means of mechanical mixing therefore stability study is mainly concerned with the types of chemicals used, mixing power (mixing speed), mixing duration (emulsification time), mixing temperature (EMT), hence knowing these parameters are very important in emulsion making since most of researcher need to know at least what combination that can give a stable emulsion that could be used for the subsequent test.

Tron eric Havre and Johan sjoblom have investigated the effectiveness of combined surfactant Phase and Asphaltene particles to produce stable emulsions, Heptane/Toluene mixture solution that contains Paraffinic and aromatic component was reported to represent the crude oil phase, they also extracted the asphaltene from the original crude and mixed it with aforementioned surfactant phase to represent the emulsifying agent, then Ultra Turrax T25 rotor was chosen as a mixture to supply the emulsifying power at speed of 9500 rpm for 30 seconds (emulsification time) at emulsification temperature of 70 °C in water bath, furthermore they also investigated the emulsion characteristic, emulsion stability as well as droplet size analysis by means of electrical field, graduated cylinder and Liquid chromatography respectively. Their study revealed that water-in-crude oil emulsions can be stabilized by means of combined surfactants and Asphaltene particle and hence they concluded that w/o emulsion can be stabilized by combination of naphthenic acid/naphthenate and asphaltene,

Lixin Xia also investigated the effect of asphaltene and resin in jet kerosene continuous phase w/o emulsion but at different emulsification conditions fore instance he never used another emulsifiers and used the hand shaking as mechanical mixing source he also used the optical microscopic visualization to characterize his emulsion together with calculating the water resolution but he emphasized on the water resolution as the best way to study the stability of emulsion however his research suggested that, there is a specific relative concentration of asphaltene and resin within which emulsions were found to stable.

In another work Brujic. J. and coworkers have produced a transparent Oil-in-water emulsion for sake of measuring the inter-droplet forces that govern these micron sized emulsion droplets, Silicone Oil and Sodium dodecyl Sulphate (SDS) were selected as oil phase and emulsifying agents respectively, their emulsion was prepared at mixing speed of 7000 s^{-1} thus resulted an emulsion with mean droplet size of 3.4 micron meter ranging from (1-10) that reported to be stable over a period of at least one year.

Jixiang Guo and frend have investigated the alkaline-surfactant-polymer as emulsifiers to stabilize emulsions made from mode oil that consisted of jet fuel as the dispersing medium, mixed with fractions from Gudong crude oil (from Shengeli oil field in China) to mimic the crude oil, however their emulsion was prepared with simple hand mixing at 60 °C, also the stability pattern was monitored by visual observation of the water resolved from the emulsion with time, from this they found that the Asphaltene component from Gudong crude oil have more polar acidic components then other fractions and these interfacial active component in the Asphaltene were found to be ionized when they are mixed with the alkali solution, thus the ionized and non ionized groups can make hydrogen bonds and lead to the formation of the acidic soap these soap acts as emulsifiers and promote stable emulsion on petroleum wells during enhanced oil recovery where the alkaline-surfactant-copolymers are injected in the reservoir to increase the productivity (Jixiang et al., 2006).

Indeed the stability effect of the alkaline-surfactant-copolymer also investigated by Minguan and his friends on stabilizing Daqing crude oil from China their study also mentioned the ability of the alkali to produce stable emulsion inside the crude oil reservoir when its used for enhanced oil recovery, however their experimental emulsion based on model oil from jet fuel and mixed with some polar fractions from daqing crude oil, the oil water to oil ratio was 50-50% and was prepared by handshaking at 45 ^{0}C (Minguan et al., 2004).

The water-in-crude oil emulsion formed from Venezuelan crude oil that having API= 24.5^0 (sour crude oil) was found to be very stable even without emulsifiers, it was reported that the emulsion did not resolved any water within a period of one week hence in the subsequent studies researchers have diluted the original Venezuelan crude oil with various amount of heptanes (Poor solvent for asphaltene) then several emulsions were made from the diluted oil by vigorous mixing at 40 ^{0}C, the results proved that the Alifatic/Aromatic ratio of the crude oil can tremendously affect the stability of the emulsion, since they attributed the stability of emulsion to the asphaltene, resin colloidal particles interaction that is in turn a very strong function of the Alifatic/aromatic fractions of the petroleum. Hence when the heptane (alifatic) is added to the crude oil (dilution) it found to induce the asphaltene to precipitate out of the crude oil, inded this precipitation increase the size and poly-dispersity of submicrone asphaltene particles that lead eventually to reduce the stability of the emulsion because of the attractive depletion force (K. Kumar et al., 2001).

Nave Aske and coworkers have developed an electric cell that can supply an electric field to the emulsion as a way to predict emulsion stability since the electric field can break the emulsion and separate the water, thus they tested that device on emulsions made from 21 different crude oils with different water cuts (30% and 20%) and from their reported results; the stability pattern was ranged from not stable at all and very stable and they concluded that the asphaltene content, aggregation state of the asphaltene and the interfacial elasticity was found to be the most important factors which could produce stable emulsions (Nave Aske et al., 2002). In another work bitumen as residue from a petroleum refinery was dispersed in water phase and produced a stable bitumen-in-water emulsion at elevated pH values (M. A. Rodriguez-Valverd et al., 2003), Minguan Li and co-workers have investigated the effects of alkaline surfactant-polymers on stabilizing crude oil emulsion that is originated from Daqing oil field (China), however their results had proved the ability of theses Alkalene surfactant to produce stable w/o emulsions inside the reservoir when they are injected during the enhanced oil recovery process, their sample was of 50-50% composition and prepared by simple hand shaking (Minguan Li et al., 2004).

In another work Andreas and friends have studied the effects of silica nano-particles on the stability mechanism of model oil emulsions, note that the heavy component of crude oil mainly asphaltene and resins were extracted from the Brazilian sour crude oil and used as coating on the surface of the silica particles to render them as solid formed emulsifiers, their model emulsion was prepared from water and mixture of heptanol plus toluene as oil phase.

the mechanical mixing energy was provided by an ultraturax mixture at 1800 rpm for one minute then at 22000 rpm for two minutes, then the stability study was carried out within a period of 30 minutes, and the percentage of water separated from the emulsion within this 30 minutes period was used to assess the emulsion stability, hence their results showed that Asphaltene could irreversibly be adsorbed as a rigid film at the oil-water interface and these coating has greatly enhanced the model emulsion stability.

Similar work also have reported by ogla and his friends have also investigated the role of Asphaltene and Resin in stabilizing water-in-oil emulsions, however their model emulsions were assessed by measuring the interfacial composition and stability, the oil models was consisted of Heptane, Toluene Asphaltene, Resin, and Native solids, they calculated the emulsion surface area from droplet sizes distribution by means of the optical microscopy, the Asphaltene and Resin used in their study were extracted from two different crude oils originated from Athabasca and Cold lake fields, they prepared the emulsion by first mixing and sonicating the Heptane with Asphaltene and Resin to form the model oil then water was added drop-wise as the mixing goes on, 17000 rpm of mixing speed was applied for 7 minutes, Although the total volume of water in the emulsion was 40% yet their emulsion was shown to separate within few minutes form it is first preparation (M. A. Rodiguez et al., 2003).

Far from crude oil emulsion other researchers reported the polymer blind mixture as comparative to emulsions since two different polymers are not compatible with each other in certain concentration range, in another word they would not form a stable solution even if their monomer and low molecular weight analogous do, hence the transition from a compatible system to an non-compatible system (emulsion) as a results of phase separation and aggregation of droplets leads to tremendous changes in rheological properties (Visco-elastic properties) of the polymer blends, interestingly surfactants are not used as stabilizers in polymer blends but rather another different additives called Compatibilizers are used to stabilize the non-compatible polymers.

K. Moran and his friends have tried to observe the contribution of Naphthenic acid in crude oil emulsions since naphthenic acid one of the natural indigenous components of the crude oil consisting of mixture of carboxylic acid with different hydrocarbon backbones, thus they have produced an emulsion that stabilized by Naphthenic acid based surfactants of Sodium Naphthenate at different concentration range of 0-10%, Still Heptane/toluene mixture was used to represent the model oil, the mixing process was carried out in water bath sonicator for ten seconds. Indeed Carlos and friend have investigated the effects of variation of internal phase volume fractions on the rheological properties of water-in-crude oil emulsions thus the water cut was varied from 5-80%.

Beside that they also investigated the effect of mixing speed (rpm), hence the range of rpm used was from 3000-11000 rpm, indeed the effect of temperature on rheological properties of the emulsion was also mentioned, hence their results had proved that temperature can tremendously effect the rheology of the emulsion (Carlos Gerardo et al., 2007,2008). Rosli Daike and coworkers have investigated the effect of commercial emulsifiers in stabilizing w/o emulsions, thus they have reported the effect of Sodim dodecyl sulphate (SDS) on stabilizing Liquid Natural Rubber (LNR) based o/w emulsions,but they focused their attentions on various concentration of emulsifiers ranged from 1-6%.

All emulsions were made at room temperature with continuous stirring for 30 minutes, however their results proved that Liquid Natural Rubber with lower molecular weight had produced emulsions with smaller droplet sizes and subsequently showed high viscosity than its high molecular weight counterpart, and thus LNR with lower molecular weight had produced more stable emulsions. In the same fashion Adam Macierzanka and co-workers have investigated the microstructure of the internal phase (dispersing phase) of the stabilized by Acylpropyleneglycols containing C_{16} /C_{18} fatty acids.

Tthe oil phase was mixture of Paraffin oil and paraffin wax, then emulsion was prepared in a glass thermostate emulsor, mechanical two blade agitator was used to supply the mechanical power at a mixing speed of 500 rpm, the phase composition of the emulsions was varied from 20-80% to 80-20%, (water-oil% respectively), however the types of emulsions were identified by measuring the electrical conductivity of the system while the emulsification is going on, that the two major types of emulsions are w/o and o/w the first is known to be less conductive since the continuous medium is oil and the resolution of water from a stable emulsion normally causes an abrupt change in the conductivity.

Indeed Lei Zhang and others have studied the correlation between the Hydrophilic-Lipophilic Balance (HLB) and the emulsion properties by means of droplet analysis thus they used surfactant with various HLB numbers to prepare their experimental water-in-oil emulsions that had been prepared in a beaker at fixed mixing speed of 500 rpm for a fixed duration of 15 minutes using two blade stirrer, in accordance with the emulsification rule of thumb they have dissolved the hydrophilic emulsifiers in the brine (aqueous phase) while the hydrophobic was dissolved in the oil phase then the two were mixed note that water was added in drop-wise in the continuous phase while the mixing process is going on, Span 80 and Tween 80 were chosen to be the major stabilizers for their study then various other fractions with different HLB ranging from 4.5-15 were produced by blending these two in different ratios then various samples of emulsions were prepared from these new fractions as well as the original emulsifiers and their droplet sizes were analyzed using the laser diffraction method with Malvern Masterizer, and the output data were analyzed and the droplet sizes ranged from 0.1 – 22 micron-meter, however their results revealed that different emulsion samples require different HLB numbers (Lei Zhang et al., 2008).

Oppositely Svetlan and friends have reported a comprehensive investigation on emulsion Rheology but focused their attentions mainly on the effect of the individual components on emulsion rheology of dilute emulsions of oil base and polymer blends (Svetlan R. Derkash et al., 2009). Also Minguan Li and co-workers studied the stability of model emulsions that was stabilized by the indigenous incompatible components of the crude oil, thus the stability was investigated by means of various apparatus such as IR, UV, and GC-MS hence the interfacial active components (Surfactants) were extracted from two different crude oils that originated from Saudi Arabia and Shengli (China).

In order to extract the interfacial active components from the crude oils, the oil to solvent ratios of 1:30 was used this extraction process was carried out by first mixing the crude with the solvent as mentioned earlier in a ratio of 1:30, then left to settle for 24 hours after that the precipitated asphaltene were dried and weighted then the filtrate (the other part of the crude oil that is dissolved in the Hexane) was poured in a silica column the percolate the remaining SARA fractions by their respective dissolving solvents, however their study proved that the stability of water-in-crude oil emulsions depends on a combination of several factors such as molecular size of the interfacial active components, aromaticity or aromatic condensation of the crude oil itself, and carbonyl group concentrations (Minguan Li et al., 2001).

Marco A. farah also odserved the dependence of water-in-crude oil emulsions on the other physic-chemical properties of the system such as dispersed phase (water) volume fractions, temperature along with some other several minor effects such as average droplets size, shear rate, droplets sizes distributions, viscosity and density of the of the oil, however they have used six different types of crude oil, the water content in their experimental emulsions was varied as 10, 20, 30,40, and 60%, but mixing speed was fixed at 10000 rpm for a fixed mixing duration of three minutes then stability pattern was verified as the amount water resolved from the stable emulsion within settling duration of four hours, and that is very normal in emulsion field just to make sure the sample is stable enough at least within the duration of the experiment.

In emulsion field every new emulsion sample of what ever application has to undergo some stability test before proceeding to its ultimate application, therefore; from their comprehensive investigation and observations they have drawn some let say general behavior about crude oil emulsions some of which shall be highlighted in the subsequent paragraphs, firstly from the observation they revealed that water-in –crude oil emulsions of high API (38) crude oils (some time referred to as either suit or light crude oils), it was very difficult to produce stable emulsions especially at high water volume fractions, also increasing the water volume fraction in emulsion would increase the temperature at which emulsion shows Newtonian behavior, moreover below wax appearance temperature (WAT), emulsions present rheological behavior of a bingham plastic in certain shear range, indeed variation of kinematic viscosity of the emulsion with temperature was observed to correspond with the ASTM equation (Marco A. Farah et al., 2005).

A. Sanfeld and others investigated the interaction between the non-deformed charged spherical droplets in concentrated water-in-oil emulsions; indeed they also investigated the repulsive interaction energy between droplets of dense w/o emulsions and their study revealed that the thickness of the repulsive electrical double layer in inversely proportional to the internal phase (water) Volume fractions (A. San feld et al., 2005).

Indeed Kristofer Paso and coworkers have observed the stability as well as flow properties of two Brazilian crude oils, how ever their emulsions were composed of 30, 50, and 70% water volume fractions, while the mixing process was carried out via Ultra- turax homogenizer at 24000 rpm for 2 minutes, the emulsification temperature also were varied as 4, 25 and 60 ^{0}C and eventually the emulsion stability was carried out via the famous process of bottle test, thus their concluded that at low water volume fraction emulsion can resists coalescence in a better manner than its high water cut counter part, another observation was that the waxy crude oil was able to form stable emulsion with water cut as high as 70%, while the heavy oil forms stable emulsions with water cut as high as 50%, this superior stability of the waxy crude oil might be attributed to the greater abundance of Asphaltene and lesser abundance of resins (Kristofer Paso et al., 2009).

In another report, Christophe Dicharry and friend have investigated the viscoelastic character of the interfacial film at the water-oil interface by means of the oscillating drop tensiometer method; hence they have proved that from the emulsions' interfacial parameters such as interfacial tension and elasticity modulus, one can predict the emulsion stability also emulsion stability was found to increase proportionally with increasing the interfacial gel strength and glass transition temperature of the gel (Christophe Dicharry et al., 2006).

Einar Eng Johnsen and his colleagues have had proposed a method for measuring the viscosity of emulsions under pressurized conditions via an apparatus that consists of rotating wheel that it would make the fluid inside to move to the opposite direction hence the torque acting on the wheel shaft is measured and transformed via a calibration model to a viscosity of the fluid, they also found that the variation of the viscosity increases with increasing the water cut (Einar Eng Johnsen et al., 2003).

2.2 Demulsification and demulsification techniques

Demulsification is the process of breaking the emulsion into it individual components mainly water and oil, and its one of the very major process in petroleum industries where emulsion happens often either naturally or deliberately, in another words Demulsification is considered as one of the most problematic and famous processes inpetro- chemical, metallurgical, beverage and food industries, wherein a massive quantity of oil contaminated aqueous waste, of water-in-oil (W/O) and oil-in-water (O/W) type emulsions, are continuously occurred. In petrochemical industries and petroleum refineries the separation of water completely from the crude oil is required before oil refining, currently chemical additives called emulsion breakers are massively used to break the water-in-oil emulsions.

Technically speaking; the resistance of a w/o emulsions to coalescence and their response to the demulsification techniques such as thermal, mechanical, electrical or chemicals depend on the Physico-chemical structure of the oil from which they are formed and emulsification conditions and history . This means that the effort and Strategies for optimizing the w/o emulsion demulsification may vary for various oil types (Tove Storm-Kristiansen et al., 1995).

Thus far, various methods for breaking emulsions were introduced: chemical demulsification centrifugal separation, electric field demulsification, freeze/thaw demulsification and so forth (Masato Kukizaki, Masahiro Goto 2008, (Delphine Daniel-David et al., 2005).

Currently plenty of methods and ways are available in treating and breaking water-in-crude oil emulsions the most common of which is chemical demulsification whereby a massive amount of chemicals are used to separate the water from the crude oils but there are some disadvantage of using these chemicals since they are expensive, toxic and environmental unfriendly, there any other alternative and sustainable demulsification methods are still in demends.

2.2.1 Chemical Demulsification

Chemical demulsification is one of very crucial techniques of resolving water-in-oil emulsions and it’s massively applied in the petrleume refineries wherein chemicals demulsifiers or emulsion breakers (surfactants) are injected to the crude oil emulsions. Basically massive amount of surfactants can be created by just manipulating the existing surfactants one way is by changing the acceptor, composition, quantities, and sequence of hydrophobic and hydrophilic groups in the long polymeric chains (Jiangying Wu et al 2004).

The very basic fundamental of chemical demulsification mechanism of what so ever type is that the demulsifiers gradually replace the emulsifiers within the water-oil interfacial film, and that would eventually cause tremendous changes to the interfacial viscosity and elasticity (Wanli Kang et al., 2006).

A. A. Hafiz and friends had synthesized some novel demulsifiers for treating water-in-crude oil emulsions their demulsifiers were a cationic polymer of of diethanol amine easter types that were produced by condensation and polymerization of the diethanolamine to diethanol amine polymer, thus the reaction taken place in a three naked flask at temperature range of 140-160 °C using different types of catalyst, however their demulsifiers were found to be effective in treating emulsion of form refining wastewater, hence the efficiency of the demulsifiers was checked by turbidity measurement (A. A. Hafiz et al., 2004).

Alejandro and friends have investigated have changed the structure of some commercially available demulsifiers (Alkylphenol polyalkoxylated resin and polyurethanes). the efficiency of the newly formulated products were assessed by several techniques such as: bottle test, rheometry, equilibrium interfacial tension, and transient changes in drop sizes distribution that was analyzed using Nuclear Magnetic Resonance, their emulsions were prepared by simply dispersing the brine in the oil without emulsifiers which means the asphaltene and resins originally existing in the crude oil did the job of the emulsifiers, indeed their results showed that the best and the highest separation were observed when emulsions were injected with resin having intermediate polyoxyethylene and polyoxypropylene moieties (Alejandro A. Pena et al.,).

Jiangying Wu and others have investigated the property and performance of 20 blocked copolymer from four different surfactant families, their emulsion were made by first diluting bitumen in 5% of toluene and centrifuged for five minutes to remove suspended indigenous small particles, then this mixture was mixed further with water, the mixing process was carried out using polytron homogenizer at 20 000 rpm for mixing duration of three minutes, the emulsion was observed to be stable without water resolution for three consecutive weeks.

Then the stable emulsion was undergone the demulsification test by using those aforementioned demulsifiers, hence the demulsification experiment was performed at 60 °C by gravitational settling methods, in another word the freshly prepared emulsion was placed in a measuring cylinder then a designated quantity of surfactant were injected the mixture (emulsion + demulsifiers) was shacked for one minute then left to settle and the amount of water separated was recorded as separation efficiency, they mentioned that while recording the separation efficiency the interface between the emulsion phase and the separated water phase was not very clear (means difficult to read), while the interface between the oil phase at the top part of the emulsion and the emulsion phase in the middle was clearly visible, indeed after one hour of settling; 1 ml of sample was taken from 3 cm depth below, the surface of the top layer and its water contain was determined and found to be in the range of (1-2%), their study concluded that the sequential block copolymer with more than 40% ethyleneoxide percentage was more effective than the others (Jiangying Wu et al., 2004).

Wanli Kang and coworkers have studied the effect of several demulsifiers namely Phenol-formaldehyde resin polyoxyethylene, polyoxypropylene and polyoxyethylene polyoxypropylene polymers, Their model emulsion was prepared by mixing purified kerosene and dewatered crude oil in a ratio of 7:3, and then water was added drop wise, the demulsification process was carried out at 45 °C.

However their results had revealed several facts as follow: from film thinning experiment it was found that the oil film between the droplets was stable at the beginning then started thinning and eventually collapsed upruptly without demulsifiers addition then when demulsifiers were added the oil film was observed to shrink gradually with demulsifiers till it was bracket. Indeed results also showed that the strength and the life time of the interfacial film was decreased when demulsifiers were added hence the curve of the interfacial elasticity was found to decrease with increasing the demulsifiers' concentration but came to a plateau of constant values beyond the critical concentration of demulsifiers (Wanli Kang et al., 2005).

Masatto and friend have used a membrane device made from material called Shirasu-porous-glass to break water-in-crude oil emulsion; generally shirasu is a type of ash that is very rich in metal oxide mainly Silicone dioxide, however their results showed that Shirasu-porous-glass membrane could efficiently break water-in-oil emulsions with droplet sizes bigger than the average membrane pore diameter (Masato Kukizaki and Mashiro Goto 2008).

Delphine and co-workers have studied the effectiveness of non-toxic silicone based demulsifiers of polysiloxane copolymers on splitting water-in-crude oil emulsions, thus for sake of experiment w/o emulsion was prepared at room temperature using polytrone homogenizer, also the total water volume fraction of the water in the emulsion was fixed at 30% (v/v), then the concentration of the demulsifiers used was 2% (w/w) dissolved in Xylene/ methanol solution (75/25 (w/w)), and their conclusion revealed that the polyoxyethylene-silicone triblock copolymers are insoluble in the water and therefore the driving force for the demulsification process is originally from the interaction between the native surface active molecules (mainly asphaltene and resin), the copolymer containing hydrophilic polyethylene oxide and hydrophobic silicone moitities (Delphine Daniel-David et al., 2005).

Similar experimental work also was reported by dalmazone and friends who had investigated the efficiency of various formulations of these aforementioned non-toxic silicone based surfactants, consisted of polydimethyle siloxane chain of various MW and Unit number, the efficiency of the demulsifiers was investigated by visual observation and measurement of water separation from emulsion as well as dynamic interfacial tension measurement, Hence they have tested silicone based formulation on two types of crude oils, from North Sea and French oil field respectively, emulsion was produced at room temperature using polytron Homogenizer to provide the mixing energy, indeed the content in the emulsion was varied at (15 and 30%), while for the demulsification process, 2% of the of the demulsifir was disoloved in xylene/methanol mixture (75/25), however their results revealed that the poly siloxane demulsifirs were very efficient in breaking water-in-crude oil emulsions in comparison with some commercial existing classical demulsifiers, furthermore; some blend of silicone-silicone and silicone-organic was selected for their sustainability and versatility reason, yet the siloxane demulsifiers are claimed non lucrative to be commercialized for economic and cost reasiom thought the current increase in ecological constraints may favor them to be used in the future or to be integrated in the demulsifiers' formulation (C. Dalmazone et al., 2005).

Svetlana and co-workers have investigated the effects of modified Chitosan derivatives in resolving o/w type emulsions, the study focused on the hydrophobically modified (HM) Chitosan derivatives relative the commercial cationic polyacrylamide flocculant and Unmodified (UM) Chitosan with various molecular weight, their experimental emulsions were made in laboratory, Sodium Dodecyl sulphate (SDDS) was selected as emulsifiers, and ultrasonic was used to provide the mixing energy for an emulsification duration of 10 minutes. However their results shoed that hydrophobically modified (HM) Chitosan derivatives with various molecular weights had shown to promot great separation compared to the others (Svetlana Bratskaya et al, 2006).

Also Abolfazl and colleagues have used the microfiltration membrane technology in separating the emulsion hence they have tested the efficiency of the hydrophobic PTFE membrane having pore sizes of 0.45 micron meter in separating the w/o emulsions, the water-in-oil emulsion was prepared in laboratory using span 80 (oil soluble surfactant) as emulsifying agent, the well known agent in oil technique was used to prepare the emulsion in another word agent in oil means the Span 80 was first dissolved in the crude oil then water was added gradually as drops, while agitation is going on, the water addition was 25 ml each minute, the mixing was carried out using pitched curved blade blender having 6 fins, however their result revealed that the permeate flux from the membrane was found to be rich in emulsifiers and poor in water, moreover; the permeate flux was found to decrease with increasing pressure and the importance of the temperature also was obvious (Abolfazl Ezzati et al., 2005).

Ing Harald Auflem and others have studied the effect of pressure on the w/o emulsion separation of North Sea crude oil, here they have prepared their emulsion by first mixing the emulsifiers (Silverson LURT emulsifiers) with the continuous phase (North Sea crude oil) then the aqueous phase was added gradually, a mixing speed of 2000 rpm was introduced to the system for a duration of one minute (emulsification time). Then the stable emulsion produced earlier was introduced to a high pressure demulsification rig, from which result showed that the emulsion stability was to some extent related to the demulsification pressure, this was explained by the fact that when the rig pressure was reduced beyond the bubble point pressure the low molecular weight portion of the crude oil could evaporate the these light would as a gas bubbles from within the sample to the top part of the system then to the surrounding just because of the difference in the density and would put the heavy components in a floatation state, this floatation effects would let the emulsifiers residing at the water-oil interface to dissolve in the gas phase (the bubbles) and that would eventually render the droplets free from their encapsulating emulsifiers' matrix, thus every groups of neighboring droplets would merge together to be separated into two phases (water at he bottom and oil at the top), another important finding of their investigation is that; by diluting the emulsion with toluene, the stability was also decreased and that is because dilution also decreases the viscosity as well as the density of the emulsion and also cause asphaltene aggregation (Ing Harald Auflem et al., 2002).

Zhiaing and friends have investigated the effects of Poly (ethylene oxide ((PEO), Poly (propylene oxide (PPO)) with variation in molecular weight, thus the PPO/PEO ratios were varied through the anion polymerization process and then the effectiveness of these modified copolymers on the demulsification of the water-in-crude oil emulsions were investigated, their experimental emulsion was made in laboratory by mixing an aqueous phase with petroleum oil taken from Shengli oil field in China, the mixing process was executed by a HT-2 Homogenizer, the water content of the emulsion was 50-50% water-in-oil emulsion, the mixing speed was fixed at 1200 rpm for an emulsification duration of 5 minutes, however the demulsification process was carried out at 50 ^{0}C, and the concentration of the demulsifiers used was fixed at 100 mg/L, the water resolution was recorded as separation efficiency for a settling period of 3 hrs, and their study had concluded that the demulsification process can be enhanced with the reduction of the PEO fraction in the surfactant formulation (Zhiqing Zhang et al.,).

Also Nael Zaki and coworkers have used the carbone dioxide to break the w/o emulsions of various actual as well as model emulsions, and that is because the dense CO_2 was assumed to fluctuate, flocculate and precipitate the asphaltene and that would reduce the strength of the interfacial film by causing the film thinning and film rupture and eventually droplets collision and phase separation, the emulsion sample used in this study was prepared by mixing via Ultra-high speed Virtishear cyclone IQ Homogenizer with emulsification (Mixing) speed of 15000 rpm, for an emulsification time of 2 minutes, then the emulsion stability was assessed by visual opservation of water separation from the emulsion for a duration of 24 hour, then only the stable emulsions were chosen for demulsification via the aforementioned CO_2 , and from their work it was concluded that CO_2 can be used successfully to treat water-in-crude emulsions of different characteristics and compositions, and the mechanism with which CO_2 break the emulsions was observed to involve the precipitation of surface active component Also Nael Zaki et al., 2003.

Abdurahman and colleagues had made a comprehensive study on water-in-crude oil stability as well as demulsification from various angles (parameters) including demulsifiers concentration that was varied from 0-5.5%, the mixing speed which was varied between 800-1600 rpm, water volume fraction was also varied from 10-80%, temperature also was indeed varied, the crude oils used in their study were originated from Iran and Malaysia, the sample of their experimental emulsion were prepared by the agent in oil technique, in which the crude oil is normally mixed with the emulsifiers first then water would be added gradually in drop wise fashion as the mixing process is going on, the mixing energy was provided by three blade propeller, and emulsion was prepared at ambient temperature of 28-30 °C for a mixing duration of 10 minutes, and their results shoed that the Iranian crude oil was found to produce more stable emulsion than the Malaysian Miri light crude oil (Abdurahman H. Nour et al., 2006).

In another work the same authors have studied the effect of the different types of the commercially available demulsifiers splitting the w/o emulsions, thus they have examined the effects of four different groups of demulsifiers namely; Amine groups, Polyhydric alcohol groups, Sulphonate groups, and polymeric groups, the methods of emulsion formulation, formation and characterization was the same as described by their previous paper, beside that the effects of the alcohol in the performance of demulsifiers also investigated (Abdurahman H. Nour et al., 2007).

Similarly they also reported in another paper, the effect of several demulsifiers on the separating water from crude oil emulsions, thus they have again compared the affectivity of different demulsifiers such as Amine, polymeric alcohole, Acid and polymeric demulsifiers, and their results shoed that amine group demulsifiers were more effective in breaking the emulsion then followed by Acid then polymeric demulsifiers, another finding was that among the most effective amine groups demulsifiers; the diacylamine demulsifier was the best and the most effective of them Abdurahman H. Nour et al., 2007).

2.2.2 Electrical demulsification

Electrical demulsification in the process of breaking of either water-in-oil or oil-in-water emulsions by the mean of electrodes, hence DC voltage would be introduced to the system that electric field voltage in generated by the means of two electrodes placed in opposed direction to each other and between which the emulsion is placed, hence as the system is conductive, it will break the energy barrier , and water molecules shall immediately be hydrolyzed into hydrogen and oxygen gases molecules.

The occurrence of this hydrolysis reaction process is normally indicated through by hydrogen bubbles that generate from the Positive electrode (cathode) and oxygen bubbles that evolve from the negatively charged electrode (anode). But, when the anode materials are made of metals with less oxidation energy than the system, these materials would dissolve in the system to produce metal ions instead of evolving oxygen bubbles. Then these metal ions would react with hydroxyl ions that produced during hydrogen generation, to give metal hydroxides.

An electrochemical reactor is a reactor shaped holding tank with two sets of metal electrodes (anodes and cathodes). These two electrodes are normally placed a certain specific distance apart one another and both of which should be merged in the system under treatment for oil contamination. The cathodes and anodes are mounted on the negative and positive outlets of a dc power supply of the reactor, respectively. Hence During the operation (emulsion treatment), the decaying metal ions are hydrolysis; for instanceinto Fe (II) (ferrous) andFe(III) ions in the case of Iron metal cathodes (Chen-Lu Yang., 2007).

Moreover; for safety reason the electrodes are normally insulated from the emulsion to prevent short circuit (I. G harpur et al., 1997), Beside the aforementioned basic principle of electrostatic demulsification, there a lot of parameters affecting the performance and efficiency of the process.

I. G harpur and co-workers have studied the ffect of 50 Hz sonosoidal electric field to treat and remove water from w/o emulsion, by using a horizontal rectangular duct as a system container (electrostatic coalescer), thus the effectiveness of the device consisted of seven electrode modules each of which was 50 Cm in length generating an electric field of 25-60 KV/cm, and their results showed that the application of the electric can cause a significant growth in drop sizes and also an increase in temperature that can induce the droplets to easily aggregate and merge (I. G harpur et al., 1997).

Woo-in Jang and friends have also investigated the electrical demulsification techniques to remove water from o/w emulsion, their intention focused on several parameters including; types of the electrode materials, polarization of the reactor, potential electrode size, temperature oil concentration, mixing rpm, pH, separation efficiency and electric power consumption.

The oil sample used in their study was taken from waste of metal cutting oil from Korea Houghton Corporation; hence the oil consists of 80% mineral oil and 20% surfactants plus some other chemicals such as anti foaming, bactericide, and anti corrosion, to prepare the experimental emulsion using the aforementioned composition; a DC motor mixture was used to prepare the emulsion, the electrostatic coalescence device was a reactor to which the o/w emulsion was injected then certain amount of electrical power was introduced to the reactor, sample of the treated emulsion was taken from the reactor and analyzed after a processing time of the 30 minutes, their results concluded that aluminum reactor was performed better and gave high separation efficiency and low energy consumption than its iron counterpart, and the best removal efficiency was observed when the reactor was a cathode indeed removal rate and energy consumption increased with increasing the applied potential, and therefore the separation percentage obtained from the aluminum reactor within 90 minute exposure time and electrical potential of 60 V was 94.05%, but it was reduced to 85.50 when the decreased to 30 V, also a wider electrode gave higher water removal and less energy consumption compared to narrower electrode, beside that the best operating temperature was found to be 50 °C , and variation of the oil volume fraction was found to have no effects on the demulsification process, Furthermore; agitating the reactor was found to reduce the separation rate but low pH was to be more effective than high pH.

When the treated sample was analyzed it was observed that there is a gradual increase in the particle sizes as the process was going on, hence their general conclusion had conformed the ability of the electrocoalescence process to treat the industrial oil-in-water emulsion (Woo-in Jang et al., 2000). Gary W. Sams and friend have investigated some parameters affecting the electrostatic coalescence and demulsification of the emulsion that including all the upstream production parameters and their results revealed that the designer should consider the production history of the well prior to selecting the suitable electrostatic equipment, therefore more vigorous and powerful electrostatic techniques are needed to treat and resolve the tight emulsions (Gary W. Sams and Mason Zaouk 2000).

Simone less and others have a device named Aibel vessel electrostatic coalesce to break petroleum oil emulsion, and the separation efficiency of the devise was evaluated in terms of percentage water resolution and droplets sizes distribution of the emulsion before and after the treatment, however their results showed that this system can effectively reduce the water content in the emulsion and also the addition of chemical demulsifiers was found to greatly affect the destabilization process (Simone Less et al., 2008).

Tsunki Ichikawa and others have applied a low electric field to break oil-in-water emulsion, thus their experimental emulsion was prepared experimentally by mixing the distinct phase in a separating funnel and mixed by means of simple hand shaking of around 100 times, the volume fractions of the two phases was also varied, the electrostatic demulsifiation device was consisted of glass container within which two stainless steel plates were fixed in opposite position (one to another) as electrodes then the emulsion sample was placed in the device and the external electric field is applied, however their results revealed that higher concentration of the electric had given high separation rate but increasing the amount of ionic surfactants does not increase, the separation efficiency, another important observation is that, though the device was very good in breaking oil-in-water emulsions; yet it could not break the w/o emulsion even at elevated electric field having frequency as high as 10 KHz, but one thing for sure is that the applied electric field could cause the rearrangement of the charges at the oil-water interfacial potential that is commonly known as Zeta potential and this would reduces the electrostatic barrier that hinder the droplets from coalloiding and this would eventually leads to the phase separationor emulsion breaking (Tsunki Ichikawa et al., 2004).

Harld Fordedal and co-worker have studied the percolation behavior of water-in-oil emulsions under the influence of the electrical field, the percolation here referred to the abrupt increase in dielectric constant of the sample when its volume fraction attains a maximum values at constant temperature, thus they have prepared two experimental emulsions for this reason one of which is a model oil that is stabilized by the naturally occurring surfactant (Asphaltene and resin) and the other is a model emulsion that is stabilized by the commercially available surfactants.

Their results proved that the dielectric constant of the emulsion was found to increase with the increase of strength of the electric field; this was observed with the water-in-oil emulsion stabilized with the indigenous interfacial active surfactants while the reverse effect was observed with the emulsion stabilized by the commercial surfactant, and from that they could conclude that the dielectric properties of the commercial surfactants are by far different than that of the indigenous surfactant (Asphaltene and resins)(Harld Fordedal et al., 1996).

Junji and colleagues have applied the electrostatic techniques to break water-in-oil emulsion hence they used some kind of metal oxide chemicals that are assumed to induce the increase in the coalescence rate of the crude oil droplet under the influence of the electric field, thus the performance of the device was assessed via video microscop from which a digital picture was captured and transferred to a computer for further analysis, their study revealed that the shapes of the droplets were observed to change from spherical shapes to hemispheres when adsorbed at the electrode surface also the metal ions used were observed to be oxidized indeed the ion concentrations of the metal ions was observed to increase at the oil-water interface, also the image analysis of the coalescence of the neighboring droplets depends on the electrical potential applied (Junji et al., 2003).

P. J. Bailes and friends have investigated the process of bubbling the emulsion with air combined with the electrostatic demulsification as a novel process for emulsion breaking, however their results concluded that the separation efficiency was enhanced by this bubbling process indeed the separation rate also was observed to increase with increasing the air flow rate (P. J. Bailesa, P. K. Kuipa 2001). Tsuneki Ichikawa and colleagues have used a low electrical field to destabilize oil-in-water emulsion hence the low electric field was assumed the reduce the thickness and weaken the strength of the repulsive double layer due to movement of the ions, thus a mathematical model of electrostatic bridge that prevent the aggregation and coalescence of the oil droplets indeed the mathematical expression of the this energy was found based on the external electric field and this potential energy between the charged droplets is just a sum of electrical double layer potential and Van der Waal's potential (Tsuneki Ichikawa et al., 2007).

Seiji Kanazawa and friends have developed an apparatus for electrostatic coalescence using the electrostatic atomization techniques; they have tested the efficiency of their system on two types of emulsion one of which was composed of water droplets dispersed in silicone oil, and the second was a stable emulsion that was prepared without using emulsifiers, the test was excuted by monitoring the movement of the positively charged oil droplets as a response to the applied electric field, thus they have first observed the marked drops in the transparent oil, then after the DC electric field was applied, the individual droplets were observed to aggregate and their traveling distance from the electrode and the traveling velocity also increasesed (Seiji Kanazawa et al., 2008).

Others have investigated the electrodynamic mechanism of the electrostatic demulsification process via simulating the effect of the field strength on an individual water droplet (Gong Haifeng et al., 2008).

A. Yakhkeshi and others have used a uniform electric field to treat oil-in-water emulsion; the hypothesis behind their investigation was that the electric current could induce the scattered find droplets within the emulsion to aggregate and come close to one another and produce bigger sized droplets through the induction of negative charges, however their emulsion was consisted from benzene as the oil phase and water, the mixing was performed by a magnetic stirrer for a duration of 15 minutes (emulsification time).

SDDS was used as emulsifying agent in a dosage range of 2-4 ppm, the dispersed volume fraction was 4% of total emulsion volume, thus their result again the usefulness of the electrostatic demulsification process on breaking the oil-in-water emulsion, and the parameters of concern were reported to be the type of the insulator at the surface of the electrode, types of the oil, oil volume fraction in the emulsion, temperature and the electrical voltage, but the voltage used in their study was 500 V, which gave separation efficiency of 80% with processing time of 60 second and 92% with processing time of 30 second (A. Yakhkeshi et al., 2010).

Mir and others have again used the non-uniform electrostatic techniques to treat an emulsion that originated from waste water and consisted of Xelene, water and metals, the have prepared an experimental emulsion that is similar to the industrial wastewater by mixing up the individual aforementioned components using the Hielscher up 400s Ultrasonic mixture, the oil phase volume fraction in the emulsion was 2% while the surfactant concentration was 1% SDDS (Sodium dodecyl sulphate), their electrostatic apparatus consisted of three compartments that are made of glass material and the two electrodes are mounted in the central chamber in paralleled position opposite to one another, three types of the electrode metals namely Iron, Tungsten and copper were tested and the best one them was selected, however their results proved that Copper electrode was the best and performed better than the others, and the highest separation was observed at electric power of 5400 V and temperature of 45 °C, Indeed for non-uniform electric field voltage, temperature, time, and types of the electrode was the most crucial parameters (Mir Masoud Hosseini et al., 2012).

Akuma Oji and friend have applied the High Voltage Dielectric Current (HVDC) in a voltage range of 4- 16 KV to break oil field emulsion, they have used a total operation time range of 10-40 minutes. The distance separating the two electrodes ranged from 60mm-244 mm, the emulsion was taken as ready made from Obagi oil field and processed directed as received without further treatment, yet it was left to settle and separate out the free water, the electrode plate was made up of Zinc, and best operation condition was observed to be the two plates spacing distance of 122 mm, or 244 mm at fixed voltage of 8 KV (Akuma Oji et al., 2012).

Byong and colleagues have used a high AC field dehydrator to treat water-in-oil emulsion the electrical voltage was ranged between 2- 20 KV, and the frequency was ranged between 60 -2000 Hz was applied on the emulsion sample that was placed between the two electrode in the coalesce chamber, thus the most prominent operating parameters were the Voltage.

The amount of chemical demulsifiers, operating temperature, operating time and residence or contact time in terms of the feed flow rate, their experimental model emulsion w/o type and contain 20%(v/v) water, an electromagnetic stirrer (Heidolph RZR 205, Germany) at 1000 rpm was used, the emulsification time was fixed at 10 minutes and after investigation the droplets sizes were found to be in the range of 15-60 Micron meter.

The electrostatic hehydrator device was made of glass chamber and the electrode were insulated with glass material to prevent possible short circuiting, prior to the demulsification certain amount of chemical demulsifiers were added to the emulsion and mixed for 5 minutes and 1000 rpm then transferred into water bath to attain the desired temperature then transferred to the electrostatic coalescer , the flow rate was monitored to give a residence time of three minutes, their results showed that the separation efficiency increased with increasing the electric field, and also adding the demulsifiers was found the increase the separation efficiency to 80%, while the temperature and the residence time were not that crucial (Byoung-Yun Kim et al., 2007).

2.2.3 Thermal Demulsification of emulsions

Thermal treatment is referred to the use of temperature to break petroleum emulsions, thus normally hotplate is used in lab scales to provide the optimal temperature beside that some researchers had treated the emulsion by reducing their temperature up to beyond freezing point then rising the temperature gradually this is known as the freeze/thaw method, however in most case thermal treatment is applied jointly with chemical to improve the efficiency.

A group of researchers have reported the usefulness of the thermal demulsification techniques in breaking crude oil emulsions, fore instance Abduraman and friends have investigated the use of hotplate in breaking w/o emulsions in comparison to the microwave demulsification techniques, the test was carried out in an experimentally prepared emulsion sample from two types of pure crude oils that were donated by PETRONAS (a Malayisan based oil and gas company), then experimental emulsion was prepared in 500 ml beaker with different volume fraction of oil and water phases, the mixing energy was supplied by standard three blade propeller at mixing speed of 1600 rpm for an emulsification time of 5 minutes at ambient temperature of 28 ^{0}C the volume fraction of the water in the emulsion was varied as 30, 40 and 50% (V/V), then emulsion was tested for stability and quality then the stable emulsion was treated to separate the water by the use of the techniques of microwave and hotplate, domestic microwave model: EMO 80855 was used, the processing time for microwave was varied as 30. 60, 90, 120,150, 180 and 210 seconds, the temperature profile of the emulsion sample was recorded via thermocouples inserted in the sample and connected to PC through PICO data logger.

The results of the microwave treatment were compared to that of hotplate treatment. Their results revealed that microwave have shown great separation efficiency over the conventional hotplate heating and that is because of the heating pattern since microwave heat materials volumetrically according to their dielectric properties thus its energy is generated within the molecules of the materials unlike the conventional hotplate in which heat is transferred from the surface of the hotplate to the bottom surface of the sample holder then to the surface of the sample then to the bulk of the sample till the top this make the conventional heating slow and non-uniform another thing is that microwaves are electromagnetic waves so they have the potential to neutralize the electromagnetic repulsive barrier (Zeeta potential) between the droplets this together with reduced viscosity as temperature increase would ease the droplets aggregation and coalescence (Abdurhaman et al.,2006).

Also Raman Morales Cherbrand and co-workers have tested the combination of three distinct techniques of Heating, Enzymatic and centrifugation to break emulsion that is originated from soybean oil extraction, the extraction process was carried out by dispersing the soybean powder at 200 rpm in 2L of aqueous water phase (there were water comes in contact with oil), the pH was increased to 8 by adding certain amount of sodium hydroxide, the stirring process had continued to 15 minutes, after which three distinct phase were separated by centrifugation. The water-oil mixture was separated to pure oil and water by certain steps; first of which the enzymetic treatment in which certain amount of the soybean cream was initially mixed with water to adjust its pH then 1% w/w of the enzyme was added then shaked at 15 rpm for 50 °C for three hours then the enzyme were deactivated by heating at 95 °C.

After that the sample was centrifuged to separate the oil, the thermal treatment was used in the second step in which that enzymetic treated sample was heated at 95 °C for 30 min then cooled in a chilled water bath and centrifuged, for the freeze thaw treatment the third step; a fresh set of enzyme-treated cream held in a freezer at -18 °C for 24 h then thawed at 30 °C for 3 h prior to centrifugation.

Tov and friend have studied the effect of heat and chemical demulsifiers on w/o emulsion resolution, their hypothesis was to observe whether the effect of these two techniques are more effective than either of them alone, their was an oil spill based w/o emulsion, but a model emulsion was prepared in laboratory with different types of crude oils to represent the natural oil spill emulsion, hence the stable w/o emulsion was prepared by mixing the crude oils with sea water of normal salinity at 10 °C by rotating flask method and their study had led to the following conclusions: w/o emulsions of paraffinic petroleum could break faster than that of the high asphaltene oil, heat treatment could break the emulsion slowly but after adding chemicals the separation rate had increased, indeed for viscous emulsion it had better to introduce the chemical demulsifiers at 10 °C while for highly viscous emulsion it had better to add the demulsifiers after heating the emulsion, moreover emulsion formed from the distillation residue could be broken with moderate heating while that with diesel oil were not broken even at high temperature, also as emulsion breaks down its viscosity reduces (Alun Lewis et al., 1995).

Chantal and friends have used the insitu emulsion burning techniques to treat the oil spill emulsions that are produced from oil spill, their objective was to find a way to minimize the oil spill pollution however they have investigated certain specific parameters that include the mechanism of the burning process, the techniques used for ignition, the environmental disturbance that burning could cause, the execution of the burning process on iced medium.

And their results had drawn so many ideas and findings fore instance they have identified the characteristics of the specific igniter that should be used to ignite the crude emulsion particularly the Helitourch was found to be one of the most effective ignition techniques for crude oil emulsion burning beside that the basic requirement for any igniter for this purpose must be composed of lightly fueled front part and heavily fueled back part, must provide quick sparking to start the ignition, must provide the heat required for the ignition, also anti-foaming additives are required to improve the flame spreading capability, the speed of the fuel pumping out of the nozzle should not be in stream, the burning efficiency by this method had reached up to 75%, and the burning residue consisted of heavily viscous and tar-like component with some minor raw emulsion(Chantal C. Gunet et al., 1995).

Bernard and colleagues have studied the possibility of stabilizing o/w emulsion using wax particles as emulsifiers and the effect of temperature on that wax particles' activities, their experimental emulsion was prepared by first dissolving the wax particles in squalane, the mixing process was performed by simple hand mixing, the type of the prepared emulsion was checked by drop test and conductivity measurement, then the stability test was performed by testing the amount of water or oil resolved from the emulsion within a fixed period of time, and their result were reported in the following conclusions: micro-wax particles could be used as emulsifiers for o/w emulsions, if the drops are generated at room temperature then increasing the temperature of the emulsion would increase the extend of coalescence and that is because at elevated temperature the wax particles at the interface would fuse and melt and by doing so; the so called interfacial barrier hindering the coalescence of the droplets would vanishes and droplets could easily come together and merge (means separation) and this barrier collapsing temperature is normally the same as the melting temperature of the pure wax particles alone, but if the emulsion were prepared at emulsification temperature that is close to wax melting temperature then it was observed to be stable even at elevated temperature (Bernard P. Binks et al., 2009).

Indeed Spencer E. Taylor and friends have studied the effect of temperature on breaking bitumen emulsions that is originated from Wolf-lake (Canada), the experimental emulsion was stabilized by ethoxylated nonylphenol surfactant, and their results that as the temperature of the system getting closer to the cloud point, emulsion could break jointly, indeed the bitumen-water interfacial tension also was found to decrease with increasing temperature and found to be very small at cloud point temperature, also they have mentioned the possibility of reusing the surfactants by separating the surfactant from the surfactant rich layer that was observed during the emulsion separation.

basically the general phenomena behind the effect of temperature on emulsion is that at low temperature below the cloud point the system was observed to poses micelles plus free surfactants that would stabilize the bitumen-water interface but at elevated temperature the ethoxylated groups could be dehydrated and consequently the hydrophilicity of the surfactants could be reduced that means their tendency to dissolve in the continuous water phase would reduce and eventually the emulsion stability would reduce and that would causes the phase separation, although at high temperature ethoxylate group have the tendency to dissolve in the oil phase but in their study they mentioned that the complex structure of the bitumen will hinder the ethoxylate group to dissolve in the bitumen (oil phae) so they would aggregate as separate phase letting the two phases to separate into pure bitumen and water (Spencer E. Taylor et al., 2011).

Guohua and Gaohong have studied the freeze/thaw method which involves the cooling of the sample to a very low temperature (below the freezing temperature -40 for exemple) then increase the temperature back gradually, to separate water from crude oil sludge produced from the pretreatment of the lubricant oil that content 38-77% water, however their emulsion was real emulsion taken from the plan and then small amount was placed in a centrifuge bottle and cooled to freezing temperature then thawed back to certain temperature then centrifuged for 5 min. at 400 rpm, then the volume of the water separated from the emulsion was read off through scales on the centrifuge tube (sample holder), their have drawn several conclusions as such the demulsification of the water-in-crude oil emulsion depends strongly on certain parameters including, the original water contents, freezing temperature.

Freezing period as well as thawing speed and temperature, also the optimal freezing temperature in their results was found to be around -40 ^{0}C for the oil sludge taken from the used oil indeed high initial water volume fraction and milder thawing would lead to increase in the volume of water separation after demulsification, beside that the optimal thawing conditions was found to be either Air at its ambient temperature or water bath at temperature below 20 ^{0}C, and the separated water was found to contain some organic contaminent, during the freeze/thawing process; the formation of the surfactant micelles also was observed theses micelles were greatly affected the quality of the separation (Guohua and Gaohong 2003).

Also Chang Lin and colleagues have used the freeze/thaw method to break water-in-oil emulsion that produced from emulsion liquid membrane; however their experimental emulsion produced using the agent in oil method wherein the surfactant (Span 80) was dissolved in the oil phase then the de-ionized was dispersed while the mixing was going on at a mixing speed of 1000 rpm to coursen the system first then the mixing speed was increased to 2000 and eventually to 6000 rpm for emulsification period of 20 minutes to get the submicron sized droplets emulsion, and from their results they have revealed tha the freeze/thaw method was very effective and easy to handle process to separate w/o emulsions, and the mechanism behind the freeze/thaw method follow the collision theory in which drops are moved close to each other gradually when the mechanical barrier capturing them is gradually removed, indeed the fundamental mechanism behind the freeze/thaw demulsification method is that during the transformation of the water phase from liquid to ice the volume expansion of the droplet could take place and that would case partial or full coalescence, and these coalesced small droplets could diffuse into the big droplets because of the interfacial area shrinking during the heating (thawing) process, also the most effective parameters in thawing process were initial the amount of the water content in the emulsion and the freezing with dry ice was found to be more effective than that with the refrigerator, but preferentially the optimal freezing temperature should be below the solidification temperature of the droplets to achieve a suitable and uniform crystallization (Chang Lin et al., 2009).

Xiaogang yang and co-workers have studied the stability pattern of asphalten stabilized emulsions and the effect of the Freeze/thawing on the demulsification process, the parameters of concern were the surface tension, Zeeta potential, the water droplets and the water separation from emulsion. Their experimental emulsion was prepared was prepared by choosing the dodecane as a model oil and deionized water as an aqueous phase, the indigenous surfactants (Asphaltene and resin) used in their study were extracted from crude oil via the n-alkane precipitation method, then the experimental emulsion which contain 30% water was prepared by mixing the dodecane with the deionised water and emulsifiers (Asphaltene and resins) the concentration of the Asphaltene was varied in the range of 3 to 9 g/l and that of Resin was varied in a range of 0.47 to 3.3 g/l, however; and system was mixed 300 time by simple hand shaking method, their results revealed that emulsion stability is a very strong function of Asphaltene and Resin concentration because their adsoption at the oil-water interface would produce a film that prevent coalescence, although their surface activities were observed to decay with increasing asphaltene concentration, also Zeeta potential of the asphaltene and resin stabilized emulsion was observed to be negative and increases with asphaltene and resin concentrations for demulsification by thawing process the separation was more easy with resin stabilized emulsions than their asphaltene stabilized counterparts. Also the air thawing was found to remove more water than the water thawing indeed the thawing with microwave heating was found to be very effective than thawing with air and water (Xiaogang yang et al.,2009).

2.2.4 Other demulsification methods

This section would consider mostly the mechanical methods that are in common use to treat the crude oil emulsion that include centrifugal, membrane and so on. A.U. Habn and colleagues have investigated the effects of ultracentrifugal demulsification on breaking w/o emulsions, the emulsions were made in laboratory by the use of several emulsifiers such as Gantrezan 119, Tween 80, and sponto 221 each with various concentration ranged between 0.05-0.01%, the oil volume fraction in the emulsion was fixed at 30%, the mixing energy was supplied by Waring Blender for a mixing period of 30s, and for the demulsification process the centrifuge efficiency was investigated bydirect measurement of the droplet sizes before and after the processing, and the centrifugal speed was varied.

Their esults showed that after centrifugation emulsion had generated cream on the surface and that is were the coalescence process is expected to occur (A.U. Habn et al., 1979).

Kashmiri L. Mital and friends have investigated the effect of ultracentrifugal method on demulsifying o/w emulsions with different concentrations of the emulsifying agent, hence their model emulsion was first stabilized by various types and concentration of emulsifiers namely Tween 20, and triton X-100, the oil to water volume fraction ratio was fixed at 50-50%, and the demulsificatiom process was carried out by centrifugation process via the high speed ultracentrifuge which was operated at the speed of 36460 rpm at ambient temperature of 25 ^{0}C for certain centrifugation time, however result showed that the rate of separation was found to be independents' concentration (Kashmiri L. Mital et al., 1972).

Beside that Abdurraman and colleagues have investigated the feasibility of using the high speed centrifuge in separating the coconut milk emulsion into pure water and coconut oil, the parameters of interest were the speed of the centrifuge (rpm), which was in the range of 6000 to 12000, and centrifugation time that was ranged between 30 to 105 min, and from their results among the four centrifugational speed (6000, 8000, 10000, and 12000) used only 12000 rpm had given the optimal separation efficiency and that was because of the general centrifugation theory which tells us that the suspended particles always move in the opposite direction of the centrifugal force, because of the density difference, the processing time was also segmented into 6 different parts of 30, 45, 60, 75, 90, and 105 minutes while temperature was fixed at 30 ^{0}C and there again the best separation efficiency was observed with the centrifugation time of 105 min (Abdurahman H. Nour et al., 2009).

Indeed N. M. Kocherginsky and friends have used the microfiltration membrane to break w/o emulsion, the fundamental theory behind that that was the oil droplets would fluctuate at the membrane pore, the factors of concern were; types of membrane, membrane pore size, the transmembrane pressure, membrane thickness and the initial water concentration, their liquid membrane emulsion was prepared by mixing kerosin and alkali aqueous solution and di-2-ethylhyxyl phosphoric acid then the mixture was agitated vigorously at 1000 rpm via mechanical mixture for an emulsification period of 1 h at ambient temperature thus their result revealed some interesting fact including the possibility of using the polymer membrane as a good choice to break w/o emulsion, though some parameters such as membrane material.

Pore sizes transmembrane pressure had very major effects on the separation process, also another important observation was that not all the membrane types are suitable for treating w/o emulsions, hence according to their results hydrophilic membrane is the only one that could break the w/o emulsions with pore sizes smaller than the droplet sizes indeed increasing the transmembrane pressure also was found to increase the separation efficiency, but membrane thickness was found to be not effective in the separation efficiency, hence the separation process is based on the interaction between the droplets and membrane not based on the sieving effects (N. M. Kocherginsky et al., 2003).

Nalin Nadarajah and colleagues have used some sorts of bacterial culture to break water-in-petroleum oil emulsions, thus they have collected the bacteria from crude oil contaminated soil, after the isolation; the bacteria is kept in cyclone fermenter on mineral salts, then various bacteria colonies were extracted and purified.

A model emulsion was prepared by first dissolving the emulsifiers in the aqueous phase then the model oil which was kerosene was added in drop-wise fashion while the agitation is going on, the mixture was a vortex mixture, the emulsification time was fixed at 3 min, for demulsification experiment I ml of the bacterial colonies was added in 9 g of model oil emulsion and mixed with the same vortex speed for 20 s and incubated at 50 °C under static condition, the demulsification efficiency was found by simply measuring the water separated from the bacterial culture treated emulsion and compared with that of the control sample, from their results they have observed that it was difficult to prepare a model emulsion of the crude oil that mimic the actual crude oil emulsionsbecause of the complexity found in the crude oil, the best separation efficiency for the biological demulsification was observed at 50 °C and that was expected since the elevated temperature reduces the viscosity of the oil and emulsion and increases the density difference between the two phases and weaken the interfacial barrier which lead automatically to droplets coalescence, the culture age was found to be not important in the demulsification and culture cultivated from crude oil medium had given high demulsification efficiency than culture cultivated from motor oil and diesel (Nalin Nadarajah et al., 2003).

Tereza Neuma and co-workers have applied have also applied the microemulsion system to break w/o emulsion of Brazilian crude oil , thus their microemulsion system was prepared in laboratory, the aqueous phase contained 5.2% HCL and oil phase was toluene and the emulsifiers was isopropyl alcohol, the demulsification experiment was carried out by direct contact method between microemulsion, and w/o emulsion in centrifuge tube for duration of 30 min with continuous mixing and fixed temperature of 70 °C, then the separation efficiency was calculated as the percentage of water separated with respect to the original amount of water used. From the result microemulsion was proven to be a suitable method to break w/o emulsions formed during the mining process of the Brazilian oil, and original water content of the system had a great effect on the process (Tereza Neuma et al., 2001). R. Del Colle and colleagues have used the alumina tubes as a filter material to split water-in-sunflower oil emulsions by using the tangential filtration process, they used a ceramic tube that was made of alumina, and hence the tube was first cantered at 1450 ^{0}C, and then impregnated by zirconic material after that the tube was calcinated and heat treated at temperature range of 600-900 °C, to discard the light organic materials, and convert the zirconium to zirconium oxide that was impregnated in the aluminia in the forms of nanoparticles aggregate then this new microporous membrane was tested in a microfiltration of aqueous system to assess its performance, the parameters investigated were the transmembrane pressure, input emulsion flow, and the results showed some interesting conclusions such as ; the ziconia impregnated model was found to be very effective and could operate at very high temperature of 900 °C (R. Del Colle et al., 2007).

Mohtada Sandrazadeh and colleagues have used the PTFE membrane to treat o/w emulsion that was originated from wastewater; the model emulsion was prepared experimentally by mixing gas oil and distilled water and components were mixed using a pitched curved blade blender with 6 fins for an emulsification duration of 10 min, their results showed that increasing temperature, pressure, as well as flow rate would affect the permeate flux, no fouling was observed and the water content of the permeate was to increase with increasing the temperature and pressure and decrease with increasing the flow rate (Mohtada Sandrazadeh et al., 2008).

Aileen Lozan and friends have used salts to induce the flocculation of oil-in-water emulsion that was stabilized by anionic emulsifiers of Sodium dodecyl sulfate (SDDS), their o/w nano emulsion was prepared experimentally by two distinct steps; one was the low energy emulsification method wherein no heat or vigorous mixing is required but rather requires only the mixing of oil, water, surfactants, alcohol and appropriate amount of salt and aqueous phase to make a bicontinuous emulsion system, and in the second step; that bicontinuous emulsion system was injected in large amount of water with slow mixing to produce nanoemulsion of fixed drop sizes which was further diluted in sodium dodecyl sulfate solution to get the desired oil-in-water emulsion (Aileen Lozan et al., 2012).

2.2.5 Microwave demulsification

Electromagnetic spectrum laying within 300MHz to 300GHz is known as microwave which known to have electric and magnetic properties, thus when they are projected to materials they obey the optical rules of Transmission Absorption and reflection depending upon the medium characteristics (Roger 1998), hence the applied field will induces a polarization effect to the medium.

The wave length vary from 1mm to 1m, in accordance with aforementioned frequency which is between 300MHz to 300GHz, beside heating and scientific research purposes some frequencies are reserved for specific purposes including these of cellular phone, radar and television satellite communication by Federal Communication commission (FCC), however the most frequently used frequency for Industrial, scientific and medical (ISM) purposes are 915 and 2450 MHz, (Thostenson and Chou., 1999) with 915 is used in this research.

Microwave is commonly preferred in material processing over its conventional counter part due to its volumetric heating; the mechanism of heat transfer in conventional heating is diffusion from the surface of the material to the bulk, while in microwave heating the temperature gradient in different location within the sample is almost invariant, another important phenomenon is that different material possess different heating pattern, and that due to the variation in material's microwave absorption capacity which in turn depends on dielectric loss that is depends on frequency (Thostenson and Chou., 1999).

I Equation of Heat transfer in Microwave

The general form of heat transfer equation consists of three principal forms which are conductive convective and irradiative form given bellow.

$$g_{MW} = \frac{hA}{V}(T_m - T_a) + \frac{\varepsilon A\sigma}{V}\begin{bmatrix}(T_m + 273.15)^4 \\ -(T_a + 273.15)^4\end{bmatrix} + \rho C_p\left(\frac{dT}{dt}\right) \tag{2.1}$$

Unless this is not the case in microwave heating in which heat is generated within the material and it’s transfer property is directly linked to the thermophysical properties of material as reported by curet and others, thus the detailed heat transfer mechanisms in microwaves will be explained in the following equation.

$$\rho c_p \frac{\partial T}{\partial t} = \mathrm{div.}(k\nabla T) + Q \tag{2.2}$$

Where: ρ and c_p are density and heat capacity of sample being heated, $\frac{\partial T}{\partial t}$ rate of temperature increase and Q is the internal energy acquired by the sample from the dissipated microwave power and could be calculated for Z directed electromagnetic wave by an equation relating power drop from surface to bottom which is:

$$Q_{(z)} = \frac{F_0}{d_p(z)} \exp\left(-\int_0^z \frac{dz}{d_p(z)}\right) \tag{2.3}$$

F_0: Microwave surface flux and d_p is the penetration depth which is strongly related to dielectric properties of the sample designated as the distance at which the microwave represents $\frac{1}{e}$ of the surface power flux and its mathematical expression is:

$$d_p = \frac{c_0}{2\pi f}\left[2\acute{\varepsilon}\left(\left(1+\left(\frac{\varepsilon''}{\acute{\varepsilon}}\right)^2\right)^{\frac{1}{2}} - 1\right)\right]^{-\frac{1}{2}} \tag{2.4}$$

While surface flux at the same conditions as Maxwell equations is calculated by the following relation,

$$F_0(x,0) = \frac{2P_{surf}}{ab}\sin^2\left(\frac{\pi x}{a}\right) \tag{2.5}$$

Where (a, b) are the dimensions of the wave guide

However, based on Maxwell equation’s perspective, the magnitude of microwave power absorbed by the dielectric samples can be estimated by the local electric field strength on the sample being treated as

$$\mathrm{Q_{abs}} = \omega .\, \mathrm{E}^2 .\, \varepsilon .\, \varepsilon'' \tag{2.6}$$

The electric field for plane wave propagation mode is solved by the following equation

$$\nabla \times (\mu_r^{-1}\, \nabla \mathrm{E}) - \left(\acute{\varepsilon}_r - j\frac{\sigma}{\omega}\, \varepsilon_0\right) k_0^2\, E = 0 \tag{2.7}$$

ω : Pulsation of microwave radiation (Rad/s)
E: electric field intensity (v/m)
ε : Complex permittivity
σ : electrical conductivity (s/m)
μ_r : relative electromagnetic permittivity of material (H/m)
k : thermal conductivity (w/m.K)

According to some previous researchers; in the above equation the radiative and convective terms are very minor and that is because sample container has very low dielectric constant therefore it does not generate much of heat and hence most of the waves are transmitted through the glass sample container to the emulsion. The density and heat capacity of emulsion are calculated from the following mixing rules:

$$\rho_m = \rho_w \phi + \rho_o (1-\phi) \tag{2.8}$$

$$C_{p,m} = C_{p,w} \phi + C_{p,o} (1-\phi) \tag{2.9}$$

II Microwave demulsification

Different materials have different heating capabilities by the incident microwave energy, hence for opaque materials the wave are totally reflected, while in transparent materials they are transverse, but in dielectric materials waves are absorbed and transformed to heat, however introducing some specific metal powder do non conducting solvent would render them microwave active and they can be heated **(**Camelia et al., 1998).

The treatment of crude emulsion is of major importance in the respective industries since, since most of the world crude oil produced in the forms of emulsion, water is normally a good microwave absorber because of it high dielectric properties, however in some rapports, at large samples the heat transfer in oil was faster than that in the water and that is imparted to the thickness of the oil, but this convention does not work with small sample hence for small sample, the heating rate of the water was faster (Barringer et al.,1994).

Emulsion was first treated via microwave by Wolf who was first started the concept of microwave demulsification since then more and more researches have been devoted to this field. The efficiency of microwave on emulsion was found to induce some effect on the treated emulsion such as, the increase in the temperature will may leads to reduction in viscosity, and this will increase the mobility of the water droplet that will in turn neutralizes the zeta potential of the dispersed droplet beside breaking the hydrogen bonding between the water and the surfactant molecules, beside that the electromagnetic wave is believed to increase the internal pressure of the water droplets leading to reduction of the interfacial film thickness (Montserrate et al., 2006).

Most of the aforementioned microwave affects depends on dielectric properties, emulsion composition, droplet size distribution, together with the operating conditions including temperature and frequency and dissolved salts fore sake of simplicity some factors are assumed constant such as negligible mass transfer, sample is assumed homogeneous and isotropic, initial temperature also homogeneous, but thermophsical and dielectric properties are temperature dependent.

As reported earlier dielectric heating is a strong function of pH, Viscosity, salt content, acid and water content (Montserrate et al., 2006). Thus it’s important to relate all of theses parameters to assess the microwave separation.With regard to separation efficiency which can be estimated by sediementation rate in the case of water-in-oil emulsion; the settling velocity of water droplets through oil is given calculated According to the force balance and Stoke’s law as

$$v_w = (\frac{\rho_w - \rho_o) g * D^2}{18\mu_o} \tag{2.10}$$

Where: D is the diameter of droplets. Similarly, if water is the continuous phase, the rising velocity of oil droplets through water is given by:

$$v_o = (\frac{\rho_w - \rho_o) g * D^2}{18\mu_w} \tag{2.11}$$

The viscosity of oil and water μ_o and μ_w are very sensitive to temperature, in this regards, as temperature increases, viscosity decreases much faster than the density difference $(\rho_w - \rho_o)$ does. Therefore, the heating either by microwave or conventional heating, increases the velocity, v_o or v_w and consequently makes the separation of emulsion faster.

The second phenomenon is molecular rotations, which may reduce or nutralizes zeta potential of emulsion Fang et al (1988). Zeta potential or a layer of electrical charges, suspend water droplets in oil in a water-in-oil emulsion, which prevents the movement and coalescence of water droplets. Since a water molecule is polar, it rotates at a high frequency under microwave irradiation. The molecular rotation raises the temperature through friction, and also neutralizes the zeta potential by disturbing the orderly arrangement of electrical charges surrounding water droplets. Without the support of zeta potential, water droplets are moved downward by gravitational force.

the advantage of applying microwave energy over its counter part is it’s ability to heat sample more uniformly than the conventional heating although in some cases local overheating may occurs causing Hotspot or thermal runaway within the sample, keeping in mind that crude oil consists of vast numbers of component that differ in their conductivity and polarity and ultimately in their absorptive patterns with asphaltene being the dominant and the major charge carrying component since they are the most polar and significant number of heteroatoms than the others(Helen et al., 2009) (Sujoy Kumar et al., 2008).

In another report they also investigated the effects of container types and water to oil ratios on emulsion stability; the types of containers used in their experiment were non reflective and partially reflective ceramic-metal complex plates with emulsion being placed in the opened exposed part, then from the data the maximum power distribution (resonance R) is found by plotting the power calculated and plotted for various parameters including dispersed phase volume fraction, emulsion thickness and plate types they found the averages power absorption for o/w emulsion is greater in sample heated with reflective surface and decrease with increasing oil volume fraction, at the same the thermal runaway estimated by plotting the difference between the maximum and minimum temperature of the sample (o/w emulsion) plotted versus irradiation time was found to increase with increasing dispersed phase volume fraction (Sujoy Kumar Samanta, Tanmay Basak , 2009). Another observation was that unlike the o/w emulsion; in w/o emulsion there was a decrease in the amplitude at metal plate-emulsion interface this situation because of small dielectric loss of the later case, beside that also it does not respond much to water volume variation.

Numerous investigations have been done in the field of microwave heating and material processing, Christian et al. 2006 have studied the absorption mechanism for emulsion containing aqueous and nano droplets; and found that absorption is attributed to the types of ions, concentration as well as their polarization. Others have studied the effect of microwave in treating industrial waste water emulsions and admitted that microwave can be used as an alternative to the existing demulsification methods; however addition of small amount of acid was reported to increase the efficiency, moreover the effect of aqueous phase composition on microwave absorption was investigated by (Montserrat et al., 2006).

N.Bjerdalen and friends have applied the microwave and ultrasonic techniques to treat the solid particles deposited at the petroleum well, since these particles consist mainly of asphaltene, resins and wax precipitated together with other solid particles such as silica, bentonite and gypsium. The parameters of concern were; temperature, Viscosity, and concentration of crude oil. The microwave device used was sumsung Mini-Chef MW 1010c that had a frequency of 60 Hz and output power of 120 V, the temperature measuring probe was of type Greenlee THH-500, while the ultrasonic device was Medson mysono 201 A19001213 that had power output of 15V and frequency of 3.5 MHz, the crude sample was originated from SANTA BARBARA, the irradiation time for microwave was 80 and 180 for crude oil and asphaltene respectively, while for ultrasinc treatment it was varied as 30, 60, 180 s, results proved that microwave irradiation could elevate the temperature of petroleum crude oil and asphaltene and decrease the viscosity while with ultrasonic treatment the viscosity was observed to increase with increasing the irradiation time (N.Bjerdalen et al.,2004).

Abduraman and colleagues have compared the separation of water from crude oil by sing conventional heating and microwave heating; the study was carried out on two different types of crude oils, and two different water to oil ratios of 30-70% and 50-50% w/o emulsions that were prepared by mixing the two phase vigorously via the standard three blade propeller at mixing speed of 1800 rpm at ambient temperature for 5 min, three types of emulsifiers namely Low sulfur wax residue (LSWR), Triton-x100 and Span 83 were used to produce the most stable w/o emulsion. For demulsification Elba domestic microwave oven was used and the temperature profile of the sample was monitored using three thermocouples that were inserted in the sample at different location (Top, Middle and Bottom), microwave processing time was varied as 30, 60, 90, 120,150, 180,210 S, their results revealed effectiveness of the microwave heating over the conventional heating in breaking w/o emulsions (Abduraman et al., 2006).

Vladan Rajakovic and coworkers have used the combined Freeze/Thaw and microwave irradiation method to spilt oil from oil-in-water emulsion that was originated from metal working oil, the splitting process was carried out via the ultrafreezer device at three distinct temperature of -20, -40 and -60 ^{0}C, for a processing or freezing duration of 10h then thawed back in Air at 20 ^{0}C then water bath at 40 ^{0}C or microwave at 95 ^{0}C, 800w, 2450 MHz, however their results showed that the effectiveness of the freeze/thawing and microwave demulsification techniques depend mainely on the oil contain of the emulsion sample, freezing time and thawing steps, thawing time, indeed microwave also believed to induce molecules to acquire more energy because of super heating and increased reaction rate, and thus microwave demulsification is proved to be the most effective method in breaking emulsions (Vladan Rajakovic et al., 2006).

A. H. Nour and coworkers have investigated the batch microwave oven with 2450 MHz in treating and breaking w/o emulsion together with effectiveness of some commercially available emulsifiers in stabilizing the petroleum emulsion, the commercial emulsifiers used in this study were Triton-X100 and Low Sulfur Wax Residu (LSWR), their experimental emulsion was consisted of 20-80 and 50-50% water to oil ratio, the crude used was given by PETRONAS (Malaka refinery), the mixing power was provided through by the standard three blade propeller, the mixing speed was fixed as 1800 rpm, at ambient temperature for an emulsification time of 8 min, however their comprehensive study have proved that microwave can provide very fast and uniform heating and have a very strong potential to be used as an alternative demulsification technique for petroleum emulsion treatment (A. H. Nour et al.,2010).

Hyder A. Abdulbari and friends have studied the stability as well as microwave demulsification of petroleum emulsion; the stability was done by assessing the effectiveness of Sorbitane monooleate (Span 83), Triton-x100, Low sulfur wax residue (LSWR), and sodium dodecyl sulfate (SDDS), the parameters of interest were; the surfactant types, surfactants concentration, water volume fraction in the emulsion (10-90%), emulsification temperature and agitation speed, the raw crude petroleum oil were originated from Iran and Malaysian oil field, emulsions ere prepared through the agent in oil method and mixture was agitated vigorously via the three blade propeller at emuksification speed of 1600 rpm at ambient temperature, the demulsification experiment was carried out using the elba microwave ovenwhose power output was 900 w and frequency of 2450 MHz, results showed gave rapid separation over the conventional gravitational settling (Hyder A. Abdulbari et al., 2011).

Montserate Fortuny and colleagues have investigated the important parameters for microwave demulsification namely salinity, temperature, water content and pH, their experimental emulsion was prepared by mixing the crude oil with saline water and homogenized using two steps emulsification techniques, thus in the first step the mixture was mixed by simple hand shaking and certain amount of water was added in a drop-wise fashion while the mixing is going on, then in the second step the system was vigorously mixed using the ultra-turax T-25 homogenizer fitted with a S25-25G dispersing tool, the water volume fraction was varied as (25, 35, 45) the mixing speed and time were fixed at 17500 and 10 min respectively, the demulsification were performed using the commercial microwave with a processing time of 15 min. results showed that increasing the microwave power could increase the demulsification process, beside that high water contained emulsions were found to give high separation efficiency and that is because of the dielectric heating, also high salt content or high pH had reduced the demulsification rate, indeed the best separation rate was observed with emulsion having water volume fraction of 45% and pH of 7 (Montserate Fortuny et al., 2007).

Rosli M. yunus and colleagues have conducted a laboratory experiment to examine the performance of microwave heating technique in breaking water-in-crude oil emulsion in comparison with the conventional demulsification techniques and their results had concluded that microwave gave better separation than the conventional beside that microwave does not need any chemicals addition and could be used as an alternative green technique to treat petroleum emulsions (Rosli M. yunus et al., 2005).

A. N. Ilia Anisa and colleagues have also used the microwave demulsification techniques to treat w/o emulsions and optimize the operating conditions to fix the best operating conditions for microwave demulsification by using the RSM software. (A. N. Ilia Anisa et al., 2011, and Abdurahman H. Nour et al., 2012).

Lixin Xia and colleagues have studied the stability of crude oil emulsion and its relation to the presence of the presence of Asphaltene and resins (the natural surfactants) followed by microwave demulsification, their experimental was produced by using jet kerosene as oil phase mixed with certain amounts of asphaltene and resin that was extracted from Daqing crude oil (China).

Thus the concentration of the asphaltene in the bulk emulsion was varied in the range of 0.3 to 0.9 w/w, and that of the resin was in the range of 1-4 w/w, the mixing process was performed by simple hand shaking. The demulsification process was carried out by using either oil bath at 90 ^{0}C, or microwave oven or microwave oven with power output of 850 w and 2450 MHz, their results revealed that stability was strongly depended on the amount of the asphaltene and resins in the daqing crude oil, and that is because the adsorption of these interfacial active components at the interfaces is believed to form a mechanical film between the droplets, also microwave demulsification had given better separation result compared to the conventional demulsification methods (Lixin Xia et al., 2004).

Abdurahman and coleugues have proposed a continuous microwave demulsification method for water-in-crude oil emulsion and found that the temperature rise within the sample at given location was linear and the rate of temperature increase of emulsion decreases at elevated temperature due to the decrease of dielectric loss of water (Abdurahman et al. 2006). however, this study have carried out in national Microwave oven, but in contrast to the previous sets, here a hole of 26 cm diameter was made on the top of oven and the beaker that is normally known to hold the sample was replaced by a rounded bottom flask.

2.2.6 Ultrsonic demulsification

Ultrasonic is the branch of physics that is dedicated to the studies of sound, the generation, transmission, control, reception and effects of mechanical waves in solids, liquids and gases (Nguyen et al. 2005). There are several major sub-branches in this research field but the more prominent ones, in addition to ultrasonic, are environmental, architectural, musical and engineering acoustics.

Ultrasonic is the study of sound with a frequency higher than audible sound, environmental acoustics deals with noise control, architectural acoustics is the study of how sound waves and buildings interact, musical acoustics deals with the design and use of musical instruments and how they affect the listener and engineering acoustics concerns the recording and reproduction of sound, thus ultrasound are well established in most engineering application and material processing such as sonochemistry, metal working, cleaning and many more, then each application have certain range of frequency. The basic requirement of establishing an ultrasonic equipment are transducer (a device that can convert electric to wave) and medium within which sound could propagate, for sonochemical application the medium is mostly water, while transducers vary with application.

In the following paragraphs some criteria and types of the existing transducers would be highlighted (Mason and lorimer 2002).

Gautam and colleagues have applied the low intensity ultrasonic field to separate oil phase that is suspended in an aqueous solution however the system consisted of rectangular chamber that was filled with matrix of porous medium within which the oil drops was assumed to be filled, three types of mesh were used that were glass beads, aluminum mesh and polyester, a rectangular piezo-electric (PZT) transducer and stainless steel reflector were mounted in the chamber in paralleled position to each other, and the distance between the and reflector was adjusted carefully to generate standing wave on the emulsion sample that was filled in chamber (between the Transducer and reflector), the acoustic field energy was produced by energizing the transducer at 680 KHz frequency using a continuous sonisoidal signals generated and amplified by KROHN- HITE 2100 A signal generator and ENI 240 L power amplifiers respectively, their experimental oil-in-water emulsion was produced by using the soybean oil and deionized water with 50-50% oil to water ratios, the emulsion was first agitated for one minute then sonicated for 8 minutes to produce a stable emulsion having 1 to 10 micro-meter sized droples that was further diluted prior to feed in the acoustic chamber for demulsification to ease the visual observation of the droplets' response to the to the ultrasonic field, results showed that the ultrasonic separation efficiency depends strongly on the feed flow rate, path length as well as the electrical power (Gautam et al., 2004).

E. Riera-Franco de Sarabia and co-workers have reported the application of ultrasound to separate the suspended particles from fluid, the basic fundamentals behind the ultrasonic particles separation depends normally on the material to be treated fore instance in the case of gas systems the very fine suspended solids particles have to be removed via the agglomeration process whereby particles collect together to increase their sizes then separate out of the suspending medium, while in the liquid systems the agglomeration rate is less efficient than that of the gas phase but generally its very useful to split and separate th fine particles from their suspending medium (E. Riera-Franco de Sarabia et al., 2000).

E. Riera and friend have studied the possibility to apply the ultrasonic agglomeration process to treat suspension and separate the suspended particles from industrial fumes and from their results they observed that the agglomeration process was not very good in liquid systems (E. Riera et al., 2000).

Ye Guoxiang and colleagues have investigated the ultrasonic electric desalting and dewatering techniques in treating petroleum emulsions in order to separate the salt and water from emulsions, their system was consisted of ultrasonic device and electric desalting and dewatering device that are connected in such a way that make the feed emulsion had to pass through the ultrasonic tube in order to enter the electric desalting and dewatering unit.

The ultrasonic equipment was designed with very specific geometry to produce an ultrasonic standing waves field, the frequency used was either 10 or 20 KHz, the initial salt content of the petroleum oil was as high as 40-70 mg/L, the process was carried out in three distinct steps that are crude oil pretreatment, ultrasonic irradiation, and electric desalting and dewatering, during pretreatment crude oil was treated to render it less viscous and flowable, then certain amount of water was added in the oil containing demulsifiers in the pipeline then the mixture was agitated by static mixture, in the second stage emulsion was treated with ultrasonic standing wave field, then in the third stage the emulsion was treated with electric desalting and dewatering process and this caused the water droplets to coalesce and settle down as separate phases, results showed that ultrasonic electric united process increases the dewatering and desalting process of the crude oil, thus the optimum treatment conditions were found to be 5% by volume of injected water, 30 micro gram/g of demulsifiers, 0.45 MPa of pressure drop of mixing, 10 KHz and 150 w of ultrasound (standing waves field), 3.4 min ultrasound irradiation time, 1.2 Kv/cm electric intensity, 20 L/h of emulsion flow rate, and processing temperature of 80 ^{0}C, thus the system was reported to be very effective, hence beside water separation, the salt separation also was found decrease from 67.5 mg/l to 3.97 mg/l at 80 ^{0}C (Ye Guoxiang et al., 2008).

Sanjay and friends had studied the mechanism of aggregation of fine particles in porous medium under the influence of the standing waves field; the parameters of interest were the bulk fluid flow rate, the ultrasonic power, and the feed concentration, the ultrasonic device was a rectangular chamber that consisted of two rectangular leads on parallel position to each other and piezoelectric transducer, the porous mesh was placed between the transducer and reflector, their results showed that the separation efficiency had reached up to 70-80% by using the porous media, also the separation efficiency was found to be directly proportional with the flow rate of the suspension, while the particle concentration was observed to have no effect on the separation efficiency (Sanjay Gupta et al., 1997).

S. Nii and friends have used a 2 MHz ultrasonic frequency generating devices to treat emulsions that were originally prepared from canola oil and water, however the parameters investigated were the ultrasonic power and processing time, however their experimental emulsion was by mixing deionized water and canolla oil and the mixing power was supplied by an ultrasonic horn sonifier (BRANSON DIGITAL).

The demousification experiment was carried out by doting a drop from the stable emulsion on microscopic lens, then the lens was soaked in an ultrasonic water bath that was consisted of glass cylinder with stainless steel plate at the bottom and transducer was mounted on the steel plate, result proved that the action of the ultrasonic power pushed the oil droplets and lead them to aggregation and eventually to massive coalescence and phase separation, beside that a remarkable increase in the velocity of the oil droplets was observed after sample was irradiated via the ultrasonic (S. Nii et al., 2008).

A. Garcia and colleagues have applied the ultrasonic standing wave resonant chamber to treat o/w emulsions, they have used an ultrasonic frequency range of between 1-2 MHz, and the apparatus used was standard research system ENI 310L RF power amplifier Tektronix oscilloscop, the experimental emulsion used in their study was prepared using an Omni-Ruptor 250 Homogenizer to provide the mixing power, the oil volume fraction in the emulsion was fixed at 10%, and for demulsification experiment several transducer types were examined to generate the standing wave in the emulsion, however; once the standing wave was generated.

The oil droplets were observed to aggregate as response to the effect of the standing waves, and thus the standing treated o/w emulsion sample had shown a great separation efficiency over the control or the gravitationally separating sample. It was also observed that at elevated ultrasonic power, acoustic streaming and heating could be produced, indeed directly contacting the emulsion sample with the transducer was found to be very effective (A. Garcia etal., 2008).

2.2.3 Summary

Crude petroleum is almost always exists in the forms of emulsion of any types such as w/o, o/w, w/o/w, o/w/o with w/o being the most prominent type encountered in petroleum institutions and that is imparted to the fact that most of the indigenous surface active agents such as asphaltene, resin long chain fatty acids are oil soluble. Water comes into contact with petroleum either inside the well or during pumping from the reservoir as well as during desalting process, this latter is very important in petroleum industries wherein water is used as a cost effective solvent to remove the water soluble salt from the petroleum prior to refining process indeed water also can be used to reduce the viscosity in the case of heavy oil transportation in pipelines.

And since the presence of water in the crude petroleum causes other problems such corrosion, and quality reduction for the refined products therefore water must be removed or reduced to minimum amount before refining starts. Various demulsification techniques are currently used to remove water from crude oil, including chemicals, conventional heating, electrical and centrifugal with chemical being the most prominent and widely used but as reported in literature it has a lot of disadvantage in many aspect including safety, cost and environmental effect, therefore more and more versatile, lucrative and sustainable techniques are needed and that is where the objective of the current work comes in. more over; emulsion formation and stability varies from one location to another or even between two different wells in the same field, Currently chemical demulsification is the most dominating technique.

In chemical demulsification; Amphiphilic copolymers called demulsifiers that categorized into anionic, cationic, nonionic and ziwitrionic are injected to the emulsion with respect to their major groups of either water soluble or oil soluble. Microwave demulsification have gained a considerable attention in resent years it first introduced to this field by Wolf, in his various lab scale experiments.

To assess this concept as discussed in the literature, same goes with ultrasonic which is very new in this field but claimed to have much potential in this area and thus in this work both microwave and ultrasonic would be assessed comprehensively in combination with chemicals to come up with a new formulation that easy to use, cost effective and environmental friendly.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This chapter describes methods and material used to carry out the research and experimental procedure followed to accomplish the objectives the study was conducted in three stages; the first stage is characterization and decolorization of crude oil, and secondly emulsions formation characterization and stability assessment, and thirdly demulsification by microwave batch process, chemicals and ultrasonic. Experimental methods involved the procedure for emulsion sample preparations, experimental-set-up for microwave equipment, sample characterization using microwave process (sample analysis, identification of emulsion type, measurements of emulsion density, viscosity, stability). Details of the experimental are discussed below.

3.2 Materials, Apparatus, and work flow

Three different methods utilized to break the emulsions are Microwave, chemical, and ultrasonic demulsification techniques but a massive screening was carried to fix the parameters of importance in producing and experimental emulsion that would mimic or represent the industrial emulsion, however the steps flow of the whole work are given as follow:

- To investigate the stability mechanisms of the emulsion by preparing several experimental emulsions and investigate their properties such as viscosity, shear rate, shear stress and gravitational settling.
- To decolorize the crude oil.
- To investigate the microscopic behavior of emulsion.

- To examine the demulsification of emulsions by microwave heating using batch process system
- To study the microwave-chemical assisted demulsification of stable water-in-crude oil emulsion.
- To study the ultrasonic chemical assisted demulsification of stable water-in-crude oil emulsion.
- To study the microwave-chemical assisted demulsification of slop oil.
- To study the microwave chemical assisted dmulsification of waste coolant.
- To study the effect of microwave power generation in demulsifying the w/o emulsions
- To analyze the overall potential of microwave and ultrasonic demulsification method as alternative to the conventional chemical demulsification method in demulsifying water-in-crude oil emulsions.

3.2.1 Microwave Oven

A domestic microwave oven was used in heating crude oil emulsion samples for the microwave demulsification study. The microwave oven is rated 800 Watt out-put power at operation frequency of 2450 MHz. The oven cavity dimensions are: 215 mm (H) 350 mm (W) 330 mm (D), with oven capacity of 23 Liters. Figures 3.1 and 3.2 show the schematic details of the domestic microwave used in this study.

A 200-500 ml round bottomed glass flask was used as the sample holder for the batch heating processes. Samples were introduced in and out of the microwave by a precise hole drilled on top of the oven. Pump was used for shifting the sample out of the oven after heating time had elapsed.

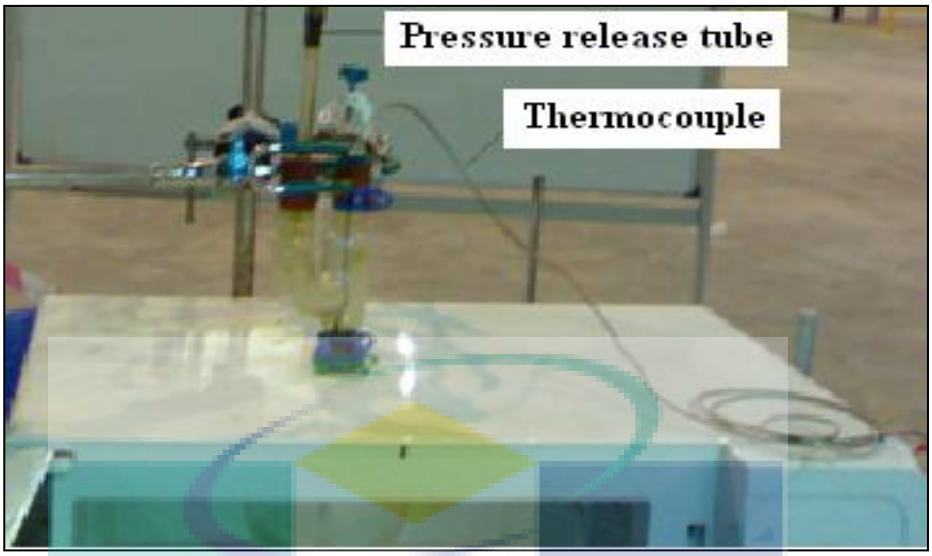

Figure 3.1: Modified domestic microwave oven

The demulsification experiments were performed using both methods; conventional heating at 70 ^{o}C and microwave irradiation (360-900W) at 2450 MHz using batch process. The demulsification efficiency was evaluated by measuring the percentage of water separated from the emulsion as a function of time. The amount of resolved water is the most appropriate measure of the emulsion stability of water-in-crude oil emulsions, since the coalescence of the droplet phase is the limiting step in the demulsification process. The data reported for this experimental study were the average of four runs.

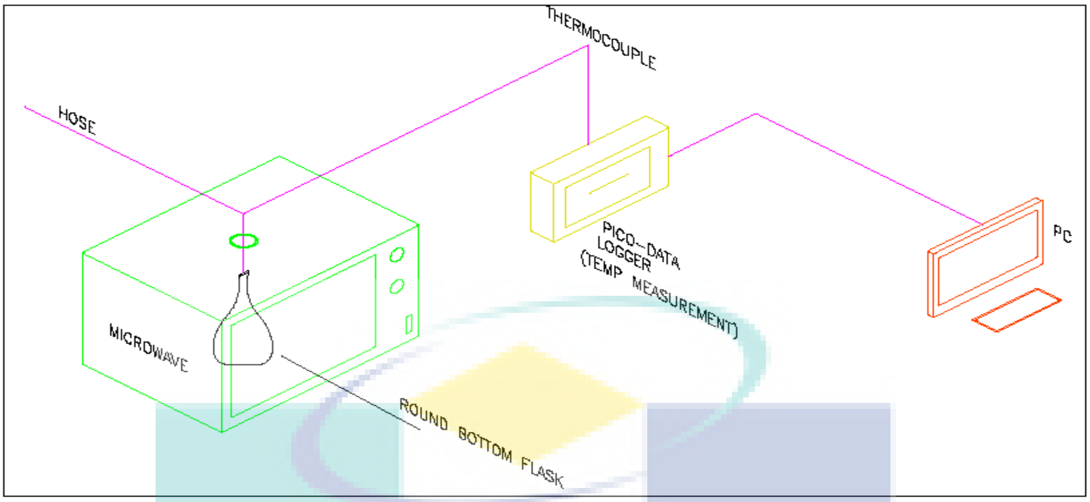

Figure 3. 2: Microwave oven and pico-data logger assembly

3.2.2 Crude Oil Emulsion

Samples of crude oils used in this study were collected from Petronas Refinery at Melaka. The samples were denoted as crude oil A (Masila+Khafji). In laboratory, samples were synthesized to different water-in-oil (w/o) emulsion ratios.

3.3 Emulsion Samples Preparation

Water-in-crude oils of different compositions were prepared in laboratory, with focusing in two distinctive fractions of 50-50 and 20-80 v/v% and prepared on the basis of oil continuous phase. The prepared emulsions were examined to identify the type of emulsion (w/o or o/w). All emulsions investigated were of type water-in-oil emulsions. Since all emulsion samples prepared were water-in-oil emulsions, therefore, the continuous phase is oil. Emulsions were made by adding internal phase (water) carefully and slowly to the mixing phase (solution with stabilizer) in a glass beaker (500 ml). Emulsions were agitated vigorously using a standard three blade propeller at speed from 500 to 2000 rpm and temperature 28-30 ^{o}C for 7 minutes. The rpm (rotation per minute) used depended on the specific emulsion and the amount of internal phase added. The concentrations of water (internal phase) in the samples were varied by volume.

However special attention was given to the effect of temperature, hence various temperature range between 30-90 ^{0}C to observe the effect of temperature on emulsion and also to estimate the temperature whne emulsion could change phase i.e. the reverse (piT) phase inversion temperature.

Several commercial surfactants supplied by local companies have been used with reference to several previous publications. The objective of screening was to assess the quality of the emulsions to be used further in demulsification experiments in terms of surfactants, their dosage and other emulsification parameters.

For the batch microwave heating process, in contrast to the previous studies the sample container have changed from the previously used beaker to a round bottomed flask, connected to joint glass tube and through hose tube to peristaltic pump. This assembly has helped to charge the raw material in this case emulsion to the microwave and shifting the products or the processed emulsion out of the oven. A 25 cm diameter hole was drilled on top on the microwave oven through which the neck of the round bottomed flask is penetrated from inside the oven to the outside assembly of the pump joint and pumps. Additionally thermocouple was inserted to the sample to record the temperature. The emulsion samples were heated with microwave radiation at 2450 MHz for a different microwave exposure time. Temperature profiles of emulsions inside the cylindrical container during the batch microwave heating were recorded by Pico-TC-08 data logger.

In order to prepare water-in-oil emulsions, the agent in-oil method was followed, that is; in this study, the emulsifying agents were dissolved in the continuous phase (oil), and then water added gradually to the mixture (oil + emulsifying agents). The volume of water settled at the bottom was read from the scale on the beaker at different times. The amount of water separation in percent was calculated as the separation efficiency. In some cases, internal phase volume fraction effects on emulsion stability and phase inversion were investigated.

3.4 Stability Measurement for Emulsion

The stability tests for emulsions prepared based on volume fraction of emulsified water, phase ratio water-oil (20-80, 50-50 %). The stability tests were carried out to understand the behavior of the crude oil emulsions. However as mentioned earlier the height of water and/or oil separated out of the emulsion was read off periodically and data were used for relative comparison and decision making for various controlling parameters estimated and reported to effect the emulsion stability these include surfactants' concentration, emulsification temperature, water to oil ratio, types, origin and composition of the oils.

3.5 Emulsifier

The emulsifying agent (surfactant) used for stabilization and preparation of the water-in-oil emulsions for this study is the commercially available Triton X-100 (non-ionic water soluble type). The emulsifier provides stability for water-in-oil emulsions. The concentrations of surfactant varied depending on the application. The entire emulsifying agent was used as manufactured without any further dilution.

3.6 Selection of Agitation Speed

The emulsions were agitated vigorously using a standard three blade propeller. The agitation speed used in this study was 1600 rpm. Some of the previous studies used speed ranging from 1000 rpm to 2000 rpm (Sjoblom et al, 1995, Abdurahman et al., 2007).

3.6.1 Selection of Agitation Period

Although several agitation periods were used for sake of screening and finally 7 minute was selected as the best and fixed therein for whole experiment since it produced the most stable emulsion. Beside the screening results this selected agitation period is also in accordance with previous results (Ease et al., 1997, Sun et al., 1996).

3.6.2 Test for Type of Emulsions

For determination of emulsions type prepared, a drop of emulsion was added in a test tube containing water and was shaken gently. If the emulsion is of w/o type, the drop will remain as droplet since the oily continuous phase is unable to mix with the water in test tube. If the emulsion prepared is of o/w type, the emulsion drop will spread Out quickly in the test tube and with gentle shake it can be seen dispersing in the test tube. Also the emulsion type was tested by filter paper tests. In this test, a drop of a water-in-oil emulsion (w/o) produces an immediate, wide, moist area, whereas oil-in-water emulsions (o/w) do not. All the prepared emulsions were of type water-in-oil emulsions.

3.7 Viscosity, Shear rate, and Shear Stress Measurement

Viscosity, shear rate, and shear stress of the water-in-crude oil emulsions in this study were determined by Brookfield Rotational Digital Viscometer Model LV/DV-III with UL adaptor and spindles 31. The Brookfield Viscometer apparatus was equipped with a water bath thermostat, a spindle set, and software of Brookfield Rheocalc Version 1.2. Selecting the right model of spindles ensure maximum sensitivity and accuracy in the range of the measured viscosities. The model of coaxial cylinders spindle was suitable for crude oil which has a low viscosity. The experimental procedures followed the standard operating procedure of Brookfield Viscometer. The measurement was carried out at least four times and the average value was taken.

Figure 3.3: Brookfield Rotational Digital Viscometer Model LV/DV- II

3.8 Surface and Interfacial Tension Measurements

For measurements of surface and interfacial tension, a standard test method (ASTM D971) is used. The Ring method was used in the determination of surface and interfacial tension as shown in figure 3.4. The equipment is Du Nouy Interfacial Tensiometer, equipped with 6-cm circumference platinum ring. The tensiometer was placed on a sturdy support, free from vibrations and other disturbances such as wind, sunlight, and heat. The wire of the ring was in one plane, free of bends or irregularities, and circular. In setting the instrument, the plane of the ring is horizontal, that is parallel to the surface plane of the liquid being tested. After the tensiometer has been calibrated, the level was checked and the cleaned platinum Ring was inserted. The dial and vernier were zeroed before any measurement was made.

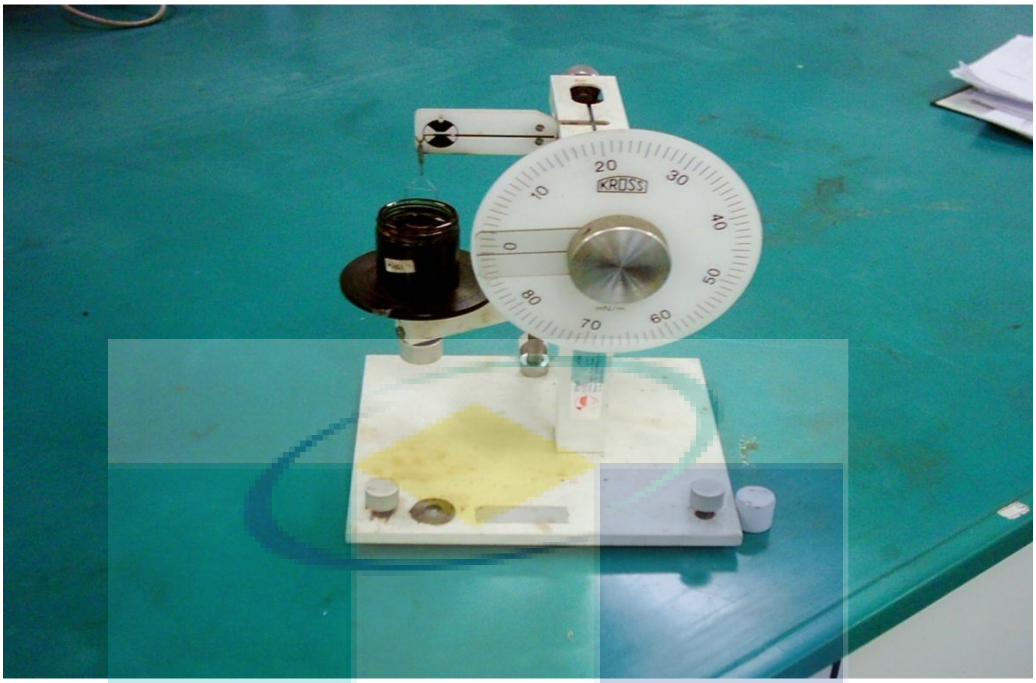

Figure 3.4: Interfacial tensiometer

3.8.1 Surface Tension

For surface tension measurement, the emulsion sample was placed on the sample platform. Then the sample platform was raised by adjusting the screw until the ring was just submerged. The platform was lowered slowly at the same time applying torsion to the wire by means of dial-adjusting screw. These simultaneous adjustments were performed carefully proportioned, while the ring system remained constant at its zero position. As the breaking point was approached, the adjustment was made more carefully. When the ring detached from the surface, the dial reading was recorded. The experiment was repeated and four measurements were recorded for accuracy.

3.8.2 Interfacial Tension

The general procedures followed for determination of interfacial tension is the same as the surface tension determination with some modifications. 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 was then poured to form the two-layer system (emulsion). Contact between the oil and the ring was avoided during the operation. After allowing sufficient time (5 minutes) for the interfacial tension to come to its equilibrium value, measurements were made in the same manner as that used for measuring surface tension.

3.9 Decolorization procedure

Decolorization of the crude oil was carried out as shown in flowchart depicted in Figure 3.5. The decolorization process was carried out by first adsorbing the crude oil in a silica gel after it was dissolved in n-hexane then the mixture was separated by filtration (to remove the solid particles), the solvent was evaporated using rotary evaporator to recover the decolorized oil as elucidated by flowchart (Figure 3.5), the detailed procedure for decolorization are below:

- 10 ml of crude oil diluted with 90 ml of n-hexane
- 5 g of silica was added to the mixture and left to settle until the solvent was transparent above the solution.
- The decolorized oil was separated from the solution by using filter paper
- The solid silica was washed with hexane with addition of some silica until the filtrate was very light in color.
- The solvent was evaporated by rotary evaporator to recover the pure decolorized crude oil

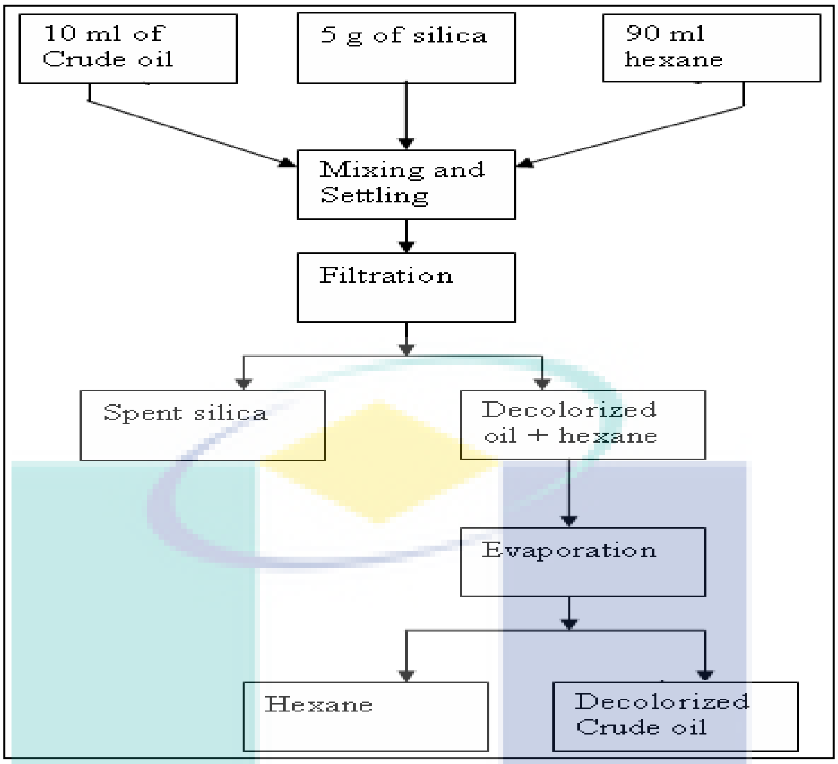

Figure 3. 5: Crude oil decolorization flowchart

3.10 Saturate aromatic resin and Asphaltene (SARA) fractionation

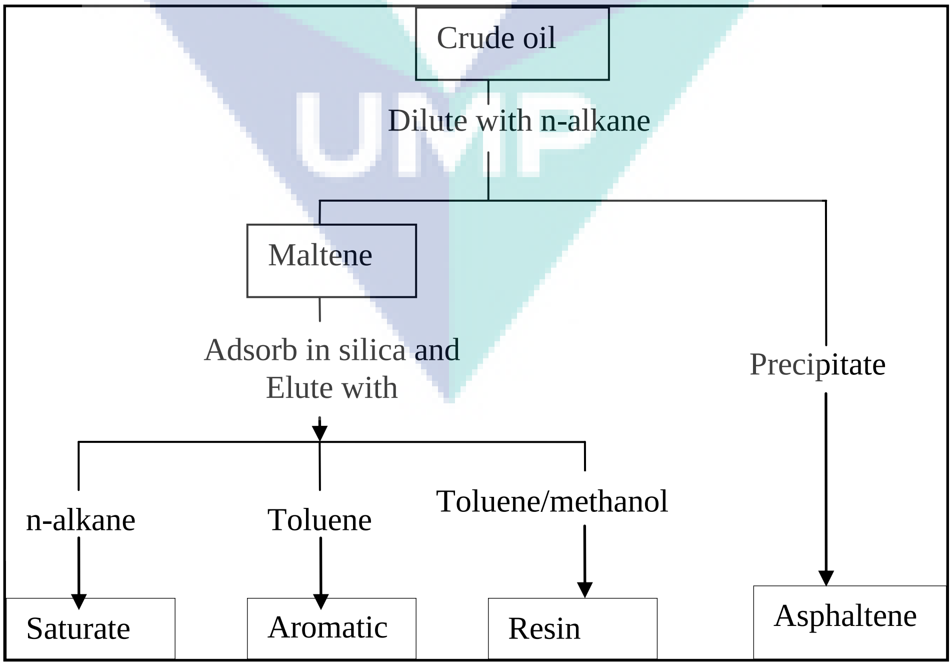

Figure 3.6: SARA fractionation flowchart

Figure 3.6 shows the procedure followed in this researche to fractionate the crude oil sample to its subfraction according to solubility range , moreover this fractionated was bases on the ASTM D2007 for crude oil fractionation (Tianguang Fan., 2002)

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter will discuss the experimental data obtained in order to accomplish the objective of the current research project. As stated earlier in the first chapter, although the main objective of the research is to investigate the effect of microwave and ultrasonic demulsification techniques on petroleum emulsions, yet the characterization and stability test of the oil samples is necessary since the emulsion being studied was prepared in laboratory; so this part will focus mainly on the method used for screening and emulsifiers selection before tackling the problem. Emulsion breaking is known to be among the very challenging techniques in petroleum industries and that because of complex nature of crude oil itself and oil water mixture that is called emulsion.

To accomplish the objective of this study several crude oils from different places were obtained and an experimental emulsion of known composition was prepared, and its rheological properties was studied thoroughly including stability test to see the resistance against coalescence.

4.2 Screening experiment for emulsifier’s selection

This section states the different ways or methods used in the production of relatively stable emulsion that can be used in further investigation, knowing this process of getting a good emulsion similar to the natural emulsion requires certain combination of water, crude oil and emulsifying agent, add to that the agitation speed and preparation time as discussed in chapter 3.

Stability studies is most probably the first cornerstone for any type of emulsion and emulsification study in various industrial as well as real life applications such as crude oil spillage, pipeline transportation, oil production from reservoir, enhanced oil recovery, in addition the wide spread food and cleaning and pharmaceutical applications (Gannam., 2005). Stability study is normally carried out to find out the optimal formulation for desired products, either to observe shelf long life as in beverage and other industrial applications excluding crude oil, or for transportation, recovery, combustion in petroleum industries and refineries, emulsions are sometime prepared in laboratory purposely for testing new demulsifiers or new demulsification techniques as in the current research.

Three types of emulsifiers have been chosen based on previous studies they are commercially named Triton-x100, SDDS and Span 80 applied in two different crude oils one was heavy type oil from Kuwait and the second was light type oil from Malaysia. The main purpose of this screening process was to find the best formulation in terms of emulsifiers' type as well as concentration, since concentration is very significant from economic point of view. Thus in every experimental emulsification studies, stability test is required to find out the best and reliable emulsion at lower cost, hencethe effectiveness of the emulsifiers was accessed by measuring the rate of water separation from emulsion (Zaki et al., 1996).

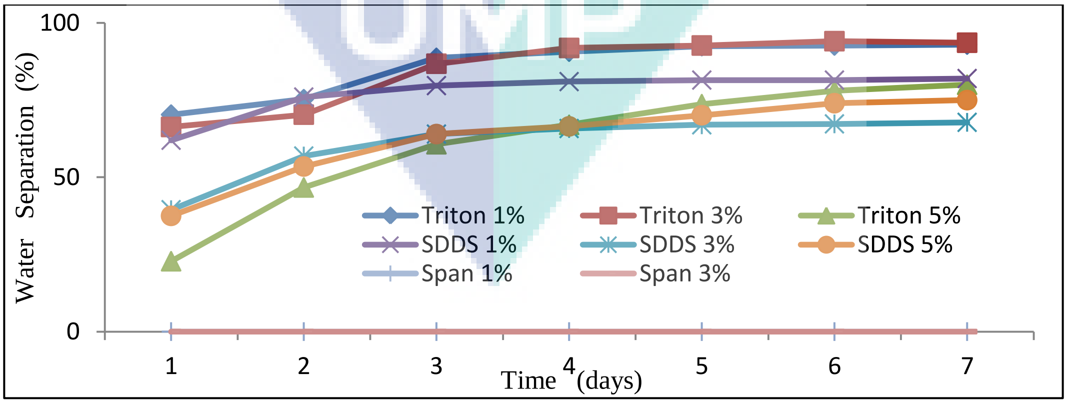

Figure 4.1: Effects of types of emulsifiers and their dosage on stabilizing 50-50% (w/o) emulsions from Miri oil (A) crude oil

Figure 4.1 shows the stability pattern of the three distinct emulsifiers with respect to concentration. The effect of three different emulsifiers on the stability of Malaysian light crude oil (miri) was depicted. The dosages of the emulsifiers were varied as 1, 3 and 5% each types. For Triton-x100, SDDS and Span-80, it was observed that at low concentration of 1% they were not efficient in stabilizing the emulsions hence more than 60% of the water in emulsion separated from the first day the emulsion was prepared, and 95% of initial water content was separated within one week.

In more details on the experimental work carried out in this research, the effects of the different concentrations of the individual emulsifiers on the emulsion stability were investigated since the stability effect was defined in terms of the percentage of water separated out of the emulsions within the observation period of one week, hence the water resolution from emulsions prepared from the three emulsifiers were discussed in details, firstly; consider the water resolved from the differently formulated emulsions in the first day from figure 4.1 was as follow.

Firstly considering the Triton x-100 stabilized emulsions the percentage of water separated in the first day was around 70%, 68% and 20% for 1%, 3% and 5% concentration respectively and from this observation, 5% result was truly in accordance with what was expected, since triton x-100 is nonionic surfactant same as Span80; so the types of interfacial barrier they make what called steric barrier and their stability was called steric stability, wherein the long chain polymeric surfactant with hydrophilic portion of around 20 ethylene oxide links. Note that a polymer with this length is never straight so it makes a bulky hydrated head groups film on the aqueous side of the interface having a thickness range of more or less $100A^0$.

These layer bump on against each other when two drops come in close proximity to one another, thus hindering inter-particles distance to reach the minimum values required for cohesion and adhesion forces to involve. Indeed such types of stabilization mechanism is suspected to cause the natural water-in-crude oil emulsion in the oil field because of bulky hydrophobic groups of natural indigenous surfactant namely asphaltene or resin. According to this perspective the current experimental result showed increase in stability (less water resolution) with increasing concentration and thus concentration was found to be the most particularly effective dosage in Triton x-100 emulsifier yet it is not the suitable choice since it lost around 20% of its water within the first day, and as time goes on; separation rate was increased until it reached 72% for the 5% concentration and 90% for each of the rest two concentrations during the total observation period of one week.

This instability might be due to low viscosity of the continuous phase together with HLB and solubility of the emulsifiers will ease the agglomeration and offer paths to the agglomerated drops and flocks to settle and sediment in accordance with stokes' law of settling velocity which says the settling velocity and separation rate of the emulsion droplets will increase with reducing continuous phase viscosity. Since Triton x-100 is nonionic surfactant but it is reported to favor partitioning in aqueous phases more than the oil phases, this may also contribute massively in lowering the stability since the surfactant are most likely assumed to be intended to produce water-in-oil types emulsion with regard to their solubility behavior, and that is by being more soluble in the aqueous droplets instead of protruding their long chain polymer part in the bulk continuous oil phase and just surround the drops to produce water-in-oil emulsion as expected,

Ghannam reported the significance of 1% triton x-100 addition in water-in-crude oil emulsion, of low water contents of 20% and found to increase emulsions stability over the emulsifiers' free emulsion, then stability decreased with increasing water contents hence the most unstable emulsion was found at 50% water concentration that is in accordance to the current study (Ghannam et al., 2005).

With regard to SDDS stabilized emulsions; the general trend for 1, 3 and 5%, stabilized emulsions were 60%, 40% and 35%, it is generally similar to it previously discussed triton x-100 counterpart although the numerical values are a bit different. SDDS is anionic surfactant and the mechanism with which anionic surfactant as reported in the literature is basically through the formation of well known electric double layer which is normally formed by the positioning of the surfactants molecules at the interface. Normally the polar head groups are attached to the water phase and the non-polar tail to the oil phase. The charge of the head groups will surround the droplets while the counter ions would be dispersed randomly in the vicinity of charged interface and altogether will form what is known as the electric double layer which acts as an electrical barrier prevents the neighboring droplets from merging or coalescing. Indeed the coalescence of the droplets is proportional to the strength or potential of this interfacial layer, although the stability of the layer is affected by many parameters such as surfactant concentration, pH, salinity and temperature, fundamentally there are two mechanisms affecting the strength of the double layer these are; the random molecular motion which tends to fix a uniform concentration in the vicinity of diffuse layer.

secondly the columbic attraction force between the adsorbed charges and the free moving charge which tends to keep the cations in close proximity to the interface, and induces repulsion when the approaching surfaces of the neighboring droplets overlap, this double layer extends over certain effective distance around 500A^0 (Angstrom) from the interface known as the Debye length which increase with increasing surfactant or electrolyte concentration.

Hence from this fact, at low concentration of 1% and 3% ; the strength of the charged interfacial layer is less effective in holding the counter ions in equilibrium at close proximity and that will lead to the reduction of Debye length and faster flocculation and coalescence of the droplets, and this will eventually leads to unstable emulsions, another explanation is that the ionic surfactants SDDS in this case are water soluble and hence will tend to dissolve in the water phase rather than oil phase and this lead them to form stables bubbles of water, SDDS gave better result than Triton x-100. This was expected to occur since SDDS is anionic surfactant which is water soluble, add to that its detergent like character will lead to the formation of foam at higher water content, this is most probably what happened in this situation of high water content (around 50%). Thus the stable bubbles making the foam are expected to be surrounded by surfactant layer. Hence this mixture of bubble plus droplets plus bulk oil will make the emulsion even more stable, however this situation was changed when the concentration was increased to 5% where triton x-100 stabilized emulsion was more stable, this may be due to the surfactant adsorption at the interface since the interface only can accommodate certain amount of surfactant concentration beyond which they either consolidate the existing monolayer and form what is known as cylindrical layer which in turns transform with increasing concentration to lamella liquid crystal or they are no longer effective in stabilizing the emulsion. Weixing and coworkers have examined the solubility behavior of some anionic surfactant and confirmed the increase of solubility with solid concentration (weixing et al., 2004).

Indeed with regard to Span80 stabilized emulsions, there was no water separation observed in all dosages tested (1%, 3% and 5%), which mean Span 80 prepared emulsions were very stable and hence from this experimental observations; Span80 was chosen as the most effective emulsifiers to produce water-in- light crude oil emulsion.

With regard to the types of emulsifiers used in this research, emulsions composed of 1% concentration of the three aforementioned emulsifiers (Triton-x100, SDDS, and Span-80), as shown in figure5.1; during the fist 24hours 1% triton stabilized emulsion had lost around 70% of its water content that means it was not stable at all so 1% triton-x100 was not sufficient in stabilizing 50-50% w/o emulsion of miri (A) crude oil, similarly SDDS stabilized emulsion had lost around 60% of its water thus 1%SDDS was not sufficient in stabilizing 50-50% emulsion of miri (A) crude oil, while that was not the case in 1%Span-80 stabilized emulsion since the curve showed there was no water separation for the whole week, but it was observed that there was some oil was floating over the emulsion layer but no water separation at all.

Indeed in the subsequent day, the separation rate of 1%SDDS stabilized emulsion was around 72% and there was very minor increase in the in the days after until the day 7. For 1%triton-x100 stabilized emulsion, the rate had augmented to around 82% by the third day after that no much increase until the day 7, in contrast to the previous two cases, the 1%span-80 stabilized emulsion was stable for the whole week with regard to water separation despite some oil had separated from the emulsion, and that may be due to the light nature of miri crude oil (low viscosity).

Secondly; the effect of concentrations on the emulsions stabilized solely by SDDS was investigated and it was found that the resolved water was ranged again as 60%, 40% and 39% for 1%, 3% and 5% respectively in day one of the test, a result which is more or less in accordance with its previous counter part (triton X-100), and indeed; the overall comment is simply that 1% concentration was not enough to stabilize 50-50% water-in-crude oil emulsions of miri light crude in both aforementioned emulsifiers (SDDS and Triton X-100).

3% and 5% SDDS stabilized emulsions had given almost identical results, unlike in the case of Triton X-100; however this situation may be attributed to what so called the critical micelle concentration(CMC) whereby the interfacial area is almost completely occupied by the surfactant molecules and most probably formed what called the surfactant monolayer which acts as a mechanical barrier in the case nonionic surfactant; (tritonx100) surrounding each drop and hinder the neighboring droplets to come together and by doing so it will automatically decelerate the sedimentation rate and confer a better stability.

In the case of SDDS the stability mechanism as described in literature is an electrostatic mechanism where by several attraction repulsion forces will interact to promote stability when repulsive forces are dominant and instability when the attractive forces are dominants, the repulsive forces for ionic surfactants (SDDS) are normally created when two charged interface approaches each other and their electric double layers overlap and its named columbic repulsion force whose function is to oppose any minimization to the separation distance and thus its in most of the times expressed as the potential energy of repulsion, however at very small separation distance (were the atomic electrons colloids reside).

There are other repulsive forces that can rises referred to as born repulsion, in the stable conditions these forces are normally balanced by what so called attractive forces created form the orientation of the dipoles which in turn categorized to either; Dipole-Dipole attraction force (Keesom dispersion forces), Dipole induced-dipole attraction (Debye dispersion forces), or induced dipole-induced dipole (London dispersion forces) (Laurier L. Schramm., 2006), however these electrostatic affect was not measured in this study since the aim was to produce water-in-oil emulsion which known to show very poor electrostatic properties, and that may be one reason why the SDDS stabilized emulsions were unstable losing most of their water contents during the first day of preparation because have poor solubility in the oil phase and that may lead then to form oil trapping surfactant micelles when they first added in the continuous phase and agitated before the addition of the water droplets, remember that in the current method used to produce the actual emulsion; the mixture of oil and surfactants was agitated vigorously for 2 minutes before adding the water as drops.

During the mixing the polar heads of the anionic water soluble SDDS surfactant would be oriented in a circle shaped micelles as they are trying to group themselves faraway from the nonpolar oil phase and some may also dive freely in the oil phase, indeed the circulated micelles my entrap some oil within the micelle forming miceller solution and that may be the reason why an unstable foam was observed to form when water was added instead of emulsion, then within a few minutes from preparation the foam would vanish and three layer would the upper most is either oil or oil rich emulsion, the down most is either water or water rich emulsion and middle layer is particularly assumed to be the surfactant or micelles rich very stable emulsion which appeared to be reddish in color and also was observed to increase with increasing surfactants concentration, this situation considered to support the idea of micelles orientation.

The increases in the amount of the surfactants will leads to more micelles and probably micelles swollen micro sized oil droplets and more freely diving surfactant which can be oriented at the interface according to their nature; and that will eventually increase the middle emulsion layer when the emulsion is put in measuring cylinder for observation, a picture of this would shown in latter sections.

In terms of quantitative observation; the addition of surfactants beyond this optimal concentration (say from 3% optimal to 5%) in this case; shall not much disperse solely but rather accumulate to the already dispersed ones (optimal condition) and consolidate the stability by forming what so called the lamella liquid crystals this claim is proved by observing the rate of stability in the following days as seen in figure 5.1, the two results were converged in the third day and remained equal until the forth day, after which the 3% had reached a plateau and the other 5% continued to separate until it reached to 70% by day 7. anyhow the results were contradictory to each other and observation marked for 50-50% miri light crude oil emulsion stabilized by SDDS was; in the previous four days; 5% concentration had given more stable emulsion with less water separation then from day four until day 7 the 3% stabilized emulsion had given a better results and reached a plateau at 60% water resolution, every emulsion produced from SDDS surfactant was not stable enough to be considered but as it is well known that every and surfactant molecule can migrate to interface and reside there with certain arrangement when its placed in mixture of two immiscible liquids, normally the polar head groups are oriented toward the aqueous polar phase, and the hydrophobic non polar tails are protruded into the hydrocarbon or oil phase, and that arrangement will lead them to construct a mechanical or potential barrier that hinder the neighboring drops from coalescence, thus in the case of SDDS the more surfactant are put; the thicker and stronger the film will be and that would lead the high stability.

Thirdly the case of span80 was totally unique and different than the other two cases hence for all observation there was no any water resolution reader may need to refer to figure 5.2. According to the theory, Span 80 and triton X-100 of same category of nonionic surfactant with triton X-100 is considered as more water soluble and span 80 is more oil soluble, indeed the mechanism of nonionic surfactants' stabilization is based on what so called steric stabilization; a mechanical film formed at the interface in the nonionic or polymer stabilized emulsion, hence when the two interface come to proximity in another word; when the two neighboring drops are close enough then the steric film is formed as a result of either head groups overlap and fluctuation in interface, this type of steric stabilization is normally stabilize or help to increase the stability of the emulsion, other type is called bridging flocculation wherein some materials are adsorbed on the particle surfaces and it normally tends to decrease the stability(Laurier L. schramm., 2006).

Finally this paragraph would be concluded by a summary of all the observations discussed. Generally at low concentration of 1% in all cases excluding Span80, the stability was very poor for miri crude oil, then when the emulsifiers increased further to 3%, the Span-80 stabilized emulsion has not shown any effect and remained stable with zero water separation, indeed the 3% triton X-100 stabilized emulsion had almost the same pattern as in 1% stabilized emulsion, while the 3% SDDS stabilized emulsion was observed to be slightly stable than at 1%, hence the separation rate was 40% during the first day and increased further to 55% in the second day then to around 60% in the following days. At 3% emulsifiers concentration, the separation rate of the triton X-100 stabilized emulsion had reduced to 20% in the first day but it had doubled in the second day to 40% then to around 55% by the third day and continued to around 70% on day 7.

Similar trend had observed with 3% SDDS stabilized emulsion which had lost around 35% of its water content in the first day, 50% in the second day, 60 % by the third day and to around 70% by the day 7, and again there was no water separated from span-80 stabilized emulsion but there were some abnormalities such forming two layered emulsion; a situation in that appeared in span80 stabilized emulsion that is contradicted the usual stability pattern of only water separating out of the stable emulsion by seeing three or two layers the top-most layer consist of either pure oil or oil rich mixture, the lowermost layer consists of either cloudy water or water rich mixture which might be referred to as micro-emulsion surfactant micelles swallowed oil droplets in the excess water phase.

Cconcerning the middles layer which appeared brownish in color is assumed to the most stable formulation within the individual emulsion samples, the point is that in span 80 stabilized emulsions; intermediate layer was found to either absent (uniform emulsion) or the dominant layer compared to the other tow types stabilized emulsions. From this observation there was a clear view and there was no minor doubt to choose the Span 80 as the best emulsifiers to be selected to produce high water contained miri light crude oil emulsion.

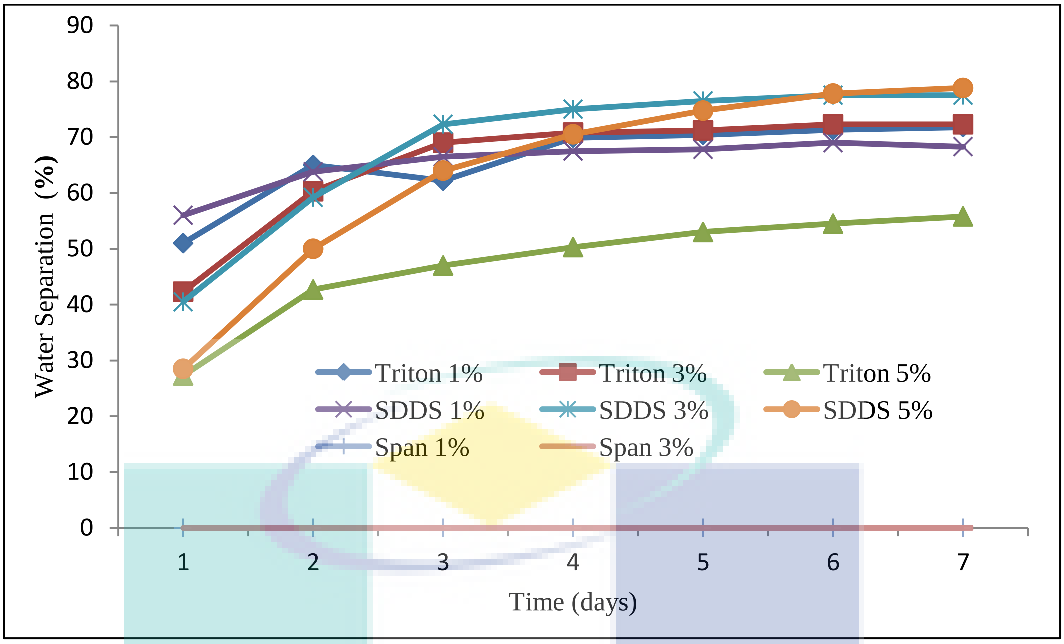

Figure 4.2: Effects of types of emulsifiers and their dosage on 50-50% (w/o) of Kuwait oil (B) emulsions

Graphs in figure 4.2 are plotted from the experimental data obtained from various emulsifiers and their dosage as stated earlier in figure 4.1, but this time in different crude oil that is apparently more viscous than the Miri (A) and it is originally from Kuwait and named as (B) in this part of the study. Emulsifiers were shown to be more active in promoting and stabilizing the emulsion in oil (B) compared to (A), thus in 50-50% water-in-oil emulsions, the effect of the different concentration of three emulsifiers had plotted in Figure 4.2, again in here the span 80 was found to promote a very stable emulsion at all concentration hence there was no water or oil separation was observed within the whole one week observation time.

The experimental results also proved that different crude oils have different stability pattern even with the same emulsifiers, this can be seen by comparing the experimental results obtained from 50-50% emulsions prepared by Triton X-100 for two different crude oils (A and B), for oil B the stability result was 50%, 40% and 26% for 1%, 3% and 5% triton x-100 respectively but thy were 70%,68% and 20% for oil (A) with the same formulation, this means Triton x-100 was more effective in oil B than oil A, a situation which could be attributed to the physical and chemical composition of the crude oils since Kuwait crude oil is heavier, denser and more viscous than miri light crude oil, and thus it is assumed to content more of incompatible materials such as asphaltene, solid particles and clays which play a very important role in promoting crude oil emulsion. Previously similar results were reported by Mervin and coworkers in different crude oil emulsions having similar formulation to the current systems, and concluded that stability is more or less a strong function of viscosity of the continuous phase (crude oils) in addition to the surfactants and agitation, and they also evidenced experimentally that heavy crude oils contains more asphaltene than the light ones.

Asphaltenes would either catalyze the mechanism of surfactant adsorption at the interface or would be located at the interface and consolidate the strength of the film formed by the surfactants molecules that acts as a mechanical barrier hindering the droplets from flocculation and coalescence and eventually promoting a stable water-in-crude oil emulsion (Fingas and Ben., 1996).

Similar observations were found with SDDS stabilized crude oil B emulsions which gave 55%, 40% and 27% just similar to the triton X-100 but in comparison with the same formulation of SDDS from the previously discussed with crude oil (A), the amount of water resolution was 60%, 40% and 39% reader may need to refer to Figure 4.1. If the effects of triton x-100 and SDDS were compared for oil B alone; it is clear that the effect is almost similar in contrast to the effects on oil (A), which was obviously fluctuating and alternating with concentrations for example at low concentration of 1%; the amount of water separated from miri light crude oil (A) emulsion were 70% and 60% for triton and SDDS respectively that means at low concentration SDDS gave better result over triton X-100.

As the concentration increased further to 3%, the water separation was 68% and 40% for triton and SDDS respectively here, still SDDS gave better result, at 5% concentration; the water separations were 20% and 39% for triton X-100 and SDDS respectively Triton gave better result this contradict the previous result, in another word; at 1% emulsifiers' concentration of triton x-100 and SDDS the percentage of water lost was around 50 and 55% respectively, this case was slightly stable compared to same composition in oil (A), in which the separation rate was 70 and 60% for triton and SDDS respectively, further more as the concentration had increased to 3%; both triton and SDDS emulsions had lost around 40% of their water content in the first day then they all reached plateau by the third day at separation range between (60-74%). Indeed when the concentration had increased further to 5%; the stability of both triton x-100 and SDDS had enhanced, and the percentage of water separation had reduced to 28% in the first day, but immediately increased the next day hence triton satbilised emulsion had reached a plateau at 40% separation by the second day, while the SDDS stabilized emulsion continuously separating and reached around 80% within one week figure 4.2.

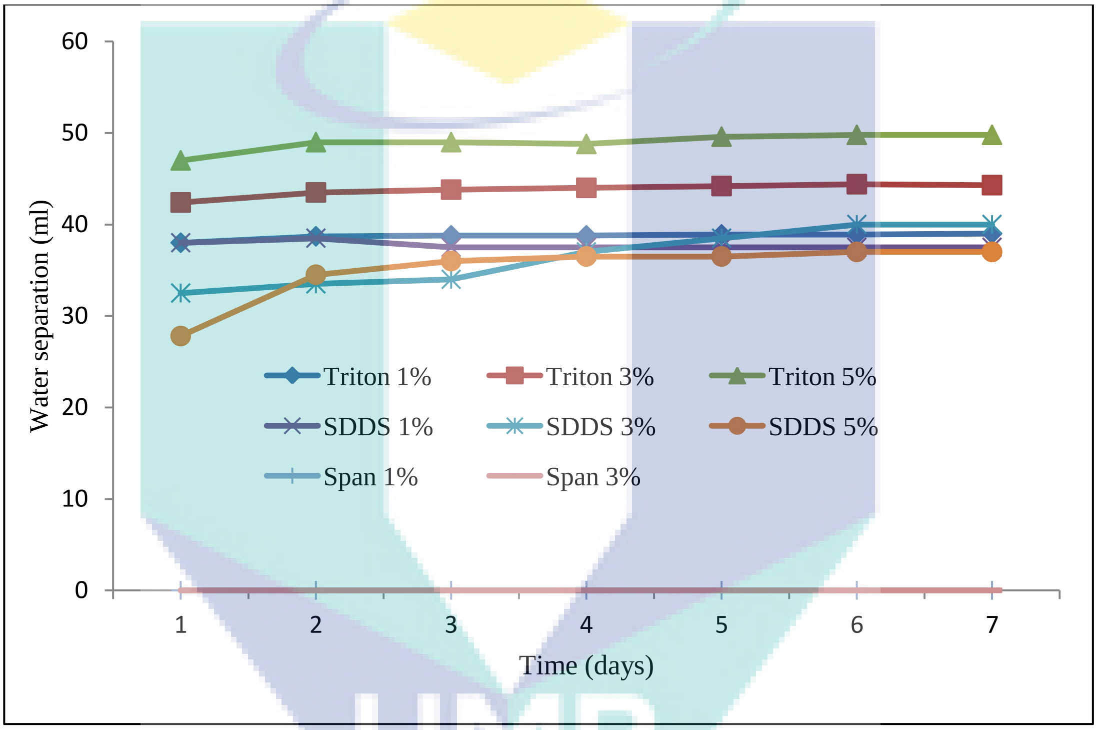

Figure 4.3: Effects of types of emulsifiers and their dosage on stabilizing 20-80% (w/o) emulsions from Miri oil (A) crude oil.

With respect to water content of emulsion and its effect on emulsifiers' action; data on Figure 4.3 were obtained from 20-80% water to oil ratio emulsions prepared from crude oil (A), how ever results in here were some how different from the 50-50% emulsion, thus for 3 and 5% Triton-x100 stabilized 20-80% w/o emulsions, it was observed that they were not stable and separated immediately to two distinct layers, more importantly the water layer was not pure water it was rather a mixture that content some oil molecules and in it and thus it was appeared as dark layer on the bottom which was quantitatively greater than the original amount of water in the emulsion (40 ml) shown in Figure 4.3, more over beside that water rich bottom layer there was also a thin emulsion layer, and finally a black oil layer on top, so altogether there were three layers, the top layer is the oil-rich layer and the middle layer might be an emulsifiers rich layer that had formed from the excess emulsifiers that may have formed some micelles at the interface between the two phase and trapped some water droplets and promoted a stable emulsion layer.

Beside that the down bottom layer that is rich in water also defiantly consists of three components with water being the most prominent element that is why it appeared as turbid water which consists of small oil droplets trapped in water and surrounded by the dissolved surfactant molecules, as the surfactant concentration was reduced further to 1% Triton x-100; the turbid water layer has reduced to 38ml, which means this concentration of triton is not enough to keep the oil drops trapped within the turbid layer so they have escaped and transferred either to the surfactant rich emulsions layer in the middle which itself had appeared tiny this time or settled on top in their bulk phase.

Regarding the other emulsifiers SDDS and its action on 20-80% w/o of miri crude oil (A) emulsions, it was observed that at high concentration of 5%; foam had formed at first instead of expected emulsion, then settled to emulsion then water started to separate, it was not so stable hence most of water had separated from the first and second days as shown in figure 4.3.

The general observation in terms of water content and its effects on emulsion stability is that at low water content the percentage of water separation was lower than that of higher water content or 50-50%, thus for triton x-100 stabilized 20-80% water-in-miri oil emulsions the separation rate was 38%, 42% and 47% for 1%, 3% and %% respectively this is strange actually to see the stability decreases with increasing emulsifiers concentration, but it was normal for SDDS stabilized emulsion and gave 38%, 32% and 28% separation rate for 1%, 3% and 5% respectively which in both cases the separation percentage was better than 50-50% emulsion means at low water content the emulsion was more stable than at 50% water content and that might be because at low water content the droplets are suspended far from each other within the bulk oil phase hence this long separating distance increase the repulsive force over the attractive force and that will hinder the aggregation and flocculation and retard the settling of the droplets and this lead to conclude that low water content emulsion is more stable than the higher water content emulsion, indeed the increase in the volume fraction of the dispersed phase also could increase the effective entropy of collision between the drops and that would lead to increase in the rate of coalescence and eventually leads to destabilization and water separation. similsr results were reported by Zaki, who investigated the effect anionic surfactants on crude-in-water emulsions prepared for pipeline transportation purposes (Nael N. Zaki., 1996). Sapan80 stabilized emulsions were always stable and no water separation was observed despite there were some oil separation.

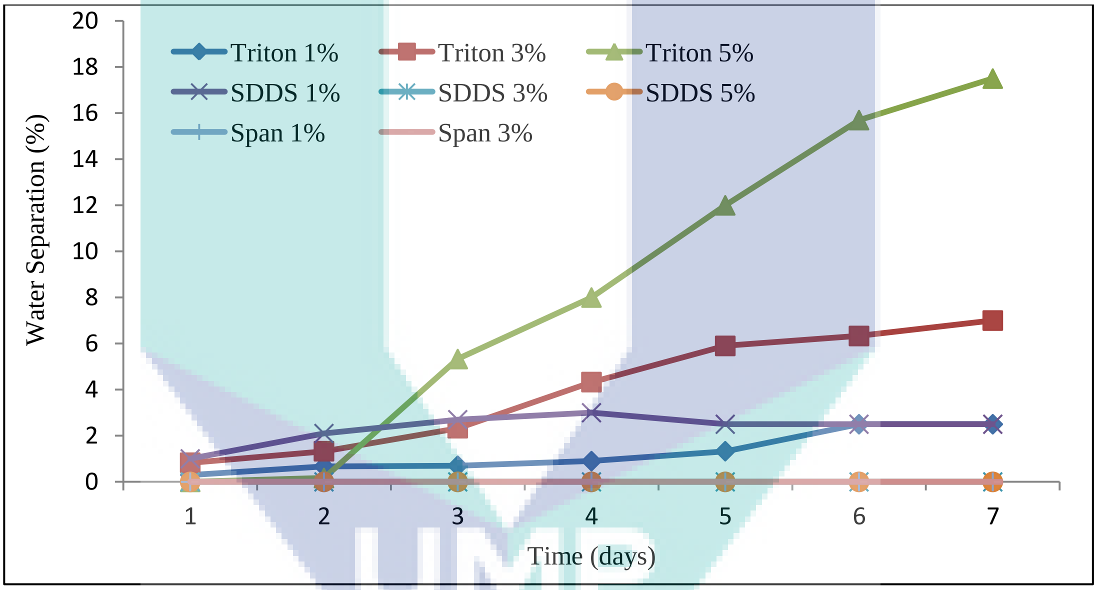

Figure 4.4: Effects of types of emulsifiers and their dosage on stabilizing 20-80% (w/o) emulsions from Kuwait crude oil (B)

Figure 4.4 shows the effectiveness of the types of emulsifiers and their dosage on 20-80% water-in-oil prepared from Kuwait crude oil (B), most emulsifiers has marked to possess a great effect with this formulation, thus all concentrations of Span80 had produced a very stable emulsion with zero water separation as usual, the water resolution from triton x-100 stabilized emulsions within their first 24hrs were 0.4%, 1% and 0.0% at 1%, 3% and 5% concentration respectively, seemingly it was 1%, 0% and 0% with SDDS stabilized emulsions, from personal perspective this is the only formulation in which all of the emulsifiers were effective and gave the most stable emulsions ever since the very beginning of this formulation. According to this result of 20-80% water-in-oil (B) crude oil; the most effective emulsifiers was Span80, followed by SDDS which gave the same result at its high concentrations of 3 and 5%, however at 1% SDDS concentration the emulsion could hold the separated levels to a very low quantity, hence the amount of water separated was less than 2% within 4 days and retained less than 4% for the whole week. The opposite was marked with the Triton x-100 induced 20-80% Kuwait oil emulsion in which stability was observed to decrease with emulsifier's concentration as proved in Figure 4.4 and that might be attributed to the solubility of the emulsifiers (triton x-100).

From these experimental observations; emulsifiers were found to have paramount contribution on emulsion stability although they alone are not enough to produce stable emulsion. Other important parameters are internal phase volume fraction and viscosity as just discussed. Importantly Span80 gave very stable emulsions, therefore Span80 will be chosen for further investigations in terms of the emulsion characteristics such as rheolgy, emulsification temperature, emulsification (rpm) and droplet sizes analysis.

4.2.1 Effects of physical parameters on emulsion Stability

Based on the last discussions on Kuwait and Miri crude oils, Span80 was found to be very effective in promoting and stabilizing the water-in-crude and since the purpose of the screening is to identify and select the most efficient emulsifiers that can be used to stabilize and produces emulsion that is stable enough to carry out the current research, thus span80 had chosen and further investigation on other crudes that are originated from Saudi Arabia (SA) and United Arab Emirate (UAE), and their stability test have carried out.

The effects of the physical parameters is also assessed by considering other parameters such as emulsification temperature (EMT) and the mixing speed (rpm), that was previously mentioned as the most candidate for emulsion formation, however this current test have not underestimated the previously discussed chemical properties such emulsifiers types, emulsion composition, and types of crude oils, properties beside the two previously discussed dispersed phase volume fractions, and since Span 80 was producing very stable emulsions at all concentrations; therefore its concentration is further reduced to 0.5% in this study, and all the preparation parameters are fixed as reported in chapter 3 (methodology).

i) Effects of Temperature on Emulsion Stability

Table 4.1 represents the effects of temperature on emulsion stability, since temperature reduces emulsion viscosity and hence its thought to accelerate separation as reported in many articles, hence span80 was used to prepare various emulsions of Saudi Arabia and United Arab Emirates crude oil, both of which are heavy oil types, two internal phase concentrations of 50-50% and 20-80%, at various emulsification temperature which was varied as (50, 60, 80 and 90 ^{0}C), the concentration of span80 was reduced further to 0.5%.

The stability of the emulsions was assessed by measuring the water settled on the bottom of measuring cylinder over a period of one week, interestingly with this one week observation time, there was no water separation at all, and thus the only comment on this result is just Span80 was very effective in producing water-in-crude oil emulsions of Saudi Arabia and United Arab Emirates crude oils with both higher and lower water content in all temperature ranges below 90 ^{0}C, but of course in reality there should be some degree of variation on the stability as the concentration are changed and this ambiguity led the author to use some other stability assessing methods such as rheology and droplets sizes which would be discussed letter.

Table 4.1 presents typical experimental values for water-in-crude oil emulsions stabilized from United Arab Emirates (UAE) and Saudi Arabia (SA) crude oils stabilized with 0.5% Span 80, from the observation carried out for a period of one week it was noticed that there were no water separation from the emulsion this result will strongly consolidate the capability of the span 80 in promoting and stabilizing water in crude oil emulsion for various crude oils thus we have a observed it is good performance on exactly four different crude oils namely; Malaysian miri, Kuwait, United Arab Emirates and Saudi Arabia.

Table 4.1: Effects of (EMT) on (UAE) and (SA) crude oil emulsion with 0.5% span80

Time (days)	Water Separation (%) for 50-50% w/o								Water Separation for (%) 20-80% w/o							
	Temperature (^{0}C) from 50-90								Temperature (^{0}C) from 50-90							
	UAE crude oil				SA crude oil				UAE crude oil				SA crude oil			
	50	60	80	90	50	60	80	90	50	60	80	90	50	60	80	90
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 4.1 above represents typical experimental values for water-in-crude oil emulsions stabilized from United Arab Emirates (UAE) and Saudi Arabia (SA) crude oils stabilized with 0.5% Span 80, from the observation carried out for a period of one week it was noticed that there were no water separation from the emulsion this result will strongly consolidate the capability of the span 80 in promoting and stabilizing water in crude oil emulsion for various crude oils thus we have a observed it is good performance on exactly four different crude oils namely; Malaysian miri, Kuwait, United Arab Emirates and Saudi Arabia. Other observation is that emulsion have been prepared over four distinct temperature levels referred to as Emulsification temperature (EMT) and still the results are the same, no water or oil separation, which means emulsions are very stables, this is different than the starting hypothesis since temperature has been reported by many articles to highly affect the stability by directly and efficiently altering the properties of the interface, interfacial film, bulk crude oil, water phases and surfactants' solubility in the oil and the water phases, this later property may dominated in the current emulsion, since there was no water resolution at lower emulsification temperature(Sunil et al., 2005).

This strong stability behavior might be primarily attributed to the elevated viscosity of both crude oils, since the viscosity of the continuous phase will play a very important role in the stability by helping the emulsifiers molecules encapsulating the droplets to resist and overcome the hydrodynamic force that is normally intent to attract the droplets and induce aggregation, coalescence and eventually separation. Even though this stability patterns had revealed that none of these separation steps could have occurred but of course this emulsification temperature variation will cause some other effects in the microstructure of the emulsion such as interfacial viscosity reduction, and droplets size evolution, and this idea had led to further investigation in terms of viscosity and droplet sizes measurement, however the results of that that will be discussed later.

Table 4. 2: Effects of Mixing speed (RPM) on UAE crude oil emulsion with 0.5% span80

Time (days)	**Water Separation (%) for 50-50% w/o**								**Water Separation for (%) 20-80% w/o**							
	Mixing Speed (RPM) from 500-2000								**Mixing Speed (RPM) form 500-2000**							
	UAE crude oil				**SA crude oil**				**UAE crude oil**				**SA crude oil**			
	500	**1000**	**1600**	**2000**	**500**	**1000**	**1600**	**2000**	**500**	**1000**	**1600**	**2000**	**500**	**1000**	**1600**	**2000**
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

ii) Effects of Mixing speed RPM on emulsion Stability

Table 4.2 above shows the effects of mixing speed (rpm) on the stability of water-in-crude oil emulsions prepared with 0.5% Span. Since mechanical mixing is very important in segmenting the internal phase into droplets producing emulsions, since mixing cause the interface between the continuous and dispersed phase to deform producing droplets, indeed at the beginning of the emulsification the drops are bigger in diameter then they are fragmented further to smaller droplets as the mixing goes on as a result of disruption process, this deformation is opposed by high Laplace pressure, which is the pressure drop between the concave side and the convex side of the curved interface is generally expressed mathematically by the well known laplace pressure

$$(\Delta \mathrm{p} = 2\gamma/R) \tag{4.1}$$

Where γ : is the interfacial tension between oil and water and R is the droplet radius, in another word; in order to break down a large droplets diameters such a pressure must be externally supplied by agitation hence high mixing speed will reduce the droplet diameters and that will increase the emulsion stability (Mamdouh T. Ghannam., 2005).

It is obvious from Table 4.2 that all mixing speed used here could produce a stable emulsion and this again reflect the effectiveness of span 80 on promoting stable water-in-oil emulsions, and again as its clear from table 4.2; even variation of (rpm) had given no effects with respect to water separation and again will lead to the conclusion that even 0.5% Span80 concentration had led to a very stable emulsion of heavy crude oils from Saudi Arabia and United Arab Emirates at various rpm and two distinct water concentrations of (50-50% and 20-80%), or another explanation to this result is that the visual monitoring of the water separation from the emulsions alone is not sufficient to analyze or investigate the stability of water-in-crude oil emulsions especially for heavy crude oil which may produce very stable emulsions that is difficult to break such as in the current case, and also its well known that in addition to water or oil phase separation; emulsion stability is also governed by some other inter-particles activities such as creaming, flocculation, coalescence, and ripening, this situation had encouraged the researcher to add some more analyzing techniques such rheological measurement including viscosity, shear stress, shear rate, droplets diameter that would be discussed in detail in the coming sections.

For better understanding of the behavior of water-in-crude oil emulsion; other parameters had been talked these are; the Rheological properties of the same crude oils with the same composition to investigate further the effects of shear forces and temperature on the viscosity of the emulsion, since it has been known from literature that emulsion viscosities are very sensitive to temperature and increase in temperature would leads to viscosity reduction and destabilization of the emulsion, and since the main objective of this study also to apply the electromagnetic energy to heat and separate water-in-crude oil emulsions, hence the study of the Rheological behavior may help to understand the stability of the emulsion.

4.2.2 Rheology of emulsion

Basically Rheolgy is the study of deformation and flow of fluid and it is very useful tool for characterizing all types' of fluids and mixtures therefore it will help to characterize and study emulsions in term of their viscosity and its variation with composition and formation conditions. Basically viscosity of emulsion is substantially greater than the viscosity of either of the two consisting phases and hence emulsions normally deviate from Newtonian behavior of the pure constructing materials, this deviation depends on the sample composition and production condition and it is a way of assessing the viscoelastic properties of most of fluids, since every fluid or mixture is by default considered Non-Newtonian when its viscosity is a function of shear rate as reported earlier in the chapter of Rheology in literature review.

Figure 4.5 is depiction of typical experimental data of viscosity variation with mixing speed (rpm) and water content for distinct crude oils from United Arab Emirates (UAE) and Saudi Arabia (SA), these data proved as expected the variation of emulsion viscosity with (rpm) as well as water content, and the effect is clear in here unlike the previous study wherein there was no effect when the visual observations of the water resolution alone is relayed upon.

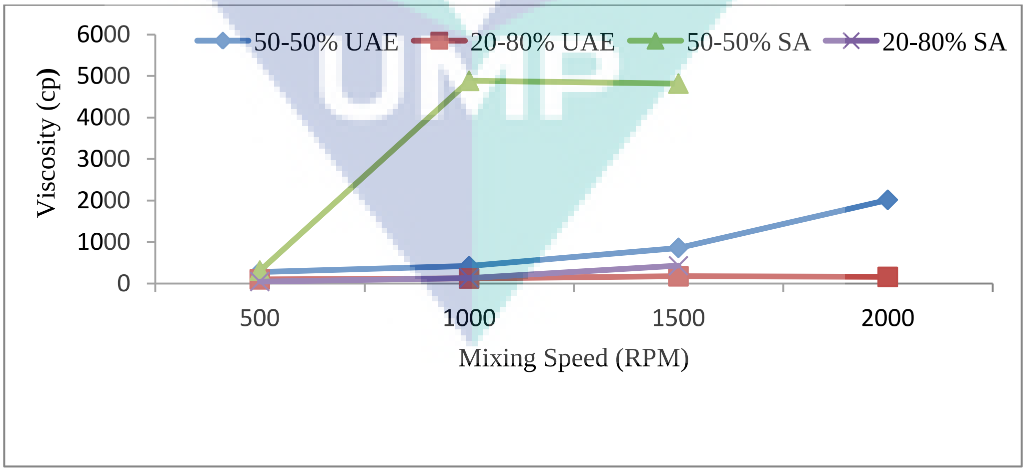

Figure 4.5: Effects of Mixing speed (RPM) and water content on emulsion stability

At 50% water volume fraction; both crude have shown a great increase in their viscosity with increasing the mixing speed (rpm), despite 50-50% (SA) crude oil was marked to show a sharp viscosity increase with increasing (rpm) to reached a plateau at 1000 (rpm) it is maximum viscosity was 4883 cp that was almost constant and there was a little decrease in viscosity at rpm (2000) and that might be due to the high turbulence that could lead to aggregation of the droplets by the action of the shear force (Einar et al.) while for 50-50% (UAE) oil emulsion; the trend was normal as expected hence viscosity was found to increase smoothly with increasing (RPM) starting from around 300cp and continues until around 2000cp. This result was in accordance with the previous finding by some researchers which attributed the governance of the stable water droplets in crude emulsion matrix to viscous and interfacial force which in tern a strong function of some other physicochemical parameters such as interfacial active components, agitation, aqueous phase concentration aqueous phase salinity and many more (Mervin F. Fingas and Ben Fieldhouse.,), they also reported in their work ; the fact that the viscosity of a stable emulsions at very low shear stress is at least three order of magnitude greater that of original crude oil.

Normally stable emulsion possess some degree of elasticity, while in unstable emulsion would have a viscosity not more than two order of magnitude of the starting oil or may be less than two order of magnitude of that of starting oil and with no or very minor elasticity From this results it's observed even within the heavy crude oils, (SA) and (UAE) in this case; emulsion stability varies with varying oil types, thus Saudi Arabian crude oil has shown to produces the emulsion with the highest viscosity over the other three types investigated so far. These results are more or less similar to previous researches done on other systems of crude oils, and fundamentally attributed to either Hydrodynamic force or Brownian motion, in another ward when the water droplets in the emulsion are of bigger droplets (probably more that 10 micro meter).

The hydrodynamic force which results from either electric double layer (with anionic surfactants) or steric barrier (with non ionic surfactants) will prevail and hence the large spheres will interact within themselves, in this case the system viscosity is a strong function of the concentration of the internal phases. Whereas in the case of small droplets (less than 1 micrometer) the colloidal surface force or Brownian motion is dominant and viscosity is no longer function of internal phase volume fraction, but at certain shear forces viscosity decrease with increase in droplet sizes (Zaki., 1996).

Moreover, in addition to the previously reported terminology regarding the emulsion viscosity increment over the viscosity of the original oil; Fingas (1966) has reported in similar manner the classification of emulsion stability by considering some other parameters of percentage of water uptake and duration, thus he categorized the emulsions as stable and unstable; Stable emulsions is the one which can hold up around 80% of its water for 30 days, while unstable emulsions; these category only can hold up 10% of its water more or less within the aforementioned period of time, thirdly; the meso-stable that possess properties between the stable and the unstable holding around 60% of its water and loosing most of its water within 7 days, the entrained emulsion a case of the entrainment of the water droplets within the oil phase matrix.

In the case of 20-80% water content at the beginning at low mixing speed they appeared to have a similar viscosity but as the (rpm) was increased further beyond 1000; the Saudi oil emulsion was appeared to exhibit higher viscosity than (UAE) indeed the letter was found to be almost constant beyond rpm (1000).

The conclusion is that emulsion viscosity had increased tremendously with increasing water content as proved by the figure 4.5, the higher viscosity was observed at high water content 50%, indeed viscosity was observed to differ with respect to the oil types hence in both fractions examined here, (SA) crude oil emulsion was found to be more viscous than (UAE) and that is surely attributed to difference in their natural compositions, this results was different from the a previously reported result which found the relative viscosity to be insensitive to oil types for north sea region (Einar et al.,2003).

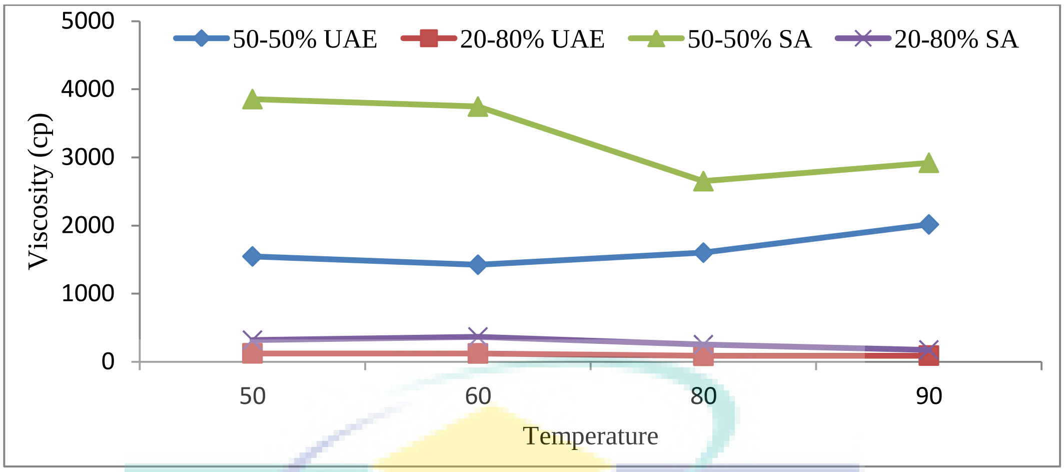

Figure 4.6: Effects of temperature and water content on emulsion stability

Figure 4.6 reveals the effect of emulsification temperature (EMT) on water-in-crude oil emulsions with the same formulations that have just discussed in the previous section; the General trends for all emulsions was similar when only the water resolution was considered as an individual parameter to assess the stability of emulsions at low temperature, but that was not always the case when the temperature is varied. Thus in the case of 50-50% SA crude oil; viscosity had decreased with temperature until 80C^0, then started to increase a situation that could attributed to either surfactants' partitioning and solubility oil properties or might be resulted from the well known phase inversion mechanism, this phase inversion was observed at 60C^0 for (UAE) emulsions.

These results were found to be in accordance more or less to some few statements that have been made by (Sunill et al., 2005).

Temperature affects emulsion mostly on its viscosity, since viscosity of all material decrease with increasing temperature beside some discrepancies observed here and would be elaborated upon later in some few sections to come.

Temperature is also reported to affect the interfacial properties of the wax; since wax can act as a surfactant by residing at the interface and helps the stabilization synergistically with the asphaltene at low temperature; and it would dissolve into the bulk crude oil at elevated temperature a situation which also contribute on stability, thirdly temperature also reported to increase internal energy of the droplets and by doing so it shall empower them to vibrate even more energetically and that would help them to jump out of their encapsulating surfactant films and thus; they may come in a close proximity, reducing the steric barrier radius to its minimum diameter to approximately equal more or less to Debye length since that is the length were the attractive foresees would overtake or even exceeds the repulsion forces such as Brownian movement and London repulsion forces.

At low water content of 20-80% no great deviation occurred and viscosity was found to decrease continuously within the observed temperature range which could be attributed to the lower water volume fraction.

4.3 Visco-elastic behavior of emulsion

Based on the common rule which claims that liquids normally deform continuously as they experience some stress, this deformation varies from liquid to another based on the type and composition of the liquid being tested, and hence the effect of the shearing forces on the behavior of the emulsions was investigated.

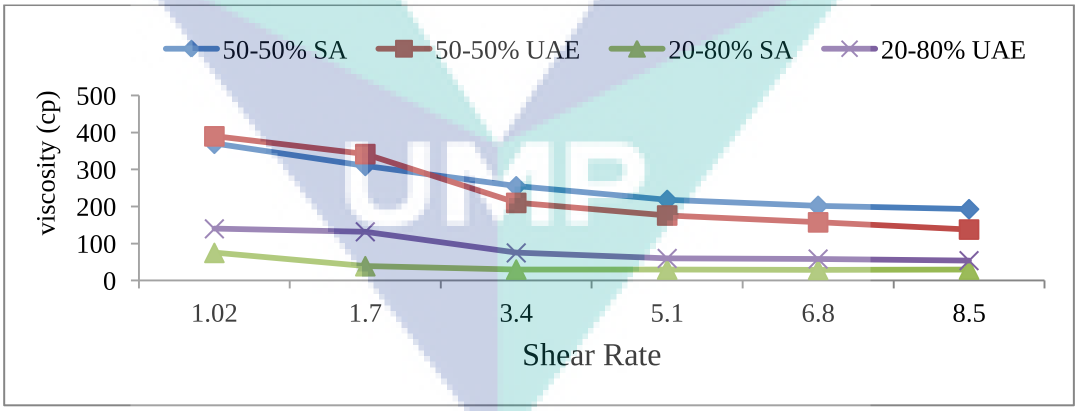

Figure 4.7: Viscosity variation with Shear Rate

In Figure 4.7 the Viscosity vs. shear rate data is plotted in this figure; as it's clear that in all cases viscosity was observed to decrease with increasing shear rate. In another word all emulsions was found to follow shear thinning behavior, as such pseudo plastic material in which the viscosity decreases with increasing shear rate, and also viscosity was found to increase with dispersed phase volume fraction hence, This is in accordance with the findings of Dou Dan and Gong from which they reported that water-in-heavy crude emulsions always possess very strong non-Newtonian behavior (Dou Dan and Gong Jing., 2006).

Another observation is that at low volume fraction the viscosity was found to reach a constant values at high shear rate and that might attributed to the fact that, at low volume fraction droplets deformation is less the inter droplet distance is higher they stay far away from each other the effect of hydrodynamic forces are reduced,

4.4 Crude oil characterization

Generally crude oil is a mixture of hydrocarbons produced in a mixture with some other components such as; minerals, clays, gases and water all together referred as reservoir fluid, crude oils are normally produced with water in the forms of emulsions, that needs to be treated in order to separate the water which is either produced with the crude oil or deliberately added for transportation or enhanced oil recovery.

Hhowever as mentioned previously emulsion is governed by a lot of factors among of which the crude oil physical and chemical properties and this make emulsions to vary from one field to another, and thus the physical and chemical characteristics of the crude oils used in this study would be given in the following sections.

4.4.1 Physical Properties

The physical properties of crude oils used in this study such as density viscosity and interfacial tension were measured in the laboratory, and results are given in table 4.3.

Table 4.3 represents the physical properties of four crude oils chosen for this study, from the physical properties, the three Saudi, Dubai and Kuwait oils have similar density of 0.9405, 0.9045, and 0.9324 respectively so they can be classified as heavy oils, unlike the Malaysian Miri crude oil which have less density of 0.8729

Table 4 3: Physical properties of the crude oils (experimental results)

Properties> oils	Density	viscosity	Interfacial tension	Pour points	API Gravity
Saudi Arabia	0.9405	173.4	9.07	-20.4	23
Dubai	0.9045	72.4	13.06		29
Kuwait	0.9324	161.8	12.78	-20	24.5
Miri	0.8729	23.7	10.88		35

With respect to viscosity again the heavy oils have higher viscosity than the Miri light crude oil please refers to Figure 5.3 to check. Indeed with respect to interfacial tension Dubai oil had the highest interfacial tension of 13.06, followed by Kuwait oil that having the interfacial tension of 12.78 then Miri oil having 10.88 and finally Saudi oil with interfacial tension of 9.07, however, from the results of stability stability study; Kuwait crude oil was found to be in contradiction with the theory; since it has the highest interfacial tension and produced the most stable emulsion and same goes to Miri which had lower interfacial tension but produced very unstable emulsion.

4.4.2 SARA fractionation

Sara fractionation is one of the methods to separate the oil compounds into polar groups namely Saturates, Aromatics, Resin and Asphaltene, Asphaltene and resin are claimed to be responsible for stability of emulsion. Normally SARA separation can be carried out by dissolving the crude oil into alkane to precipitate the Asphaltene Fraction then the rest is adsorbed in Silica column the other fractions were eluted using appropriate solvent.This study is aimed to fractionate the crude oil after decolorizing, because decolorizing the crude oil is helpful to monitor and investigate the emulsion characteristics. So only the United Arab Emirates oil (Dubai) was underwent this fractionation and the weight percent of the polar components was measured, Asphaltene content was 0.071, wax content was 0.472 and resin content was 0.119

4.5 Crude Oil decolorization

The declorization process is carried out in order to facilitate the microscopic analysis of the emulsion in terms of its droplet size, this is only for heavy crude oil namely Kuwait crude oil in this study since the droplets visualization is more clear in the light crude oils; so only a sample of heavy crude is decolorized for the purpose of droplet analysis, and the effect of different parameters such as mixing speed (rpm), Emulsification temperature (EMT).

The surfactant concentration on the emulsion droplets has been studied thoroughly, the decolorization steps are as stated in the methodology chapter (Chapter 3), firstly sample of crude oil is diluted with solvent (hexane) then the solid adsorbent (Silica) was added and the mixture was left to settle, after that the mixture underwent filtration process to separate the solids, and the solvent was evaporated using rotary evaporator to recover the decolorized oil, and solvent, then the solvent is recycled, the solid particle from this process is washed with the solvent in order to remove all crude oil, until the solvent appeared almost colorless, indicating no more oil is trapped within the adsorbent. Sample of decolorized oil would be shown next.

Figure 4.8: Samples of raw crude oil and silica

Figure 4.9: Mixture of crude oil plus hexane plus silica

Figures 4.8 and 4.9 represent the very first steps in crude oil decolorization hence figure 4.8 is samples of the raw crude oil and the solid adsorbent before being mixed, after that in Figure 4.9 is a mixture where crude oil is dissolved in hexane with certain ratios then silica is added to them so all the three flask of Figure 4.9 actually content the same sample.

Figure 4.10: Filtration Process

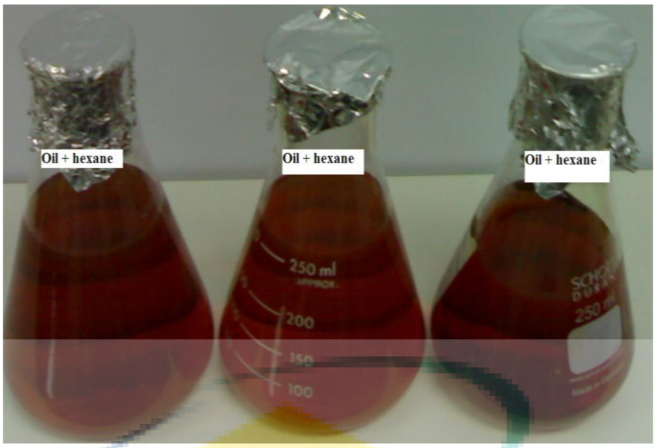

Figure 4.11: Crude oil plus hexane

Figures 4.10 and 4.11 represents the filtration steps in here after the is settled, in here the mixture is separated using filter paper, hence the solid adsorbents are held up on the filter and the crude oil hexane mixture is collected at the bottom.

Figures 4.12 and 4.13 represent the crude oil-Hexane separation process; in here the crude oil-hexane mixture is heated using rotary evaporator to recover the solvent hexane and use the decolorized crude oil.

Figure 4.12: Rotary evaporator

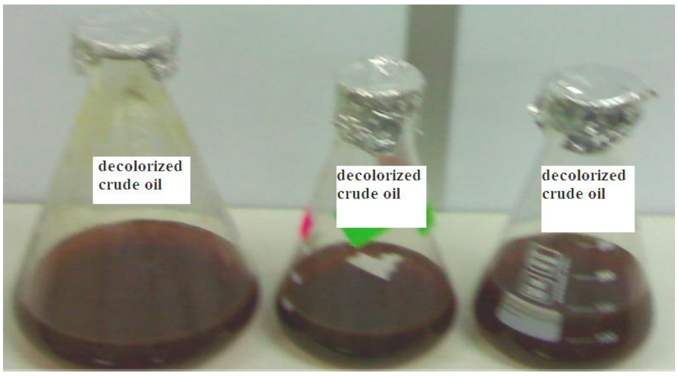

Figure 4.13: Decolorised crude oil

Figure 4.14 represents the photograph of the decolorized crude oil from the rotary evaporator and the solid adsorbent after the decolorization.

Figure 4. 14: Samples of processed crude oil and Silica

4.6 Stability study with decolorized Kuwait crude oil

Before demulsifying emulsion of whatsoever type, it is necessary to control the coalescence of the drops; one way to do so is to determine the size of droplets versus time and also droplets size have a great effect on emulsion viscosity and stability (Abdurahman et al., 2007). Information about droplets is vital to control, predict, measure and report the droplet size of emulsions prepared for different purpose (EL-Hamouz A. et al., 2009). Various studies and techniques have been proposed for drop size measurement including thermogranulometry, optical microscopy, unfortunately not adaptable in compact and concentrated water-in-crude oil emulsion (Abdurahman et al., 2006), add to that the black color of the crude oil which will hinder the observation of droplets under the microscope have lead the researcher to conduct such investigations by using model emulsion, Model-emulsion is a term used to describe a dilute emulsion that prepared by mixing for instance Heptanes and Toluene being considered as the Hydrocarbon phase and aqueous phase (Josef D. et al., 1997).

The disadvantage of this process is that it would not reflect the complete behavior of emulsion and as if the original crude oil was used, since crude oil contains thousands of hydrocarbons, heavy metals and clays. That would not exist in the model emulsion, since the actual crude oil emulsion characterization is difficult especially when they are concentrated, opaque and highly viscous (Abdurahman et al., 2006), therefore a method of decolorizing the crude oil may contributes tremendously in emulsion characterization in terms of droplets sizes, Zeta potential, Scanning electron microscopy and so forth.

However, in this study; research microscope devise is used to observe and monitor the droplets and their sizes in a sample of decolorized crude oil from Kuwait (Alsyaheen), since Emulsion characterization is a very important task to choose optimal ways of preparing or breaking, and even the stability of water-in-crude emulsion is defined as the resistance of the suspended water droplets against coalescence which is function of various factors as such: presence and amount of surfactants, viscosity, specific gravity, temperature, droplets size and size distribution, and aging (Gonglun Chen et al., 2005) results and illustrative figures would be shown in the upcoming paragraphs

4.6.1 Effect of stirring intensity on emulsion stability

Mechanical energy is of paramount importance in preparing an emulsion, since this vigorous agitation breaks the large liquid droplets into smaller ones and reduce the interfacial free energy and that will directly influences the viscosity, droplets size and size distribution and promotes stable emulsion, indeed in this section all the parameters discussed earlier such as water resolution, viscosity shall be considered with this decolorized crude oil in addition to droplet sizes, therefore the experimental results of decolorized crude oil-in-water emulsions and their microscopic generated pictures are shown in the next paragraphs.

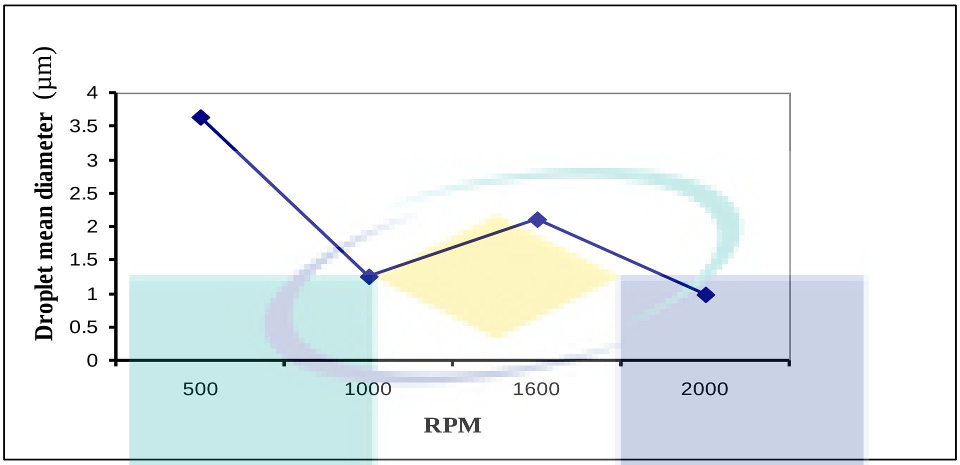

Figure 4.15: Droplets diameters vs. rpm for 50-50% (w/o) decolorized Kuwait crude oil emulsions

In the previous figure; the effects of the mixing speeds (rpm) on the droplet sizes was depicted; the mean droplet diameter vs. rpm was plotted, and it was observed that the droplets' diameter is reduced with increasing rpm, this evident from the fact that increasing the mechanical energy will hammer the larger droplets and render them fragmented into smaller ones (Gonglun Chen et al., 2005), and that may influences the surface area of the interface and drop-drop interaction which will lead to increase in emulsion viscosity as shown in the next figure 4.17; when viscosity is plotted against rpm.

The picture of figure 4.16; are the microscopic picture of the decolorized oil emulsion prepared at different rpm and denoted a, b, c, and d for 500, 1000, 1600,2000 rpm respectively, it's clear at lowermost rpm of 500,the droplets are more or less uniform and distributed far away from each other and not really seemed to aggregate, or coalesce, in the vicinity of each droplets there exists some black films around each droplet that may be either the surfactant molecules or the solid and metal components that exists naturally in the crude oil, Since it is well known that; minerals, metals and clays are opaque and cannot transmit any light so if they were to exist in this system they could have been dark or black and they does as expected.

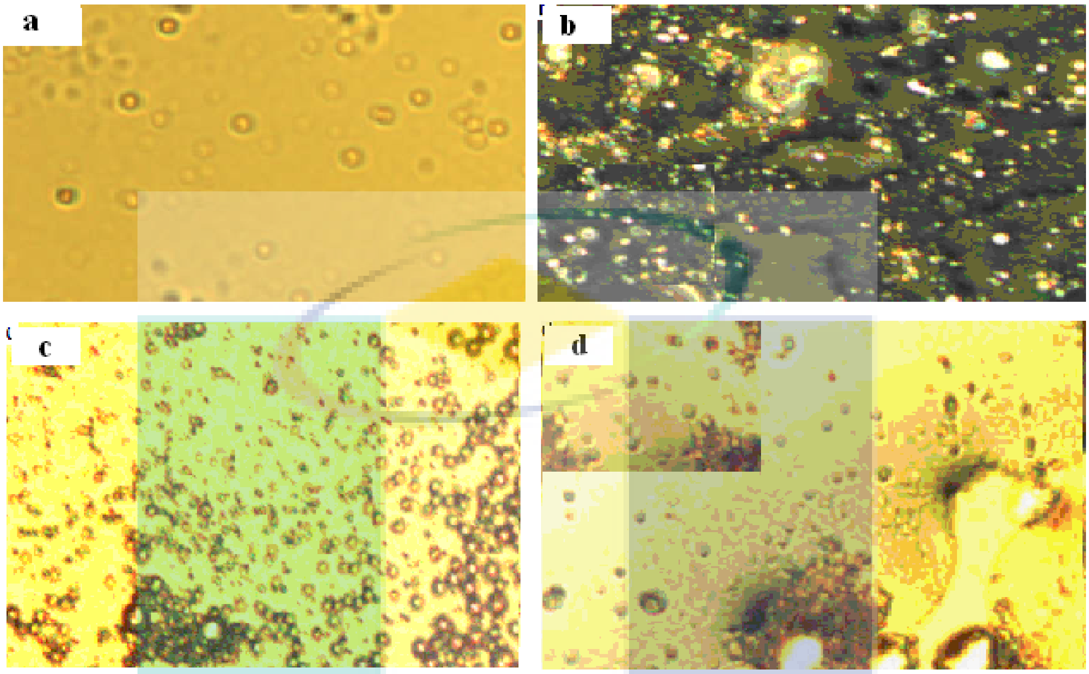

Figure 4.16: Mean droplet diameter as a function of rpm, a-500, b-1000, c-1600, d-2000

From the figure 4.16; above the effects are clear now, partitions, a, b, c, and d, represents the emulsions produced with various mixing speeds of 500, 1000, 1600, and 2000 respectively, here even the inter-particle distance also apparent more or less, thus at mixing speed of 500 the droplets are bigger in size, and easily collided as they appeared in the forms agglomerate and most of the droplets are easily disappeared evidencing the unstable behavior of the emulsion at this particular rpm (500).

Another observation is that the emulsion type which is clearly water in oil emulsion consisting of continuous oil phases appeared yellow-brownish and water droplets dispersed on it.

when the mixing speed was increased to 1000 rpm for the same emulsion (all the other parameters other than mixing speed are fixed constant), the emulsion morphology has totally changed compared when it was at rpm 500 refer to the figure above compartment (b), the droplet has reduced to a very small the quantitative changes of the droplets from RPM 500 to 1000 can be observed from the graph of droplets sizes Vs. RPM, and emulsion appeared to be mostly like multiple emulsion and the distribution of the droplets is not uniform, as the mixing speed is increased further to 1600 there the morphology return back as when it was at rpm 500, but the droplets are more smaller and appeared as nicely shaped spheres see the compartment (c) of the figure 4.16 and some areas like they turning to a very small sized spheres, and finally when the rpm is increased further to 1800, the morphology was the constant the spheres were uniform and small but their quantity has reduced a situation that could explained by the fact that this vigorous mixing may have reduced the droplet sizes into even more smaller and turned the emulsion into non-emulsion instead with Nano-sized droplets that could be seen even in the microscope whose scales are in micro size.

In most parts of the compartment (d) picture are just like single phase was shown, thus from the author’s perspective, the emulsion prepare via mixing speed (rpm) of 1000 and 1800 are very stable and have similar character to micro-emulsion which not frequently encountered in crude oil applications while emulsions prepared from with 500 and 1600 rpm were more or less close to macro-emulsions that is normally encountered in crude oil industries, to ensure the effect of rpm on emulsion stability; the viscosity values were plotted as functions of rpm and the effect was clear from figure 4.17 which shows the increase of viscosity with increasing rpm, these viscosity values on the tells that the current produced via all the rpm’s was in the meta stable emulsion categories, since their viscosity is more than two times the starting oil viscosity which was 161.8 cp for undecolorized Kuwait oil.

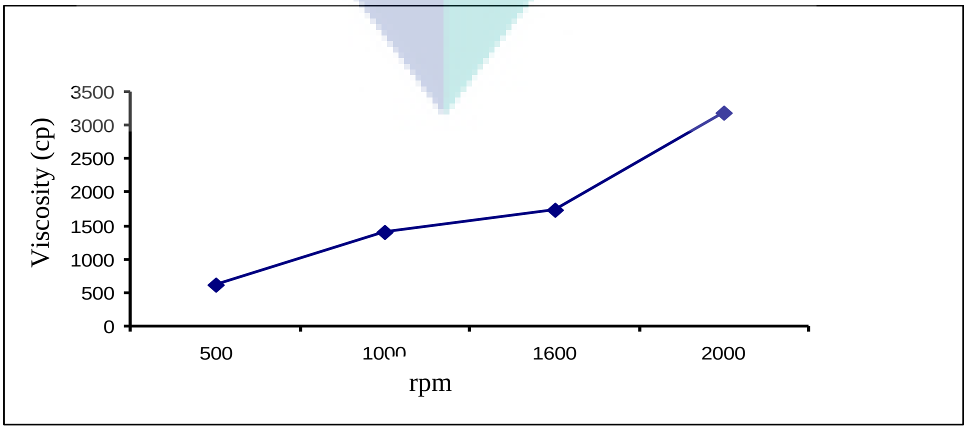

Figure 4.17: Effects of rpm on emulsion viscosity

Some additional observation in this figure is that, from rpm 500 to 1000 the viscosity was found to increase linearly, then after that from rpm 1000 to 1600 the increasing rate was slow see the figure then from rpm 1000 to 1800 the viscosity increasing rate was sharp indication finite droplets sizes leading to high viscosity. Beside that in order to relate all the parameters that affect the emulsion stability a plot of mixing speed (rpm) vs. percentage of water separation was produced reader can refer to the next coming plot.

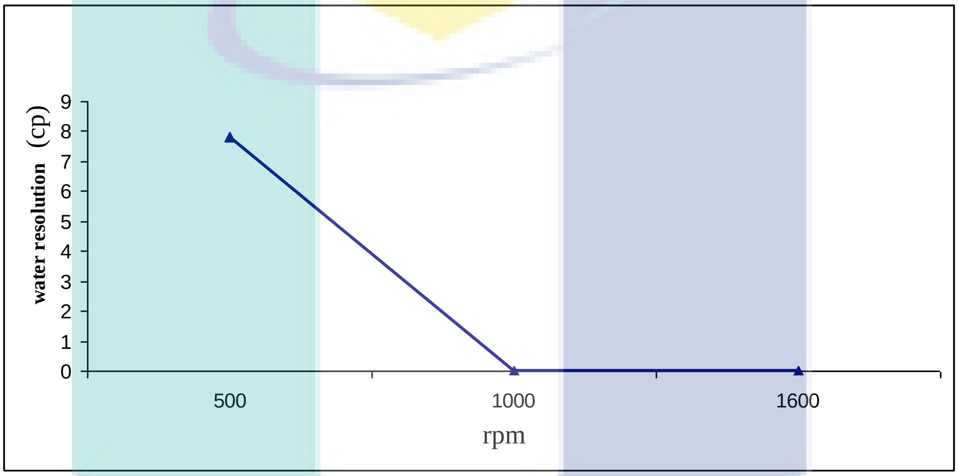

Figure 4.18: Effects of rpm on water resolution

In figure 4.18 the water resolution from the same 50-50% water-in-decolorized oil emulsions were investigated, the testing period was 10 hours with half an hour interval of reading, so if the separation is considered as a parameter, then only 500 rpm produced emulsion lost some amount of its water, the rest were all stable with zero water separation and was expected ever since its droplet sizes and viscosity was analyzed and this lead to draw some conclusions regarding this particular case.

In correlating the droplet sizes to the viscosity of prepared emulsion by observing the graphs in figures 4.15 and 4.17 where the same rpm is plotted vs. the emulsion droplet sizes and viscosity respectively, at high droplet sizes of around 3.6 µm (low rpm) emulsion was found to be less viscous of around 600 cp, then increased to around 1700 cp as the droplets reduced to ≈ 2 µm, then further increasd to ≈3000 cp when the droplet diameter was reduced to ≈ 1 µm wherein emulsion was looked very thick. From this result; obviously there is a direct correlation between and dependence of emulsion viscosity on droplets diameter which in tern directly related to the stirring intensity all this will straighten the droplets to withstand again coalescence and eventually promote emulsion stability as evidenced by figure of water resolution which show the percentage of water resolution from the aforementioned emulsion as a function of rpm, Knowing the reading was taken for every half an hour interval for 10 hours successively. the result was in accordance with the researcher expectation which is; at low rpm the was water separation means less stable emulsion was produced then decreased to zero as the stirring intensity increased, finally the conclusion is that; the higher the rpm; the smaller the droplets sizes and the higher the viscosity and stronger the stability, next the effect of temperature on the same aforementioned parameters would thoroughly delineated.

4.6.2 Effect of temperature on decolorized emulsion stability

Usually the liquid viscosity as well as interfacial tension decrease with increasing temperature, and this was shown previously just in here the effect of temperature on droplets deformation, droplets aggregation and droplet coalescence was aimed to be observed qualitatively by means of crude oil decolorization and microscope with analysis tools, the result shall be shown in figures to come:

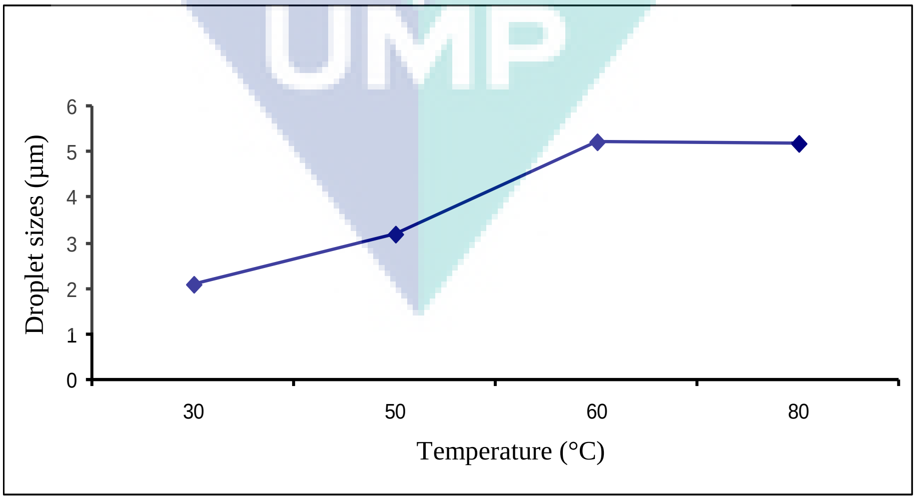

Figure 4.19: Effects of temperature on droplet sizes

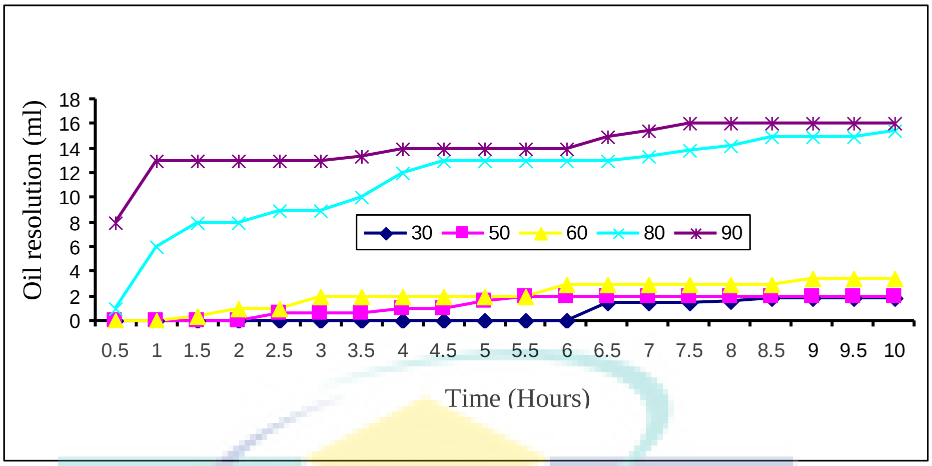

Figure 4.20: Effect of temperature on water resolution

The effect of processing temperature on emulsion stability was experimentally tested as depicted by the curve in the last three Figures (4.19, 4.20, and 4.21); for water resolution measurement; emulsion was field in a measuring cylinder and the amount of water settled or oil floated was measured as time goes on, reading was taken for each half an hour interval for 10 hours successively at different emulsification temperatures which was varied from 30-90 °C, all the other parameters are fixed as the previous emulsion (rpm, 1600 and span 80, 0.5).

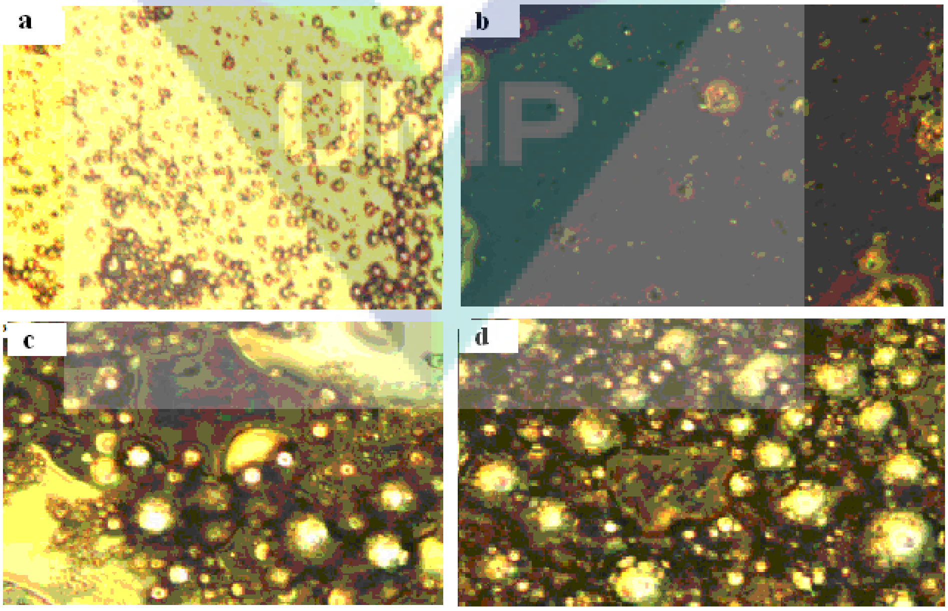

Figure 4.21: Pictures of Effects of temperature on droplet sizes

From the observation the effect of emulsification temperature (EMT) on emulsion stability was apparently pronounced and there was a direct correlation between the temperature and emulsion stability evaluated by both droplet mean diameter measurement and oil resolution (Figures 4.19 and 4.20), from Figure 4.20 the maximum oil resolution after 10 hours of settling was 1.8, 2, 3.4, 15.4 and 16% at their respective EMT of 30,50,60,80 and 90 °C.

Another interesting observation is that at the lowest temperature of 30 °C emulsion was very stable with no oil resolution for the first 6 hours then started to separate, while all other emulsions, started to separate at earlier time, for example; 50 and 60 °C emulsions started to resolve at 2 and 1 hours respectively, furthermore; 80 and 90 °C emulsions started to resolve within the first 30 minutes, and that might be due to the viscoelastic pattern of the emulsion and viscosity reduction with elevated temperature may be the main reason, these results were supported by the results plotted in Figure 4.19 as the variation of mean droplet sizes as a function of temperature is plotted, at lower temperature of 30 °C; the droplet sizes were relatively small around 2 micron meter.

The current emulsion was survived against coalescence for quite long time presumably 6 hours, but as temperature increased the droplet behavior has dramatically changed and more bigger droplets are produced accompanied with drastic reduction in emulsion viscosity which caused rapid coalescence to occur, and that was evidenced by emulsion picture snapped at different EMT in Figure 4.21 (a-d) which showed the evolution of emulsions ‘droplets as EMT increases this pattern could be considered in such way as just opposed to the trend observed previously in Figure 4.16 (a-d). However, Figure 4.21 (a-d) represents the morphology of emulsion at different E.M.T., the results were in accordance with the researcher’s hypothesis and some other previous work as well, at low temperatures of 30 and 50 °C, the droplets were relatively small in sizes and scattered uniformly with minor agglomeration, but as EMT increases to 60 °C; more bigger droplet are produced.

furthermore at 80 °C; even more bigger drops are produced and the agglomerated and partially coalesced droplets could be clearly visible refer to Figure 5c, the reason behind this behavior is that, as temperature increases; the emulsion viscosity is reduced and the internal energy of the molecules increased and that may increase the pressure required to induce the interfacial film thinning, drainage, rapture and eventually reduces the coalescence time and ultimately leads to emulsion resolution.

Thus far it is reasonable to some conclusion about the effect of EMT on emulsion stability, the optimal EMT of water-in-crude oil emulsion stabilized by (SM) emulsifiers lies between 30-50 °C and this was in accordance with findings from previous researchers namely: Rusli and coworkers have reported the optimal EMT to prepare Liquid Natural Rubber emulsion is between 28-70 °C with respect to some fixed parameters, others have carried out an experimental investigation on coal-oil-water slurry and believed the optimal EMT was 30 °C.

Abdurahman and coworkers have performed excessive experiments on EMT and concluded that elevated temperature will alter the interfacial tension, affects the adsorption of emulsifiers, reduces its viscosity and affect the vapor pressure of the liquid phase; hence emulsion stability mostly decreases with increasing temperature.

4.7 Effect of surfactant concentration

Surfactant existence is one of the most influential factors in emulsification, however; their types and dosage are also claimed to crucial from efficiency and economical points of view respectively, hence low concentration and high efficiency and preferential, and therefore experimental data was presented in Figure 4.22; to find out the best concentration of (SM) emulsifiers that needed to prepare water-in-crude oil emulsion Knowing most of the previous researchers have done their investigation either in different condition or in model emulsion which will help to be considered in this study, however in Figure 4.22.

Four different concentrations of surfactants molecules were used namely (0.1, 0.125, 0.25 and 0.5), emulsion stability was evaluated by measuring the percentage of water or oil resolution as a function of time, and readings were taken every half an hours for 10 hours successively. From the graph; it is clear that emulsion stability was increased as emulsifiers' concentration was increased; the most stable emulsion was encountered at 0.5% concentration, at medium concentration of 0.25 the emulsion still could considered stable since the total water resolution after ten hours still less than 10% of total content of the emulsion, on the contrary at low concentration of 0.15 and 0.1%; emulsions were not stable and started to separate into two and even three in some cases immediately, and that is due to low emulsifiers' concentration in which the droplet could not be fully encapsulated therefore agglomeration and coalescence will take place easily. The reverse will hold true for high concentration, similar results were reported by authors in (Gonglun Chen et al., 2005, EL-Hamouz A. 2009).

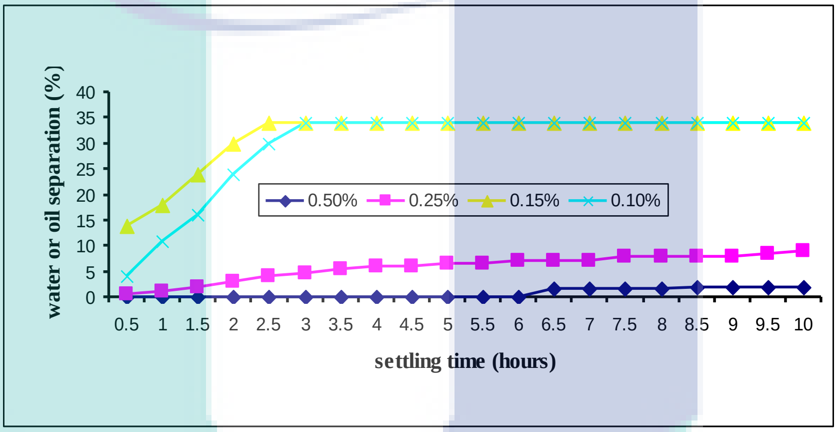

Figure 4.22 : Effects of emulsifiers' concentration on emulsion stability

4.8 Conclusions

Laboratory tests have shown that optical microscopic can be an effective tool for characterization of W/O emulsions. This study demonstrated the effects of impeller speed, E.M.T., and surfactant concentrations on droplets size, viscosity and stability of W/O emulsions. The optimal impeller speed was found to be in the range 1600-2000 rpm, EMT was 30 °C, while emulsifier's concentration was 0.5%, therefore these parameters would be maintained to produce the emulsion that is desired to be used in this study.

4.9 Demulisification

This section reports and discusses the experimental results carried out to meet the objectives of the current research, hence this chapter consists of Three main parts, that are Microwave-chemical assisted demulisification, and Ultrasonic-chemical assisted demulsification, as well as chemical demulsification that would be iteratively applied to several petroleum based emulsions from different production regions of the world then a qualitative comparison between the aformrntioned techniques was carried out. Microwave demulsification would be tackled first, and main investigated parameters of volume rate of heat generation, dielectric constant, dielectric loss, loss tangent, temperature distribution and microwave exposure time were discussed. Based on the results, optimal demulsification parameters such as microwave exposure time, temperature distribution, and heating rate of temperature increase for microwave demulsification were specified.

4.9.1 Working equation for Microwave Demulsification Study

Using microwaves as a source of heat in the processing (heating, melting, drying, and thawing) of materials is advantageous because it results in faster, and more uniform heating than conventional heating do. This study focus on the application of microwave in demulsifying water-in-crude oil emulsions. Since microwave heats materials volumetrically, it is possible to calculate the volume rate of microwave heat generation from energy balance equation as:

$$q_{MW} = \frac{hA}{V}(T_m - T_a) + \frac{\varepsilon A \sigma}{V}\left[(T_m + 273.15)^4 - (T_a + 273.15)^4\right] + \rho C_P \left(\frac{dT}{dt}\right) \qquad (4.1)$$

Where q_{MW} : Volume rate of heat Generation

h : Convective heat transfer coefficient

V : Volume of water separa$\boldsymbol{\rho}$ted

A :Sample Container area

$T_{m:}$: Temperature of emulsion
T_a : Ambient Temperature
ε : Emissivity of Surface
σ : Stafan-Boltzman constant
Cp : Heat capacity of emulsion
dT/dt: Rate of Temperature increase

Equation 4.1 assume that the rate of heat transfer from emulsified water droplets to continuous phase (oil) is very fast and rapid; therefore, water and oil practically have the same temperature (Fang et al. 1995). The right hand side of Equation 4.1 comprises of three terms, convective heat transfer, radiative heat due to microwave and conductive heat in the sample respectively. From result of experimental data, the effect of radiative heat and convective heat are very small. Since the sample container (glass) has low dielectric constant, therefore, its heat generation is assumed to be negligible. Therefore, the rate of temperature rise would be given by:

$$\frac{dT}{dt} = \frac{q_{MW}}{\rho C_P} \tag{4.2}$$

As shown in equation 4.2 the temperature rise is linear since q_{MW} is a constant, depending on the electric field at the location. For calculation of the volume rate of heat generation in equation 5.1 the density (ρ) and the heat capacity (C_P) of the emulsion can be calculated from the mixing rules as:

$$\rho_m = \rho_w \Phi + \rho_o (1-\Phi) \tag{4.3}$$

And

$$C_{Pm} = C_{Pw}\Phi + Cpo(1-\Phi) \tag{4.4}$$

Where σ_m : Density of emulsion

Φ : Volume fractions of water

σ_o : Density of oil

σ_W : Density of water

Considering that emulsion is heterogeneous mixture of water and oil, and heat is generated separately in the suspended phase (water droplet) and continuous phase (oil), Equation 4.3 can be applied separately for water and oil with individual attenuation factors. The total volume rate of heat generation of emulsion to be used in Equation 4.3 is given by:

$$q_{MW} = q_{MW,w} * \phi + q_{MW,o}(1-\phi) \tag{4.5}$$

The dielectric constant and dielectric loss of water used for the model in this study was given by wolf, (Wolf. 1986)

$$\varepsilon'_{r'w} = 85.215 - 0.33583T \tag{4.6}$$

$$\varepsilon''_{r'w} = 320.658\,T^{-1.0268} \tag{4.7}$$

Where ε' : Dielectric constant of water

ε'' : Dielectric loss of water

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

$$\varepsilon'_{r'o} = 2.24 - 0.000727T \tag{4.8}$$

4.9.2 Measurement of Penetration depth and wavelength

Gallawa (1989) reported that, there is a direct relationship between the frequency and the wavelength. There is also a relationship between the frequency and the degree, or speed of heating, as well as the depth of penetration. The wavelength (which is the distance between positive peaks or negative peaks of two adjacent waves) is equal to the speed of light divided by the frequency. For practical purposes, the speed of light does not change. Therefore, the only two variables in equation are the frequency and the wavelength, their relationship as follows:

$$\lambda_m = \frac{c}{f} \tag{4.9}$$

Where: λ_m (m) is wavelength, c (ms^{-1}) is speed of light, and f is frequency (Hz).

The above relation indicates, the higher the frequency, the proportionately shorter the wavelength, and the lower the frequency, the proportionately longer the wavelength. This is an inverse relation.

Tanmay (2004) related the microwave penetration depth D_p and wavelength of radiation in the medium λ_m to dielectric constant ε'_r and dielectric loss (loss factor) ε''_r in the following manner.

$$D_p = \frac{c}{\sqrt{2} * \pi * f \left[\varepsilon'_r \left(\sqrt{1 + \left(\frac{\varepsilon''_r}{\varepsilon'_r} \right)^2} - 1 \right) \right]^{1/2}} \tag{4.10}$$

And

$$\lambda_m = \frac{c\sqrt{2}}{f\left[\varepsilon'_r\left(\sqrt{1+\left(\frac{\varepsilon''_r}{\varepsilon'_r}\right)^2}+1\right)\right]^{1/2}} \tag{4.11}$$

The two most common techniques for dielectric properties measurements are the resonant cavity, or cavity perturbation method, and the transmission and reflection method.

4.9.3 Experimental result for Microwave heating

Samples of water-in-oil emulsions were prepared with different ratio as described in chapter 3. In this study the microwave power level was fixed at the maximum of 800 watt and considered as a constant parameter, then irradiation time is other crucial parameter was varied additional parameter was the types of crude oils used in this study and the water content of the emulsions which was specified as 50% to represent the high water content emulsions and 20% to represent the low water content emulsions, the power was fixed at 800 watt because there had some modification on the system (Microwave), to overcome some splashing and uncertain heating that normally encountered at high power level, the modified system had been seen in chapter 3.

a) The Temperature Profiles of the individual components

At the beginning of the microwave heating; the heating properties of the pure components (water and crude oils) were carried out before embarking on the emulsions.

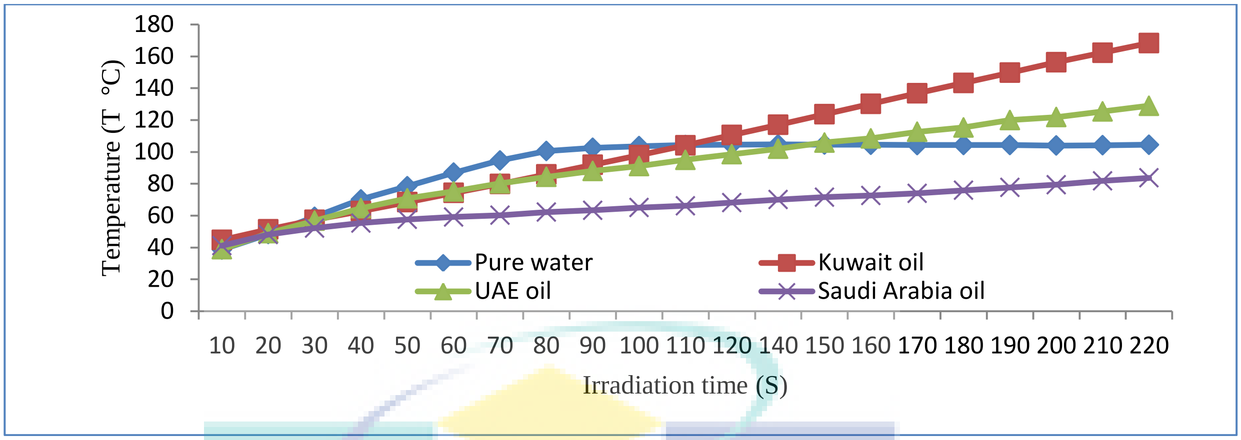

Figure 4.23: Heating of pure water and pure oils at 800 Watt for 3.5 minutes

Figure 4.23 depicts experimental data of the pure components of the emulsion; this was to give some references or control values to get some green lines or quantitative values of the individual components of the mixture, as it's clear from the Figure 4.23, in all cases initially within the first 20 seconds; all components had a similar temperature of more or less 50 °C and gradually the temperature trend for each component taken several paths, thus water had the path with the maximum values of temperature compared to the others within the interval from 20 seconds until 90 seconds, in that interval; the trend is in accordance with the theory which consider water as more polar than hydrocarbons (oil) and supposed to absorb and generate more energy from the incident electromagnetic wave that could be evidenced by the increase of the temperature(Alvin et al.,2009).

however at 90 seconds, the temperature reached a plateau at around 100 °C and remained constant till the end of the irradiation period of 210 seconds, that plateau could be attributed to the fact that the dielectric properties (would be discussed latter on) which responsible of converting the electromagnetic wave into energy reduce with increasing temperature, note that an increase in irradiation time will increase the sample temperature. . Indeed Kuwait and UAE oils that had to some extend equivalent trend evidenced by the overlap of their two curves within the irradiation period between 20 s to 80 s, they also appeared to be the components with the second highest temperature path in this particular interval, but after that interval or after 80 s was elapsed; the path of the Kuwait oil had increased even more and intersect with water path at 105 °C, after that it exceeded the water path, and continued sharply to170 °C at the end of the irradiation time, this in a direct disagreement with the electromagnetic theory which strongly relates microwave heating with polarity and conductivity, however authors attributed this strange thermal behavior of the Kuwait crude oil under the microwave heating to the existence of some ionic elements or fatty acids within the crude oils.

UAE oil had taken another path with a bit lower temperature than Kuwait oil and intersected with water curve at 145s, then exceeded the water path and reached around 120 °C at the end of the irradiation time, finally Saudi Arabian crude oil was observed to have the lowest thermal properties with a maximum temperature of around 80 °C' , this is some how in accordance with the electromagnetic theory, during the whole irradiation time of 220 seconds, thus in summary one can say Kuwait oil has the maximum thermal capacity followed by UAE oil, water then Saudi Arabian crude oil.

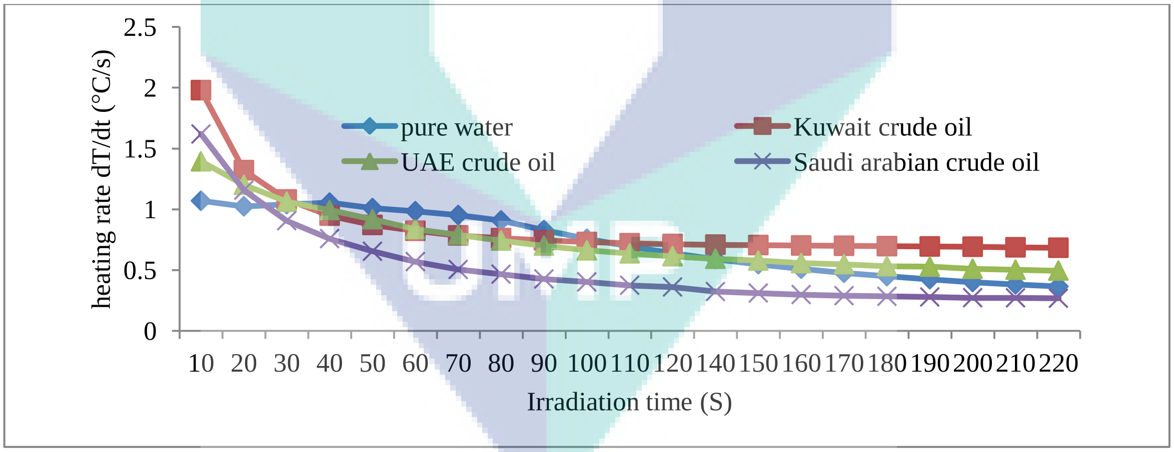

Figure 4.24: Heating rates of the pure components at 800 Watt and 3.5 minutes

Figure 4.24 represents the heating rates of the same individual components, and shows the temperature increases with time, and that would give a clear idea on how materials would responds to microwave and the wave absorption and heat generation varies with time, since it's well known that microwave is energy conversion and materials absorb microwave energy by two mechanisms of ionic conduction and dipole rotation that depends strongly on the temperature of the sample, polarity of the sample as well as conductivity of the sample, hence in the current experimental observations, in contrast to what had been seen with temperature vs. time curve every component have different initial rate of temperature increase, although it reduces very fast in first and after 30 s of radiation all of them would converge at heating rate of around 1.2 °C /s and from that convergence point as it can be seen from the figure; the heating rate of water had exceeded the others, hence the heating rate of the Kuwait and UAE oils was observed to decrease after they have converged with the water curve, at a values that is a bit lower than the that of the convergence values, regarding the Saudi Arabian crude oils the heating rate was drastically decreased with regard to the other components.

Regarding the water again; the heating had reached a second maximum of around 1.2 ^{0}C/s, after which it started to decrease until it crosses the curves of both Kuwait and UAE oils which have had reached a plateau at around 0.8 and 0.5 °C /s respectively but it has not reached the Saudi Arabian crude oil whose plateau was at around 0.4 °C /s, Generally it’s clear from this experimental results that, crude oil from Kuwait had ended up having the maximum heating rate at the beginning of the process (at low temperature) and at the end of the process (at high temperature), followed by the crude oil from Saudi Arabia which had the second highest heating rate at the beginning at beginning and the lowest heating rate at medium and high temperature, bearing in mind that the irradiation temperature range was (0-3.5 minutes).

UAE crude oil has medium heating rate based on this experiment at the beginning at low temperature and medium as well as at high temperature, and finally water had the lowest heating rate at low temperature and have the highest at medium temperature and medium heating rate at high temperature, however these results were not in accordance with the literature according to which water should have had the maximum heating rate over all types of oil and that is because first, water is a polar molecules with permanent dipoles and secondly it has higher dielectric properties than the non-polar hydrocarbon oils, however this contradiction may be as a result of the fact that crude oils are mixture of thousands of component including charges carrying components including fatty acids, heavy metals such as Sulfurs and other Asphaltene composing of heavy metals such as Vanadium nickel and nitrogen components all of these may have contributed synergistically and gave the current unusual results, however most of the previous articles claimed that water would have higher heating rate than crude oils but the current experimental work showed the opposed, but in some cases yes it does for example the case of the crude Saudi Arabia; it does have lower heating rate and also lower temperature than water.

Now the heating properties and character of the individual component have been shown, in the next upcoming couples of sections, thus massive discussions would take place to delineate the major factors and parameters behind the microwave heating of different type emulsions including water-in-crude oil emulsions prepared from different crude oils that had just being discussed, together with some other industrial emulsions including Slop oil emulsions and waste coolant.

b) The Volumetric rate of heat generation of the individual components

Basically materials absorb microwave energy through by the dielectric properties and that is the reason why some time microwavic material processing is referred to energy conversion instead of heat transfer, since microwave also does not obey the common rule of conventional heating in which heat is transferred either through conduction or convection from the high temperature location to lower temperature location, thus its important for an investigator to have some rough idea on how the heat is generated within the volume of the sample as the irradiation goes on, together with the dielectric properties of the component which are a function of temperature.

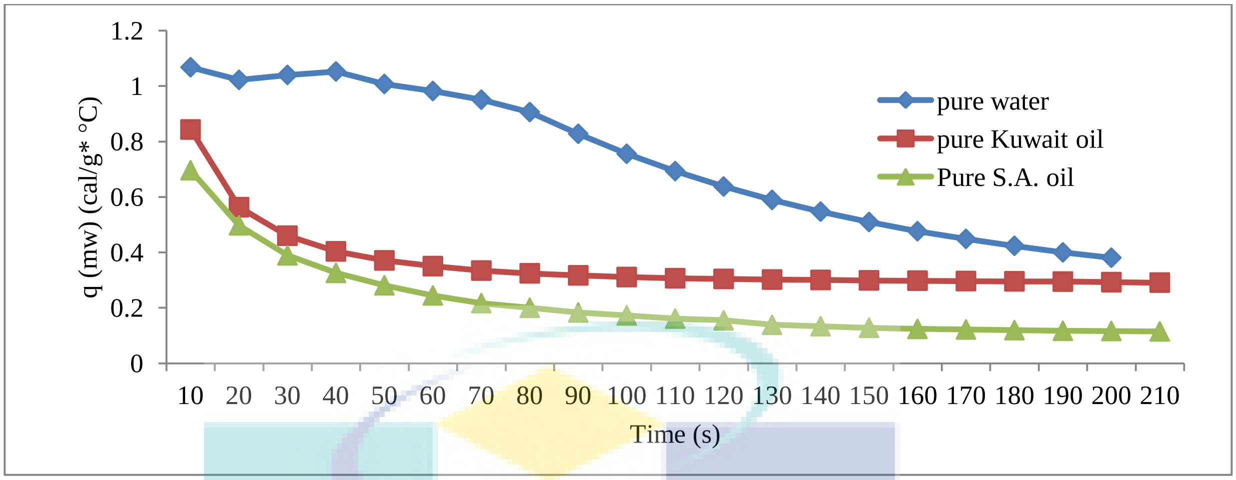

Figure 4.25: The volumetric rate of heat generation of the singles phases at 800 watt for 3.5 minutes

Figure 4.25 represents the experimental results of the volume rate of heat generation of different materials at their single phase states via microwave energy, the values of volumetric heat generation was calculated by inserting the temperature data in equation 4.2, indeed the term ρC of the system was determined using equations 4.3 and 4.4, hence figure 5.3 depicted the data of the pure substance at their single phase states namely pure water, pure Kuwait oil and pure S.A. oil, at the beginning of the irradiation specifically within the first 10 seconds all materials were found to have the highest capacity to generate heat from the incident electromagnetic waves, then in the subsequent period two distinct trends were observed, in one of which the volumetric heat generation of the crude oils were found to decrease with increasing the irradiation time until they reached after 60 seconds were elapsed, despite that Kuwait crude oil was found to have high capability to generate more heat than Saudi Arabia oil, form the same figure; the curve of the Kuwait crude oil was started at 0.8 cal/g*°C, and reached plateau at 0.4 cal/g*°C ,while that of the Saudi Arabia had started at around 0.7 cal/g*°C and reached plateau at around 0.3 cal/g*°C and that may be due to the elemental composition of each crude as reported earlier in the literature. Secondly; water was found to have different trend that had the highest quantitative values of the volume rate of heat generation over the crude oils this behavior is in accordance with the theory, since water possess high polarity and high dielectric properties as well, another significant information is that the highest values of heat generation in water sample were observed at intermediate irradiation time (from 30s to 100s), unlike the crude oils whose maximum heat generation was observed at the beginning then decreased as the irradiation goes on until the plateau.

c) The Dielectric properties of the individual components

The upcoming Figure 4.26 shows the dielectric properties of same previously discussed single phase components, however the result was found to be in accordance with the theory in the sense that water had the highest dielectric constant and dielectric loss; another significant observation is that all crude oil were shown to possess very little dielectric properties and this rise some ambiguities since it has already seen previously that crude oils are generating heat out of the electromagnetic wave almost in the same fashion as water does. Moreover the temperature raise of the Kuwait crude oil had even exceeded that of the water (refer to Figure 4.26 and 4.27) this is to some how in contradiction with the general rule of thumb of the electromagnetic

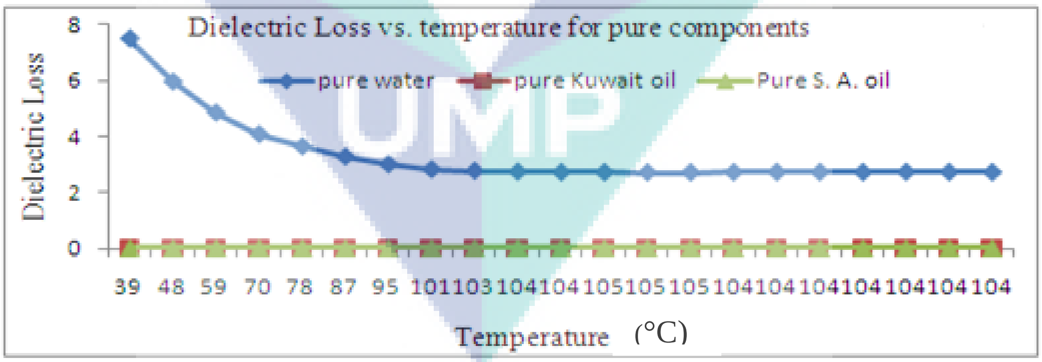

Figure 4.26: Dielectric Loss of the pure components,

theory where only the dielectric materials can absorb the incident wave and convert them to heat, however researcher attributed this to the fact that, crude oils naturally consists of thousands of component among of which some charge carrying elements or ions that could align and rearrange or even move Within the sample as a response to the incident wave, then this movement would lead to energy generation that is evidenced by the rise in sample temperature, no much research have been done thus far on how the trace elements on the crude oil could contribute to the heating process other than the well known fact that microwave does not penetrate the opaque materials although dimethyl-siloxane which is used as a demulsifiers would be delineated in later sections.

Avijid and coworker have investigated the thermal profile of some mineral like porous metals and postulated that electrically conducting minerals does penetrate microwave power but their penetration is just limited to their skin depth which is a function of material permittivity, conductivity and angular frequency (Avijid et al., 2009), they also concluded that smaller particle size correspond to high heating rate for powder of that materials, more specifically Kappe (2005), and Ruren (2007), were quoted by A.D. Mohammed and coworkers postulating that conductivity principle which defined as the migration of ions as a results of the incident electromagnetic field, is much more stronger than the other effect of the dipole rotation and thus systems containing ions are heated more rapidly and efficiently than the that polar solvent, even though it depends on ion concentration in the system.

d) Wavelength and penetration depth of the individual components

This section would elaborate about the behavior of the electromagnetic wave itself when it penetrates through materials, in terms of wavelength and penetration depths.

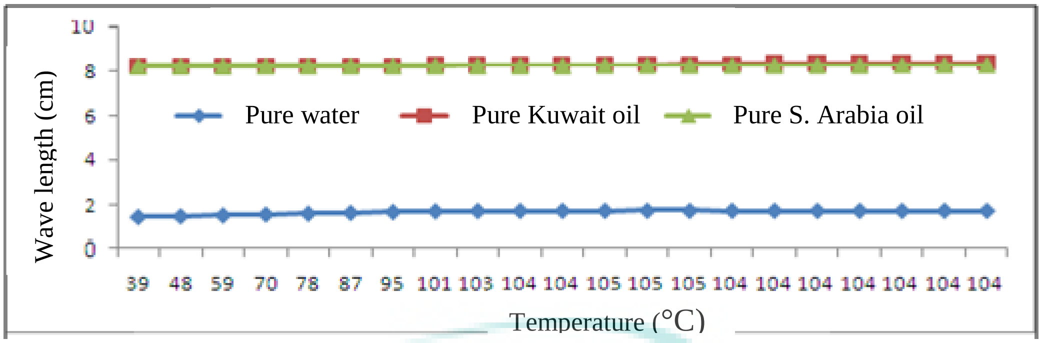

Figure 4.27: wave length of the pure components, (0.05 and 0.1% are the concentration of the demulsifiers used)

Figure 4.27 represents the wavelength of microwave power on the pure components respectively, from experimental data depicted in the figure it was clear that microwave had a very short wave length water hence the wave length was around 1.7 cm and 8 cm for water and crude oils respectively, this means there must be some dissipation of microwave in another word the electromagnetic waves are dissipated in the medium, absorbed and converted to energy while its passing through the emulsion, and that was clearly evidenced by the increase in the sample temperature as the irradiation goes on, and that is due to the ion mobility or ionic conduction factor were mentioned in earlier section of this study equation 4.10.

4.9.4 Thermal properties and energy generation of emulsions

The proceeding section had discussed experimentally the basic mechanisms of microwave-material interaction to gain some fundamental ideas on how the individual components of this study (Pure water and pure crude oils) could interact or respond to the incident electromagnetic energy and how does that effect to rise their temperature.

I. The Temperature Profiles of Water-crude oil emulsions

However, no much shall be added in the proceeding couple of paragraphs other than just observing the same previously discussed parameter namely temperature profiles, heating rates, volumetric heat generation and so forth, for various types of water-in-crude oil emulsions.

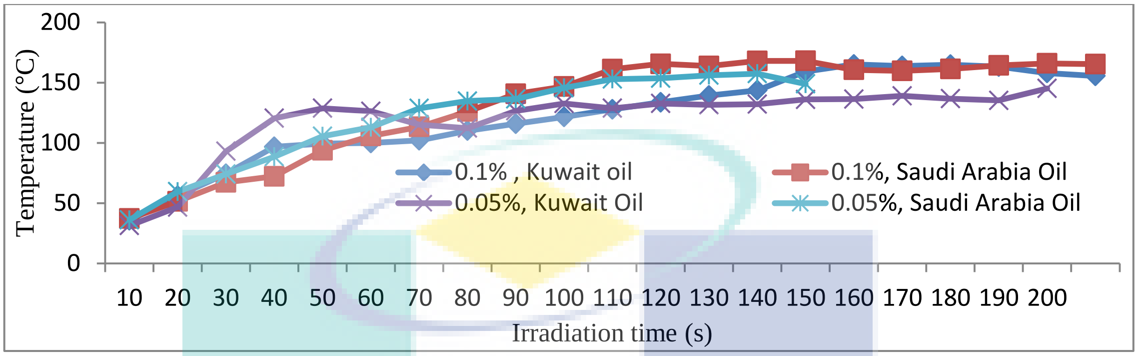

Figure 4.28: Temperature profiles of 50-50% w/o emulsions containing 0.1and 0.05% demulsifiers at 800 watt for 3.5 minutes the numbers 0.05 and 0.1% are the concentration of the demulsifiers used)

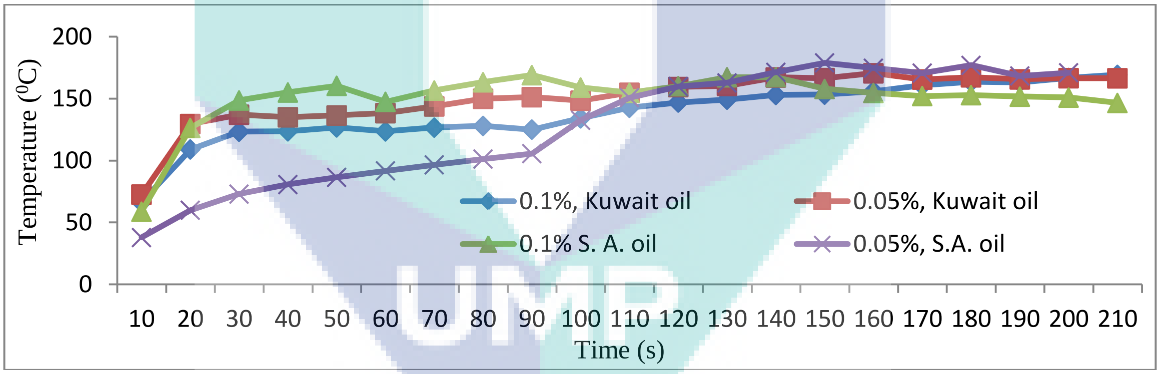

Figure 4.29: Temperature profiles of 20-80% w/o emulsions containing 0.1 and 0.05% demulsifiers at 800 watt for 3.5 minutes (the numbers 0.05 and 0.1% are the concentration of the demulsifiers used)

Figure 4.28 and 4.29 reveal the data of the temperature profiles obtained in this study for two different crude oils that are originally from Middle East as shown figure 4.29, note that water content of the emulsion is considered as parameter of study and hence figure 4.28 represent high water cut of 50-50% w/o emulsion and Figure 4.29 represent the low water cut of 20-80% w/o emulsions, then as mentioned in the scope of this study; certain other specific parameters such as oil types, and demulsifiers' concentration on the temperature profile of the emulsions at fixed irradiation time would be discussed particularly on each figure. This is to gain some ideas on how and at what temperature the sample is being heated indeed this experimental values of the temperature profiles would be used latter on in the modeling of system to determine the volumetric heat generation of each system as well as the wave characteristics on the sample including dielectric properties. On the first hand concerning the demulsifiers (Poly-dimethyl-siloxane) effect on 50-50% w/o emulsions (Figure 4.28).

At the beginning of the microwave irradiation all emulsions had the same values of temperature which is to some how close to the ambient temperature, but it raised very rapidly to around 50 °C in just 20 seconds, then within the period from 20 seconds to 50 seconds each component had different trend, thus the curve of the 0.1% demulsified Kuwait oil emulsion and that of the 0.05% demulsified Saudi Arabia crude oil emulsion have had almost similar trend in such a way that their gradual temperature increase as function of irradiation time had almost similar numerical values within this period (20-50 second), hence the temperature increment is ranged from around 35 to more or less 100 °C for within 20 and 50 seconds respectively.

Furthermore; 0.05% demulsified Kuwait oil sample's trend have had even greater temperature of around 140 °C, then 0.1% demulsified Saudi Arabia crude oil emulsion had the trend with the lowest temperature reader may refer to figure 4.28 for more details, then starting from 50 second until the end of the irradiation time, the trends were just opposite to what they were at 50 seconds, generally all curves reached plateaus at various temperature maximum but the difference was not that big for all samples, and maximum temperature of the 50-50% w/o emulsions was found to be more or less 130 °C.

In more details; 0.1% demulsified Kuwait and Saudi Arabia oil had an equal and the highest temperature curve of around 150 °C then followed by 0.05% demulsified Saudi Arabian crude oil having plateau at around 145 °C, then finally 0.05% demulsified Kuwait oil which had its temperature plateau at around 140 °C, as said earlier the difference is not that big but it could be said that heating is enhanced with the addition of more demulsifiers (0.1). On the other hand Figure 4.28 represents the temperature profile of 20-80% w/o emulsions, this time all the parameters had held constant except the water cut of the emulsion, its clear from the figure that water cut does to some how effects the heating process, however the general trends of temperature profile were more or less similar for the two different water cuts and all samples were heated almost in the same fashion, the only strange observation is that at 50-50% w/o emulsion, the 0.05% demulsified Kuwait oil emulsion samples had the highest temperature at the beginning and lower temperature at the end.

Basically the 0.1% demulsified Kuwait oil emulsion sample had the lowest temperature at the beginning and high temperature at the end. But for 20-80% w/o emulsions; the sample of 0.1% demulsified Saudi Arabian oil, had the maximum temperature at the beginning and minimum temperature at the end, reader may refer to Figures 4.28 and 4.29 for more details, but the conclusion is that the effect of demulsifiers in rising the temperature or improve the heating was observed at low water cut, in another word demulsifiers work better at low water cut.

II. Rate of temperature increase of Water-crude oil emulsions

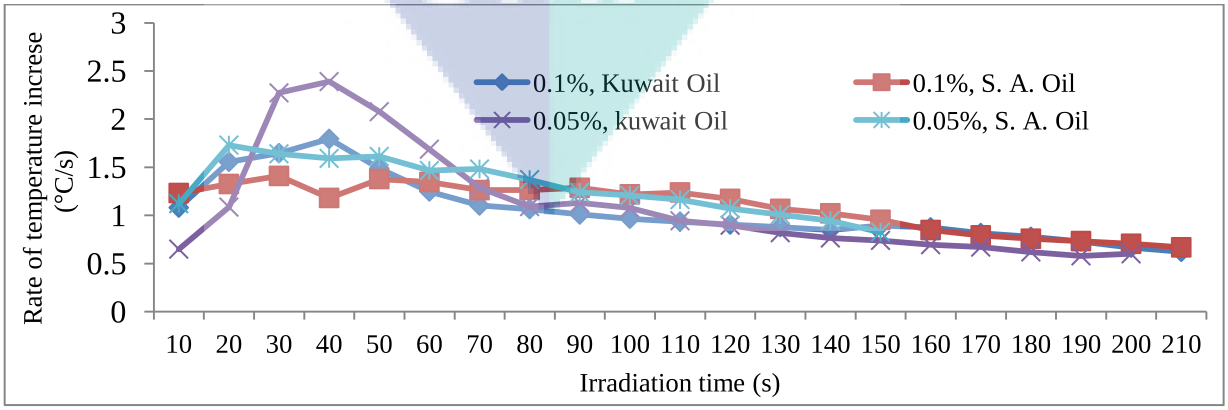

Figure 4.30: Rate of temperature increase vs. irradiation time for 50-50% w/o emulsions (the numbers 0.05 and 0.1% are the concentration of the demulsifiers used)

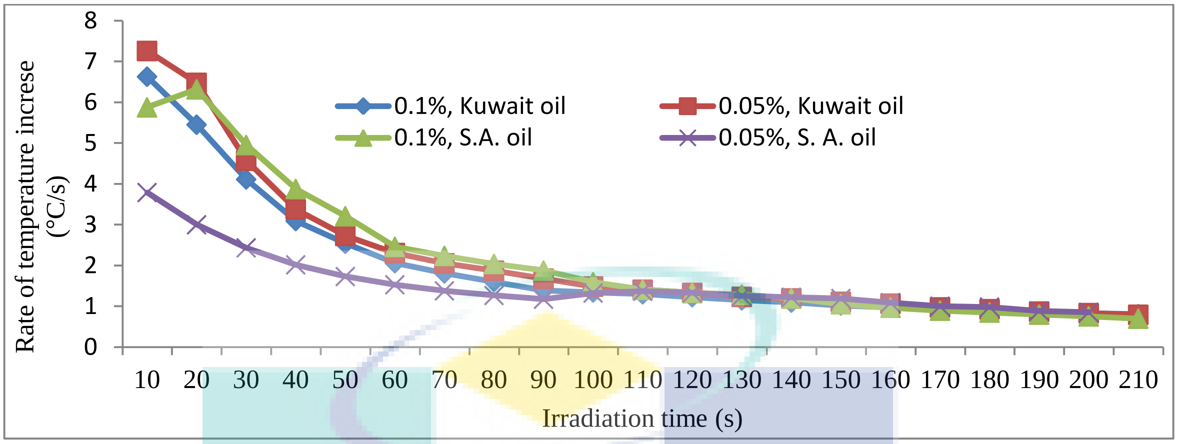

Figure 4.31: Rate of temperature increase vs. irradiation time for 50-50% w/o emulsions (the numbers 0.05 and 0.1% are the concentration of the demulsifiers used)

Figures 4.30 and 4.31 reveal the rate of temperature growth for 50-50% and 20-80% w/o emulsions respectively plotted against the processing time or (irradiation time). With regard to the curves in Figure 4.30, almost all samples seemed to have similar trend, (increase at the beginning to some maximum values then decrease back to some plateaus), the detailed discussion of the temperature rate fluctuation with irradiation time for figure 4.30 could be given by segmenting the course of the curves into three distinct regions according to their behaviors.

Region one is designated to the time interval from (0 to 20 sec), in this interval the temperature rate was almost in linear increment with time, but 0.05% demulsified Kuwait oil had some how lower increment value than the others at the beginning then increased rapidly to the same levels at others,

Region two lies within the time interval starting from 20 to 60 second, in this interval the temperature rate had experienced an increase for some samples and decrease for others, however the critical values were observed in the forms of either concave or convex that happened at 35 sec, where 0.05% demulsified Kuwait oil had the maximum values of 2.4 (°C /s), then followed by that of 0.1% demulsified Kuwait which was 1.8

(°C/s), unfortunately the temperature rate for Saudi Arabia were observed to decrease with temperature in this second interval, hence the minimum values were found to be 1.5 and 1.2 (°C/s), for 0.1 and 0.05% demulsified Saudi Arabia crude oils respectively,

Region three is the interval 60 seconds to the end where all of the curves reach certain steady state values with Saudi Arabia crude oil having the highest values. Indeed Figure 5.9 represents the temperature rate for 20-80%, w/o emulsions; generally the heating rate was much higher than it was for 50-50% w/o emulsion, and also the highest temperature rate was observed in the very first 10 seconds, and it was 7.3 (°C /s), for 0.05% demulsified Kuwait oil samples, this is the sample with the highest temperature rate, in contrast 0.05% demulsified Saudi Arabia emulsion was found to possess the lowest heating rate of 4 (°C /s), this may be due to crude oil composition, then 0.1% demulsified Kuwait and Saudi Arabia crude oils were found to have intermediate heating rates of 6.8 and 5.8 (°C /s), respectively.

III. Volumetric rate of heat generation vs. temperature of Water-crude oil emulsions

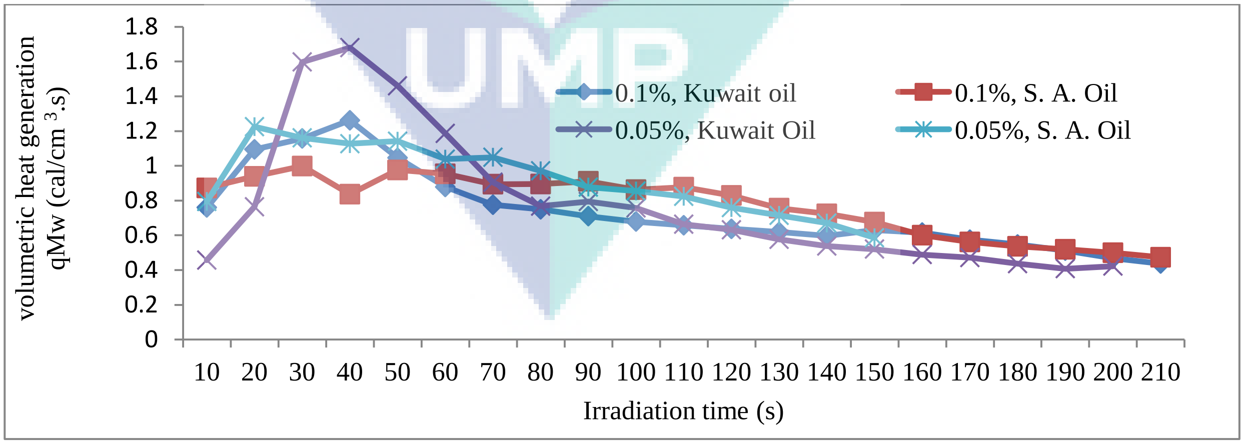

Figure 4.32: Volumetric heat generation vs. time for 50-50% w/o emulsions

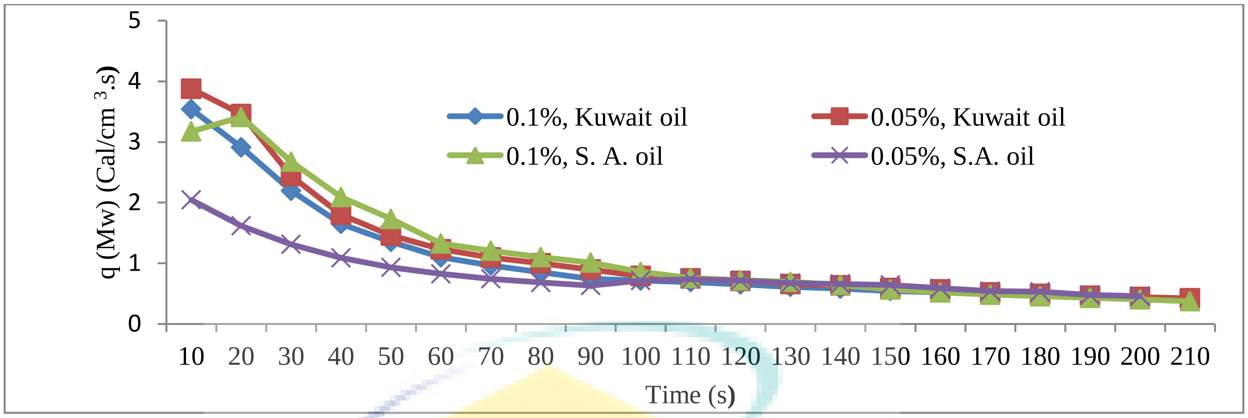

Figure 4.33: Volumetric heat generation vs. irradiation time for 20-80% w/o emulsions

The values of the volumetric rate of heat generation in figure 4.32 and 4.33 were calculated from equation 4.2 where the density and heat capacity of the mixture were determined by equations 4.3 and 4.4 respectively, indeed equation 4.2 is a rearranged version of the general heat transfer equation, but the other terms of conduction, convection and radiation are assumed negligible.

Since microwave heat materials volumetrically and uniformly without temperature gradient, also the system is assumed well mixed therefore the heat distribution within the mixture component is assumed uniform hence there is no temperature gradient or conductive heat transfer within the mixture components, and also the conductive term is dropped because the sample container is transparent to electromagnetic wave and hence it generate no heat, and therefore the temperature rate was the main and varying parameter in calculating the volume rate of heat generation, and that was evidenced by the curves that had an identical trends as that of the temperature rates, the only difference is their numerical values which were a bit smaller reader may refer to figures (4.30, 4.31, 4.32, and 4.33) to check this fact.

Indeed In relating these results (of Figures 4.30 and 4.31, 4.32 and 4.33) to that of their individual component counter parts (of figure 4.24); researcher observed that; the temperature rate and heat generation profiles of 50-50% w/o emulsions had similar profile to pure water profile and that means the heating rate or heat generation of 50-50% w/o emulsion (higher water cut emulsions) was brought about by the influence of the water molecules, or dipole rotation while the heating rate and heat generation profiles of the of 20-80% w/o (low water cut emulsion)s were found to have similar temperature rate profile as the pure oils, that means heating rate in these samples was dominated by the ion mobility and ion concentrations, and heat is generation from the friction resulted when the rapid and random movement of ions is opposed by the viscous bulk fluid.

IV. Dielectric constant vs. temperature of Water-crude oil emulsions

Dielectric constant is defined as the ability of material to accommodate or obstruct microwave energy as it passes through and is regarded as the single mechanism through which the polar and conducting material could interact with microwave that lead to the energy generation within the materials.

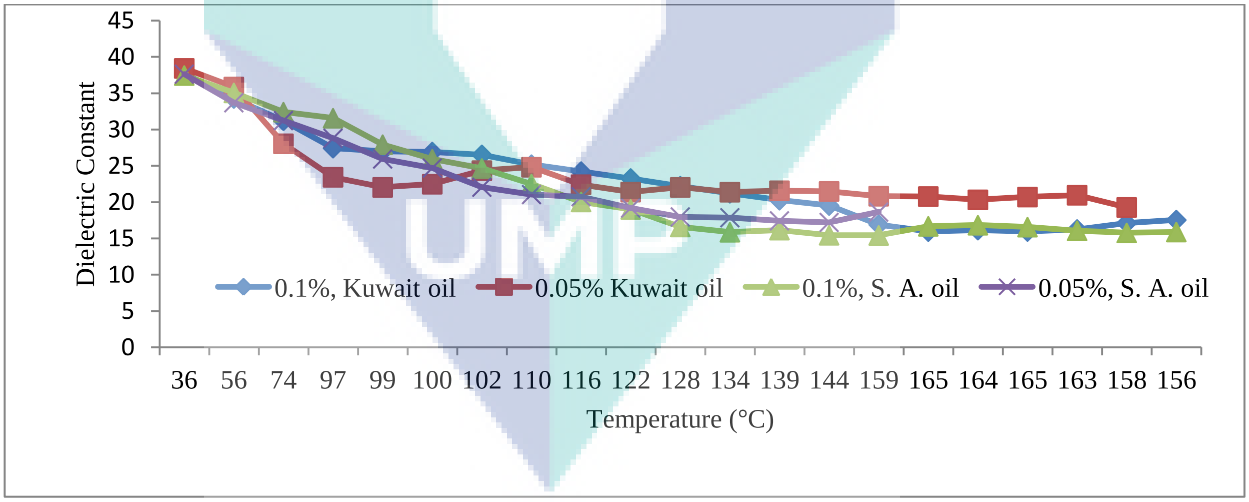

Figure 4.34: Dielectric constant Vs. Temperature for 50-50% w/o emulsions

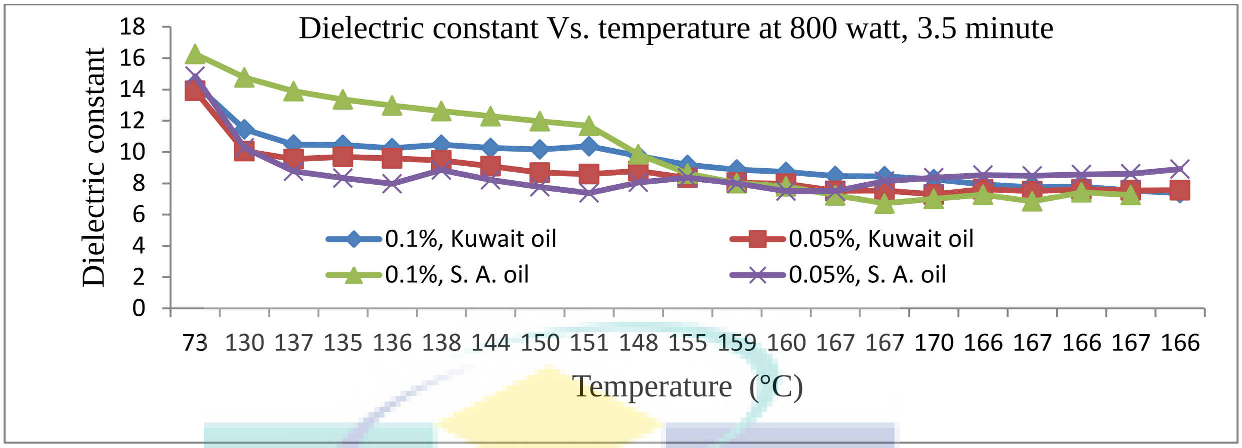

Figure 4.35: Dielectric constant Vs. Temperature for 20-80% w/o emulsions (800W, 3.5 min)

Figures 4.34 and 4.35 contains the calculated results of the dielectric constant for 50-50 and 20-80% w/o emulsions respectively, for 50-50% w/o emulsion all samples had similar curves that is all started at one point that is located between 35-40 (values of dielectric constant) then decreased gradually in a fluctuating pathways until they all reached a constant values of 23 more or less when temperature reached (130 °C), however the real steady plateau was achieved at temperature of 162, where 0.05% demulsified 50-50% Kuwait oil emulsion had the maximum dielectric constant values of (22), then followed the Saudi Arabian sample of the same composition having dielectric constant of (20), the rest two 0.1% demulsified Kuwait and Saudi Arabia samples had identical dielectric constant values of (18) in that particular interval.

With regard to 20-80% w/o emulsion; the curves of all samples were found to start at almost similar values more or less 15 then immediately started to decrease each taking distinct path with 0.1% demulsified Kuwait oil having the path with the highest values of dielectric constant followed by 0.1% demulsified Saudi Arabia, and 0.05% demulsified Kuwait then 0.05% demulsified Saudi Arabia, but all paths were converged at a plateau that is seemed to have very close values of more or less (11) when temperature reached 150 °C, in comparing the two curves one can conclude the following; the dielectric constant of the 50-50% w/o emulsion was higher than the dielectric constant of the 20-80% w/o emulsion and this again will consolidate the domination of the water molecules, also in 50-50% samples; low demulsifiers concentration gave high values of dielectric constant and the opposite was observed with the 20-80% w/o emulsions

V. Dielectric Loss Vs. temperature of Water-crude oil emulsions

Dielectric loss or loss factor is a term given to the ability of conductive and polar materials to dissipate or accommodate the electromagnetic wave that is obstructed by the action of the dielectric constant, and thus help material to convert more energy in the forms of heat, and its characterized to decrease with increasing temperature as would be seen in the graphs.

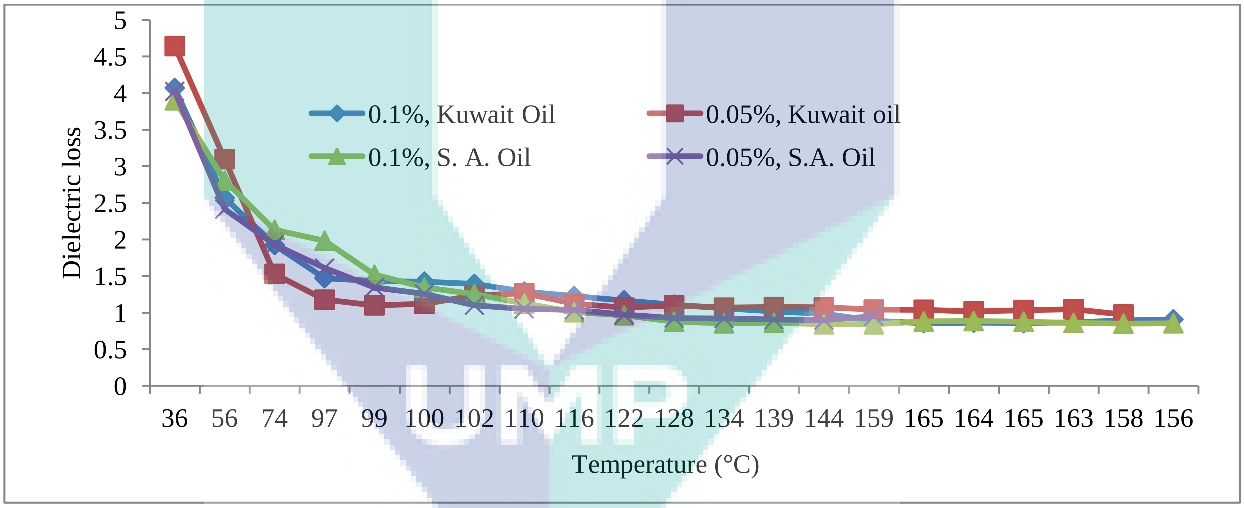

Figure 4.36: Dielectric Loss vs. Temperature for 50-50% w/o emulsions

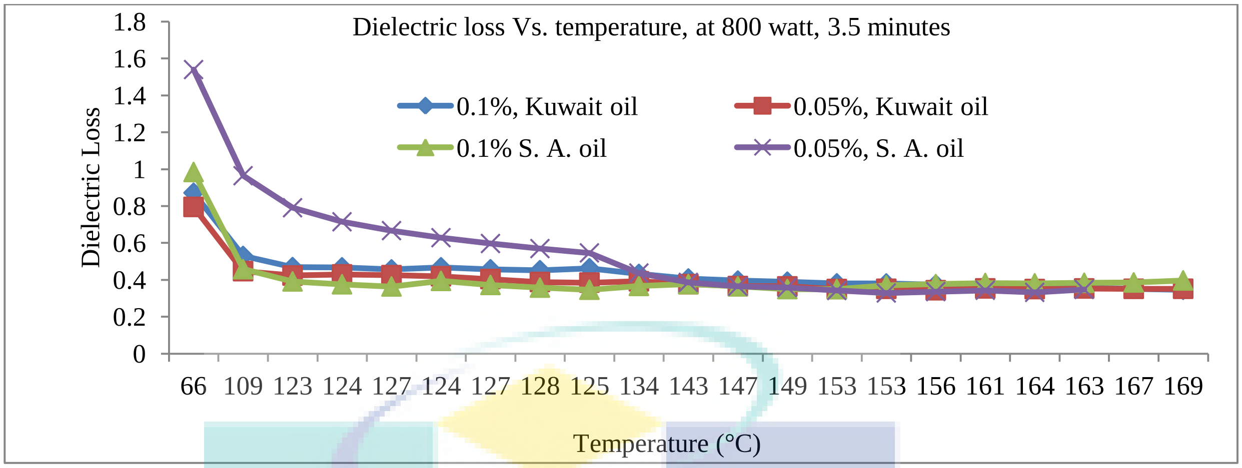

Figure 4.37: Dielectric constant vs. Temperature for 20-80% w/o emulsions (800 W, 3.5 min)

Figures 4.36 and 4.37 represent the values of the dielectric loss of various samples of 50-50 and 20-80% w/o emulsions that are demulsified by various concentrations of polydimethyl –siloxane that is used as dumlsifiers in this research. Particularly; Figure 4.36 represents the dielectric loss of 50-50% w/o emulsions of two crude oils, however; from first glance one can realize that not all the wave absorbed by the sample are converted to energy, this fact could be seen if one compare the values of the dielectric constant and dielectric loss of the 50-50% w/o emulsions or Figures 4.34 and 4.36, it is clear that the maximum values of the absorbed wave (Dielectric constant) was within the interval of (35-40) (Figure 4.34), but the maximum value of the portion that is converted to heat (dielectric loss) was within the interval of (4-5) (Figure 4.36), this is almost ten time reduction in the values of absorbed electromagnetic wave, that may be due the small sized sample used in this experiments.

The other observation is that the dielectric loss curves was shown to decrease sharply and reached its minimum value very fast when the sample temperature is $90\ ^{0}$C, this in contradiction to the dielectric constant curves whose reduction was slow and gradual, in summary it can said that dielectric constant and Loss have certain proportionality but not direct hence more waves are dissipated and only less are converted to energy, and this applies on the 20-80% sample as well, with regard to dielectric loss of

20-80% w/o emulsions; its clear from figure 46.37 that all systems had almost identical values lies in the interval between (0.8-1) except 0.05% demulsified Saudi Arabia that had the value of (1.6) almost double of the others, then as temperature increase; the profiles of the dielectric loss (Figure 4.37) had decreased gradually till they reached a constant values of (0.4).

VI. Wave length vs. temperature of Water-crude oil emulsions

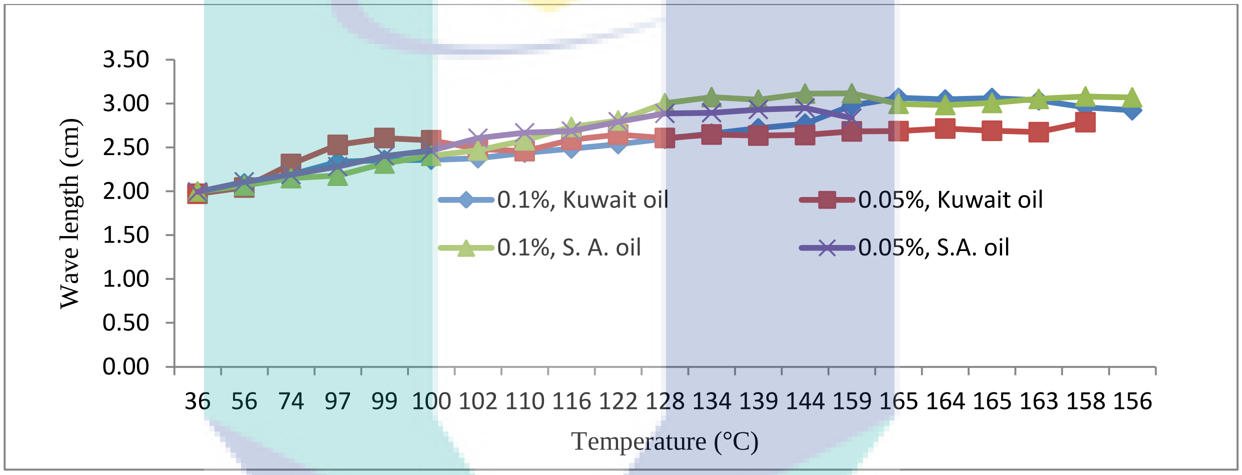

Figure 4.38: Wave length Vs. Temperature for 50-50% w/o emulsions (300W, 3.5 min)

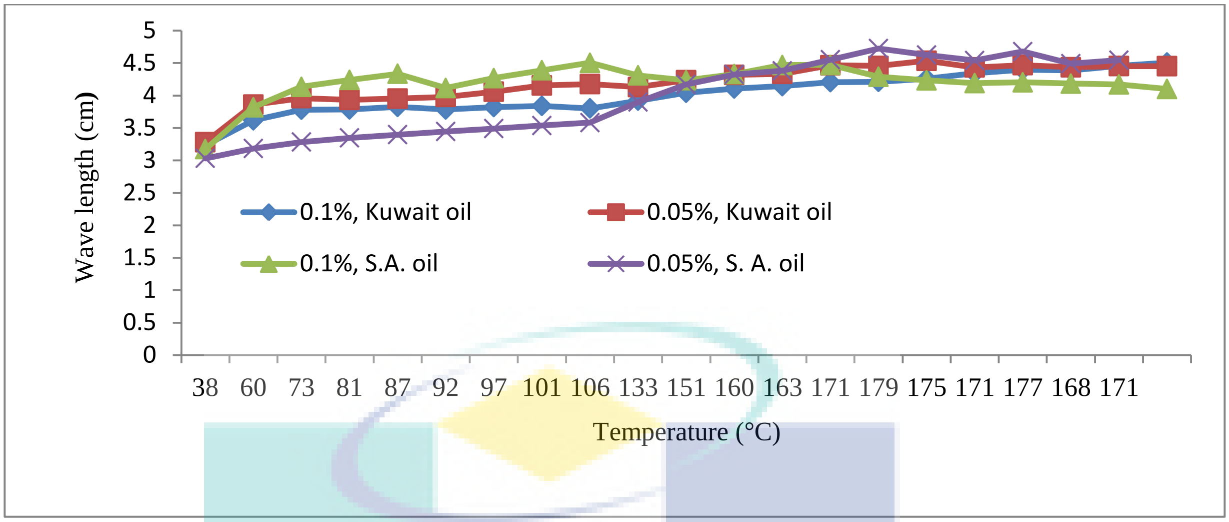

Figure 4.39: Wave length Vs. Temperature for 20-80% w/o emulsions (800W, 3.5 min)

Figures 4.38 and 4.39 reveal the wavelength of the microwave on 50-50 and 20-80% w/o emulsions respectively, this is very important to know since shorter wave length would result in faster and efficient heating, indeed the wavelength also reported to vary with temperature, in fact these claims were evidenced clearly on the current result, as given in Figure 4.38, which showed the wavelength on samples of 50-50% w/o emulsions as function of sample temperature, generally; all samples showed very similar profiles of the wavelength as a function of temperature the initial wavelength for all samples was almost identical and located around 2 cm at 36 °C, and final value was 3 cm more or less, hence the effect of oil types as well as demulsifiers' concentration was very minor for 50-50% w/o emulsions.

With regard to 20-80% w/o emulsions, the values of the wavelength was to some how greater than that of it 50-50%, but particularly within 20-80% samples all sample appeared to have similar wavelength that had an initial value of around 3 cm and final value of around 4 cm, from this results it could be said that the amount of water in the emulsion does effect the wavelength and that may affect the heating pattern as well, since energy generation is proportional to the wavelength, however there was no much data previous data to elaborate or explain this result exclusively but the only evidence that lead to accept this result is that the sample wave much more less than the bulk sample diameter which was found to be 9.5 cm.

VII. Penetration depth vs. temperature of Water-crude oil emulsions

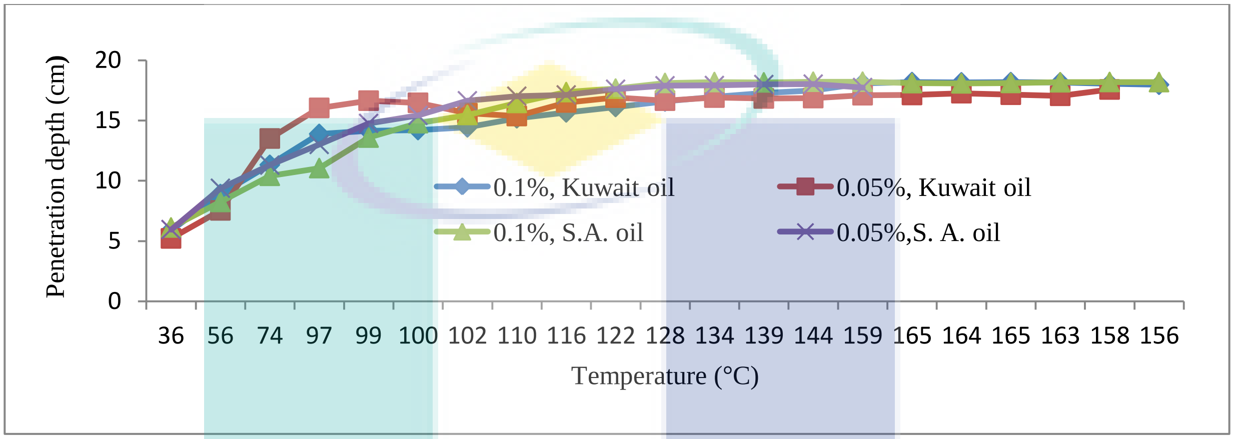

Figure 4.40: Penetration depth vs. Temperature for 50-50% w/o emulsions (800W, 3.5 min)

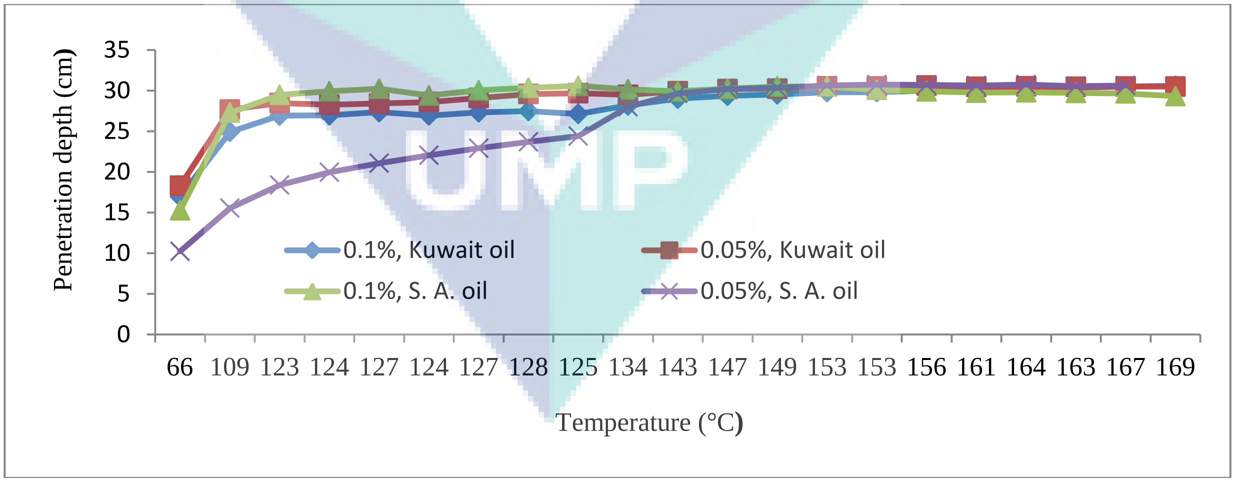

Figure 4.41: Penetration depth Vs. Temperature for 20-80% w/o emulsions (800 W, 3.5 min)

Figures 4.40 and 4.41 describe the penetration depth of the electromagnetic waves on the samples of 50-50% and 20-80% w/o emulsions, so the penetration depth for 50-50%

w/o emulsions was found to be almost equal for all compositions, and varies with temperature, hence its starting value was 5 cm for all samples at the very beginning of the irradiation when the temperature was just 36 °C, then it increased slowly until it reached a constant value of 15 cm when temperature was 102 °C, however comparing this result to that of 20-80% w/o emulsions of Figure 5.19; its clear that water cuts does greatly affect the penetration depth, hence the difference was around two order of magnitude greater for 20-80%, whose initial value was around 15 cm for the three samples and it was around 10Cm for 0.05% demulsified 20-80% S.A crude oil at 66 °C, then increased gradually with temperature then all the values were converged at plateau of around 30 cm, when temperature 143 °C. From this observation it can be said that the actual concentration of demulsifiers does not affect much the penetration depth nor the oil type only water cut does, another information is that the penetration depth was found to increase with increasing temperature and in that to some how in accordance with the theory which defines penetration depth as the depth where the power is reduced to 37% of the surface values, (R. S. Shavan et al., 2010), also davinder have reported the gradual dependence of penetration depth on sample temperature (Davinder et al., 1997).

4.9.5 Microwave Demulsification of Petroleum based emulsions

The preceding section had discussed the demulsification process in terms of thermal properties but this section would tackle the efficiency of microwave in breaking several types of emulsions, including experimental as well as real emulsions, and the microwave performance would be assessed in terms of water resolution.

I. Effects of demulsifiers' concentration and irradiation time on demulsification

This section is aimed to investigate the synergistic effect of the chemical assisted microwave demulsification in terms of water separation from the stable emulsion, together with the irradiation time for 50-50 and 20-80% w/o emulsions of Kuwait and Saudi Arabia.

II. Kuwait oil

The effect of microwave in breaking w/o emulsions was assessed in this section, in terms percentage of water resolved from the emulsions.

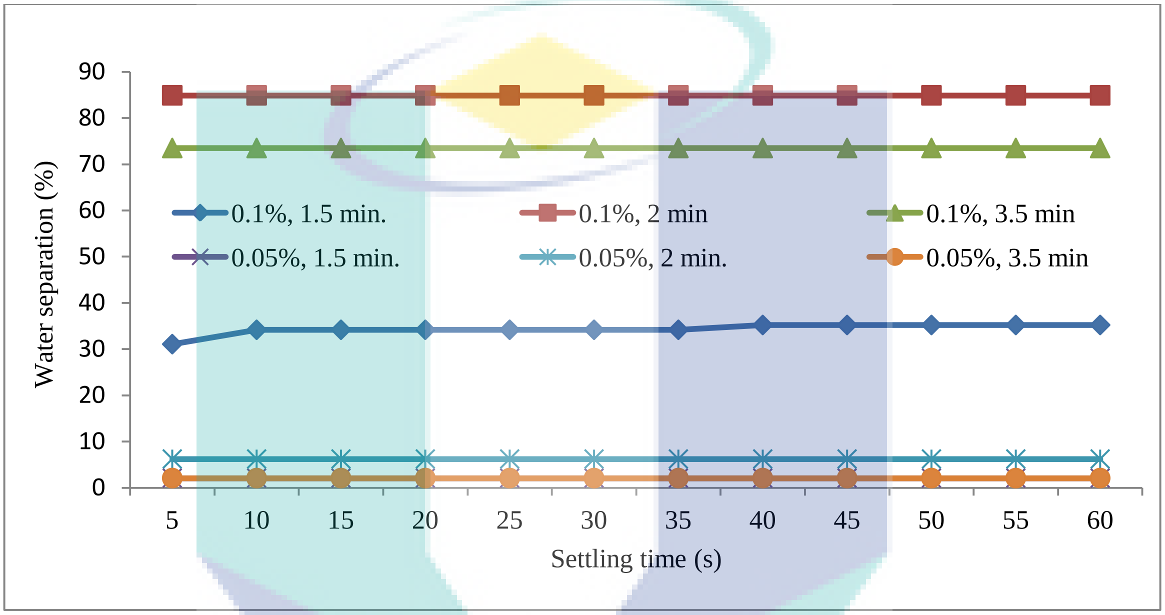

Figure 4.42: Percentage of water separation for 50-50% w/o emulsion (Kuwait oil)

Figure 4.42 reveals the experimental results obtained from 50-50% w/o emulsions of Kuwait crude oil, as stated earlier many parameters are to be discussed in this paragraph but currently Figure 4.42 is particularly devoted to observe the synergistic effects of the demulsifers' concentration and Irradiation or processing time on the emulsion separation efficiency, which in turn evaluated by pouring the processed samples in measuring cylinder and the separated amount of water is read of as settled layer at the bottom of the cylinder for duration of 1 hour (settling time). Indeed two different concentrations of demulsifiers (0.1% and 0.05%), and three different irradiation times (1.5, 2 and 3.5 minutes) were investigated on 50-50% w/o emulsion. However; the results showed that a composition with 0.1% v/v concentration of demulsifiers and 2 minutes of irradiation time had given the best separation efficiency of almost 87%. But when demulsifiers' concentration was increased to 0.7%; the separation also increased to 96%. Then followed by sample 0.1% demulsifiers and 3.5 minutes irradiation which had a separation efficiency of around 75%,

Although this result is quite good but, supposedly 3.5 minutes irradiated sample should have had greater yield than 2 minute irradiated sample based on theory and previous articles. But this situation may be due to the modification on the system where a pressure release long hose was introduced to avoid the pressure build up that is easily leads to splashing or explosion, hence during the experiment it was observed that after irradiation time reached 2 minutes; some vapor had seen to escape from the system. Therefore its assumed that during 3.5 minutes exposure time there was much losses compare to 2 minutes irradiation time, on the other hand 0.05% demulsifiers concentration and 1.5 microwave exposure time were found to be non effective for 50-50% w/o emulsions.

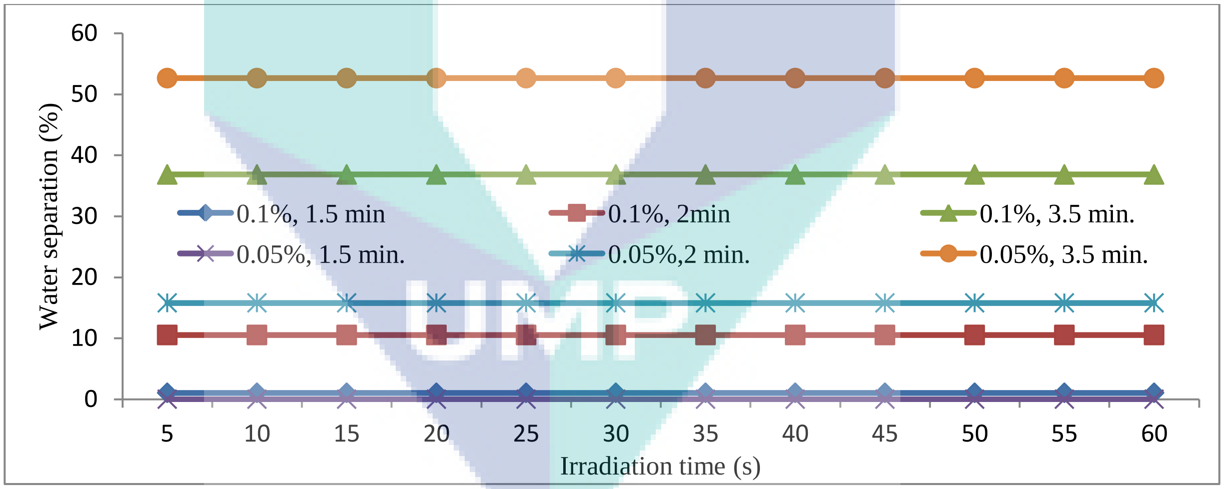

Figure 4.43: Percentage of water separation for 20-80% w/o emulsion (Kuwait oil)

Figure 4.43: was plotted to investigate the effect of water volume fraction on the emulsion since it well known systems with different composition will respond differently to any external effect, and it was in this result thus system of 20-80% w/o emulsion composed of 0.05% demulsifiers and 3.5 minute irradiation time have had the maximum yield of 52%

more or less water resolution followed by 0.1%, 3.5 minutes which had water resolution of around 37%. Other interesting observation in here is that, low demulsifiers concentration had given much higher yield which was around 52% and 35% for 0.05% and 0.1% demulsified emulsions respectively, hence from this result for low water content Kuwait oil of 20-80% w/o emulsion low demulsifiers' concentration and long irradiation time would give a better yield, so the conclusion is that the quantitative values of the parameters used to demulsify 50-50% and 20-80% w/o emulsions are just opposite to one another.

III. Saudi Arabia oil (S.A.)

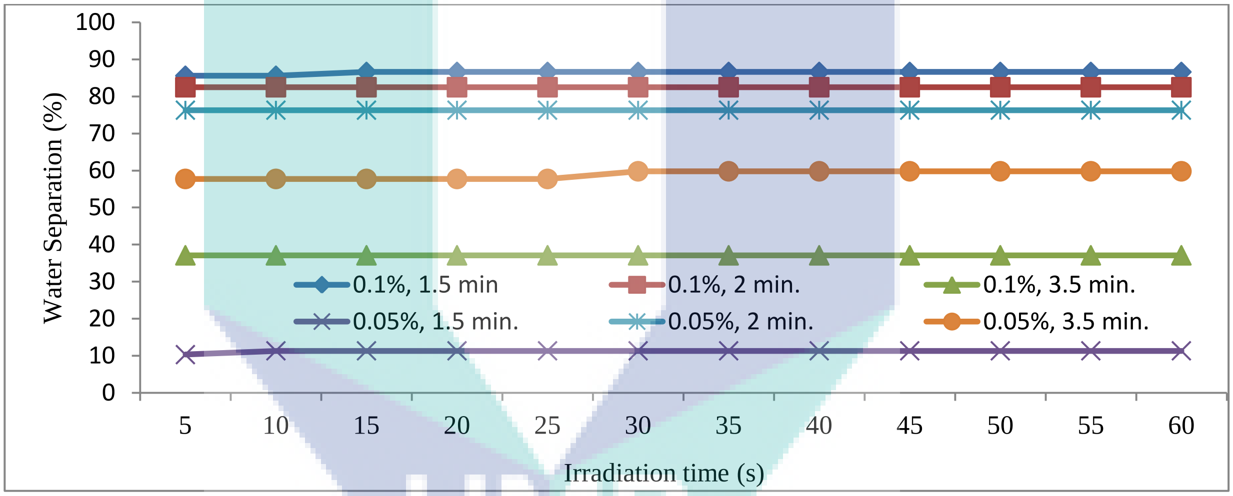

Figure 4.44: percentage of water separation for 50-50% w/o emulsion (Saudi Arabia oil)

Figure 4.44 represents the experimental results of 50-50% w/o of (S.A.) emulsion, all parameters are fixed as same as its Kuwait homologue, so this can help to observe the effects by considering oil types as independent parameter. From these results it was observed that the profile is almost same as it was with Kuwait oil, in a sense that high demulsifiers concentration and short irradiation time would give high yield.

From figure 4.44; it was observed that three samples had the highest values namely sample of 0.1% emulsifiers and 1.5 minutes irradiation had separation efficiency of around

85%, but the same samples again had 82% separation efficiency when the irradiation time had increased to 2 minute; in fact this result sound ambiguous and could be attributed to the thermal properties of the samples that may lead to vapor escaping from the heating sample before 2 minutes and that vapor may take some water with it and that would lead reduction of the water contained in the emulsions.

The other sample with high yield was that with 0.05% demulsifiers' concentration and 3.5 minutes irradiated sample which had around 59% of its water separated. Generally the effect in Saudi Arabia Crude oil is high than crude oil for 50-50% emulsions but fortunately the samples with maximum yields are still having the same compositions.

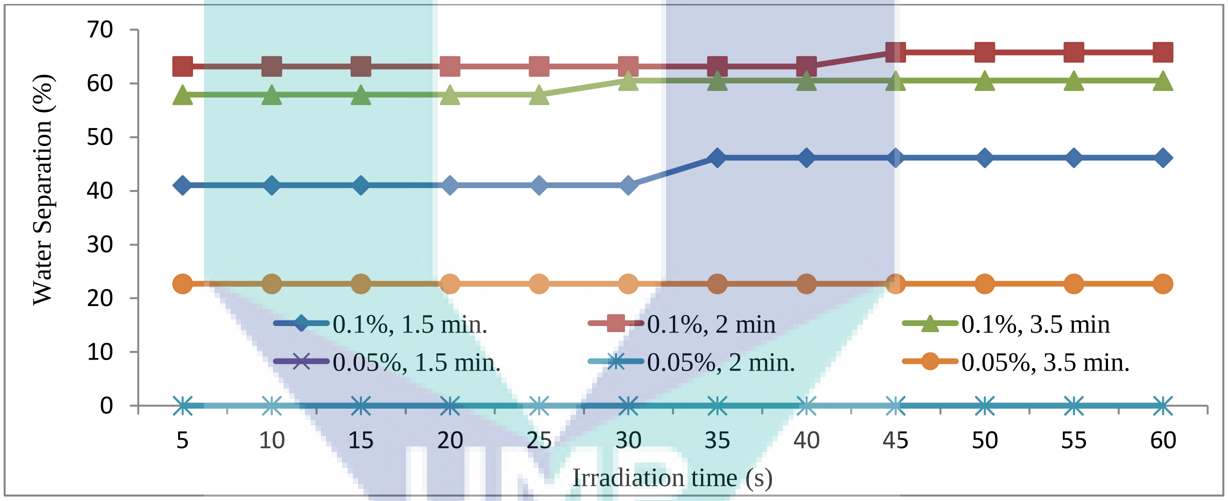

Figure 4.45: percentage of water separation for 20-80% w/o emulsion (Saudi Arabia oil)

Figure 4.45 represents the separation efficiency for 20-80% w/o emulsions of S.A. crude oil produced using the same parameters as 50-50% emulsion, only the water content is varied purposely to observe its effect on separation efficiency. This time the effect was in same fashion as 50-50% w/o emulsions, hence in this types of (S.A) crude oil; the water volume fraction does not affect much on the separation efficiency but demulsifiers' concentration and irradiation time do effect, hence the maximum separation efficiency of (62%) was observed in sample having 0.1% demulsifiers that is irradiated for 2 minute.

indeed when the same sample irradiated further to 3.5 minutes; the separation efficiency had reduced to around 58%, furthermore it was also observed in this 20-80% w/o (S. A.) crude oil that; low concentration of demulsifiers did not give much effect; this is a reverse of the 20-80% Kuwait oil in which low demulsifiers concentration and high irradiation time gave better yield (Figure 4.43)

4.9.6 Microwave demulsification of slop oil and waste coolant emulsions

This section would investigate the validity of the current technique on real life sample; hence two samples of industrial emulsion namely light slop oil and waste coolant were supplied by two local companies. Microwave has shown great effects on demulsification of slop oil and waste coolant emulsions, as would be presented in the upcoming paragraphs.

Table 4.4: Microwave demulsification of the slop oil

	Demulsifiers' concentration			
Settling time (S)	**0.0**	**0.2%**	**0.4%**	**1%**
	Separation efficiency (ml)			
5	35	42	47	53
10	35	42	47	54
15	35	42	47	54
20	35	42	48	54
25	35	42	48	54
30	35	42	48	54
35	35	42	48	54
40	35	42	48	54
45	35	42	48	54
50	35	42	48	54
55	35	42	48	54
60	35	42	48	54

Table 4.4 presents the experimental data obtained from microwave chemical assisted demulsification of the slop oil emulsion.

Based on the previous crude oil results; the irradiation time was fixed at 2 minutes and only demulsifiers' concentration were varied as (0.0, 0.1, 0.2, 0.4 and 1%) whose separation efficiencies were (35, 42, 48 and 54 ml respectively).

Generally the current result showed that microwave was effective in separation water from slop oil emulsion, but the separation rate was increased with increasing demulsifiers concentration, hence 1% demulsifiers concentration had given the maximum yield.

Another interesting observation is that the amount of chemical needed to separate water from slop oil emulsion was more than that of the crude oil, and that was expected since slop oil is the oil that is settled in bottom of the storage tanks and that is surely contain other impurities and solid particles that would increase its viscosity and stability. Therefore increased demulsifiers concentration would reduce the viscosity and leads to a better separation. Actually the data on Table 4.4 and 4.5 were gotten from 100 ml of waste emulsion being treated in each run.

Table 4.5 reveal the experimental results of the waste coolant treated with microwave, however no chemicals were added in this particular emulsion since it seemed very light and hence 100 ml of the waste coolant sample was filled in the sample container and exposed to microwave without any pretreatment.

Table 4.5: Microwave demulsification of the waste coolant

	Irradiation time (min)			
Settling time (S)	**0.5 min.**	**1 min.**	**2 min**	**4 min.**
	Separation (ml)	**Separation (ml)**	**Separation (ml)**	**Separation (ml)**
5	0.3	10	40	43
10	0.3	10	42	43
15	0.3	12	42	43
20	0.3	12	42	43
25	0.3	12	42	43
30	0.3	13	42	43
35	0.3	13	42	43
40	0.3	13	42	43
45	0.3	13	42	43
50	0.3	13	42	43
55	0.3	13	42	43
60	0.3	13	42	43

The only parameter that is investigated here was the irradiation time which was varied as (0.5, 1, 2, and 5 minutes), from the results the separation efficiancy was observed to increase with increasing irradiation time and hence the maximum separation was 43 ml out of 100 ml, sample treated, these values on the table are in millimeters, and not as percentages, although the maximum amount of water separated was found to be 43 ml out of 100ml in another word less than the 50% but this should not be the ultimate results since waste coolant is water based emulsion that presumably contains more than 50% water and thus further investigation is needed to get better separation.

4.9.7 Chemical demulsification of w/o emulsions

The demulsification performance of two surfactants from two families including amine, and polysiloxane groups were evaluated using the experimental water-in-oil emulsion.

The oil resolution rates of the water-in-oil emulsion with addition of these surfactants are shown in Figure 4.46 and 4.47which show the effect of hexylamine demulsifiers on different types of crude oils denoted as oils (A and B), with two different volume fractions (50-50% and 30-70% respectively), water-in-crude oil emulsions, The dosage of the surfactant is varied from 0.5% considered as the lowest and 3% as highest based on the total volume of emulsion.

I. Effects of amine group demulsifiers

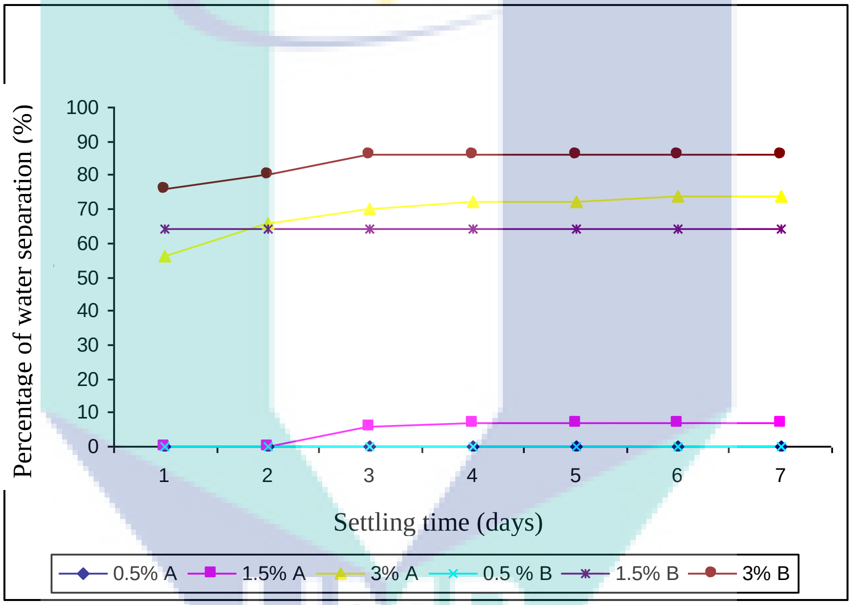

Figure 4.46: Separation efficiency for 50-50% w/o emulsions (Amine group)

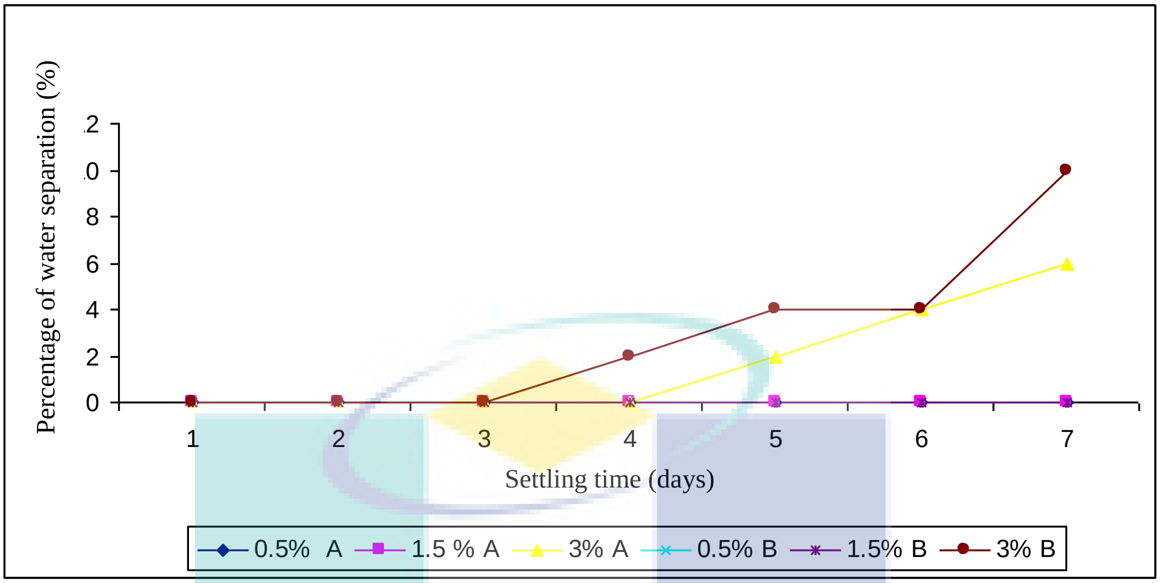

Figure 4.47: Separation efficiency for 30-70% w/o emulsions (Amine group)

Figures 4.46 and 4.47 were plotted from the experimental data of the current work, they show the effect of different concentration (0.5-3%) of amine group demulsifiers on breaking 50-50% (Figure 4.46) and 30-70% (Figure 4.47) w/o emulsions.

Ffrom Figure 4.47; it is obvious that at low concentration of demulsifiers (0.5%) the two curves are laying in the X axis which means zero separation, for both crude oil A and B but it is increased with increasing the demulsifiers' concentrations, thus the maximum separation yield obtained for crude oil A with 50-50% w/o emulsion at 0.5, 1.5 and 3% demulsifiers concentrations were 0%, 14% and 72% respectively. While for oil B were 0%, 64% and 86% respectively (Figure 4.46), this might be attributed to the interaction of demulsifiers molecules with the existing emulsifier's film at the oil water interface.

At low concentration of demulsifiers the diffusion rate at the interface is expected to be low because of low bulk concentration of demulsifiers and hence they would not be able to neutralize the interfacial film hence no separation occurred. In contrast to previous statement; as the demulsifiers concentration increased the diffusion rate at the interfacial film also expected to be increased and that will induce the interfacial film drainage, thinning then rupture and finally that will lead to the collision of the neighboring droplets due to intermolecular and vander-wals attraction force and separate as a water layer at the bottom while the pure oil phase will separate at the top. Some researcher stated that the demulsifiers molecule will be absorbed gradually into the oil-water interfacial film and replace the emulsifiers, that replacement decreases both the strength and the life of the film and the film thickness until it collapsed (Wanli Kanga et al., 2006).

II. Effects of Silicon group demulsifiers

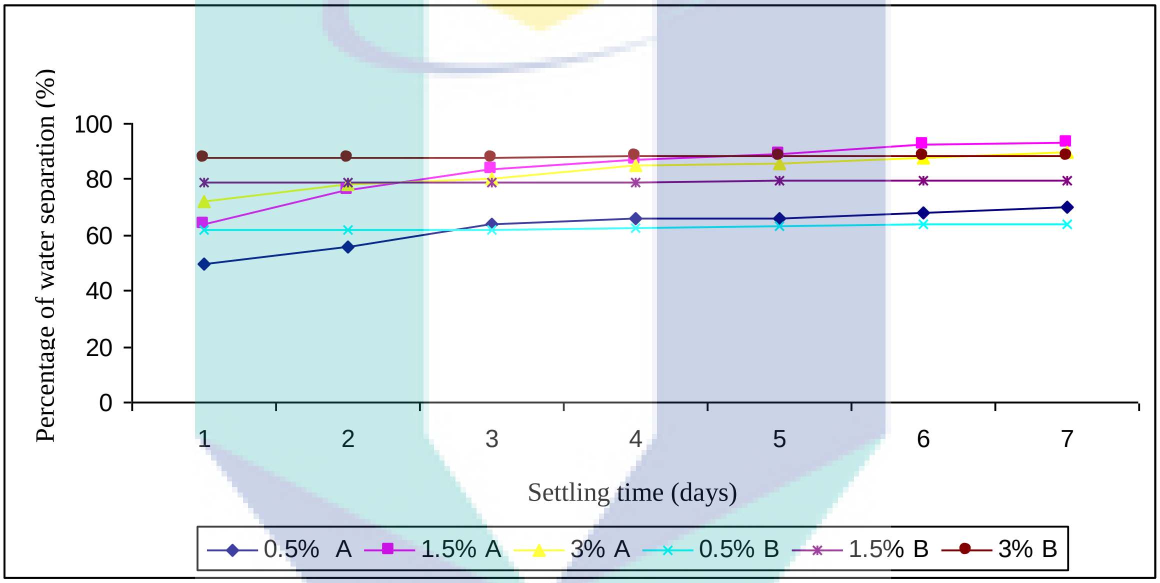

Figure 4.48: Separation efficiency for 50-50% w/o emulsions (Silicon group)

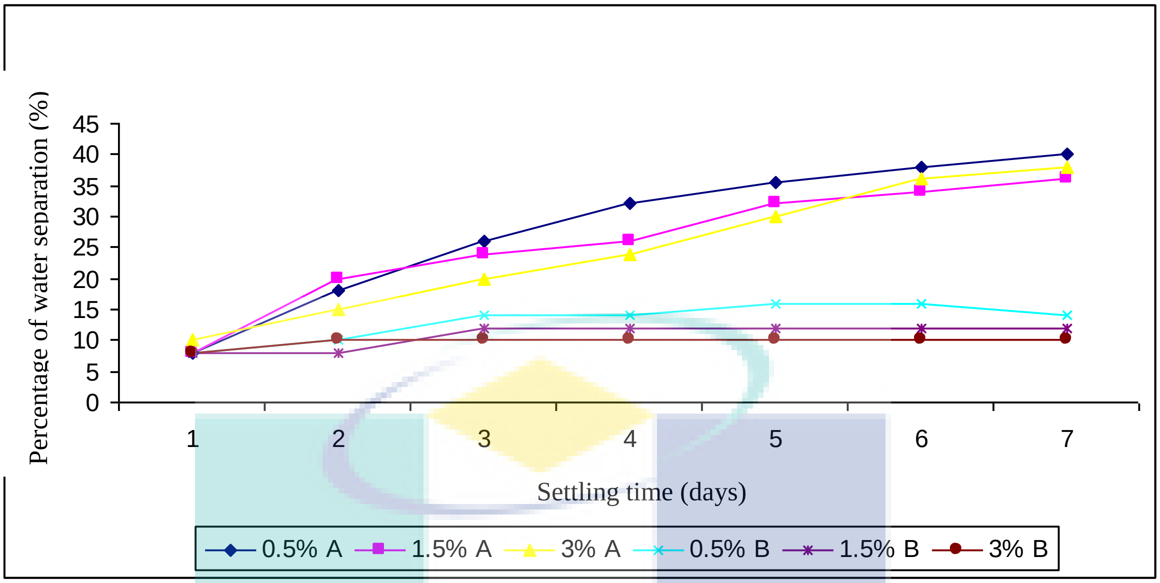

Figure 4.49: Separation efficiency for 30-70% w/o emulsions (Silicon group)

Figures 4.48, 4.49 represent data of 50-50% and 30-70% w/o emulsions respectively, and From which it is clear that at 0.5% demulsifiers concentration; the maximum separation efficiency of silicon demulsifiers on 50-50% w/o emulsion of oils A and B were 70 and 63.8% respectively while that of 1.5% were 93 and 79.4% and for 3% was 90 and 88.4% respectively.

It is obvious from the results that in all cases silicon demulsifiers gave high separation in crude A than B. At low water cut emulsions of 30-70% w/o emulsions; the maximum separation was 40 and 14% at demulsifies' concentration of 0.5%, 36 and 12% at 1.5%, 38 and 10% at 3%. It is noticed that if the water cut is low in the emulsion; the demulsifiers performance is low too, that the emulsion is more stable at low water concentration. From Figure 5.26, for high water cut emulsion of 50-50%, all of the three concentrations of silicon demulsifiers gave high percentage of water separation in contrast to the amine group which was not given any separation at low concentration of 0.5%. The second observation is that in silicone demulsifiers, the maximum separation for 50-50% w/o emulsion was observed at the medium concentration of 1.5 percent for crude oil A while for oil B the maximum water separation was observed at 3%, Therefore; it could be concluded that for silicon demulsifiers the optimal concentration of demulsifiers lies between 1.5 and 3% therefore further investigation need to be carried out to get the best concentration.

For low water concentration of 30-70% as shown In Figure 4.49, the lowest concentration of silicon demulsifiers (0.5%) gave more separation than the other two concentrations (1.5 and 3%), and correlated to previous work done by (D. Daniel et al., 2008) who found that polysiloxane demulsifiers could promote a good separation even at a very low concentrations.

4.9.8 Ultrasonic Demulsification of w/o emulsions

This section is considered one of the most significant parts of this research, and devoted to investigate the effect of ultrasonic in demulsifying w/o emulsions prepared from Kuwait oil at various concentration of chemical demulsifiers precisely (0.1,0.3, 0.5, 0.7%), with varying sonication time.

Based on literature most of the previous research on w/o emulsions were oriented toward the standing wave concept, in which droplets are aggregated or agglomerated according to the density and contrast factor to either pressure nodes or pressure antinodes of the standing that normally produced from a resonator, but this standing wave concept does not work well with viscous systems as the case of the current emulsions, thus in this investigation; a simple cleaning bath was used synergistically with the chemical demulsifiers and results would be discussed next.

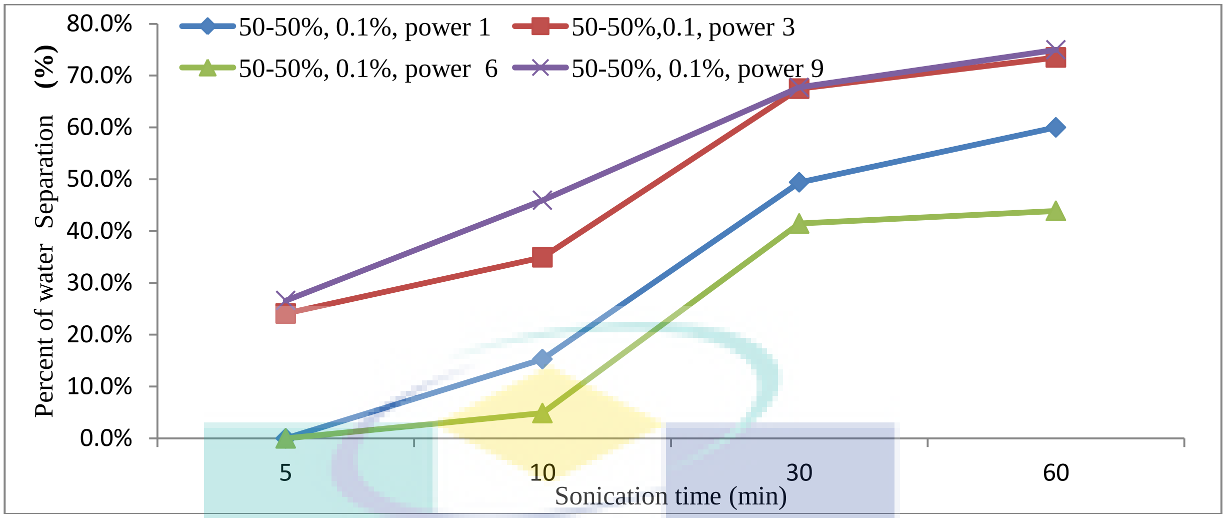

Figure 4.50: Separation efficiency for 50-50% w/o emulsion, at 0.1% demulsifiers

Based on the current experimental data; chemical assisted sonication process was found to be very effective in treating w/o emulsions, four types of power levels were used and designated low (1), medium (3), high 6, and very high (9).

Figure 4.50 shows the separation efficiency of ultrasonic at one single concentration of 0.1%, and four power levels.

It is clear from the figure that at 0.1% demulsified sample; power 3 and 9 gave the maximum separation efficiency of around 70%.

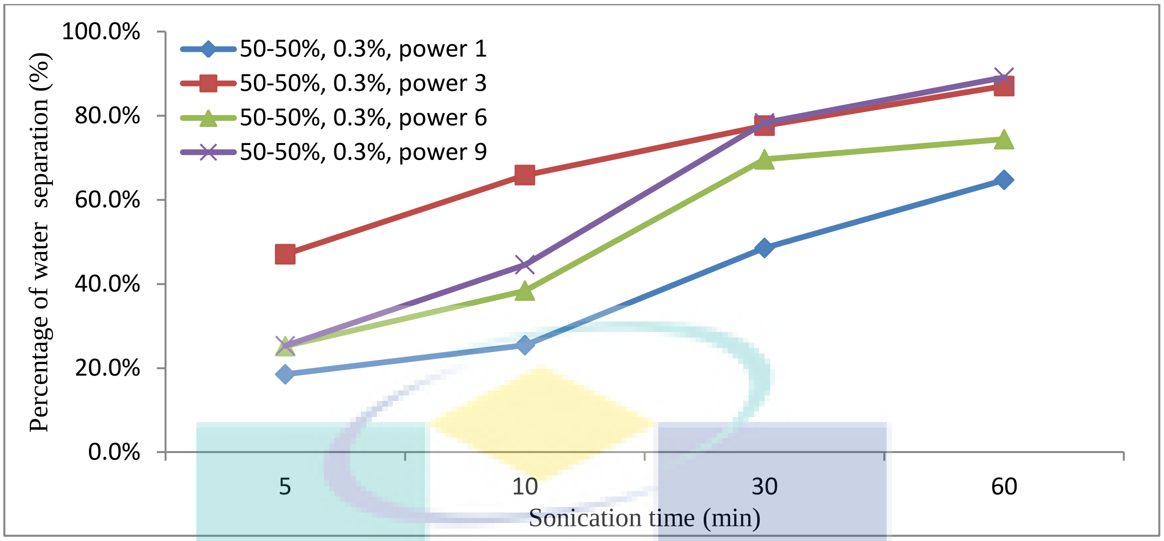

Figure 4.51: Separation efficiency for 50-50% w/o emulsion, at 0.3% demulsifiers

Figure 4.51 is depicted to investigate the effect of demulsifiers' concentrate ion on the ultrasonic w/o emulsion splitting process, hence the amount of the demulsifiers was increased further to 0.3%, but all the other parameters are fixed. However, the result was as expected with power 3 and 9 having the maximum efficiency again that reached 80% more or less water separation, and also the proportional effect of the amount of the demulsifiers on the separation efficiency was apparently pronounced.

If one compared the Figures 4.50 and 4.51, one can see clearly that when the demulsifiers' concentration was 0.1%, the resulted penetration separation efficiency was 70%, but when the demulsifiers' concentration was increased to 0.3%; the separation efficiency was increased to 85%, also prolonged sonication time was found to produce better separation, that can be observed from both Figures 4.50 and 4.51 where curve were seen to have their greatest or maximum amount of efficiency as one goes toward the maximum sonication time of 60 seconds or 1 hour.

From these results it can be said that the ultrasonic chemical assisted demulsification process was found to enhance with increasing demulsifiers' concentration. The amount demulsifier used are much less than the amount used when chemical alone is used, and this would consolidate and encourage the idea of silicone based chemical assisted ultrasonic demulsification of water –in-crude emulsion to be developed further as a sustainable, versatile and cost effective technique in treating water-in-oil emulsions. Indeed two more demulsifiers' concentrations of 0.5%and 0.7% were tested along with the same four power levels and result would be reported in the next section.

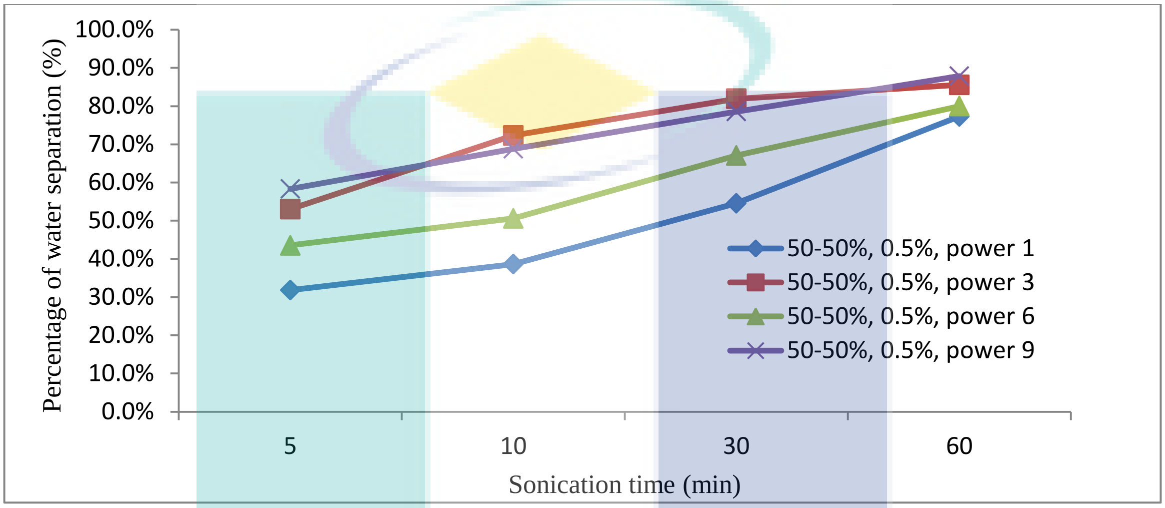

Figure 4.52: Separation efficiency for 50-50% w/o emulsion, at 0.5% demulsifiers

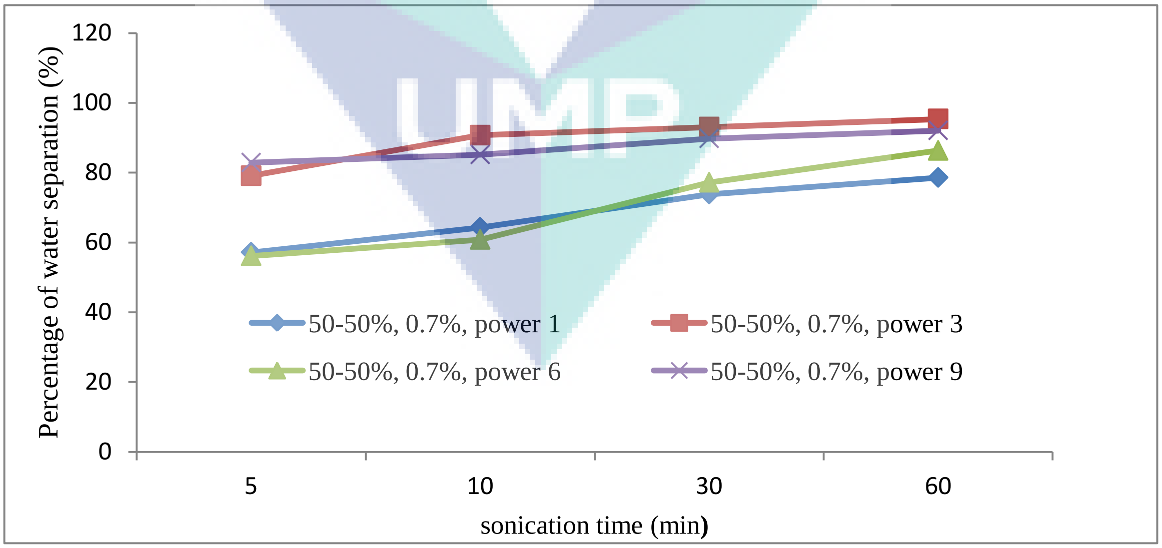

Figure 4.53: Separation efficiency for 50-50% w/o emulsion, at 0.7% demulsifiers

Figures 4.52 and 4.53 were plotted from the experimental data obtained from 50-50% w/o emulsions that is demulsified by the addition of 0.5 and 0.7% respectively; al the other parameters including power levels were held constant.

The effect was found to be similar with previous discussion in a sense that when demulsifiers was increased to 0.5%; the separation efficiency was increased too from 85% at 0.3% concentration to 90%. When demulsifiers were increased further to 0.7%, it resulted in even better separation efficiency of 97% (Figure 4.53).

From these results it was observed that increasing the ultrasonic power would increase the separation yield and the most effective power levels were found to be (3 an 9), another observation is the demulsifiers' which was also found to perform better with in creasing concentration, this result could explained by the fact that chemical demulsifiers would contribute massively on reducing emulsion viscosity, and also undo the stabilizing action of emulsifiers at the interface, and that would induce to water droplets to aggregate, additionally ultrasonic is assumed on one had to disperse the chemicals uniformly in the sample and on other hand to create air bubbles within the emulsion sample in the same manner as it does in cleaning, these bubbles are normally created at low power level and they either disrupted immediately or travel along pathways within the sample to evaporate, these activities may be the driving force governing the ultrasonic demulsification at low power level, since the mechanical ultrasonic would insert certain pressure on the droplets when its first contacted with the droplet, that pressure is called primary acoustic radiation force, then after that, beside that bubbles are created when the waves are interacted with some dissolved gases such dissolved oxygen (DO), or Carbon dioxide, that are assumed to exist within the emulsion sample.

Aalso the wave induced droplets would produce another type of pressure force that is known as secondary acoustic radiation pressure that act to move the neighboring droplets. This movement will lead to the aggregation of the droplets, indeed the movement of these aggregating droplets is facilitated by the collapsing and evaporating bubbles that would open pathways to the droplets to come together, collect agglomerate and eventually separate as water layers.

4.9.9 Optimizations

The optimization process for whole the experimental results was carried out using the response surface methodology (RSM), since the results were discussed in several sections the optimization process also would be executed in different section in accordance with the experimental data.

I. Stability investigation

The optimization process of stability study was carried out in terms of the interaction between the parameters of study that are; the emulsification speed (RPM), water content, the origin or types of the crude oils , in order to get the optimal combination that can give the desired response, hence the optimal conditions were depicted in Table 4.6 and Figure 4.54 from which the optimal conditions that gave the optimal viscosity of 4883 cp were rpm of 1952.68, water content of 46.74 %, Saudi Arabian (SA) crude oil. However very similar results were obtained from the experimental data, hence the experimental viscosity of 50% water contained Saudi Arabian crude had reached a plateau of 4883 cp when the rpm was beyond 1000.

Table 4.6: Solutions of optimal conditions

experiment	RPM	Water (%)	Crude oils	Viscosity	desirability
1	1865.45	48.08	SAUDI ARABIA	4883	1
2	1917.26	47.27	SAUDI ARABIA	4882.99	1
3	1987.23	46.23	SAUDI ARABIA	4882.99	1
4	1817.12	48.86	SAUDI ARABIA	4883	1
5	1803.61	49.09	SAUDI ARABIA	4882.99	1
6	1994.47	46.12	SAUDI ARABIA	4882.99	1
7	1782.07	49.45	SAUDI ARABIA	4883	1
8	2000.00	50.00	UNITED EMIRATES	2440.55	0.49484
9	2000.00	49.66	UNITED EMIRATES	2400.68	0.486594
10	500.01	20.00	UNITED EMIRATES	530.642	0.099823

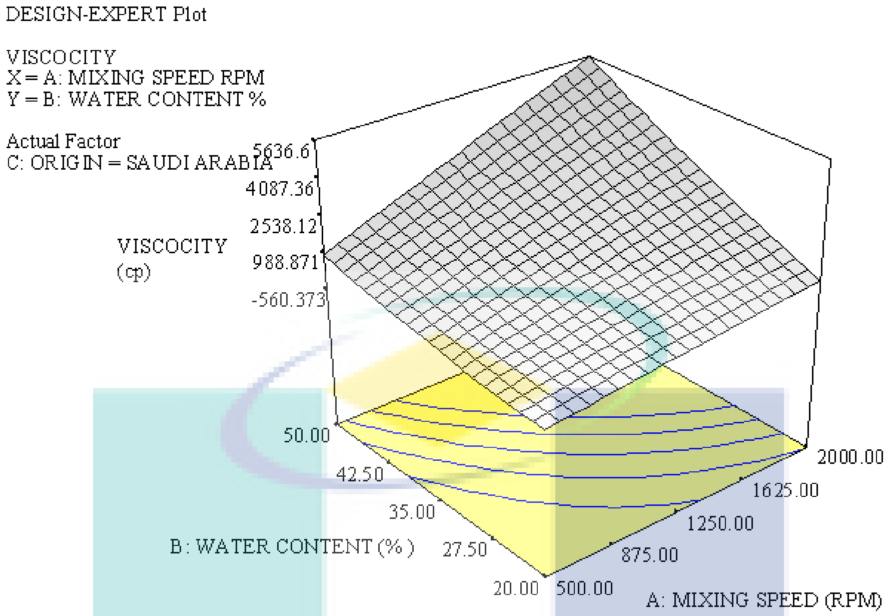

Figure 4.54: Response surface plots representing the effect of mixing speed (rpm), water content and their interactions on emulsion viscosity

II. Microwave demulsification of Kuwait crude oil

The optimization of chemical assisted microwave demulsification of Kuwait crude oil was studied via the response surface methodology (RSM), hence the effects of chemical demulsifiers' concentration, water content, irradiation time, settling time and their interaction on water resolution from the emulsions is shown in Tables 4.7 and Figure 4.54

Table 4.7: RSM Solutions of optimal conditions

Experiment	**Settling Time (%)**	**Irradiation time**	**Chemical Concent-tration (%)**	**Water comtent (%)**	**Separation Percent (%)**	**desirability**
1	59.98	3.49	0.10	49.47	78.5582	0.925303
2	60.00	3.49	0.10	49.33	78.3425	0.922762
3	60.00	3.45	0.10	49.99	77.7804	0.916141
4	52.69	3.50	0.10	50.00	76.6509	0.902838
5	60.00	3.04	0.10	50.00	76.3939	0.89981
6	45.23	3.50	0.10	50.00	74.5963	0.878637
7	59.98	3.50	0.10	50.00	74.4149	0.876501
8	5.81	3.50	0.10	49.97	73.8595	0.869958
9	28.04	3.49	0.10	50.00	72.1042	0.849283
10	60.00	3.50	0.07	23.87	42.7132	0.5031

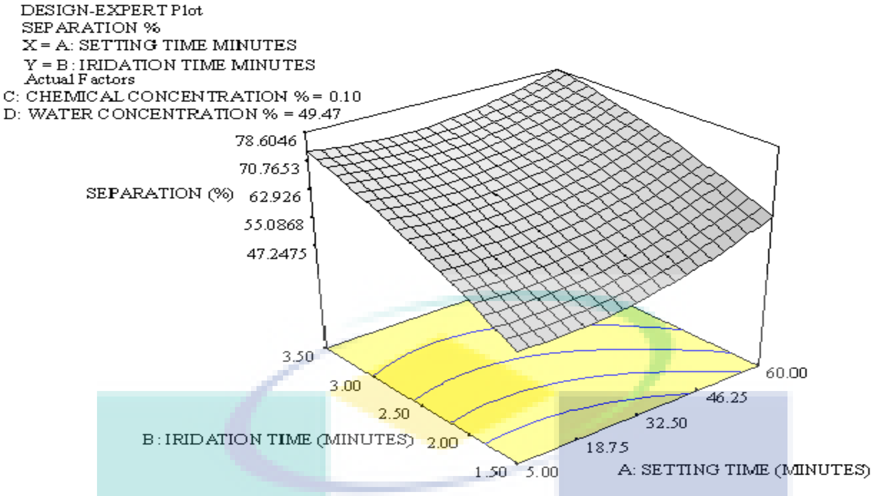

Figure 4.55: Response surface plot representing the effect of microwave irradiation time, settling time and their interaction on the water separation on

Which show the interaction between the independent variables that govern the microwave demulsification of w/o emulsion; hence the graphs in Figure 4.55 indicate the increase of the dependent response variable (water separation percent (%)) with increasing the irradiation time as well as the settling time, indeed from Table 4.6 it was observed that the optimal separation percentage of 78.5582% was obtained at water content of 49.47%, chemical or demulsifiers' concentration of 0.1%, irradiation time of 3.49 min, and settling time of 59.98%, however these expected values have some similarities with the experimental values whereby the optimal separation efficiency of 87% was obtained with 50% water content, 0.1% chemical demulsifiers' concentration and 2 minutes irradiation Time

III. Microwave demulsification of Saudi Arabia (SA) crude oil

Response surface methodology is also used to find the optimal values of all the aforementioned factors that would give the optimum or desired separation of water from the water-in-oil emulsion of Saudia Arabian types of crude oil.

Table 4.7 and Figure 4.55 present the solution of the optimal condition and response surface contour plot respectively, hence based on Table 4.7, it was found that the optimal demulsifiers' concentration, water content, irradiation time and settling time were; 0.1%, 50%, 2.02 min and 8.29 min respectively.

Table 4.8: RSM Solutions of optimal conditions

experiment	Settling Time (min)	Irradiat-tion time(sec)	Chemical Concent-ration	Water Content (%)	Separation (%)	desirability
1	8.29	2.02	0.10	50.00	78.1567	0.902502
2	7.49	2.00	0.10	50.00	78.1519	0.902446
3	6.98	2.02	0.10	50.00	78.1487	0.90241
4	9.36	2.03	0.10	50.00	78.1122	0.901989
5	8.60	2.01	0.10	49.83	78.0821	0.901641
6	11.79	2.07	0.10	50.00	77.8871	0.899389
7	8.59	2.05	0.10	50.00	77.8464	0.898919
8	5.00	1.87	0.10	50.00	77.8084	0.89848
9	17.06	2.09	0.10	49.72	77.4907	0.894811

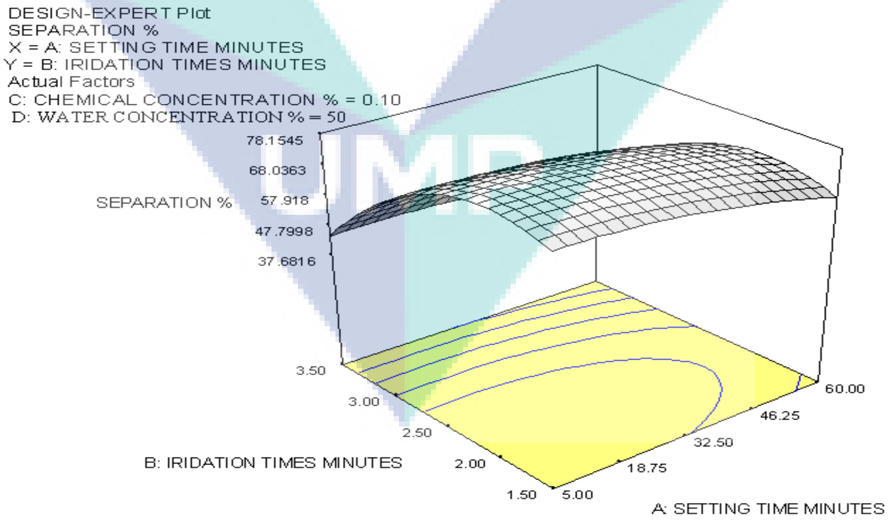

Figure 4.56 Response surface plots representing the effect of microwave irradiation time, settling time and their interaction on the water separation on emulsion

Figure 4.56 presents the response surface of the interaction between the irradiation time and the settling time on the response which is the percentage of water separated from the emulsion, however the plot had reached plateau at 2 min irradiation time, this 2 min could be considered as the optimal irradiation time, unlike the Kuwait crude oil in which the optimal irradiation time had reached until beyond 3 min.

IV. Microwave demulsification of Slop oil emulsion

Chemical assisted microwave demulsification techniques also applied to break some actual petroleum based emulsions, including the slop oil, that was a way to examine the applicability of the microwave demulsification techniques from laboratory based emulsions to actual industrial based emulsions, thus Table 4.9 and Figure 456 presents the optimal operating parameters and their interactions that generated from the response surface methodology, on the response variable which always the percentage of water separated from the emulsions after their exposure to the microwave energy

Table 4.9: RSM Solutions of optimal conditions

Experiment	**Settling Time (min)**	**Chemical Concentration (%)**	**Water Separation (ml)**	**Desirability**
1	27.35	1.00	52.6485	0.980473
2	27.07	1.00	52.6485	0.980472
3	27.88	1.00	52.6485	0.980472
4	25.79	1.00	52.6483	0.980462
5	17.78	1.00	52.6419	0.980106

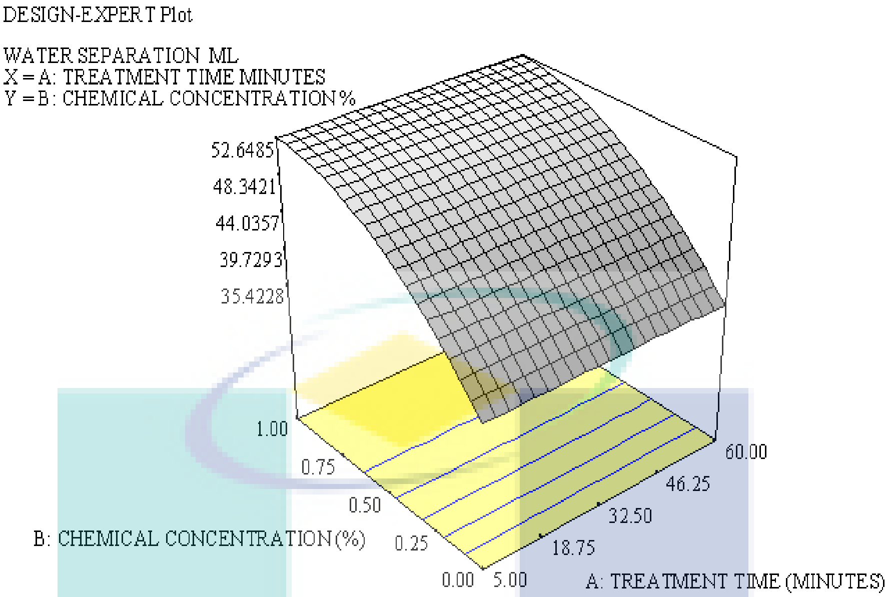

Figure 4.57: Response surface plots representing the effect of Chemical demulsifiers' concentration,, settling time and their interaction on the water separation on Slop oil emulsion

From Table 4.9; a good or optimal response of 52.6485 ml was obtained at 1% chemical demulsifiers' concentration and 27.35 min settling time, that was quite similar to the experimental results whereby the optimal response of 54 ml was obtained at 1% chemical demulsifiers' concentration and 25 min of settling time, while Figure 4.56 represents the contour of the response surface plots of the interacting independent parameters, hence Figure 4.57 also shows that the separation percent increase with increasing the chemical demulsifiers' concentration and settling time have no much effect on the response.

V. Chemical demulsification of the petroleum emulsions

The application of response surface methodology to study the formulation of the chemical demulsifiers was always as discussed previously, hence the response is always the amount or percentage of water separated from the treated emulsion, hence two types of chemical demulsifiers were investigated namely Amine group and silicone group demulsifiers, with different concentration on two types of crude oil named (A and B), the experimental emulsions tested were consisted of two distinct water volume fractions that are 50-50 and 30-70% w/o emulsions, since the chemical demulsification is based on gravitational and concentration deriving forces therefore the emulsion was left to settle slowly after chemical treatment for the period on one week (7 days), and the amount of water separation was taken every day till the day 7.

Table 4.10 presents the optimization solution for the optimal conditions that produced the optimal yield of separation efficiency, hence it’s obvious from Table 4.10 that Silicone based chemical demulsifiers were very effective in breaking the w/o emulsions of both crude oils, another observation is that the silicon demulsifiers were very effective on emulsions with high water content (50-50%) than emulsions with low water content (30-70%), hence from Table 4.10; silicon based chemical demulsifiers gave an optimal response range of (96 to 97%) for both crude oils at 50-50% water contents, and from this optimal condition it could be concluded that silicone based demulsifiers were found to be more effective than the amine based demulsifirs.

Table 4.10: RSM Solutions of optimal conditions

Experiment	**Chemical Concentrztion (%)**	**Settling Time (days)**	**Chemicals**	**Water Content (%)**	**Crude oil**	**Water Separation (%)**	**desirability**
1	2.65	6.10	SILICONE	50 : 50	A	96.9998	1
2	2.51	6.33	SILICONE	50 : 50	A	97.0001	1
3	2.44	6.48	SILICONE	50 : 50	A	97.0001	1
4	2.52	6.30	SILICONE	50 : 50	A	97.0002	1
5	2.36	6.65	SILICONE	50 : 50	A	97	1
6	2.35	6.70	SILICONE	50 : 50	A	96.9999	1
7	2.96	5.85	SILICONE	50 : 50	A	97	1
8	2.18	4.89	SILICONE	50 : 50	B	97	1
9	2.93	2.71	SILICONE	50 : 50	B	96.9999	1
10	2.08	5.55	SILICONE	50 : 50	B	97	1
11	1.99	6.34	SILICONE	50 : 50	B	97	1
12	2.01	6.15	SILICONE	50 : 50	B	97.0002	1
13	1.96	6.67	SILICONE	50 : 50	B	97.0002	1
14	2.02	6.06	SILICONE	50 : 50	B	96.9999	1
15	2.43	3.77	SILICONE	50 : 50	B	97.0002	1
16	2.63	3.20	SILICONE	50 : 50	B	97	1
17	3.00	7.00	AMINE	50 : 50	B	84.4192	0.870301
18	3.00	6.24	AMINE	50 : 50	B	81.4406	0.839594
19	3.00	7.00	AMINE	50 : 50	A	52.2036	0.538181
20	1.24	7.00	SILICONE	30 : 70	A	37.7762	0.389446
21	1.25	7.00	SILICONE	30 : 70	A	37.7749	0.389432
22	2.55	7.00	AMINE	30 : 70	B	14.8998	0.153607
23	1.71	6.01	SILICONE	30 : 70	B	13.3776	0.137913
24	1.97	7.00	AMINE	30 : 70	A	12.3799	0.127628
25	1.91	7.00	AMINE	30 : 70	A	12.3609	0.127432

Figure 4.58 represents the response surface plots of Silicone based chemical demulsification' concentration, settling time and their interactions on the water separation for 50-50% w/o emulsion made from crude oil A, thus the water separation observed to increase with increasing the chemical demulsifiers' concentration, however these optimized results were similar with the experimental results wherein the maximum separation was of 93% were observed with silicone demulsifiers at water 50-50% w/o emulsions of crude oil A based emulsions.

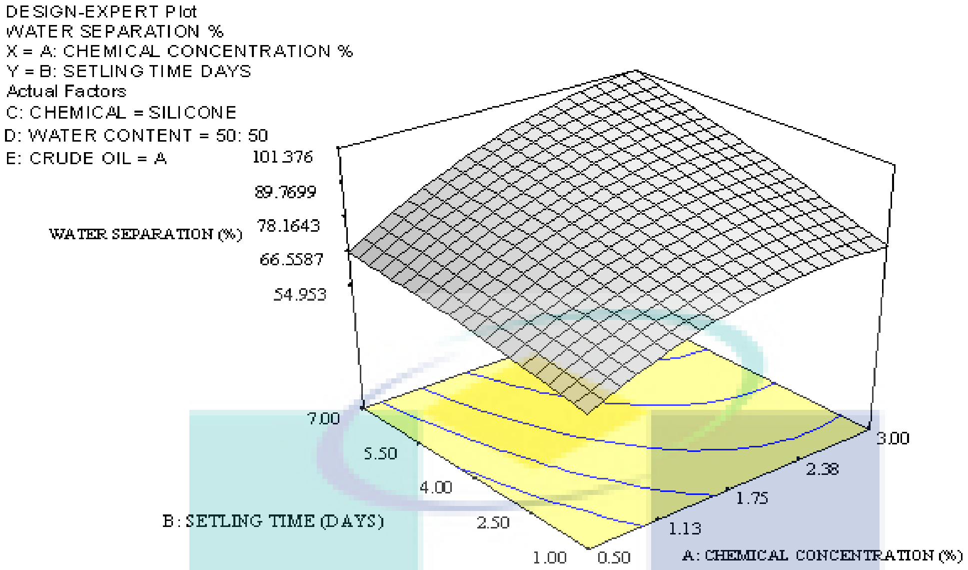

Figure 4.58: Response surface plots representing the effect of Chemical demulsifiers' concentration, settling time and their interaction on the water separation of w/o emulsions

VI. Ultrasonic demulsification of the petroleum emulsions

The optimal conditions for breaking the water-in-crude oil emulsions by ultrasonic demulsification technique was studied via the response surface methodology, since the current experimental emulsion was found to be very difficult to break with ultrasonic alone; therefore certain amount of chemical demulsifiers were added in order to accelerate the separation process, thus certain factors were considered including the effect of varying the ultrasonic power, chemical demulsifiers' concentration, sonication time and their interaction in separating water from crude oil emulsion was investigated, the RSM solutions of the optimal condition are shown in Table 4.11

Table 4.11: RSM Solutions of optimal conditions

Experiment	**Chemical Concentration (%)**	**Ultrasonic Power (watt)**	**Sonification Time (min)**	**Water Separation (%)**	**Desirability**
1	0.65	8.24	50.00	86.6092	0.896971
2	0.68	8.32	50.00	86.5704	0.896483
3	0.70	7.87	50.00	86.5029	0.895634
4	0.67	5.90	50.00	86.1058	0.890639

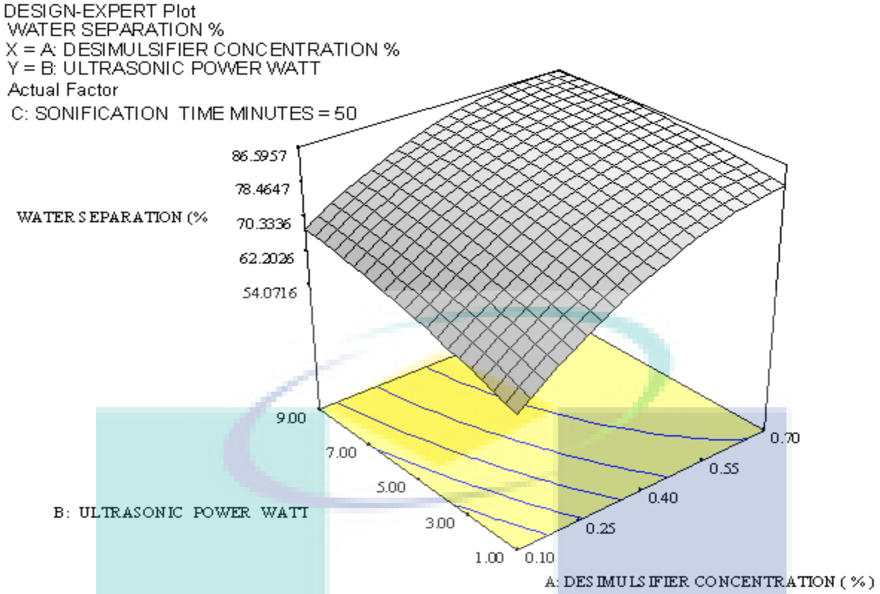

Figure 4.59: Response surface plots representing the effect of Chemical demulsifiers' concentration, ultrasonic power and their interactions on the separation of w/o emulsions

Within the various optimum conditions depicted in Table 4.11, the maximum response of water separation of 86.6092 was obtained from experiment 1 in Table 4.11, at ultrasonic power of 8.24 watt, chemical demulsifiers' concentration of 0.65, and sonication time of 6 min. These result is comparable to the experimental results from which the maximum separatiom separation of 97% was obtained from ultrasonic power of 9 watt, chemical demulsifiers' concentration of 0.7%.

Figure 4.59 also presents the response surface plots of and from this one can conclude that the chemical assisted ultrasonic demulsification techniques was found to be very effective in treating petroleum based emulsions and water separation

CHAPTER 5

Conclusions

5.1 Conclusions

The current research was devoted to investigate the behavior of water-in-crude oil emulsions in terms of formation, formulation, stabilization, and destabilization via various methods such as (microwave batch, Chemical and ultrasonic) and determine synergistic effect of their integration on experimentally formulated emulsions as well as real life emulsions. The principal objective of this project work was to develop a better fundamental understanding of the mechanisms of emulsion stabilization, mechanisms of emulsions breaking, as well as the potentials of microwave technology and ultrasonic demulsification technologies as sustainable alternatives in demulsification of water-in-crude oil emulsions. Based on the objective of the research; the current results were analyzed in chapter 4, hence chapter4 was devoted to the formation, formulation stabilization, and designated to destabilization by the means of the various techniques mentioned earlier.

Hence from chapter 4 the following conclusions were drawn:

From the screening results, it was found that Sorbitan monooleate (Span 80), had performed much better than its counter part of SDDS and Triton X-100 emulsifiers, hence span 80 is very good to produce an emulsion of heavy crude oils, Span 80 also worked quite better with light crude oils.

Other observation is that it is very challenging to produce a stable experimental emulsion of Miri light crude oil.

Further more, it was also observed that it was difficult to observe the droplet of the heavy crude oils under the microscope hence the current researchers got it done by removing the black color of the crude oil (Decolorization). It is possible to decolorize the crude oil, Moreover, emulsion viscosity and stability is a direct function of mixing Speed and emulsifiers' concentration, finally; the best Formulation of current emulsion was found to be 0.25% emulsifiers (Span 80) and 1600 rpm. chapter 4 also reveal the destabilization of the emulsion with the optimal stability character resulted from the integration of chemical microwave or chemical assisted ultrasound, demulsifiers concentration and irradiation time was considered as main parameters for this process, and that had resulted the following;

From Microwave chemical assisted demulsification of various types of w/o emulsion; 0.1% demulsifiers and 2min irradiation time was found to be the effective formulation for 50-50% w/o emulsion because it gave as high as 87% more or less water separation for this particular emulsion.

with 20-80% w/o emulsions; low concentration of demulsifiers (0.05%) and prolonged irradiation time of 3.5 minutes had given the best effects, although the percentage of water separated was less than that of 50-50% emulsions.

With 20-80% (w/o) emulsions; the maximum water separation observed was 60% of the total volume contained in the emulsion. Beside that with 0.7% demulsifiers' concentration, separation reached 96%. Indeed regarding pure chemical demulsification; two types of demulsifiers were used namely Hexylamine, and poly (dimethyl siloxane), for two different volume fraction of 50-50% and 30-70%, and the best results are summarized in the following: For 50-50% w/o emulsions, the maximum separation from hexylamine was around 75%, at 3% hexylamine concentration regardless of oil types, while the maximum separation from Siloxan was around 90% at 3% siloxane concentration But for

30-70%, hexylanine gave around 10% separation while siloxane gave around 40% separation so this was the reason behind the selection of siloxane to assist microwave and ultrasonic.

And finally with regard to ultrasonic-chemical assisted demulsification; it was found that, this combination was very effective in separating the emulsion, hence the separation was increased with increasing demulsifiers concentration and prolonged irradiation time, and the maximum separations were observed at 0.7% demulsifiers and 1 hour sonication time and power level of 3.

Indeed for sake of comparison Hence ultrasonic-chemical integrated system gave the highest separation rate for water-in-crude oil emulsions which reached 97% at power level of 3, compare to microwave-chemical integrated system which gave maximum separation efficiency of 87% at the aforementioned concentration of 0.1%, but when the demulsifiers were increased to 0.7% microwave had given a maximum separation of 96%, and finally the optimal conditions to break the break the petroleum based emulsion was obtained with the of optimization function of the design expert software, however results were to some extent in aggrement with experimental conditions.

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