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

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

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A thesis submitted in fulfillment
of the requirements for the award of degree of
Bachelor of Chemical Engineering

FACULTY OF CHEMICAL AND NATURAL RESOURCES ENGINEERING
UNIVERSITI MALAYSIA PAHANG

DECEMBER 2010

I declare that this thesis entitled “Demulsification of Water-In-Crude Oil Emulsions via Microwave Heating Technology” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.”

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To my respected supervisor,
beloved father and mother

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ABSTRACT

Traditional methods to separate water-in-crude oil emulsions like chemical demulsifiers are not environmentally-friendly, slow, separation not efficient, not cost effective and consume space for separation. The potentials of microwave energy in demulsification of water-in-crude oil emulsions were investigated. In this study, stability tests, gravity settling, microwave heating and microwave separation were studied. Microwave demulsification was applied in 50/50 and 20/80 water-in-crude oil emulsions with microwave exposure time varied from 120-180 seconds. As the sludge is heated, viscosity is lowered, and rapid coalescence of liquid phases takes place. Once the liquid phases coalesce, separation occurs through natural gravity. No chemicals are needed to force separation. Three different parameters were being investigated on the effect of separation namely volume ratio of water-in-oil emulsions, different emulsifiers and power generations of microwave. The four emulsifiers used were SDDS, Span 83, Triton X-100 and Tween 80. The power generations were 360 and 540 watts respectively. 20/80 water-in-crude oil emulsion was the most stable among two volume ratios. Newtonian fluid was determined from stability tests. Viscosity decreased, shear stress increased and shear rate increased over rpm. Surface and interfacial tensions were determined. Water and oil separation efficiencies via gravity settling were low. Volumetric heat generation rate of microwave was high. Water and oil separation efficiencies of microwave were more efficient than gravity settling. Microwave causes molecular rotation and ionic conduction thus fast heating.

ABSTRAK

Kaedah-kaedah tradisional untuk mengasingkan emulsi air-dalam-minyak mentah seperti agen demulsi kimia adalah tidak mesra alam, lambat, pemisahan tidak efisien, tidak jimat kos dan mengambil ruang untuk pemisahan. Keupayaan gelombang mikro dalam proses demulsi emulsi air-dalam-minyak mentah dikaji. Dalam kajian ini, ujian kestabilan, pemendakan graviti, pemanasan gelombang mikro dan pemisahan disebabkan gelombang mikro dikaji. Proses demulsi gelombang mikro diguna dalam 50/50 dan 20/80 emulsi air-dalam-minyak mentah dengan masa terdedah gelombang mikro berbeza dari 120-180 saat. Apabila kelodak dipanaskan, viscosity direndahkan, dan percantuman cepat fasa cecair mengambil tempat. Sebaik sahaja fasa cecair bercantum, pemisahan berlaku secara graviti semulajadi. Tiada bahan kimia diperlukan untuk pemisahan berlaku. Tiga parameter dikaji untuk kesan pemisahan antaranya ratio isipadu emulsi air-dalam-minyak, agen emulsi yang berbeza dan kuasa generasi gelombang mikro. Empat agen emulsi yang diguna adalah SDDS, Span 83, Triton X-100 dan Tween 80. Kuasa generasi adalah 360 dan 540 watt. 20/80 emulsi air-dalam-minyak mentah adalah paling stabil antara dua ratio isipadu. Fluid Newtonian ditentukan melalui ujian kestabilan. Viscosity menurun, daya tegang meningkat dan kadar tegang meningkat apabile rpm meningkat. Tension permukaan dan antara dua permukaan ditentukan. Pemisahan air dan minyak melalui pemendakan gravity adalah rendah. Kadar generasi pemanasan isipadu gelombang mikro adalah tinggi. Pemisahan air dan minyak gelombang mikro adalah lebih efisien daripada pemendakan gravity. Gelombang mikro menyebabkan putaran molekul dan konduksi ion kesannya pemanasan cepat.

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LIST OF ABBREVIATIONS

DLVO : Van der Waals interaction, electrical double layer theory

R/A : Resin to Asphaltene ratio

MPS : Multi-Phase Separation

MESB : Mechanical Emulsion Breaker

mw : microwave

o/w : oil-in-water emulsion

w/o : water-in-oil emulsion

SDDS : Sodium Dodecyl Sulfate

T X-100 : Triton X-100

mins : minutes

SR : Shear Rate

Visc. : Viscosity

SS : Shear Stress

rpm : rotations per minute

hr : hour

hrs : hours

LIST OF SYMBOLS

50/50 or 50-50: emulsion of 50 volume % water in 50 volume % of crude oil

20/80 or 20-80: emulsion of 20 volume % water in 80 volume % of crude oil

v_w : Settling velocity (cm/sec)

ρ_w : Density of water (g/cm3)

ρ_o : Density of oil (g/cm3)

g : Gravity

D : Droplet diameter (cm)

μ_o : Viscosity

P_o : Microwave surface power (W)

m : Mass of sample (g)

A : Sample container area (cm^2)

α_E : Electromagnetic attenuation factor (cm-1)

f : Frequency of incident microwaves

P_z : Microwave power transmitted (W)

δ : Loss tangent

q_{mw} : Volumetric heat generation rate ($cal/cm^3.s$)

λ_m : Wavelength (cm)

D_p : Penetration depth (cm)

$\varepsilon'r$: Dielectric constant

$\varepsilon''r$: Dielectric loss

c : Speed of light (cm/s)

h : Convective heat transfer coefficient ($cal/s.cm^2.^oC$)

v : Volume of water separated (cm3)

T_m : Temperature of emulsion (^oC)

T_a : Temperature of ambient (°C)

σ : Stefan-Boltzmann constant

ε : Emissivity of surface

Cp or Cp_m : Heat capacity of emulsion (cal/g.°C)

ρ : Density of emulsion (g/cm^3)

dT/dt : Rate of temperature increase

ϕ : Real water ratio inside emulsions

ρ(water) or ρ_w : Density of water

ρ(oil) or ρ_o : Density of oil

ρ_m : Density of emulsion

CHAPTER 1

INTRODUCTION

1.1 Problem Statement

In many oil fields, following the initial gas-oil separation process, the oil must be treated to remove water, salt, or H_2S. Most pipeline quality oil must have its water content reduced to the 0.2% to 2% by volume range. Because salt water is generally associated with oil in the reservoir, its production along with the oil is not unusual. Almost all well streams contain water droplets of various sizes. If, because of their higher density, they collect together and settle out within a short period of time they are called free water. A more difficult separation problem arises when the oil and water are produced as an emulsion. Most oilfield emulsions are the water-in-oil type, where individual water particles are dispersed in a continuous body of oil. An inverted, or oil-in-water, emulsion can also occur, especially when the ratio of water to oil is very high. Two things are necessary to produce an emulsion of water and oil: agitation and an emulsifying agent. In order to “break” the emulsion and separate the oil from the water, a variety of processes have been developed. Conventionally, chemicals are normally added continuously to the produced fluids, as far upstream from the treating or separation facilities as possible. This is the simplest and least expensive method currently endorsed by most of the oil companies. The addition of microwave heating is necessary and economically attractive when the space for chemical addition is limited in offshore production facilities. As older fields begin to produce increasingly higher water cuts, and when water injection projects are begun in depleting fields, the need for emulsion treating processes can increase. Small amounts of water can cause problems, particularly if the salinity is high. Salty crude will cause severe problems during the refining process by producing corrosive compounds under high temperatures and depositing mineral residues within the refining equipment. Untreated water in crude oil can also cause high wastewater loads when piping to refineries. Produced water, after separation and treatment, is normally disposed of by injection into disposal wells, reinjection into the reservoir as part of a waterflood project, or pumping to open pits where it is allowed to evaporate or drain. At some offshore locations, the water may simply be pumped into the ocean [Karl, 1986]. Traditional method using chemical addition to separate water-in-crude oil emulsions will cause pollution and environmental problems whether to mainland organisms or marine aquatics. So, a better alternative has been discovered which is microwave heating. It is environmentally friendly, not space confining and time-saving.

1.2 Objectives

1. To study the separation or demulsification (breaking emulsions) of water-in crude oil emulsions via microwave heating technology.
2. Analyze the overall performance of microwave heating as an alternative method for water-in-crude oil emulsions breaking compared to chemical addition.

1.3 Scopes

In order to achieve the objectives, the following scopes have been identified:

a) Characterization of emulsions in terms of chemical and physical properties such as density, viscosity, surface tension, interfacial tension, shear stress, shear rate, rotations per minute (rpm) and temperature.
b) To examine the demulsification of water-in-crude oil emulsions via microwave heating technology using batch process system.
c) To study the effects of varying the microwave power generation at 900, 720 and 540 watts.
d) Evaluation of volume rate of microwave heat generation.
e) Comparison between microwave heating technology and conventional method (chemical addition and hot plate).
f) To evaluate temperature profile at different locations for emulsions.

1.4 Rationale & Significance

The rationale and significance of separation of water in crude oil emulsions via microwave heating method will be compared with conventional method of using chemicals.

Firstly and most importantly, microwave heating method is an environmentally friendly method. It does not cause pollution to the environment. It does not need any chemical addition to separate crude oil emulsions. Traditional and present way of using chemicals to demulsify crude oil emulsions will create polluted waste water problem.

Secondly, microwave heating method is cost effective. It does not need the purchase of large quantities of chemicals which are expensive to separate crude oil emulsions. It only requires microwave heating machine to demulsify water in crude oil emulsions. The lower cost of using microwave heating method outweighs chemical method in comparison.

Thirdly, microwave heating method is time-saving and efficient. It requires only a short period of time for the effective separation of water in crude oil emulsions. On the other side, chemical method will take a lot of time for the settling process to take place. In industrial real site, it may take at least a week to separate water in crude oil emulsions using chemical method.

Fourthly, microwave heating method is not space confining. Because it only takes a brief period for separation, space used by microwave heating method will only takes a short time for separation. Microwave heating method is necessary when the space for chemical addition is limited in offshore production facilities. Unlike microwave heating method, chemical method takes a long time for separation and eventually takes up a lot of space for storage to let separation happens.

Lastly, microwave heating method is a clean technology. It does not produce any side effect to the environment. It is energy efficient and environmentally benign. It dramatically eliminates the use of chemicals. Microwave heating method to separate crude oil emulsions is superior to the conventional chemical method. It offers significant additional benefits, notably the efficiency of separation.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Water is normally present in crude oil reservoirs or is injected as steam to stimulate oil production. Water and oil can mix while rising through the well and when passing through valves and pumps to form in most cases relatively stable dispersions of water droplets in crude oil (w/o), which are usually referred to as oilfield emulsions. The formation of emulsions creates problems during the production, transport of multiphase oil-water-gas mixture to the land based process plants from the production sites. Formation of these emulsions during oil field production is a costly problem, both in terms of chemicals used and due to production losses. To reduce the water content of the produced crude oil, the water/crude oil emulsions have to be broken (demulsified) [Abdurahman H. Nour *et al.*, 2008]. Thus, it is important to understand the mechanisms responsible for formation, stabilization and controlling of these emulsions. There are many types of methods used to demulsify water-in-crude oil emulsions such as chemical additions, membrane separations, electrical, mechanical, conventional heating and microwave heating. In this context, microwave heating method will be used to demulsify water-in-crude oil emulsions. Many parameters had been considered in the previous researches. This study enhances microwave heating technology by varying the power generation and usage of different emulsifiers and demulsifiers.

2.1.1 Background

Emulsion is a thermodynamically unstable system consists of dispersed phase scattered across continuous phase. The dispersed phase (solid or liquid) is immiscible with the continuous phase. There are two types of water-crude oil emulsions, which are water-in-oil emulsions (meaning water is the dispersed phase and oil is the continuous phase) and oil-in-water emulsions (meaning oil is the dispersed phase and water is the continuous phase). Most well reservoir produced oil type is water-in-oil emulsions.

Microwaves are electromagnetic waves with wavelengths from 1mm to 1m, or with frequency from 0.3 GHz to 300 GHz. Microwave irradiation are being studied as a tool for demulsification. This is due to the fact that microwave irradiation offers a clean, cheap and convenient heating process that in most of times results into better yields and shorter reaction times [Coutinho et *al.*, 2007].

The heating of liquids using microwaves can be explained by the interaction of matter with the electric field of the incident radiation, causing the movement of ions as well as that of induced or permanent molecule dipoles. The movement of such species can cause heat generation. The two main dielectric heating mechanisms are: dipole rotation and ionic conduction. Electric dipoles are formed by the redistribution of electric charges. The action of an electric field causes the orientation of dipole moments parallel to the electric field, while the action of an electromagnetic field results in the rotation of the dipoles caused by the high number of times that the electromagnetic field is alternated. In liquids, the electric dipoles cannot rotate instantaneously and the time required for the movement of the dipoles depend on the molecular mass, on the viscosity of the medium and on the forces exerted by the neighboring molecules. For frequencies comprised between low and very high, electric dipoles slightly delay with respect to electric field variations and a portion of the energy that the electric field provides for dipole rotation is stored. Such energy will be turned into heat resulting from the friction with neighbouring molecules. This heating mechanism is called dipole rotation. When the irradiated sample is an electric conductor or semiconductor formed by ions (such as NaCl aqueous solutions), these ions can move through the material so as to follow the variations in electric field. The resulting electrical currents heat the sample as a consequence of the electrical resistance. This mechanism is called ionic conduction [Coutinho et *al.*, 2007].

Separation occurs mainly because of coalescence, flocculation and sedimentation. Stability (instability) of an emulsion is caused by the coupling of coalescence and flocculation, which follow a multiplication principle rather than an additivity principle. This means that the total result of the application of a stabilizer (destabilizer) depends very much on both flocculation and coalescence processes [Sjöblom et *al.*, 2005].

Coalescence is the process in which two or more emulsion drops fuse together to form a single larger drop, and is irreversible as Figure 3.2 indicates. As already mentioned, for large drops approaching each other (no background electric field), the interfaces interact and begin to deform. A plane parallel thin film is formed, which rate of thinning may be the main factor determining the overall stability of the emulsion. The film thinning mechanism is strongly dependent on bulk properties (etc. viscosity) in addition to surface forces [A. Hannisdal, 2005].

Flocculation is the process in which emulsion drops aggregate, without rupture of the stabilizing layer at the interface. Flocculation of emulsions may occur under conditions when the van der Waals attractive energy exceeds the repulsive energy and can be weak or strong, depending on the strength of inter-drop forces. The rate of flocculation can be estimated from the product of a frequency factor (how often drops encounter each other) and the probability factor (how long they stay in contact). The first depends on the driving force for droplet movement whereas the latter depends on the interaction energy of the droplets [Binks, 1998]. The driving forces for flocculation can be (1) *body forces,* such as gravity and centrifugation causing creaming or sedimentation, depending on whether the mass density of the drops is smaller or greater than that of the continuous phase. Since drops of different size move with different velocities, drops are also subjected to aggregation during creaming/sedimentation. Gravitational sedimentation is used industrially in for example hydrocyclones or traditional settling tanks (2) *Brownian forces* or (3) *thermocapillary migration* (temperature gradients) may dominate the gravitational body force for very small droplets, less than 1 μm [Danov et *al.*, 2001].

The discovery of enhanced separation of oil-water emulsions and dispersions using microwave radiation was first disclosed in 1986 by Wolf, N. O. in U.S. Pat. No. 4,582,629. In this disclosure, Wolf demonstrated through several benchtop experiments that modest amounts of microwave power applied to oil-water emulsions could increase oil-water separation rates by more than a factor of two compared to simple heating alone. Results suggested that microwaves were enhancing the separation rate through a mechanism distinct from heating alone. Wolf postulated that microwaves were successful because of direct heating of the bulk of the emulsion and disruption of surfactant molecules present in the interfacial film.

Since Wolf's pioneering work, independent confirmation of his general results were obtained by several researchers. For example, Nikola *et al.*, with the support of the EPRI Center for Materials Production developed a novel apparatus for testing continuous separation of emulsions using microwave radiation. Purta found significant reduction in the time required to separate oil and water phases of emulsions using only small amounts of microwave energy and with temperature rises of only 20 degrees C.

A research report, prepared by Fang, C. S.; Chang, B. K. L.; Lai, P. M. C.; Klaila W. J. presented systematic data on the effectiveness of microwave radiation in separating water-oil mixtures and emulsified oil-water-solid sludges. The authors concluded that microwave radiation was more effective in heating thick, viscous emulsions than gas or oil-fired heaters. Enhanced emulsion breaking with microwave radiation was also reported. They found evidence that enhanced separation rates were due to reduction of the zeta potential, which suspends water droplets and solid particles in an emulsion.

Following the original disclosure of Wolf, a comprehensive series of patents were generated which disclosed novel concepts for applying microwaves to oil-water emulsions. Among these are U.S. Pat. Nos. 4,853,507; 5,055,180; 4,810,375; and 4,853,119. All of these patents assert the advantages of enhanced emulsion breaking properties through the application of microwave radiation. While generally applicable to any type of emulsion or suspension, one of the largest potential users of microwave-enhanced emulsion breaking technologies is the petroleum industry. Most of the patents referenced previously discuss applications in this specific industry.

2.2 Stability of Crude Oil

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

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

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

The effect of the water content, agitation speed, resin/asphaltene (R/A) ratio, surfactant concentration, and temperature on crude oil emulsion stability has been shown in past journal. For water content, lower water (v/v) in water-in-oil emulsions, a higher solids concentrations was found allowed easier emulsification and slowed the settling process. There is a correlation between dynamic viscosity and mixing speed, which is; as increasing the mixing speed, resulting in increase of the viscosity of the emulsion, which means the stability of the emulsions increases. High resin/asphaltene (R/A) ratios decrease the water-in-oil emulsion stability. The effectiveness of water-in-oil emulsion stabilization increases with increasing surfactant concentration and decreases with increasing temperature [Abdurahman H. Nour *et al.*, 2008].

The microwave heating process was examined for emulsions samples. Results of this study showed that, microwave radiation is a dielectric heating technique with the unique characteristics of fast, volumetric and effective heating is feasible and has the potential to be used as an alternative way in the demulsification of water-in-oil emulsions. From temperature distribution profiles of irradiated emulsion, it appears water-in-oil emulsions has been heated quickly and uniformly by microwaves rather than by conventional heating. This new separation technology does not require chemical addition. Furthermore, microwave radiation appears to provide faster separation than the conventional heating methods [Abdurahman H. Nour et *al.*, 2010].

I will enhance this microwave heating technology by varying the power generation, usage of different emulsifiers and demulsifiers.

Water-in-crude oil emulsion creates a lot of problems, especially foaming and corrosion in pipeline. Most of the oil companies use chemicals to demulsify water-in-crude oil emulsions, which may require additional cost and sometimes affect the chemical properties of the crude oil itself. So, to demulsify water-in-crude oil emulsions, it is required an easy, applicable, safe, cost effective method. So, I will be using microwave method in demulsification process to remove water-in-crude oil emulsions, which cause corrosion in pipelines.

2.2.1.2 Stability Investigation of Water-in-Crude Oil Emulsion

Experimental data are presented to investigate the stability of water-in-crude oil emulsions in both creaming and coalescence states were measured as a function of sodium chloride concentration. Also the stability of w/o emulsion is investigated over a wide range of parameters. These parameters are salt concentration (0-5.5%), mixing speed (800-1600 rpm), water concentration (10-80%) and temperature.

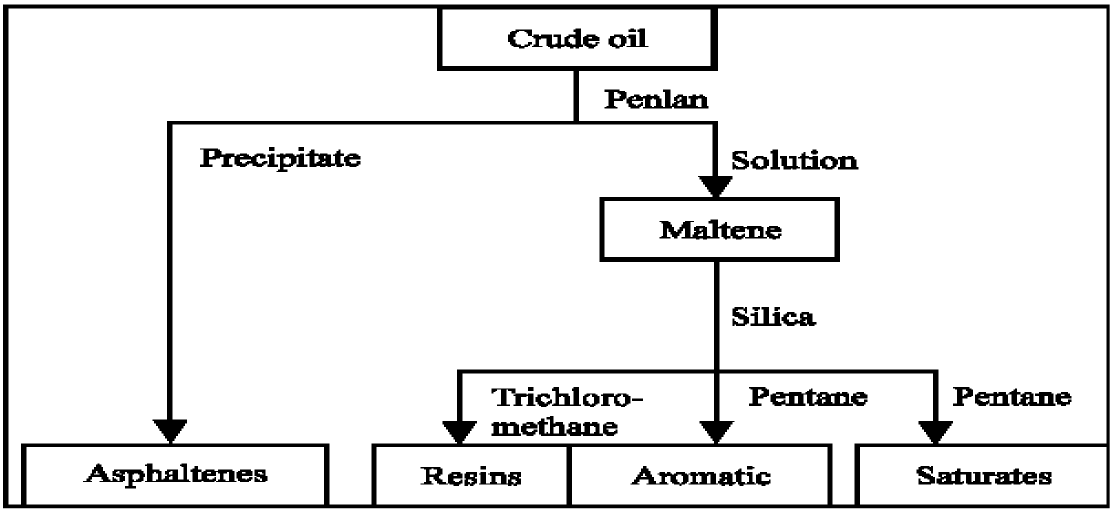


Fig 2.1: Separation of Crude Oil Fractions

The percentage of water separated is the best indicator of emulsion stability. Separation of water layer was used as a measure of physical instability for water-in-oil emulsions. It is pronounced that separated water was increased for emulsions having high salt concentrations. A long duration is necessary for separation of water-in-oil emulsions with no heat and salt is remarkable for sedimentation experiments. However, an unstable emulsion can be eventually destroyed leading to complete separation of the two phases. From the diffuse ion theory, as salt concentration increases, the internal energy of the system increases. Consequently, the emulsions are not thermodynamically stable and droplets (water) merge with each other to produce big droplets and increase the coalescence rate. Coalescence is one of the possible mechanisms of destruction of emulsions, which occurs when the energy of adhesion between two droplets is larger than the turbulent energy causing dispersion. Interfacial tension is an important factor in emulsion stability. It arises because the intermolecular forces in the interior of a liquid are equal in all directions. The interfacial tension falls to low values at higher sodium chloride (NaCl%) concentration. To investigate the effect of salt on the emulsion stability, one would go into the free energy of the system. For a constant volume of droplets, as the droplet stretches, its surface area as well as the free energy of the surface increases. On the other hand, the longer the droplet dimension and smaller the radius, the lower is the rotational energy. The results indicated that as salt concentration (NaCl%) increases, the density difference increases and interfacial tension decreases, the chance for the molecules to collide with each other increases.

It is found that as the volume fraction of water in w/o emulsions decreases, the separation time for water to separate from the emulsion decreased. The concentration of surfactant mainly affects the viscosity of emulsion. Experiments show that the viscosity of emulsion increases as surfactant concentration increases. It also shows that the viscosity of emulsion increases greatly as internal volume fraction (water) increases.

The stability of emulsions again was determined by measuring the water separation from the emulsions at room temperature (30°C) using surface-active agents (asphaltene and resin). When surface-active agents added to the emulsions, the interfacially active agents were adsorbed or deposited at the interface of the oil/water system. The process takes place over a period of time until the system attains equilibrium. The figures shown that the emulsions made by asphaltenes were more stable than those made by resins or mixture agents (asphaltenes+resins).

Significant changes in temperature cause changes in interfacial tensions, viscosities, nature (hydrophilicity-lipophilicity) of the surfactants, vapor pressures of the liquid phases and in the thermal agitation of the molecules. Thus, emulsions tend to be very sensitive to temperature changes. Emulsions are more stable when the temperature is near the point of minimum solubility of emulsifying agents [Abdurahman H. Nour et *al.*, 2006].

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

The effect of chemical demulsifiers in demulsification of water-in-oil emulsions were assessed experimentally by Abdurahman *et al.* (2007). The relative rates of water separation were characterized via graduated beakers. Four groups of demulsifier with different functional groups were used in this research work namely amines, polyhydric alcohol, sulphonate and polymer. The effect of alcohol addition on demulsification performance was also studied.

Triton X-100 was used beside asphaltenes and resins originally present in crude oil to stabilize the emulsions. Four chemical demulsifiers namely amine groups, polymeric, sulphonate and polyhydric alcohol were used to perform demulsification tests. Oil producer is interested in two aspects of demulsification; the rate of speed at which separation takes place and the amount of water left in the crude oil after separation. In terms of emulsion characterization, this study used a variety of surfactants to get a high stability for water-in-oil emulsions. Coalescence needs to be minimized to obtain any useful rheological information. In this regard, as shear rate increases, the viscosity decreases. From the experiment, emulsions exhibit Newtonian behavior up to a water content of 20%.

Water-phase pH has a strong influence on emulsion stability. The stabilizing, rigid-emulsion film contains organic acids and bases, asphaltenes with ionizable groups and solids. The pH of water affects the rigidity of the interfacial films. pH also influences the type of emulsion formed. Low pH (acidic) generally produces w/o emulsions, whereas high pH (basic) produces o/w emulsion. The optimum pH for demulsification is found at 10 without demulsifier. Addition of a demulsifier enhances demulsification.

The interfacial pressure of demulsification process is defined as the difference between the interfacial tension of the oil containing stabilizer/aqueous phase and that of the same system when a destabilize is added. Results showed that the higher the interfacial pressure value, the higher the instability of emulsion and vice versa. Based on results, demulsifiers can be divided into three groups. The first group consists of the demulsifiers such as amine group, sulphonate and polyhydric alcohols group which have interfacial pressure values ranging from 4.1 to 7.5 which can destabilize the emulsion. The water separated is up to 80%. The second group comprises Polyethylene Glycol (PEG) 600, Polyethylene Glycol (PEG) 1000, AOT, propylamine which have interfacial pressure values ranging from 2 to 6 and can partly break the emulsion. The amount of water separated from this group is in the interval of 25 to 67%. The third group consist of poly PO terminated, polyethylene block PEG, polyethylene oxide (PEO) 100000, trioctylamine, Propylene glycol (PG), ethylene glycol (EG) and NaDBS which have interfacial pressure values ranging from -8 to 2.8 and could not destabilize the emulsion. The percentage of water separation is less than 15%.

All amine groups showed the water and oil separations. This could be attributed to a very specific interaction between the amine added and the naturally occurring constituents in the interfacial film.

The larger agglomerates have a larger sedimentation velocity than the individual particles and require larger forces to hold them at the interface. According to Stoke’s Law, as droplets agglomerate, the density flocs decreases because of entrained continuous phase (oil), but their radius increases, resulting in a higher sedimentation velocity because of the squared dependency on the radius.

Effect of alcohol addition on demulsification performance of oil soluble demulsifiers studied as well. Butanol does not affect the destabilization if used alone as destabilizer, but they can enhance the destabilization process when used together with a demulsifier. Butanol is grouped into medium chain alcohol which is slightly soluble in water and more soluble in non-polar or weakly polar compound.

2.3 Demulsification

2.3.1 Chemical Demulsification

2.3.1.1 Chemical Demulsification of Water-In-Crude Oil Emulsions

Chemical demulsification is the most widely applied method of treating water-in-crude oil emulsions and involves the use of chemical additives to accelerate the emulsion breaking process. The effect of chemical demulsification operations on the stability and properties of water-in-crude oil emulsions was assessed experimentally. In this regard, Amine Demulsifier, Polyhydric Alcohol, Acid and Polymeric demulsifiers were used. The amine group demulsifiers promoted best coalescence of droplets. In contrast, polymeric demulsifier group is the least in water separation.

All amine groups showed the water and oil separations. This could be attributed to a very specific interaction between the amine added and the naturally occurring constituents in the interfacial film. After a prolonged duration, decylamine separated highest percentage of water, followed by octylamine, hexylamine, pentylamine, dioctylamine, trioctylamine and propylamine. Oil separation from water-in-oil emulsions through the addition of amine group also showed the same descending sequence as before but with a higher percentage of oil separation. The observed descending sequence of amine demulsifier efficiency was due to high molecular weight factor of amine which acts as flocculants in adsorption and interaction activities.

All polyhydric alcohols (polyethylene glycol PEG 1000, polyethylene glycol PEG 600, ethylene glycol EG and propylene glycol PG) are aliphatic alcohol compounds which contain two hydroxyl groups as their functional groups. PEG 1000 can separate higher percentage of water than PEG 600. While for EG and PG, there was no separation of water. All polyhydric alcohol demulsifiers are able in separating oil from the emulsion. PEG 600 has the highest separation, followed by PEG 1000, EG and PG. Based on the solubility properties, low molecular weight alcohols are water soluble such as methanol and ethanol.

From experimental results obtained in this paper, it was found that the amine demulsifiers were more effective in emulsion breaking than polyhydric dmulsifier group. It can be concluded that the amine demulsifiers for hydrogen bonding is much stronger than the polyhydric alcohols demulsifier group.

Six acid demulsifiers were tested separately. Butanoic acid has the highest percentage of separated water, followed by octanoic acid (long time of induction) and formic acid. Hexanoic, pentanoic and heptanoic acids have much lower percentages. The classification of the demulsifiers in terms of decreasing efficiency is therefore butanoic, formic, octanoic, hexanoic, pentanoic and heptanoic acids. The efficiency of blended butanoic/octanoic, formic/octanoic and hexanoic/octanoic (50/50 o/w) were better than the single demulsifiers. This may be attributed to the presence of the low molecular weight octanoic acid which effectively increases the efficiency of water separation compared to the performance of each demulsifier used alone. All acid demulsifiers permit oil separation. The highest was given by butanoic acid followed by formic acid. Acid demulsifiers were less in both water and oil separations.

Amine demulsifiers group were more effective in emulsion breaking than polyhydric and acid demulsifiers. Decylamine is the best in separation of both water and oil from emulsion.

This method takes very long time to complete demulsification of water-in-crude oil emulsions. A faster and more effective method to separate water from crude oil emulsions, which is microwave heating technology is preferred [Abdurahman H. Nour et *al.*, 2007].

2.3.1.2 Development of New Demulsifiers for Oil Production

Formation of emulsions comprising oil and water commonly occur in the extraction, production and processing/refining of petroleum oil. It is often necessary to separate the water from the oil in order to effectively prepare the oil for further processing and/or refinement. Demulsifiers are typically composed of one or more surfactants dispersed in a solvent system and may be derived from alcohols, fatty acids, fatty amines, glycols and alkylphenol condensation products, for example.

The ecological impact of offshore crude oil extraction has been subjected to increasing scrutiny. Several international and national environmental regulatory agencies have determined that demulsifiers containing nonylphenol alkoxylates and related compounds have a deleterious effect on the marine environment. Moreover, conventional demulsifier chemicals typically do not meet a biodegradation level of greater than 20% as established by these regulatory agencies. Consequently, the likelihood exists that a vast majority of conventional demulsifiers will be banned from offshore use in the near future.

A need therefore exists for petroleum oil demulsifiers with an improved environmental profile. In particular, a need exists for environmentally friendly water-in-oil demulsifiers that are biodegradable and have a low toxicity in the marine environment.

The present invention provides environmentally friendly demulsifiers for the breakdown of petroleum oil applications. The demulsification formulations of the present invention are biodegradable and are low in toxicity. The demulsifiers include a poly(tetramethylene glycol) and an alkylene glycol copolymer linked to the poly(tetramethylene glycol) by a difunctional coupling agent.

It is a demulsifier comprising about 5% to about 90% by weight of poly(tetramethylene glycol) and about 1% to about 50% by weight of an alkylene glycol copolymer linked thereto by about 5% to about 90% by weight of a difunctional coupling agent.

The demulsification formulations of the present invention meet or exceed regulatory standards for biodegradability and aquatoxicity (i.e., the present demulsifiers are non-mutagenic, non-reprotoxic or endocrine disrupting).

2.3.2 Multiple Stage Demulsification Process

2.3.2.1 Systematic Crude Oil Dewatering

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

The first stage is the Multi-Phase Separation (MPS). The “multiphases” (oil, water and solids) are separated in the first stage: the oil is pumped through the MPS profiles and as it passes through the inlet the oil is swirled on to the MPS profiles, the small water droplets merge to form larger drops. These are bound by the gravitational and adhesion forces of the profiles and directed down into the water collecting area. The solids slide down the profiles into the sludge holding tank. This operation is also suitable for deoiling.

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

The third stage is Membrane Filtration. In the third and final stage, the oil flows through a water-repellent membrane which dependably retains the last remaining water droplets.

Although this crude oil dewatering unit is fully automated and no chemicals is needed, the process is a complicated one involving three stages. Furthermore the construction and installation cost will come into account when using this process. A more simplified and cost-effective method will be considered for the demulsification of crude oil emulsions which is through microwave heating.

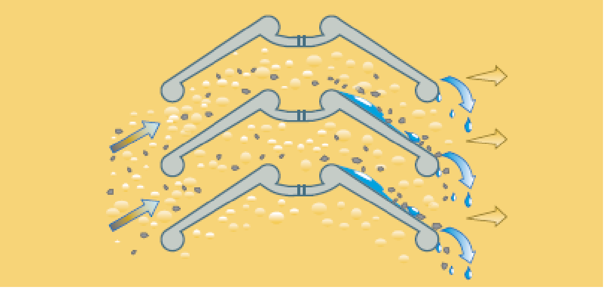


Figure 2.2: Multi-Phase Separation (MPS) Process

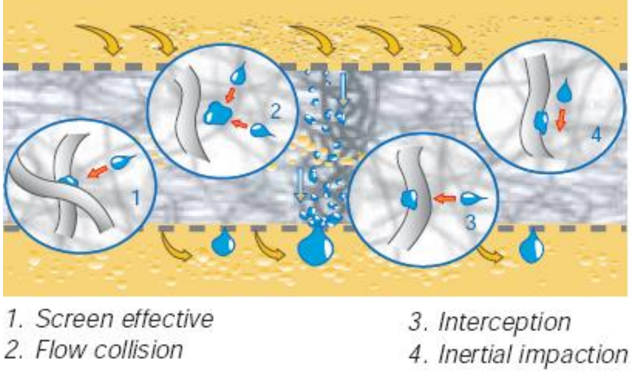


Figure 2.3: Mechanical Emulsion Breaker (MESB) Process

2.3.3 Microwave Heating Technology

Microwave heating technology is a relatively new method in demulsifying water-in-crude oil emulsions. Microwave heating technology is clean, cheap and fast in separating water-in-crude oil emulsions compared to conventional method of using chemical additives. It also provides better yields in comparison. Besides that, microwave heating is environmental friendly. On the other hand, chemical additives can cause serious wastewater pollution to the surroundings.

Electromagnetic radiation in the frequency range 300 MHz-300GHz are known as microwaves, microwave energy is a non-ionizing radiation that causes molecular motion by migration of ions and dipole rotations, but does not cause changes in molecular structure and wavelengths ranging from a few cm to a few mm [Chartterjee *et al.*, 1998]. It can cause heat generation.

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

A batch microwave heating process of 2450 MHz was examined on crude oil emulsions.

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

From the result obtained in this research, it was found that the rate of temperature increase of emulsions decreased at higher temperature due to decreasing dielectric loss of water. [Abdurahman H. Nour et *al.*, 2010].

Laboratory tests have been shown that microwave radiation can be faster to separate emulsified water from oil mixtures. Results also showed that the temperature occurred by microwave always higher than that occurred by conventional heating (hotplate). Microwave has feature of penetrating power, it distributes energy within the bulk of most materials, rather than just on its surface [Abdurahman H. Nour et *al.*, 2006]. Microwave radiation is a dielectric heating technique with unique characteristics of fast, volumetric and effective heating is feasible and has the potential to be used as an alternative way in the demulsification of water-in-oil emulsions.

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

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

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

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

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

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

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

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

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

$$v_w = \frac{(\rho_w - \rho_o) g D^2}{18 \mu_o} \qquad \text{(Equation 1)}$$

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

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

$$P_o = \frac{453.2 + 59.8\ln(m)}{A} \qquad \text{(Equation 2)}$$

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

$$P_{\aleph} = P_o e^{-2\alpha\aleph} \qquad \text{(Equation 3)}$$

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

$$\propto_E = \frac{2\pi f}{c}\left[\frac{\varepsilon'_r}{2}\sqrt{1 + \tan^2\delta - 1}\right] \qquad \text{(Equation 4)}$$

The above equation will be used for calculation of the volume rate of heat generation by microwave radiation but not in my research as:

$$q_{MWz} = \frac{2\propto_E}{4.184} P_z \qquad \text{(Equation 5)}$$

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

$$\lambda_m = \frac{c}{f}\left[\frac{\varepsilon'_r\left(\sqrt{1+\left(\frac{\varepsilon''_r}{\varepsilon'_r}\right)^2}+1\right)}{2}\right]^{-1/2} \qquad \text{(Equation 6)}$$

and

$$D_p = \frac{c}{2\pi f}\left[\frac{\varepsilon'_r\left(\sqrt{1+\left(\frac{\varepsilon''_r}{\varepsilon'_r}\right)^2}-1\right)}{2}\right]^{-1/2} \qquad \text{(Equation 7)}$$

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

$$q_{MW} = \frac{hA}{V}(T_m - T_a) + \frac{\varepsilon A\sigma}{V}\left[(T_m + 273.15)^4 - (T_a + 273.15)^4\right] + \rho C_p\left(\frac{dT}{dt}\right) \qquad \text{(Equation 8)}$$

The above equation assumes that the rate of heat transfer from emulsified water droplets to the continuous phase (oil) is very rapid; therefore, water and oil practically have the same temperature. The right hand side of equation above comprises of three terms, convective heat transfer, and radiative heat due to microwave and conductive heat in the sample respectively [Abdurahman H. Nour *et al.*, 2010].

2.4 Comparative Studies

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

In conventional thermal heating, energy is transferred to the material through convection, conduction and radiation of heat from the surfaces of the material. In contrast, microwave energy is delivered directly to the material through molecular interaction with the electromagnetic field. Because microwaves can penetrate materials and deposit energy, heat can be generated throughout the volume of the material. The transfer of energy done not rely on diffusion of heat from the surfaces and it is possible to achieve rapid and uniform heating of thick materials. In addition to volumetric heating, microwaves can be utilized for selective heating of materials. The molecular structure affects the ability of the microwaves to interact with materials and transfer energy. When materials in contact have different dielectric properties, microwaves will selectively couple with the higher loss material. In multiple phase materials, such as W/O emulsions, some phases may couple more readily with microwaves.

In terms of emulsion breaking, the separation is much faster with microwave heating than room temperature (gravitational) and conventional heating separation. Results showed microwave radiation can raise the temperature of emulsion, reduce viscosity and the result a separation of water from oil. As microwave is a nonionizing radiation that causes molecular motion by migration of ions and dipole rotations, therefore microwave induced molecular rotation of water molecules and causes in reduction of zeta potential.

Laboratory tests have been shown that microwave radiation can be an effective tool to separate emulsified water from oil mixtures. This new separation technology does not require chemical technology. Results also showed that the temperature occurred by microwave always higher than that occurred by conventional heating (hotplate). Microwave has feature of penetrating power, it distributes energy within the bulk of most materials, rather than just on its surface. Molecular rotations can reduce zeta potential which suspends water droplets and solid particles in an emulsion [Abdurahman H. Nour et *al.*, 2006].

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

For this research the type of method used was experimental batch method. In this research, crude oil samples from Petronas Refinery, Melaka City was collected.

In this study, microwave heating concept was to separate water in crude oil emulsions. The concept of microwave is very recent in breaking the emulsion of crude oil, which was started in the year 1986. Microwave method is considered as a cost effective method in the laboratory and all the feed and the raw materials proves that the microwave is the best methods in terms of applicability in a way that it is not space confining. Crude oil industry can benefit from this concept, since this can be considered as one of the easiest and cheapest process.

3.2 Materials

3.2.1 Emulsifying Agents

An emulsifier (also known as an emulgent) is a substance which stabilizes an emulsion by increasing its kinetic stability. One class of emulsifiers is known as surface active substances, or surfactants.

3.2.1.1 SDDS

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

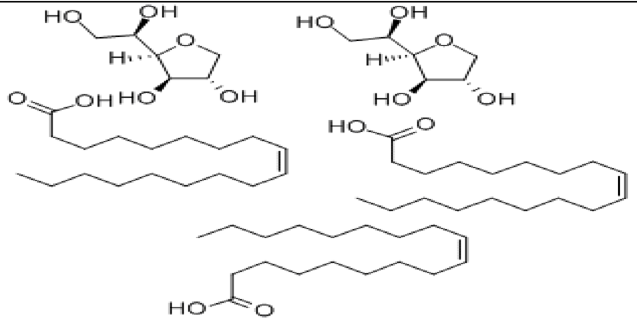
Table 3.1: Properties of SDDS

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

3.2.1.2 Span 83

Span 83 is mainly used for cosmetics, textiles, pharmaceuticals, paints, petroleum products, oil, industries such as powder for emulsifier, by solvents, stabilizers, lubricants, softener, antistatic agents, finishing agent, dispersing agent, cosolvent, anti-rust agent. Its preparation or sources is from sorbitol and oleic acid anhydride reaction in the system.

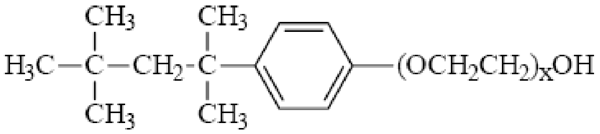
Table 3.2: Properties of Span 83

Other names	Span No 3, Sorbitan Sesquioleate, Anhydrohexit olsesquioleate, Crill 16, Crillk 16, Emasol41s, E msorb2502
Molecular Structure	
CAS number	[8007-43-0]
Molecular formula	$C_{66}H_{130}O_{18}$
Density	0.989 g/mL at 25 °C(lit.)
Melting point	Decomposes
Vapor pressure	0.81 psi (20 °C)
Flash point	113 °C

3.2.1.3 Triton X-100

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

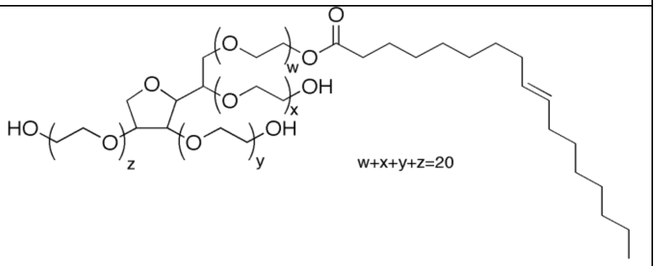
Table 3.3: Properties of Triton X-100

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

3.2.1.3 Tween 80

Tween 80 is a nonionic surfactant and emulsifier derived from polyethoxylated sorbitan and oleic acid, and is often used in foods. Tween 80 is a viscous, water-soluble yellow liquid. Properties of Span 80 are as in the table below:

Table 3.4: Properties of Tween 80

Other names	Polysorbate 80, polyoxyethylene (80) sorbitan monooleate, (x)-sorbitan mono-9-octadecenoate poly(oxy-1,2-ethanediyl, POE (80) sorbitan monooleate
Molecular Structure	
CAS number	[9005-65-6]
Molecular formula	$C_{64}H_{124}O_{26}$
Appearance	Amber colored viscous liquid
Density	1.06-1.09 g/mL, oily liquid
Melting point	-20.556°C (-5°F)
Boiling point	>100°C (212°F)
Solubility in water	Very soluble
Vapor pressure	<0.1 kPa (@ 20°C)
Flash point	113 °C

3.3 Equipments

3.3.1 Microwave Oven

In this research, Elba domestic microwave oven model: EMO 808SS, its rated power output were 360 and 540 watts and its operation frequency is 2450 MHz was used in heating water-in-oil emulsion samples. A 250 mL beaker was used as sample container.

3.3.2 Thermocouple

A thermocouple is a junction between two different metals that produces a voltage related to a temperature difference. Thermocouples are a widely used type of temperature sensor for measurement and control and can also be used to convert heat into electric power. They are interchangeable, are supplied fitted with standard connectors, and can measure a wide range of temperatures.

Any junction of dissimilar metals will produce an electric potential related to temperature. Thermocouples for practical measurement of temperature are junctions of specific alloys which have a predictable and repeatable relationship between temperature and voltage. Different alloys are used for different temperature ranges.

Certain combinations of alloys have become popular as industry standards. Selection of the combination is driven by cost, availability, convenience, melting point, chemical properties, stability, and output. Different types are best suited for different applications. They are usually selected based on the temperature range and sensitivity needed. Thermocouples with low sensitivities (B, R, and S types) have correspondingly lower resolutions. Other selection criteria include the inertness of the thermocouple material, and whether it is magnetic or not. Standard thermocouple types are listed below with the positive electrode first, followed by the negative electrode.

In my research study, I used thermocouples type J. Three thermocouples type (K-IEC-584-3) will be connected to Pico-TC-08 data logging and then connected to microwave oven as shown in Figure 4. The thermocouples were inserted to different locations top, middle and bottom of the emulsion sample to measure local temperatures.

3.3.3 Data Logger

A data logger is an electronic device that is used to record measurements over time. Pico data loggers require no power supply and simply plug into a parallel, serial or USB port on your PC. By connecting suitable sensors, Pico data acquisition products can be used to measure temperature, pressure, relative humidity, light, resistance, current, power, speed, vibration... in fact, anything that you need to measure. Pico data loggers are supplied complete with PicoLog — this powerful but flexible data acquisition software allows you to collect, analyze and display data. With PicoLog the data is viewable both during and after data collection, in both spreadsheet and graphical format. The data can also be exported for use in other applications. In my research study, the data logger was connected to PC using the Pico Log R5.08.3 software.

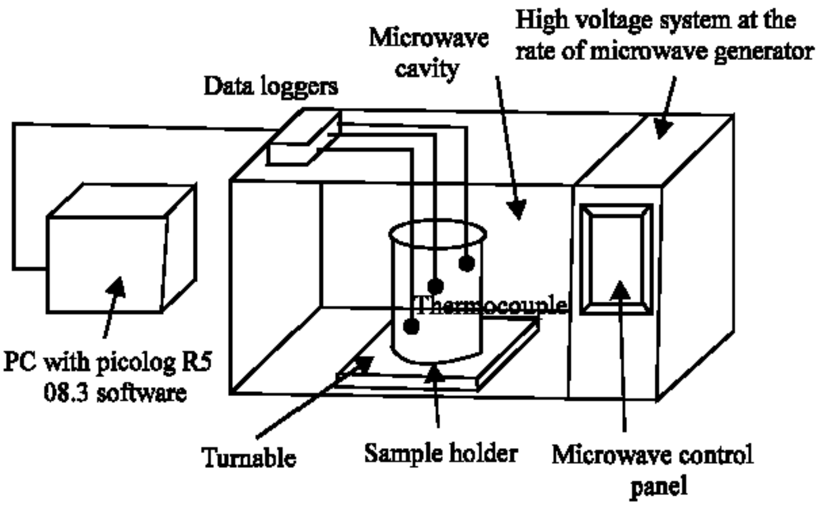


Fig. 3.1: Elba Microwave Oven

3.4 Method of Research

3.4.1 Emulsion Preparation

Firstly, the exact volume ratio of oil was poured into 250 mL beaker. Then the exact volume percentage of emulsifier, 1 vol. %, was added in. Then the mixture was taken for agitation. Clock was started once the three-blade propeller started blending the mixture. The speed of the propeller was increased gradually starting from the lowest. After 2 mins of blending, water was added into the beaker gradually while the speed of the propeller was also increased gradulally. The purpose of increasing the speed of propeller gradually was to make sure that the sample mixed thoroughly. The water depending on the exact volume ratio was added all before 6 mins. At 6 mins, the speed of the propeller was adjusted to the required speed, 800 rpm. The mixture was left for blending for 3 mins at the required speed. The propeller was stopped at 9 mins of blending. The volume used for Brookfield stability test was 10 mL, volume for gravity settling 50 mL and volume for microwave heating 100mL.

3.4.2 Brookfield Stability Test

Brookfield viscometer was used. Actually only 6-7 mL of emulsions was needed. The emulsions was poured into the container of viscometer. Then, press "Motor On/Off" button. Without putting spindle, the viscometer will zero its value. After the calibration was done, the "Spindle 31" was screwed into the upper part of the viscometer. Then the speed of the spindle rotation was fixed at 50 rpm, viscosity, shear stress and shear rate were recorded once their values were stable. The speed of the rotation then was changed to 100, 150 and 200 rpm respectively to measure viscosity, shear stress and shear rate.

3.4.2.1 Shear Stress

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

3.4.2.2 Shear Rate

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

3.4.2.3 Viscosity

Viscosity is a measure of the resistance of a fluid which is being deformed by either shear stress or tensional stress. Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction.

3.4.2.4 RPM

Revolutions per minute (abbreviated rpm, RPM, r/min, or $r \cdot min^{-1}$) is a unit of frequency of rotation: the number of full rotations completed in one minute around a fixed axis. It is used as a measure of rotational speed of a mechanical component.

3.4.2.5 Temperature

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

3.4.3 Surface and Interfacial Tension Measurement

Tensiometer was used. Firstly, surface tension of water was measured. The ring was hooked on the hooker well above the liquid surface presumably. Settings were fixed. 100 mL of tab water was poured into the container then the ring was lowered down by turning rotator until it was totally immersed into the water. Then set the value to zero. After that the ring was slowly taken up by rotating the rotator in opposite direction. It must be rotated slowly. The ring will create an upward water surface when the ring was pulled up. At one point the upward water surface will burst, that was when we stopped rotating. The surface tension was read from the panel. The above steps were repeated for crude oil but care must be taken since crude oil was not see-through clear so we must instinctively feel the point where the ring is totally immersed. For interfacial tension, 50 mL water was first added into the container then 50 mL crude oil was added slowly so as not to mingle up the two liquids. Once it was done, it was placed inside tensiometer and the ring was lowered down slowly not to the surface of oil but the surface between water and oil. Care must be taken as we cannot see through oil layer so the interface shall be roughly estimated and felt. Then the reading was set to zero again. The ring was then heighten up slowly and at one point, you will feel the bursting of the surface on the ring that was when the interfacial tension was read from the panel. Repeat the same procedures for interfacial tension of 20/80 water/crude oil emulsions.

3.4.3.1 Surface Tension

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

3.4.3.2 Interfacial Tension

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

3.4.4 Gravity Settling

The required emulsions were prepared like the procedures above. Then it was poured into a measuring cylinder. The measuring cylinder was covered up with aluminium foil to reduce the evaporation of liquid. Then separation of water and oil and total volume were recorded at 10 mins, 30 mins, 1 hr, 2 hrs, 6 hrs and 12 hrs.

3.4.5 Microwave Heating

Firstly on the installed program Picolog Data Logger, click “File”, then “New Settings”, then “Ok”. Maximum numbers of samples was fixed at 5000. Then click “Ok” twice. The channels which I had fixed the three thermocouples were selected. For example, Channel 1, 2 and 3, “Edit” each respective channels, then select “Type J”, then “Ok”. Then under “File”, click “New Data”, enter “File Name”, then “Save”. Click “red icon” once the microwave oven started to heat to start recording the temperature at every seconds. Stop recording when the heating was completed. Then for the microwave oven, settings were needed to fix. “MIC R-D” button was pressed, then “MINUTES” (180s for 360 W and 120s for 540 W). Then “POWER” was pressed at 40% (360 W) or 60% (540 W) depending on individual experiments. “Start” the microwave oven and “Record” simultaneously on the Picolog Data Logger software. “Stop” the heating of oven once the sample caught fire inside. From the recorded temperature over time, “Copy to clipboard” and it was pasted in Ms Word and saved. The graph of rate of temperature increase was also copied over (“Copy to clipboard”) to Ms. Word and saved. After heating, the emulsions sample was poured into a measuring cylinder and was covered wity aluminium foil to reduce evaporation. Then separation of water and oil and total volume were recorded at 10 mins, 30 mins, 1 hr, 2 hrs, 6 hrs and 12 hrs.

3.4.6 Calculations

Firstly, water and oil separation efficiencies or % of water and oil separation was calculated as below:

$$\%\ \text{of Water Separation} = \frac{(\text{Volume of water separated,mL})}{(\text{Original volume of water,mL})} \times 100\% \quad \text{(Equation 9)}$$

$$\%\ \text{of Oil Separation} = \frac{(\text{Volume of oil separated,mL})}{(\text{Original volume of oil,,mL})} \times 100\% \quad \text{(Equation 10)}$$

The temperatures of sample against time when being microwave heated were being recorded down by Picolog data logger. The rate of temperature increase, dT/dt was then calculated as below:

$$\frac{\mathrm{dT}}{\mathrm{dt}} = \frac{\text{Temperature average of every consecutive 20s}}{\text{Time being heated}} \qquad \text{(Equation 11)}$$

Then the real water ratio inside the emulsions, ϕ was calculated as below:

$$\phi = \frac{\frac{\text{Percentage of water}}{\rho(\text{water})}}{\frac{\text{Percentage of water}}{\rho(\text{water})} + \frac{\text{Percentage of oil}}{\rho(\text{oil})}} \qquad \text{(Equation 12)}$$

where ρ(water) = density of water = 1.0 g/cm^3 and ρ(oil) = density of oil = 0.85 g/cm^3.

Then density of the emulsion mixture, ρ_m was calculated using “mixing rule equation” as below:

$$\rho_m = \rho_w\phi + \rho_o(1-\phi) \qquad \text{(Equation 13)}$$

where ρ_w = density of water and ρ_o = density of oil.

Then heat capacity of the emulsion mixture, Cp_m was calculated as below:

$$Cp_m = Cp_w\phi + Cp_o(1-\phi) \qquad \text{(Equation 14)}$$

Then ultimately, volumetric heat generation rate, q_{mw} was calculated as below:

$$q_{mw} = p_m\, Cp_m\, (dT/dt) \qquad \text{(Equation 15)}$$

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 Introduction

The results of this study is discussed in four major parts, which are stability tests, gravity settling, microwave heating and microwave separation. All the experiments were carried out using 50-50 Tapis – Heavy Crude Oil. In this research, three different parameters were being manipulated to study the effect of these parameters on stability of emulsions and also the effect on water and oil separations. The first parameter was the concentration of the emulsions which are 50% volume water in 50% volume oil and 20% volume water in 80% volume oil. The second parameter was the use of four emulsifiers being SDDS, Span 83, Triton X-100 and Tween 80. The third manipulated parameter was power generation of microwave oven which are 360 watts and 540 watts.

Most of the results here are presented in two-way form, which are table-form and graph form. The use of table will show readers the exact value of the effect on parameter while the use of graph will let readers understand better the trend and for comparison purpose for different identities of parameter. Besides presenting all of the results of my research, explanations are also given to share the theories behind the occurrences. Lastly, results and discussions made are being supported by many materials being most of them journals. If you have any doubts, feel free to clarify it from me. Until then, sit back, relax and enjoy reading the core part of my research!

4.2 Stability Tests

For large drops approaching each other (no background electric field), the interfaces interact and begin to deform. A plane parallel thin film is formed, which rate of thinning may be the main factor determining the overall stability of the emulsion. The film thinning mechanism is strongly dependent on bulk properties (etc. viscosity) in addition to surface forces [A. Hannisdal, 2005].

4.2.1 Effect of Shear Rate to Shear Stress

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm. The temperature of the emulsions was maintained at 25 ^{o}C.

Table 4.1: Shear Stress, D/cm^2 at Different Shear Rate

SR,1/sec	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**T X-100, 20/80**	**Tween 80, 50/50**	**Tween 80, 20/80**
17	18.1	14.7	26.0	9.08	1.02	22.6	48.8	26.2
34	30.8	26.3	45.2	15.6	1.94	32	59	37.7
51	41.8	36	61.6	20.7	2.04	41.3	66.2	48
68	50.1	44.1	76.8	26.5	1.84	40.3	47.8	58.8

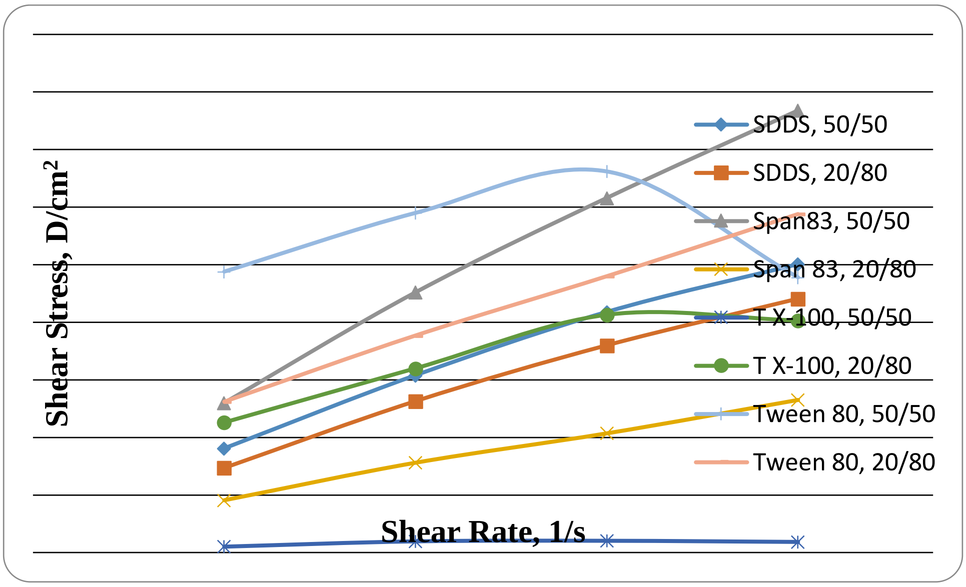


Fig. 4.1: Shear Stress vs. Shear Rate

From Fig. 4.1, Span 83 50/50, Span 83 20/80 emulsions are Newtonian fluid because shear stress increases linearly over shear stress. A fluid whose stress at each point is linearly proportional to its strain rate at that point is called Newtonian fluid. Newtonian fluid is any kind of fluid continues to flow, regardless of the forces acting on it.

SDDS 50/50, SDDS 20/80, Triton X-100 50/50, Triton X-100 20/80, Tween 80 50/50 and Tween 80 20/80 emulsions are Non-Newtonian fluids as the shear stress does not increase linearly over shear rate. They are pseudoplastic type of Non-Newtonian fluid when the line in the graph starts to form an upward curvature. It can be concluded that phase inversion occur from w/o to o/w. This situation occurs because, as the emulsion’s shear rate increases, temperature of the emulsion increases which causes the intermolecular forces between molecules increases. Consequently, the phase of the emulsion converts from w/o to o/w. For the inversion of w/o to o/w, it could be as the volume of the dispersed phase increases, the continuous phase must spread out further to cover all of the droplets, this cause the likelihood of impacts to increase, thus decreasing the stability of the emulsion. This means that, the emulsion might not break when increasing the volume of the dispersed phase. In fact this increment caused an emulsion to invert from one phase (w/o) to another (o/w).

From Fig. 4.1, most of the emulsifiers had shear stress increased over shear rate. This means shear stress decreased over time. Span 83, 50/50 water-in-oil emulsions had the highest shear stress at the final shear rate, meaning it had the highest shear stress at the initial time. Triton X-100 50/50 emulsions had the least shear stress at the initial time. At initial time from highest to lowest shear stress accordingly were Span 83 50/50, Tween 80 20/80, SDDS 50/50, Tween 80 50/50, SDDS 20/80, Triton X-100 20/80, Span 83 20/80 and Triton X-100 50/50. At final time which corresponds to initial shear rate, Tween 80, 50/50 had the highest shear stress while Triton X-100 50/50 had the least shear stress. At final time from highest to lowest shear stress accordingly were Tween 80 50/50, Tween 80 20/80, Span 83 50/50, Triton X-100 20/80, SDDS 50/50, SDDS 20/80, Span 83 20/80 and Triton X-100 50/50. Overall it was observed that Tween 80 had among the highest shear stress throughout time over two concentrations of emulsions. Triton X-100 had among the least shear stress throughout time over two concentrations of emulsions.

From Fig. 4.1 also, most of the emulsions showed greater shear stress at 50/50 concentrations than 20/80 concentrations.

4.2.2 Effect of Shear Rate to Viscosity

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm. The temperature of the emulsions was maintained at 25 ^{o}C.

Table 4.2: Viscosity at Different Shear Rate

SR,1/sec	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**T X-100, 20/80**	**Tween 80, 50/50**	**Tween 80, 20/80**
17	106.2	87.0	153.0	56.4	6.00	141.6	290.9	154.8
34	90.6	77.4	132.9	45.9	5.70	95.4	175.8	112.2
51	82.0	71.0	120.8	40.6	4.00	83.4	135	93.8
68	73.6	64.8	112.9	38.8	2.70	52	92.7	86.1

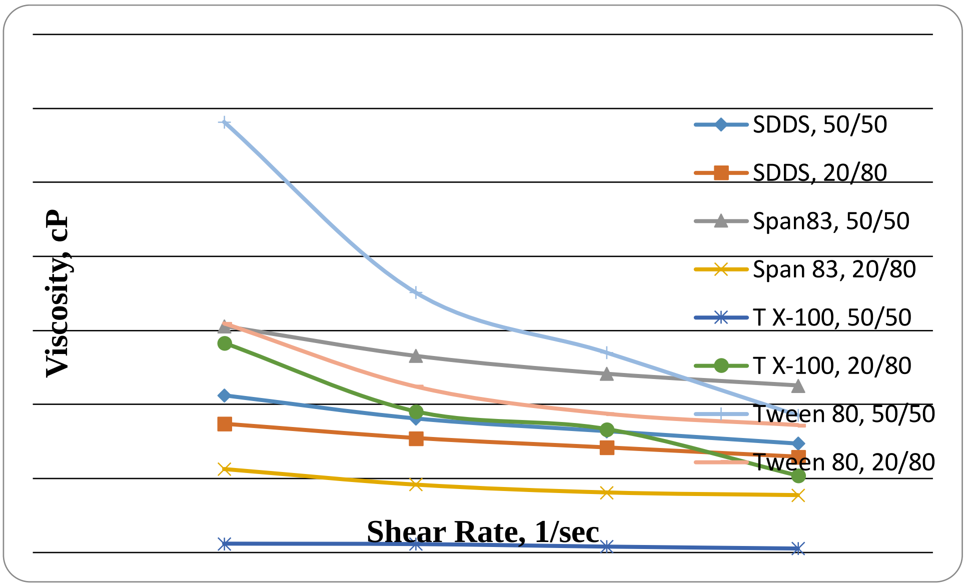


Fig. 4.2: Viscosity vs. Shear Rate

From Fig. 4.2, all of the emulsions showed greater viscosity at 50/50 concentrations than 20/80 concentrations except emulsions with Triton X-100. The viscosity increased linearly with increasing of water cut due to the increase of hydrogen bonds, leading to decrease in the molecular distances of the emulsion system as well as an increase of resistance to flow. As the dispersed phase function (water) of dispersion is increased, the dispersion rheology changes significantly due to the frequency of droplet interaction increases. Therefore, as the results coalescence faster in high cut, the number of the droplets in an aggregates change with time. Since any change in the dependence of the viscosity on rate of shear could not be observed, the decreased in viscosity would be brought about the broadening of the droplet size distribution [Ilia et *al.*, 2010].

From Fig. 4.2 also, all the emulsifiers had shear stress decreased over shear rate. This means viscosity increased over time. Span 83, 50/50 water-in-oil emulsions had the highest viscosity at the final shear rate, meaning it had the highest viscosity at the initial time. Triton X-100 50/50 emulsions had the least viscosity at the initial time. At initial time from highest to lowest viscosity accordingly were Span 83 50/50, Tween 80 50/50, Tween 80 20/80, SDDS 50/50, SDDS 20/80, Triton X-100 20/80, Span 83 20/80 and Triton X-100 50/50. Generally the trend of viscosity vs. shear rate at initial time is almost similar to the trend of shear stress vs. shear rate at initial time. At final time which corresponds to initial shear rate, Tween 80, 50/50 had the highest viscosity while Triton X-100 50/50 had the least viscosity. At final time from highest to lowest viscosity accordingly were Tween 80 50/50, Tween 80 20/80, Span 83 50/50, Triton X-100 20/80, SDDS 50/50, SDDS 20/80, Span 83 20/80 and Triton X-100 50/50. The trend of viscosity vs. shear rate at final time is similar to the trend of shear stress vs. shear rate at initial time. Overall it was observed that Tween 80 had among the highest viscosity throughout time over two concentrations of emulsions. Triton X-100 had among the least viscosity throughout time over two concentrations of emulsions.

4.2.3 Effect of RPM to Viscosity

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm. The temperature of the emulsions was maintained at 25 ^{o}C.

Table 4.3: Viscosity, cP at Different RPM

rpm	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**T X-100, 20/80**	**Tween 80, 50/50**	**Tween 80, 20/80**
50	106.2	87.0	153.0	56.4	6.00	141.6	290.9	154.8
100	90.6	77.4	132.9	45.9	5.70	95.4	175.8	112.2
150	82.0	71.0	120.8	40.6	4.00	83.4	135	93.8
200	73.6	64.8	112.9	38.8	2.70	52	92.7	86.1

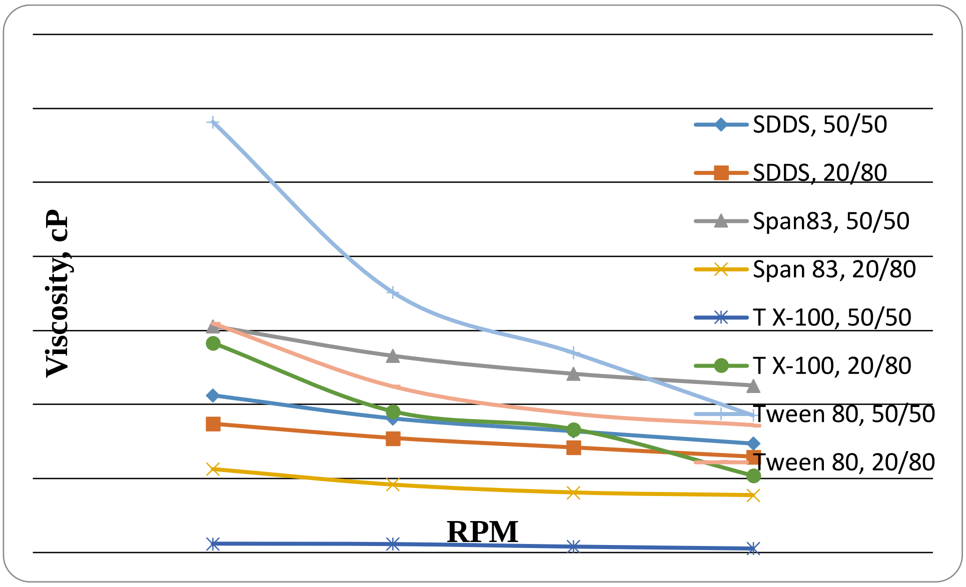


Fig. 4.3: Viscosity vs. RPM

From Fig. 4.3, all the emulsions had viscosity decreased over increasing rpm, which may be caused by the intermolecular forces become low at high shear rate. Higher viscosity of emulsions shows that the stability of the emulsions is higher. When the shear rate increases, viscosity of the emulsions decreases and it causes stability of the emulsions decreases. An increase in water cut of emulsions is inversely proportional towards viscosity of the emulsions.

At lowest rpm, Tween 80, 50/50 had the highest viscosity while Triton X-100 50/50 had the least viscosity. At lowest rpm, viscosity from highest to lowest accordingly were Tween 80 50/50, Tween 80 20/80, Span83 50/50, Triton X-100 20/80, SDDS 50/50, SDDS 20/80, Span 83 20/80 and Triton X-100 50/50. At highest rpm, Span 83, 50/50 water-in-oil emulsions had the highest viscosity while Triton X-100 50/50 emulsions had the least viscosity. At highest rpm, viscosity from highest to lowest accordingly were Span 83 50/50, Tween 80 50/50, Tween 80 20/80, SDDS 50/50, SDDS 20/80, Triton X-100 20/80, Span 83 20/80 and Triton X-100 50/50. Overall it was observed that Tween 80 had among the highest viscosity throughout the 4 rpm over two concentrations of emulsions. Triton X-100 had among the least viscosity throughout the 4 rpm over two concentrations of emulsions.

From Fig. 4.3 also, most of the emulsions showed greater viscosity at 50/50 concentrations than 20/80 concentrations.

4.2.4 Effect of RPM to Shear Stress

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm. The temperature of the emulsions was maintained at 25 °C.

Table 4.4: Shear Stress, D/cm^2 at Different RPM

rpm	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**T X-100, 20/80**	**Tween 80, 50/50**	**Tween 80, 20/80**
50	18.1	14.7	26.0	9.08	1.02	22.6	48.8	26.2
100	30.8	26.3	45.2	15.6	1.94	32	59	37.7
150	41.8	36	61.6	20.7	2.04	41.3	66.2	48
200	50.1	44.1	76.8	26.5	1.84	40.3	47.8	58.8

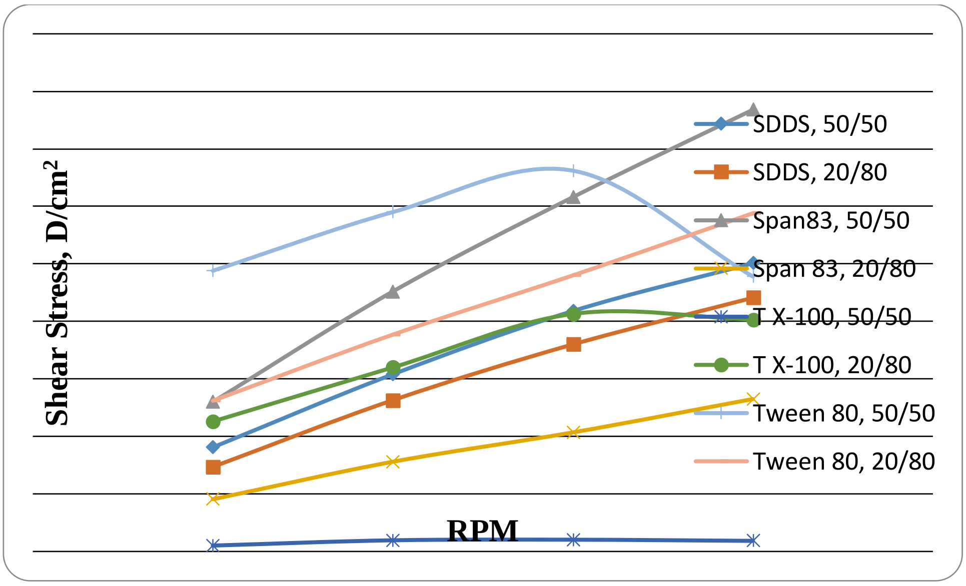


Fig. 4.4: Shear Stress vs. RPM

From Fig. 4.4, all the emulsions generally had shear stress increased over increasing rpm. At lowest rpm, Tween 80, 50/50 had the highest shear stress while Triton X-100 50/50 had the least shear stress. At final time from highest to lowest shear stress accordingly were Tween 80 50/50, Tween 80 20/80, Span 83 50/50, Triton X-100 20/80, SDDS 50/50, SDDS 20/80, Span 83 20/80 and Triton X-100 50/50. At highest rpm, Span 83, 50/50 water-in-oil emulsions had the highest shear stress while Triton X-100 50/50 emulsions had the least shear stress. At initial time from highest to lowest shear stress accordingly were Span 83 50/50, Tween 80 20/80, SDDS 50/50, Tween 80 50/50, SDDS 20/80, Triton X-100 20/80, Span 83 20/80 and Triton X-100 50/50. Overall it is observed that Tween 80 had among the highest shear stress throughout the 4 rpm over two concentrations of emulsions. Triton X-100 had among the least shear stress throughout the 4 rpm over two concentrations of emulsions.

From Fig. 4.4 also, most of the emulsions showed greater shear stress at 50/50 concentrations than 20/80 concentrations.

4.2.5 Effect of RPM to Shear Rate

The below water-in-crude oil emulsions sample was prepared at 1.0 % volume concentration of emulsifier, agitated at 800 rpm. The temperature of the emulsions was maintained at 25 ^{o}C.

Table 4.5: Shear Rate at Different RPM

rpm	**SR, 1/s**
50	17.0
100	34.0
150	51.0
200	68.0

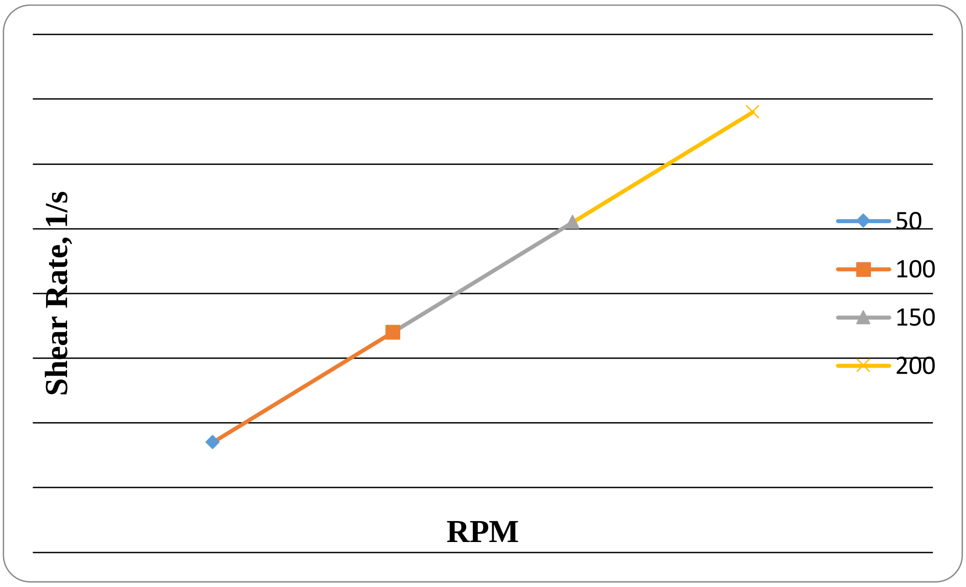


Fig. 4.5: Shear Rate vs. RPM

From Fig. 4.5, all the emulsions with all the emulsifiers had the same shear rate over increasing rpm. The shear rate increased linearly over increasing rpm.

4.2.6 Surface & Interfacial Tension

The droplet size resulting from a given mixing process will have great importance for the overall stability of the emulsion through the surface energy of the droplets [A. Hannisdal, 2005].

Surface tension of water was 54.76 mN/m.

Surface tension of oil was 24.6123 mN/m.

Interfacial tension is an important factor in emulsion stability. It arises because the intermolecular forces in the interior of a liquid equal in all directions. The interfacial tension falls to low values at higher sodium chloride (NaCl%) concentration [Abdurahman H. Nour *et al.*, 2006]. Interfacial forces try to maintain a spherical shape of the droplet. Interfacial films on the surface of the dispersed water droplets hinder droplet coalescence, causing stabilization of water emulsions in crude oil [Coutinho et *al.*, 2007].

Interfacial tension of 50/50 water/oil emulsions was 1.109 mN/m.

Interfacial tension of 20/80 water/oil emulsions was 8.634 mN/m.

4.3 Gravity Settling

4.3.1 Water Separation

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm.

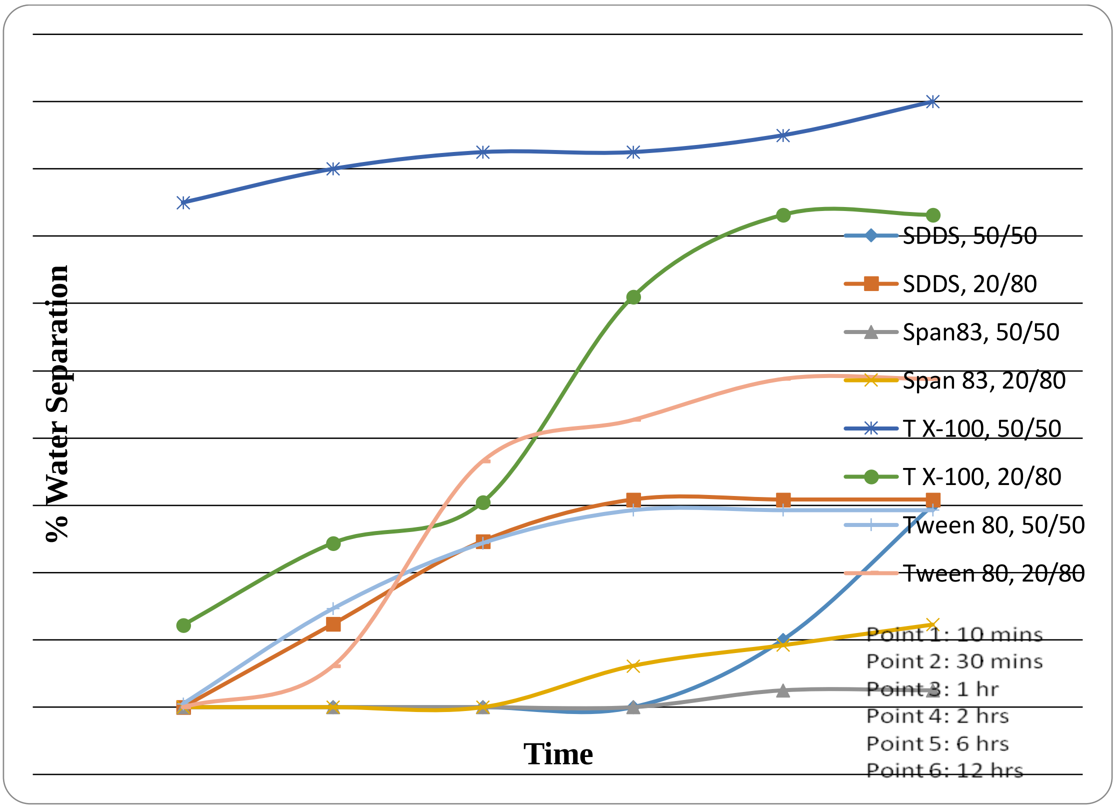


Fig. 4.6: Percentage of Water Separation vs. Time

For all four emulsifiers at 1.0 volume concentration, agitated at 800rpm, from Fig. 4.6, Triton X-100 with 50/50 of water-in-crude oil emulsions had highest percentage of water separation compared to other emulsifiers with two different emulsions-ratios. After 12 hours, Span 83 with 50/50 emulsions had least percentage of water separation among others. The final percentage of water separation after 12 hours ranked from the highest to the lowest were Triton X-100 with 50/50, Triton X-100 with 20/80, Tween 80 20/80, SDDS with 20/80, SDDS with 50/50, Tween 80 with 50/50, Span 83 with 20/80 and Span 83 with 50/50. From the rankings, it was observed that Span 83 had the most stable emulsions (in terms of water binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios. Triton X-100 had the least stable emulsions (in terms of water binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios.

4.3.2 Oil Separation

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm.

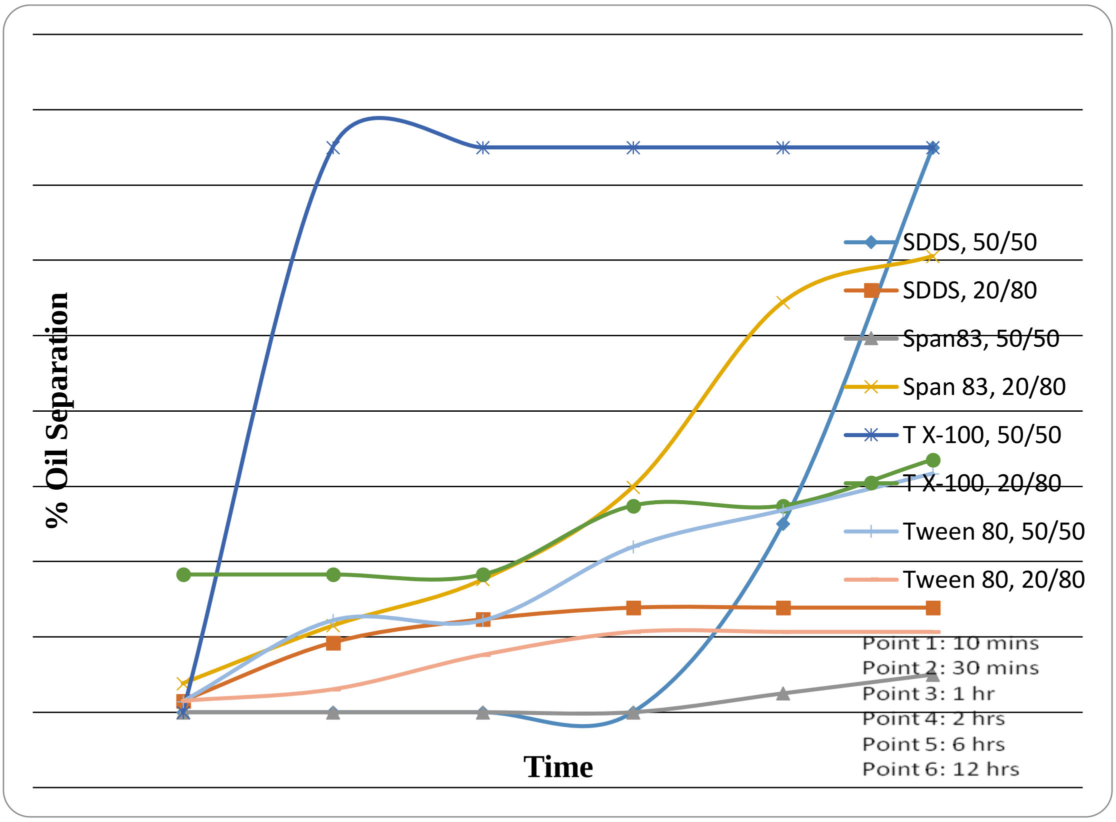


Fig. 4.7: Percentage of Oil Separation vs. Time

For all four emulsifiers at 1.0 % volume concentration, agitated at 800rpm, from Fig. 4.7, Triton X-100 with 50/50 of water-in-crude oil emulsions had highest percentage of oil separation most of the time compared to other emulsifiers with two different emulsions-ratios. After 12 hours, Span 83 with 50/50 emulsions had least percentage of oil separation among others. The final percentage of oil separation after 12 hours ranked from the highest to the lowest were Triton X-100 with 50/50, SDDS with 50/50, Span 83 with 20/80, Triton X-100 with 20/80, Tween 80 with 50/50, SDDS with 20/80, Tween 80 with 20/80 and Span 83 with 50/50. From the rankings, iw was observed that Tween 80 had the most stable emulsions (in terms of oil binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios. Triton X-100 had the least stable emulsions (in terms of oil binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios.

4.4 Microwave Heating

4.4.1 Temperature Increment

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm.

360 Watts

Table 4.6: Temperature (°C) over Time at 360 Watts

Time, s	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**T X-100, 20/80**	**Tween 80, 50/50**	**Tween 80, 20/80**
20	35.0771	33.581	28.0338	49.4352	28.68	30.829	29.3186	32.3081
40	46.2775	37.089	27.983	47.798	28.67	34.525	29.3735	37.3525
60	70.0885	63.4655	27.9765	64.663	28.68	40.408	47.158	42.5445
80	69.9575	60.462	38.825	62.8335	42.99	42.8145	64.6585	49.397
100	69.556	61.7955	61.032	65.6815	62.85	47.725	75.8588	57.7895
120	75.032	71.2685	73.0515	83.849	78.34	51.9025	80.4005	63.9115
140	76.738	71.2945	75.341	73.6995	81.74	58.2085	87.6365	69.895
160	86.554	73.3512	84.683	92.2525	91.47	62.1045	98.612	73.2045
180	88.851	76.002	86.6414	83.114	88.45	68.8817	92.665	76.6795

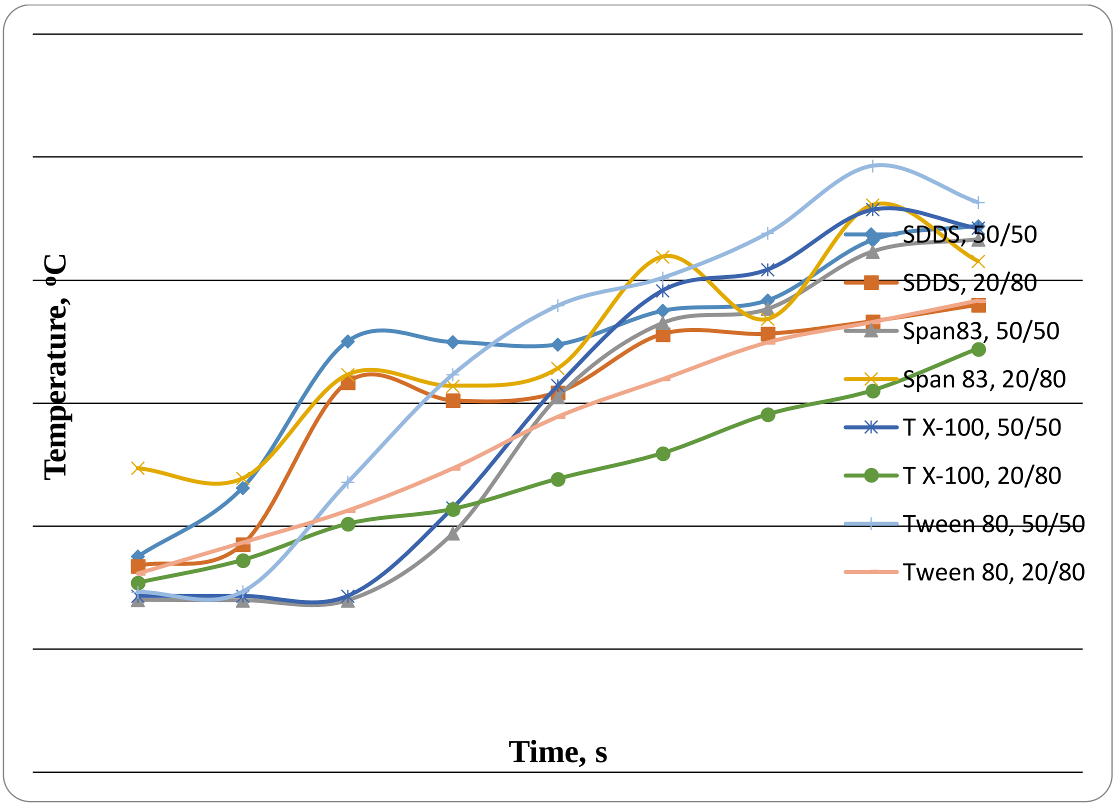


Fig. 4.8: Temperature vs. Time at 360 Watts

540 Watts

Table 4.7: Temperature (°C) over Time at 540 Watts

Time, s	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**Tween 80, 50/50**	**Tween 80, 20/80**
20	33.5233	43.3743	28.9143	37.9033	29.7819	29.1814	31.259
40	49.5755	54.488	31.0445	46.024	30.07	31.06	39.4079
60	64.27	55.4145	67.4095	54.9635	46.6695	65.2255	53.049
80	68.9815	59.6781	78.2865	58.172	58.2645	76.591	59.1005
100	82.5933	73.291	89.0455	65.749	78.222	96.677	59.772
120	86.6678	84.02	99.2865	70.9495	91.8062	103.413	74.9723

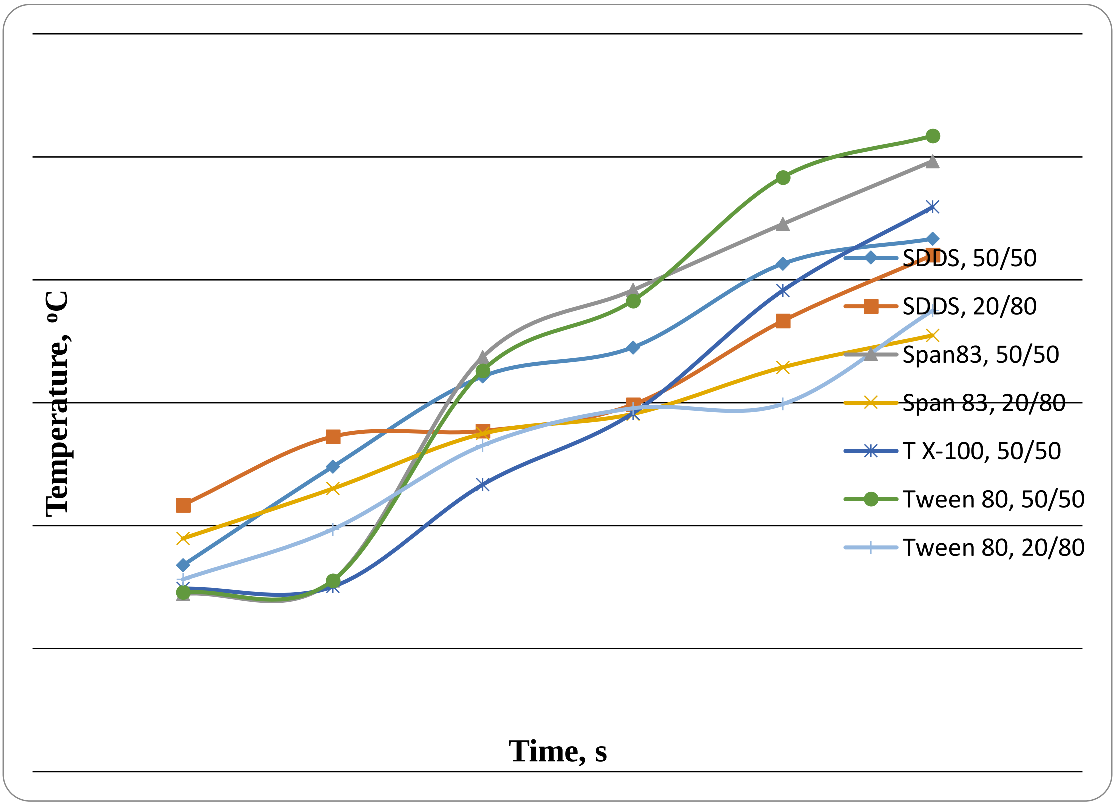


Fig. 4.9: Temperature vs. Time at 540 Watts

From Fig. 4.8 and Fig. 4.9, it is clear that temperature of emulsions increased with radiation time. This was due to continuous supply of heat in the form of radiation. In Fig. 4.8 and Fig. 4.9 line of 20-80% w/o is above 50-50% w/o because the initial temperature of the emulsion of 20-80% w/o emulsion was higher than the other emulsions but by comparison temperature increase of 50-50% emulsions was higher than 20-80% due to small dielectric loss of water. Higher amount of water in 50-50% w/o emulsion will cause less dielectric loss in the emulsion and higher temperature increase in the emulsion, whereas lower water cut will cause higher dielectric loss in 20-80% w/o emulsions.

The temperature increase can cause reduction in the viscosity of the rigid film formed by natural surface agents in the water-oil interface, making easier the coalescence between said dispersed drops [Coutinho et *al.*, 2007].

It has been recognized that the acceleration of reactions by exposure to microwaves results from material-wave interactions, leading to thermal effects easily estimated by temperature measurements (the so-called dielectric heating) and specific effects (not purely thermal) generally associated with the selective absorption of microwave energy by polar molecules. [Perreux et *al.*, 2007].

At enhanced temperatures, besides reducing the viscosity, higher levels of applied energy are required, contributing to an improved demulsification performance. Therefore, both the viscosity reduction effect and the enhanced energy should contribute toward the increase of demulsification efficiency [Coutinho et *al.*, 2007].

4.4.2 Rate of Temperature Increase

360 Watts

Table 4.8: Rate of Temperature Increase (°C/s) over Time at 360 Watts

Time, s	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**T X-100, 20/80**	**Tween 80, 50/50**	**Tween 80, 20/80**
20	1.75386	1.67905	1.40169	2.47176	1.434	1.54145	1.46593	1.6154
40	1.15694	0.92723	0.69958	1.19495	0.71675	0.86313	0.73434	0.93381
60	1.16814	1.05776	0.46628	1.07772	0.478	0.67347	0.78597	0.70908
80	0.87447	0.75578	0.48531	0.78542	0.53738	0.53518	0.80823	0.61746
100	0.69556	0.61796	0.61032	0.65682	0.6285	0.47725	0.75859	0.5779
120	0.62527	0.5939	0.60876	0.69874	0.65283	0.43252	0.67	0.5326
140	0.54813	0.50925	0.53815	0.52643	0.58386	0.41578	0.62598	0.49925
160	0.54096	0.45845	0.52927	0.57658	0.57169	0.38815	0.61633	0.45753
180	0.49362	0.42223	0.48134	0.46174	0.49139	0.38268	0.51481	0.426

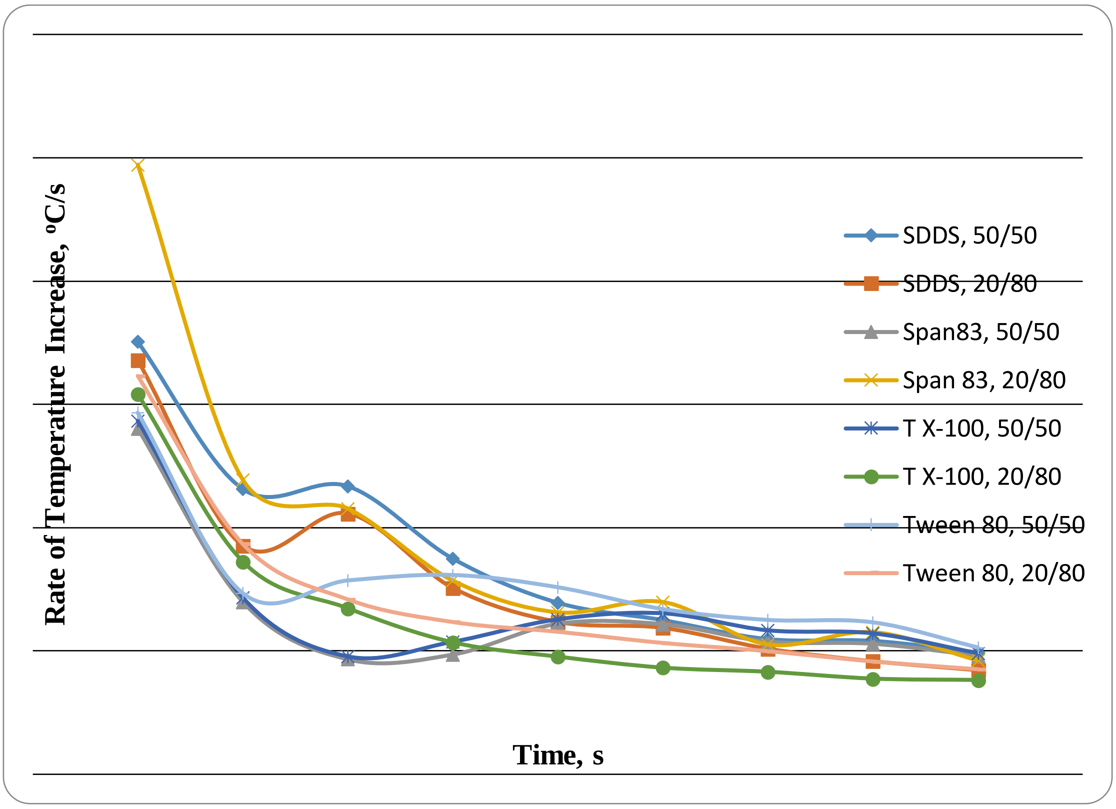


Fig. 4.10: Rate of Temperature Increase over Time at 360 Watts

540 Watts

Table 4.9: Rate of Temperature Increase (^{o}C/s) at 540 Watts

Time, s	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**Tween 80, 50/50**	**Tween 80, 20/80**
20	1.67617	2.16871	1.44571	1.89517	1.4891	1.45907	1.56295
40	1.23939	1.3622	0.77611	1.1506	0.75175	0.7765	0.9852
60	1.07117	0.92358	1.12349	0.91606	0.77783	1.08709	0.88415
80	0.86227	0.74598	0.97858	0.72715	0.72831	0.95739	0.73876
100	0.82593	0.73291	0.89046	0.65749	0.78222	0.96677	0.59772
120	0.72223	0.70017	0.82739	0.59125	0.76505	0.86178	0.62477

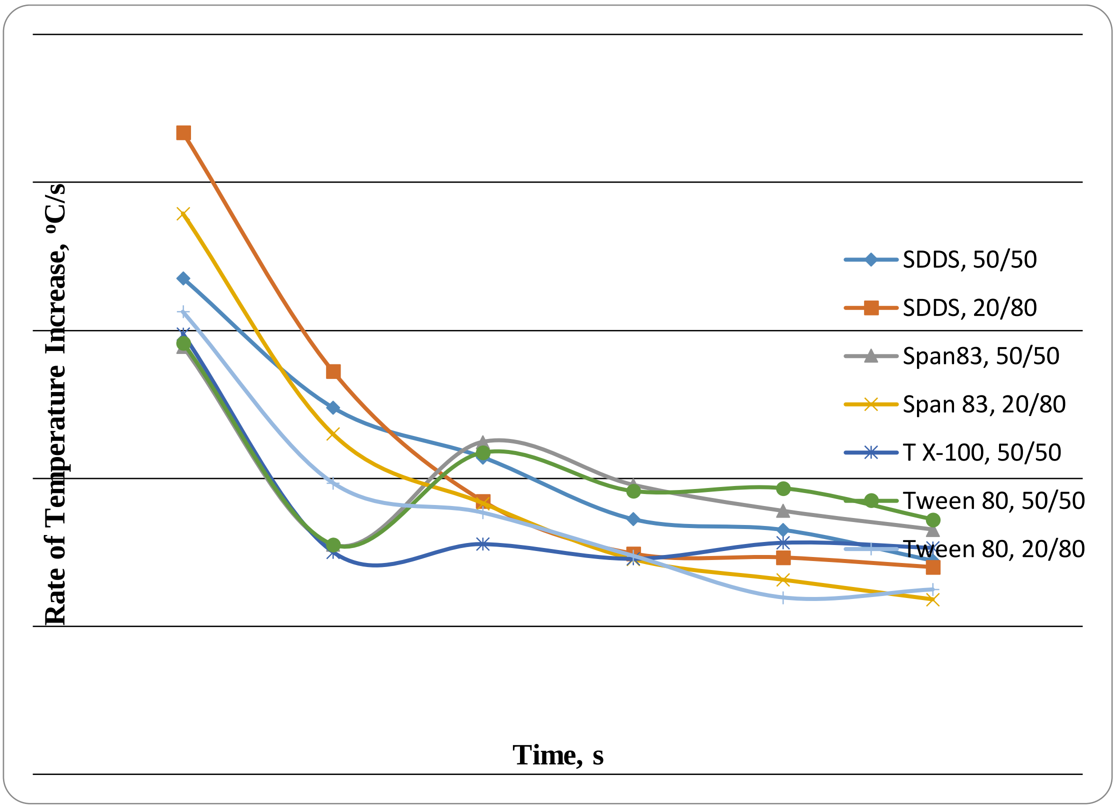


Fig. 4.11: Rate of Temperature Increase over Time at 540 Watts

The rate of temperature increase of emulsions decreased as radiation time increased due to decreasing dielectric loss of water. Decrease in rate of temperature increase of 20-80% w/o emulsion was higher than 50-50% and 50-50% w/o emulsion according to Table 4.8 and Table 4.9.

4.4.3 Volumetric Heat Generation Rate

4.4.3.1 360 Watts

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm and heated at 360 watts.

Table 4.10: Volumetric Heat Generation Rate (cal/cm^3.s) over Time at 360 Watts

Time, s	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**T X-100, 20/80**	**Tween 80, 50/50**	**Tween 80, 20/80**
20	1.15691	0.8379	0.9246	1.23349	0.94592	0.76924	0.96698	0.80614

40	0.76316	0.46272	0.46146	0.59632	0.47279	0.43073	0.48439	0.466
60	0.77055	0.52786	0.30757	0.53782	0.31531	0.33608	0.51845	0.35385
80	0.57683	0.37716	0.32013	0.39195	0.35447	0.26707	0.53314	0.30813
100	0.45882	0.30838	0.40259	0.32777	0.41458	0.23816	0.50039	0.28839
120	0.41245	0.29638	0.40156	0.3487	0.43063	0.21584	0.44196	0.26578
140	0.36156	0.25413	0.35498	0.2627	0.38513	0.20749	0.41292	0.24914
160	0.35684	0.22878	0.34912	0.28773	0.37711	0.1937	0.40655	0.22832
180	0.32561	0.21071	0.31751	0.23043	0.32414	0.19097	0.33958	0.21259

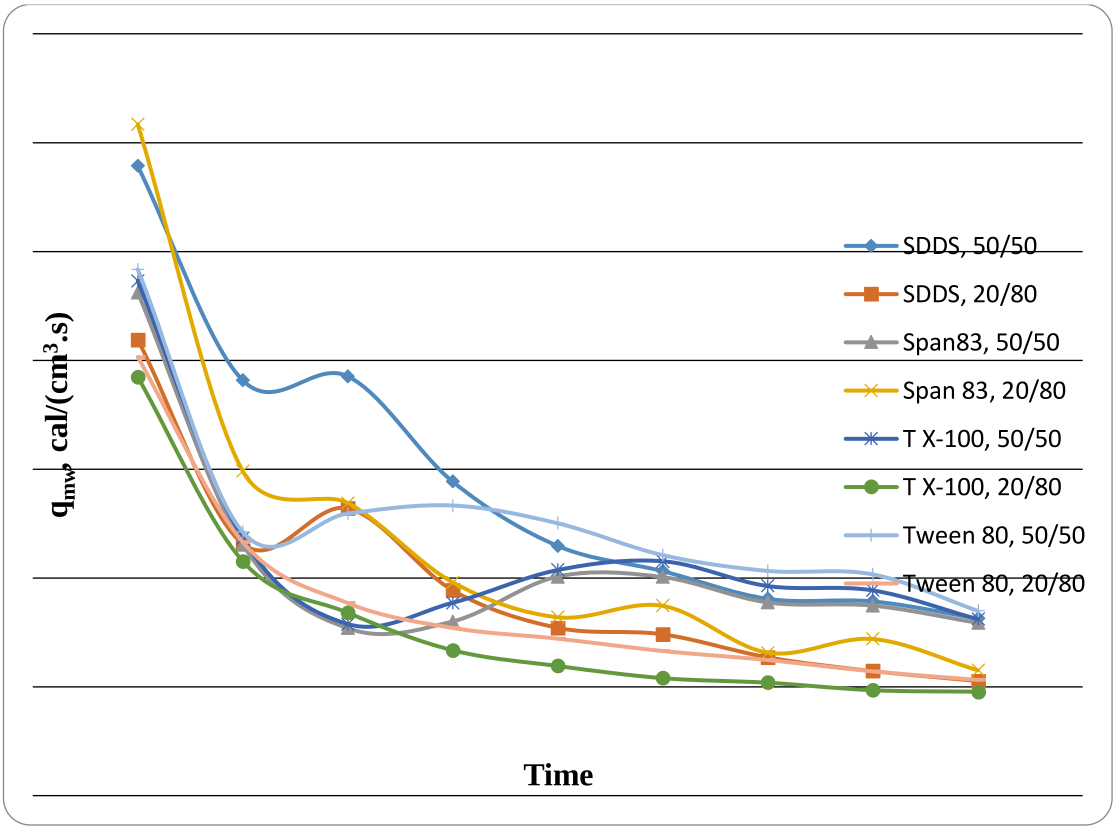


Fig. 4.12: Volumetric Heat Generation Rate vs. Time at 360 Watts

Generally, all emulsions had decreasing volumetric heat generation rate over time. Span 83 at 20/80 water-in-crude oil emulsions had the greatest volumetric heat generation rate initially while Triton X-100 at 20/80 emulsions had the least volumetric heat generation rate initially. At the final time of 180s, all emulsions had very close volumetric heat generation rate with the most was Tween 80, 50/50 emulsions and the least was Triton X-100, 20/80 emulsions.

4.4.3.2 540 watts

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm and heated at 540 watts.

Table 4.11: Volumetric Heat Generation Rate (cal/cm^3.s) over Time at 540 Watts

Time, s	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**Tween 80, 50/50**	**Tween 80, 20/80**
20	1.10566	1.08226	0.95364	0.94575	0.98226	0.96245	0.77996
40	0.81754	0.67978	0.51195	0.57419	0.49588	0.51221	0.49165
60	0.70658	0.46089	0.74109	0.45714	0.51308	0.71708	0.44122
80	0.56878	0.37227	0.64551	0.36287	0.48042	0.63153	0.36866
100	0.54481	0.36575	0.58738	0.32811	0.51598	0.63772	0.29828
120	0.47641	0.34941	0.54577	0.29505	0.50465	0.56846	0.31178

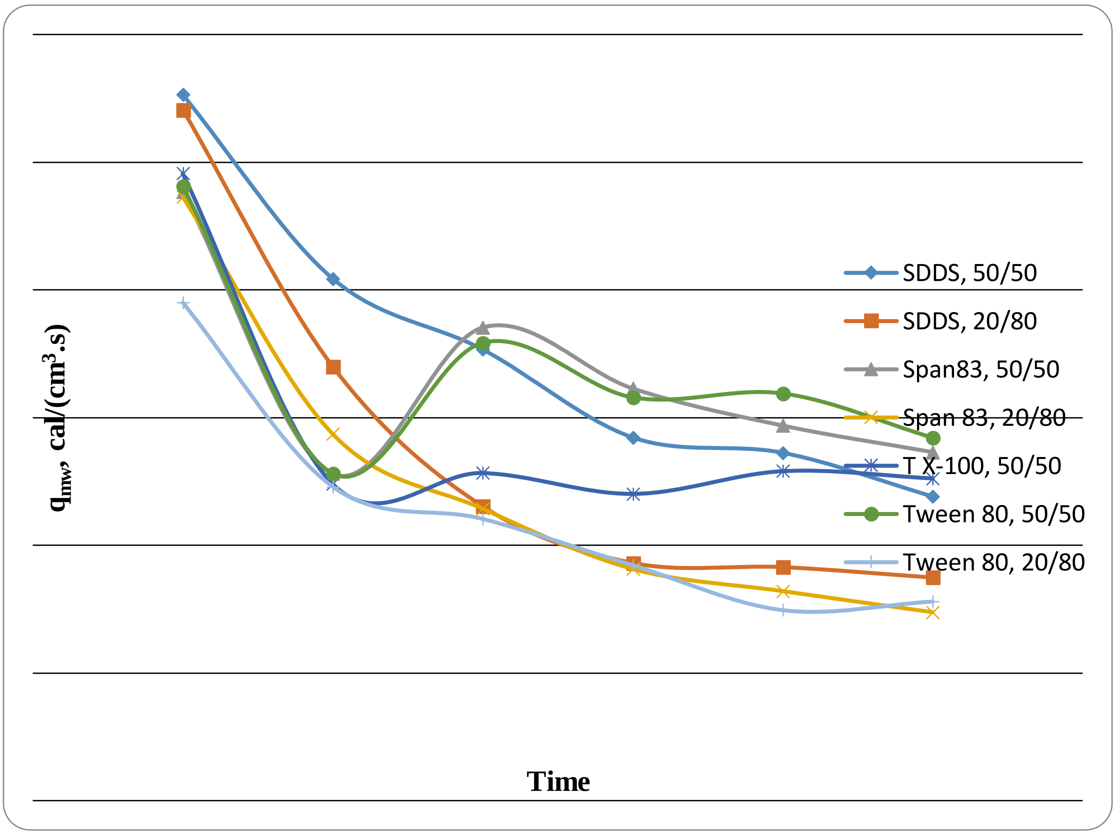


Fig. 4.13: Volumetric Heat Generation Rate vs. Time at 540 Watts

Generally, all emulsions had decreasing volumetric heat generation rate over time. SDDS at 50/50 water-in-crude oil emulsions had the greatest volumetric heat generation rate initially while Tween 80 at 20/80 emulsions had the least volumetric heat generation rate initially. At the final time of 180s, the greatest volumetric heat generation rate was Tween 80, 50/50 emulsions and the least was Span 83, 20/80 emulsions.

4.4.3.3 Comparison of Volumetric Heat Generation Rate over Power Generation

As compared between Fig. 4.12 and Fig. 4.13, most of the emulsions at 540 watts had greater volumetric heat generation rate initially. At the final time of 180s, all of the emulsions had greater volumetric heat generation rate at 540 watts.

From Fig. 4.8 through Fig. 4.13, it was observed that when the microwave power generation increased from 360W to 540W, temperature of all emulsions increased faster with radiation time. This was due to higher amount of radiation supplied to the emulsions converts into heat and increases temperature of the emulsions. This situation caused rate of temperature increase and volume rate of heat generation of emulsion supplied with 540W was higher than 360W.

4.4.3.4 Different Power Generations

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm. The volumetric heat generation rate of individual emulsion at a certain power was taken as an average over time.

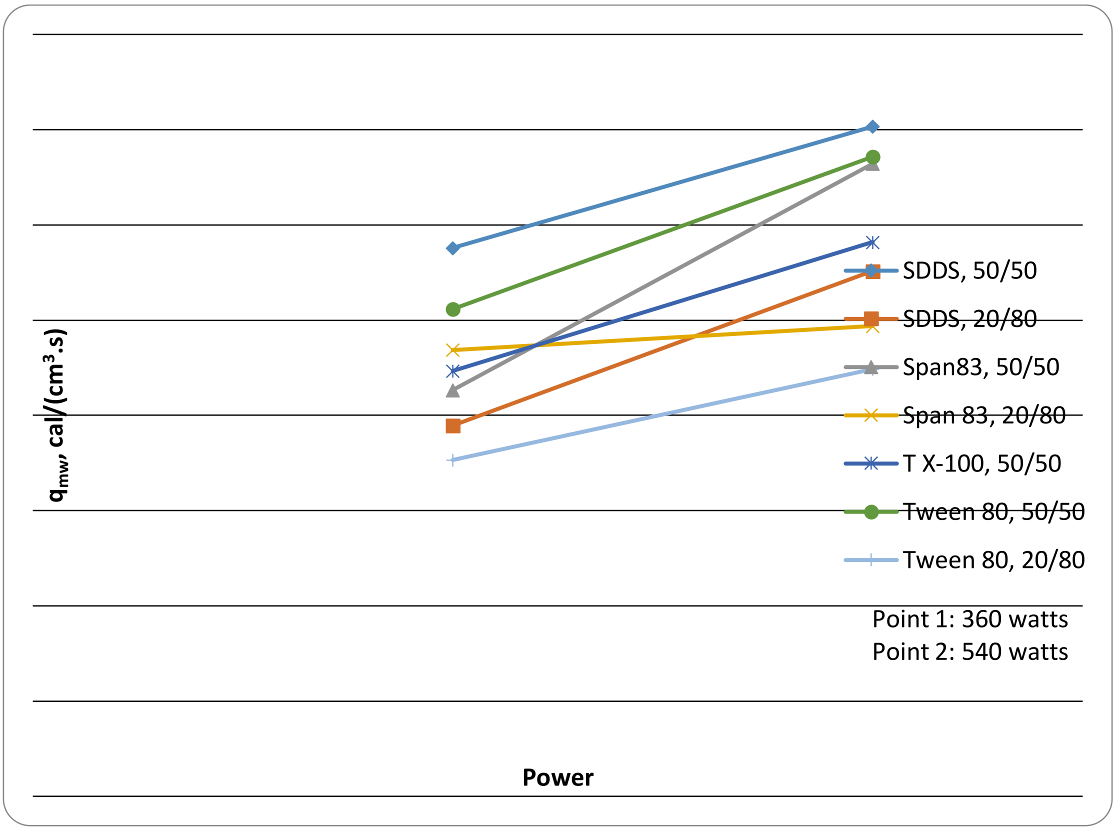


Fig. 4.14: Volumetric Heat Generation Rate vs. Power

For SDDS, the volumetric heat generation rate was higher for 50/50 water-in-crude oil emulsions than 20/80 emulsions. For Span 83, at 360 watts, the volumetric heat generation rate for 20/80 emulsions was higher than 50/50 but at 540 watts, inversely the volumetric heat generation rate for 50/50 emulsions was higher than 20/80. For Tween 80, the volumetric heat generation rate was higher for 50/50 water-in-crude oil emulsions than 20/80 emulsions.

For frequencies comprised between low and very high radiation frequencies which is ideal for dipole rotation and ionic conduction, electric dipoles slightly delay with respect to electric field variations and a portion of the energy that the electric field provides for dipole rotation is stored. Such energy will be turned into heat resulting from the friction with neighboring molecules. This heating mechanism is called dipole rotation. When the irradiated sample is an electric conductor or semiconductor formed by ions (such as NaCl aqueous solutions), these ions can move through the material so as to follow the variations in electric field. The resulting electrical currents heat the sample as a consequence of the electrical resistance. This mechanism is called ionic conduction [Coutinho et *al.*, 2007].

The lower the water contents in the emulsion sample, the greater the energy that might be applied to the sample will reach the set-point temperature. This effect is well-known and can be described mathematically through the so-called “dielectric heating equation”

$$p = 2\pi f \epsilon_o \epsilon'' E^2 = \sigma E^2$$

where the power dissipated per unit volume (p) is related to the permittivity of free space (ϵ_o), the loss factor (ϵ''), the electric-field intensity (E), and its frequency (f). Because the electrical conductivity (σ) effects are usually included within the loss factor, it is evident from the equation above that the power dissipation is proportional to the electrical conductivity. As a consequence, the greater the water content in the emulsion, the greater will be the power dissipation per unit volume of the sample and thus the heating effect [Coutinho et *al.*, 2007].

As the volume of moving ions which are hydrogen ions and hydroxide ions increases, which means as the volume of water cut increases, more electrical current passes through the sample heating it, eventually volumetric heat generation rate will be higher for 50/50 water-in-oil emulsions.

4.4.3.5 50/50 Water/Crude Oil Emulsions

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, 50/50 water/oil ratio and agitated at 800 rpm. At 360 watts, all the emulsions were heated for 180 seconds owing to slow heating rate. At 540 watts, all the emulsions were heated for only 120 seconds owing to fast heating rate.

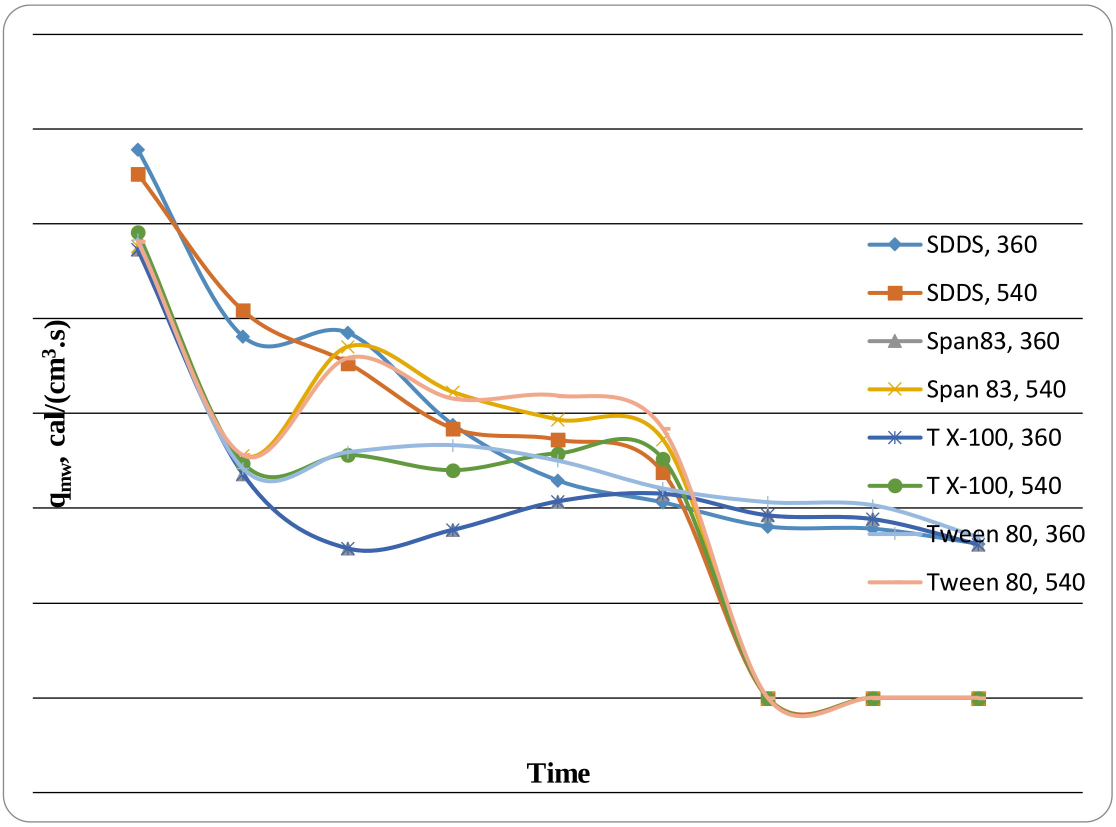


Fig. 4.15: Volumetric Heat Generation Rate vs. Time at 50/50 Water/Oil Emulsions

For the same emulsifiers, the volumetric heat generation rates at particular time were almost the same owing to the fact of almost similar chemical properties and the same emulsifier used despite different volume ratio of water and oil. Initially, SDDS had the greatest volumetric heat generation rate while all the other emulsions had almost the same volumetric heat generation rates. We take 120 seconds as the final time seeing emulsions at 540 watts were heated until that time only. At 120 seconds, all the emulsions had near volumetric heat generation rates.

4.4.3.6 20/80 Water/Crude Oil Emulsions

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, 20/80 water/oil ratio and agitated at 800 rpm. At 360 watts, all the emulsions were heated for 180 seconds owing to slow heating rate. At 540 watts, all the emulsions were heated for only 120 seconds owing to fast heating rate.

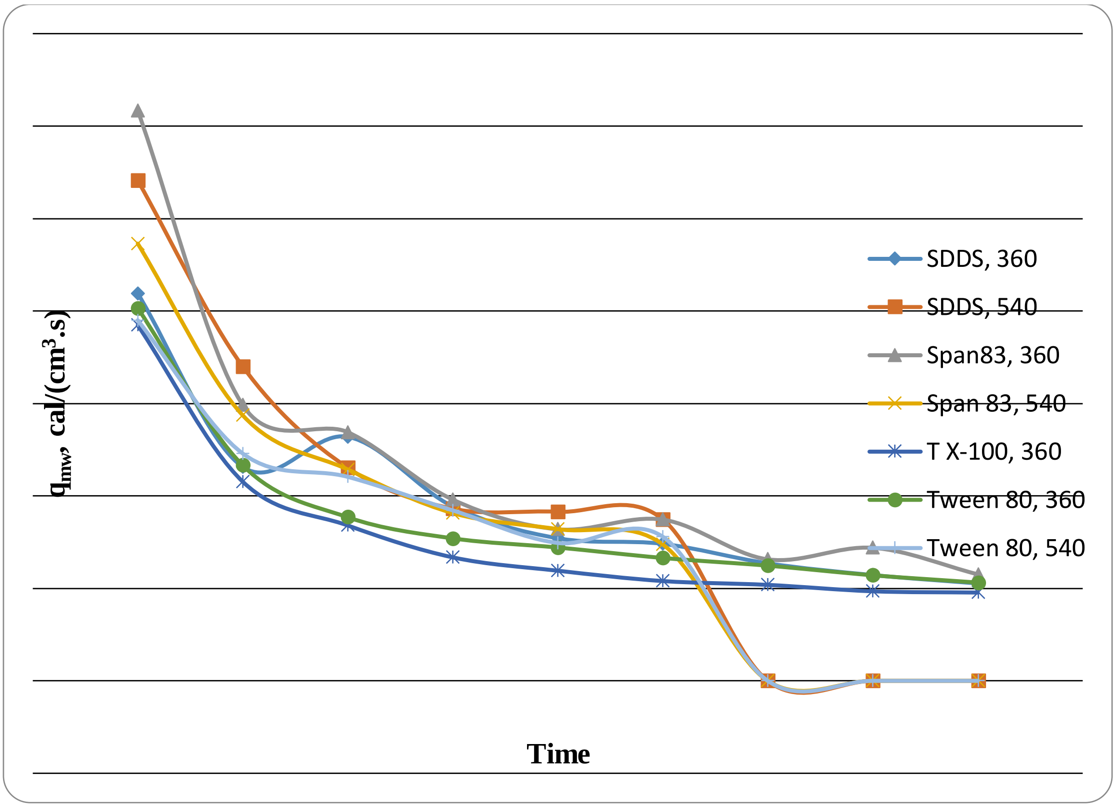


Fig. 4.16: Volumetric Heat Generation Rate vs. Time at 20/80 Water/Oil Emulsions

For the same emulsifiers, the volumetric heat generation rates at particular time were almost the same owing to the fact of almost similar chemical properties and the same emulsifier used despite different volume ratio of water and oil. Initially, Span 83 had the greatest volumetric heat generation rate while all the other emulsions had almost the same volumetric heat generation rates. We take 120 seconds as the final time seeing emulsions at 540 watts are heated until that time only. At 120 seconds, all the emulsions had near volumetric heat generation rates.

4.5 Microwave Separation

4.5.1 Water Separation at 360 Watts

Because dielectric properties are influenced by medium composition, it is necessary to determine the relationship between these properties and the emulsion water content. This is especially important in demulsification processes, where water content variations are expected to occur [Coutinho et *al.*, 2007].

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm and heated at 360 watts.

Table 4.12: Percentage of Water Separation at 360 Watts

Time	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**T X-100, 20/80**	**Tween 80, 50/50**	**Tween 80, 20/80**
10 mins	100	25.1572	0.54348	7.89474	6.18557	100	15.7895	86.0215
30 mins	100	28.481	2.1978	36.8421	8.29016	100	17.8947	92.3913
1 hr	99.3865	25.4777	3.2967	42.328	20.8333	100	19.1489	90.1639
2 hrs	100	31.8471	3.31492	66.4894	27.0833	100	21.2766	93.4066
6 hrs	100	95.5414	46.4088	79.7872	41.6667	100	22.3404	98.9011
12 hrs	100	95.5414	55.2486	93.0851	54.1667	100	31.9149	98.9011

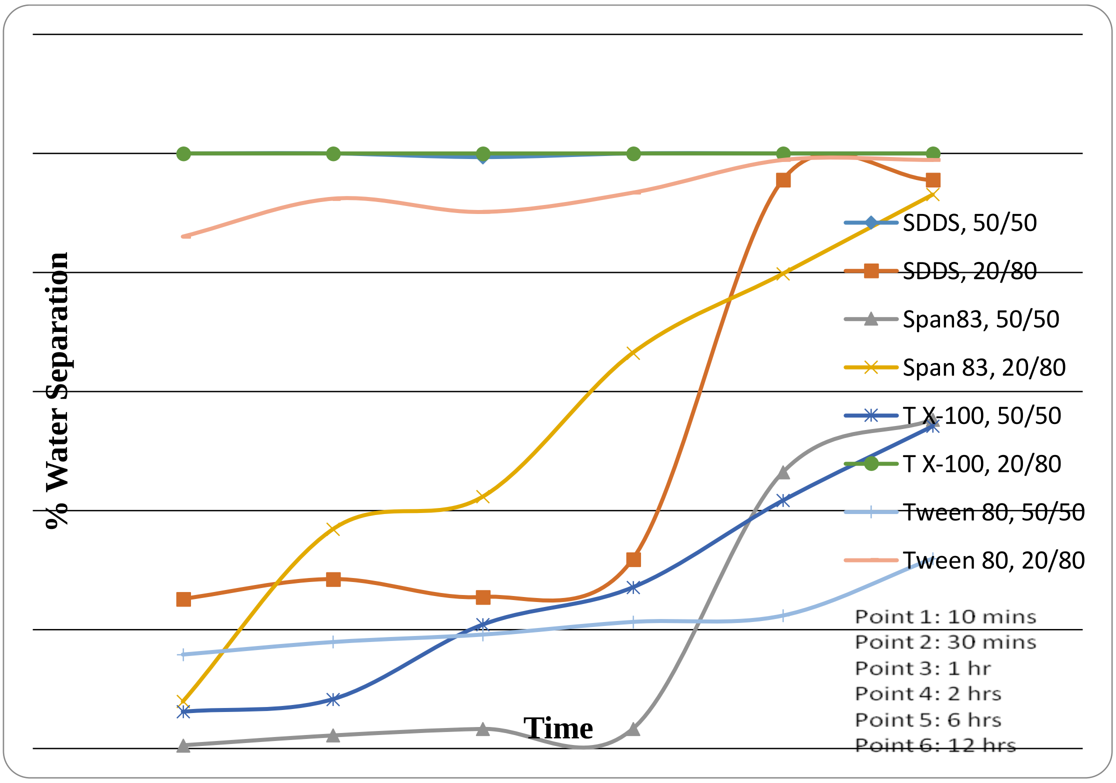


Fig. 4.17: Percentage of Water Separation vs. Time

For all four emulsifiers at 1.0 % volume concentration, agitated at 800rpm, from Fig. 4.17, Triton X-100 with 20/80 of water-in-crude oil emulsions had highest percentage of water separation finally compared to other emulsifiers with two different emulsions-ratios. After 12 hours, Tween 80 with 50/50 emulsions had least percentage of water separation among others. The final percentage of water separation after 12 hours ranked from the highest to the lowest were Triton X-100 with 20/80, SDDS with 50/50, Tween 80 20/80, SDDS with 20/80, Span 83 with 20/80, Span 83 with 50/50, Triton X-100 with 50/50 and Tween 80 with 50/50. From the rankings, it was observed that that after microwave heating, Span 83 had the most stable emulsions (in terms of water binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios. After microwave heating, SDDS had the least stable emulsions (in terms of water binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios.

4.5.2 Oil Separation at 360 Watts

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm and heated at 360 watts.

Table 4.13: Percentage of Oil Separation at 360 Watts

Time	**SDDS, 50/50**	**SDDS, 20/80**	**Span83, 50/50**	**Span 83, 20/80**	**T X-100, 50/50**	**T X-100, 20/80**	**Tween 80, 50/50**	**Tween 80, 20/80**
10 mins	90.2439	86.478	6.52174	1.97368	3.09278	94.9721	18.9474	99.4624
30 mins	92.6829	85.443	4.3956	2.63158	4.14508	92.6966	21.0526	96.4674
1 hr	93.2515	85.1911	5.49451	39.0212	5.20833	92.5141	25.5319	94.9454
2 hrs	91.358	88.3758	5.52486	43.883	6.25	92.5141	29.7872	93.4066
6 hrs	92.5926	86.7834	14.3646	54.5213	6.25	93.0398	59.5745	93.4066
12 hrs	93.8272	86.7834	29.8343	65.1596	6.25	92.3295	65.9574	93.4066

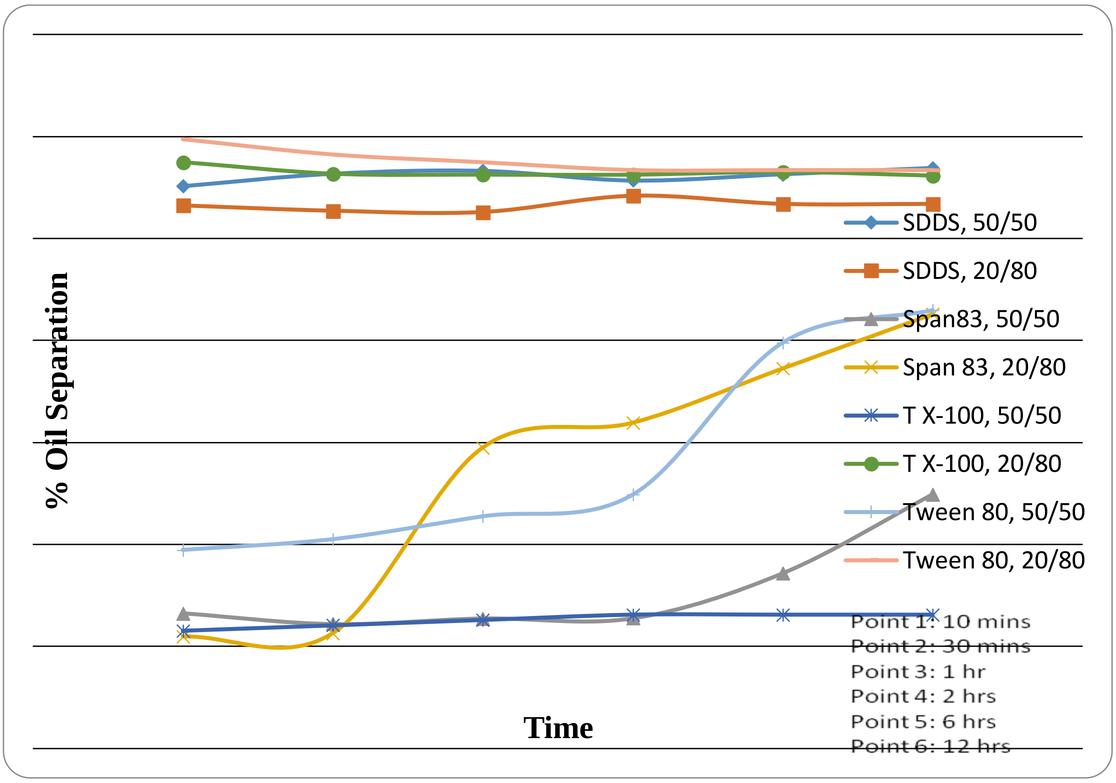


Fig. 4.18: Percentage of Oil Separation vs. Time

For all four emulsifiers at 1.0 % volume concentration, agitated at 800rpm, from Fig. 4.18, SDDS with 50/50 of water-in-crude oil emulsions had highest percentage of oil separation finally compared to other emulsifiers with two different emulsions-ratios. After 12 hours, Triton X-100 with 50/50 emulsions had least percentage of oil separation among others. The final percentage of oil separation after 12 hours ranked from the highest to the lowest were SDDS with 50/50, Tween 80 with 20/80, Triton X-100 with 20/80, SDDS with 20/80, Tween 80 with 50/50, Span 83 with 20/80, Span 83 with 50/50 and Triton X-100 with 50/50. From the rankings, it was observed that after microwave heating, Span 83 had the most stable emulsions (in terms of oil binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios. After microwave heating, SDDS had the least stable emulsions (in terms of oil binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios.

4.5.3 Water and Oil Separation at 360 Watts

From Table 4.12 and Table 4.13, after microwave heating, Span 83 had the most stable emulsions (in terms of water and oil binding) among all four emulsifiers at 1.0 % volume concentration with two volume ratios of water-in-crude oil emulsions, agitated at 800 rpm and heated at 360 watts. SDDS Span 83 had the least stable emulsions (in terms of water and oil binding) among all four emulsifiers at the same conditions like the previous statement. Stability (instability) of an emulsion is caused by the coupling of coalescence and flocculation, which follow a multiplication principle rather than an additivity principle. This means that the total result of the application of a stabilizer (destabilizer) depends very much on both flocculation and coalescence processes [J. Sjöblom et *al.*, 2005].

4.5.4 Water Separation at 540 Watts

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm and heated at 540 watts.

Table 4.14: Percentage of Water Separation at 540 Watts

Time	**SDDS, 50/50**	**SDDS, 20/80**	**Span 83, 50/50**	**Span 83, 20/80**	**Tween 80, 50/50**	**Tween 80, 20/80**
10 mins	93.9891	59.7826	2.08333	0	72	18.7166
30 mins	97.2376	65.9341	3.125	23.5602	77.7778	18.8172
1 hr	98.8889	93.9227	3.15789	47.3684	80.8081	21.5054
2 hrs	100	93.9227	4.21053	78.9474	85.2792	37.6344
6 hrs	100	99.4475	48.4211	84.2105	91.3706	32.2581
12 hrs	100	100	63.1579	89.4737	93.401	48.6486

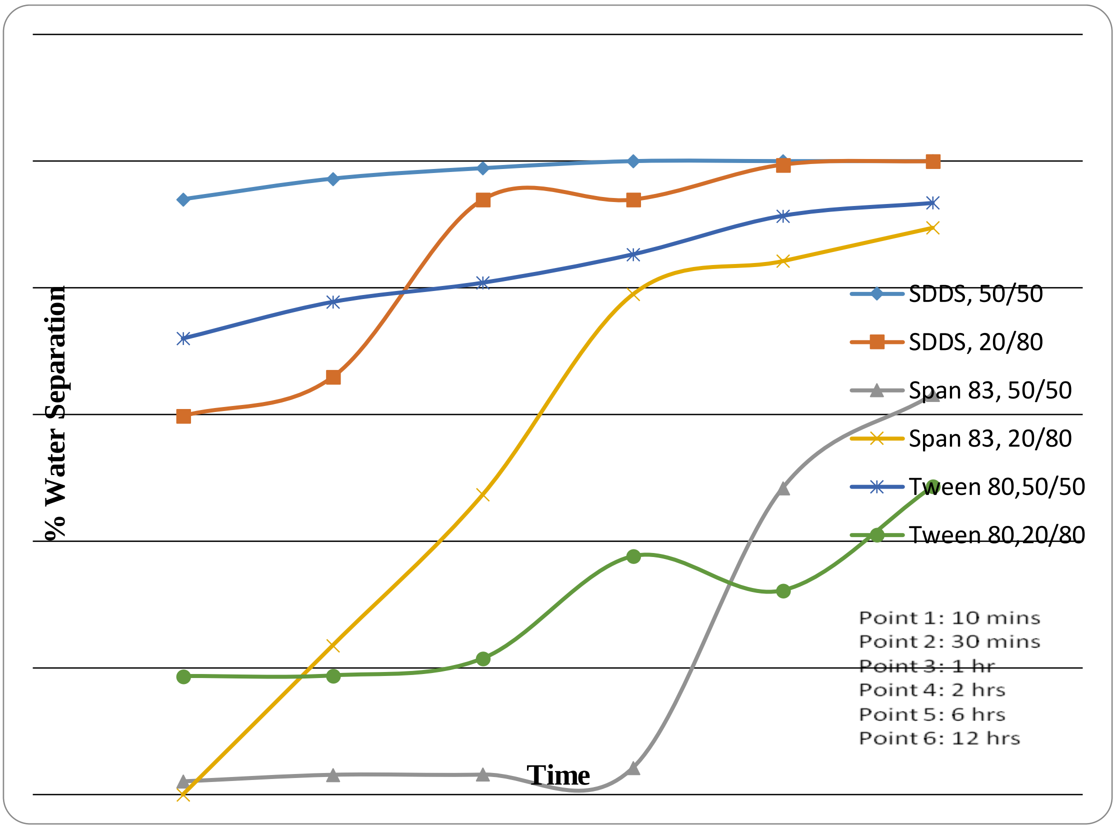


Fig. 4.19: Percentage of Water Separation vs. Time

For all four emulsifiers at 1.0 % volume concentration, agitated at 800rpm, from Fig. 4.19, SDDS with 50/50 of water-in-crude oil emulsions had highest percentage of water separation finally compared to other emulsifiers with two different emulsions-ratios. After 12 hours, Tween 80 with 20/80 emulsions had least percentage of water separation among others. The final percentage of water separation after 12 hours ranked from the highest to the lowest were SDDS with 50/50, SDDS with 20/80, Tween 80 with 50/50, Span 83 with 20/80, Span 83 with 50/50, Tween 80 with 20/80. From the rankings, it was observed that after microwave heating, Span 83 had the most stable emulsions (in terms of water binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios. After microwave heating, SDDS had the least stable emulsions (in terms of water binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios.

4.5.5 Oil Separation at 540 Watts

All the below water-in-crude oil emulsions samples were prepared at 1.0 % volume concentration of emulsifiers, agitated at 800 rpm and heated at 540 watts.

Table 4.15: Percentage of Oil Separation at 540 Watts

Time	**SDDS, 50/50**	**SDDS, 20/80**	**Span 83, 50/50**	**Span 83, 20/80**	**Tween 80, 50/50**	**Tween 80, 20/80**
10 mins	95.082	96.4674	3.125	1.28866	52	71.5241
30 mins	93.9227	94.7802	4.16667	1.96335	59.596	72.5806
1 hr	93.3333	94.6133	3.15789	7.23684	64.6465	75.2688
2 hrs	95.5556	94.6133	6.31579	52.6316	69.0355	67.2043
6 hrs	94.4444	94.6133	8.42105	75	73.0964	94.086
12 hrs	96.6667	94.6133	18.9474	80.2632	76.1421	94.5946

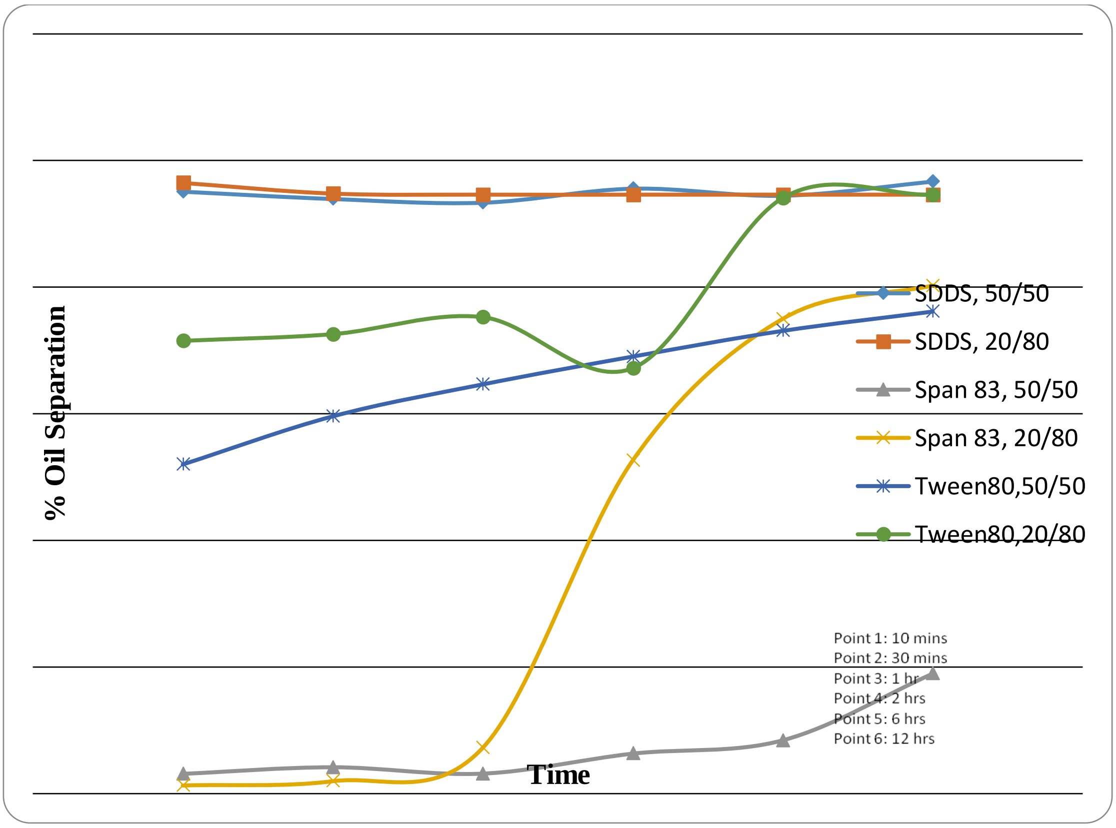


Fig. 4.20: Percentage of Oil Separation vs. Time

For all four emulsifiers at 1.0 % volume concentration, agitated at 800rpm, from Fig. 4.20, SDDS with 50/50 of water-in-crude oil emulsions had highest percentage of oil separation finally compared to other emulsifiers with two different emulsions-ratios. After 12 hours, Span 83 with 50/50 emulsions had least percentage of oil separation among others. The final percentage of oil separation after 12 hours ranked from the highest to the lowest were SDDS with 50/50, SDDS with 20/80, Tween 80 with 20/80, Span 83 with 20/80, Tween 80 with 50/50 and Span 83 with 50/50. From the rankings, it was observed that after microwave heating, Span 83 had the most stable emulsions (in terms of oil binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios. After microwave heating, SDDS had the least stable emulsions (in terms of oil binding) among other emulsions with different emulsifiers, both at 50/50 and 20/80 emulsions-ratios.

4.5.6 Water and Oil Separation at 540 Watts

From Table 4.14 and Table 4.15**,** after microwave heating, Span 83 had the most stable emulsions (in terms of water and oil binding) among all four emulsifiers at 1.0 % volume concentration with two volume ratios of water-in-crude oil emulsions, agitated at 800 rpm and heated at 540 watts. SDDS had the least stable emulsions (in terms of water and oil binding) among all four emulsifiers at the same conditions like the previous statement. Stability (instability) of an emulsion is caused by the coupling of coalescence and flocculation, which follow a multiplication principle rather than an additivity principle. This means that the total result of theapplication of a stabilizer (destabilizer) depends very much on both flocculation and coalescence processes [J. Sjöblom et *al.*, 2005].

Comparison between stability of emulsifiers between gravity settling and microwave heating, we can see that somehow after microwave heating, the chemical properties of the emulsifiers will alter. For example in my study, Triton X-100 had the least stable emulsion (in terms of water and oil binding), but SDDS had the least stable emulsion (in terms of water and oil binding) after exposing to microwave heat.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From Chapter 4, I will make conclusions based on my research. I will make conclusions from stability tests first, then gravity settling, microwave heating and finally microwave separation.

Here are the conclusions from stability tests. Only Span 83 emulsions are Newtonian fluid given the fact that shear stress increases linearly over shear rate. The other SDDS, Triton X-100 and Tween 80 emulsions are all Non-Newtonian because the shear stress does not increase linearly over shear rate. As shear rate and RPM increase, viscosity of emulsions will decrease curvingly. As RPM increases, shear stress will increase. Shear rate increases linearly at the same pace at increasing RPM for all emulsions. Surface tension of water is greater than oil. Interfacial tension of lower water cut is higher than higher water cut.

Here is the part of gravity settling. Water and oil separation increases over time. Span 83 has the most stable emulsions (in terms of water binding) among other emulsions because of the least volume of water separated. Tween 80 has the most stable emulsions (in terms of oil binding) among other emulsions because of the least volume of oil separated. Triton X-100 has the least stable emulsions (in terms of water and oil binding) among other emulsions because of the greatest volume of oil separation. The stability of all these emulsions are free from thermal heating.

Here is the part for microwave heating. The temperature of liquid sample emulsions will increase over time. The rate of temperature increase will decrease over time due to decreasing dielectric loss of water. All emulsions have decreasing volumetric heat generation rate over time. All emulsions also showed an increase of volumetric heat generation rate from 360 watts to 540 watts of microwave power. During the microwave heating of a material, radiation penetrates the material so that heat transfer occurs from within the material up to the surface of it. This kind of transfer causes the global warming of the material and a quick increase of its temperature [Coutinho et *al.*, 2007]. The greater the water content of the emulsions, the higher the temperature increase thus higher heating effect.

Finally, here is the microwave separation part. Water and oil separation increases over time and the water and oil separation of microwave heating are greater than gravity settling. Span 83 has the most stable emulsions (in terms of water and oil binding) among other emulsions because least volume of water separation. SDDS has the least stable emulsions (in terms of water and oil binding) among other emulsions. At 540 watts of microwave power generation, water and oil separation are higher than 360 watts. For comparison of heat effect on emulsion with different type of emulsifier, we can see that at gravity settling, Tween 80 has the most stable emulsions while Triton X-100 has the least stable emulsions, while after microwave heating, they are no longer the most and least stable emulsions. We can conclude that heat will have effect on the chemical properties of emulsifier in binding water and oil.

5.2 Recommendations

Here are some of my humble recommendations. Actually in my research, I had four parameters manipulated being concentration of emulsions, types of emulsifier, different power generations and volume % of emulsifier added. But here, with constraints, I can only put in the first three parameters listed above being two concentration of emulsions, four types of emulsifier and two power generations. The demulsification of w/o emulsions via microwave heating can be studied by increasing more variants under each parameter, then we will have a thorough understanding of the microwave demulsification process. Secondly, we can introduce and manipulate temperature in our stability tests as temperature plays an important role in viscosity of the emulsions. Thirdly, my research was only about batch microwave heating so we can try out continuous heating and I strongly believe the separation efficiency will be much, much greater. Finally ‘Safety First’ as we are dealing with crude oil which is highly flammable while applying heat, extra carefulness must be preserved.

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APPENDICES

A Brookfield Stability Tests

All the emulsions were prepared at 800 rpm. Stability tests were carried out at 25 ^{o}C. Visc. represents viscosity, SS is shear stress and SR is shear rate.

Table A.1: SDDS, 0.1 vol%; 50/50

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	99.0	16.5	17.0
100	84.3	29.7	34.0
150	99.4	51.0	51.0
200	96.3	66.9	68.0

Table A.3: SDDS, 1.5 vol%; 50/50

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	93.6	15.9	17.0
100	81.6	27.7	34.0
150	75.6	38.5	51.0
200	72.1	48.9	68.0

Table A.5: Span 83, 0.1 vol%; 50/50

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	12.0	1.73	17.0
100	5.70	1.94	34.0
150	3.60	1.53	51.0
200	3.75	2.45	68.0

Table A.7: Span 83, 1.5 vol%; 50/50

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	129.6	22.0	17.0
100	116.4	39.6	34.0
150	105.6	53.8	51.0
200	93.3	63.4	68.0

Table A.2: SDDS, 0.1 vol%; 20/80

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	148.2	25.1	17.0
100	114.6	38.0	34.0
150	94.4	47.9	51.0
200	86.1	58.7	68.0

Table A.4: SDDS, 1.5 vol%; 20/80

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	103.2	17.6	17.0
100	86.4	29.5	34.0
150	74.0	37.6	51.0
200	66.4	45.4	68.0

Table A.6: Span 83, 0.1 vol%; 20/80

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	219.0	36.9	17.0
100	161.4	44.9	34.0
150	119.2	52.6	51.0
200	77.1	61.7	68.0

Table A.8: Span 83, 1.5 vol%; 20/80

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	91.2	15.2	17.0
100	67.2	22.8	34.0
150	58.2	29.7	51.0
200	52.0	35.4	68.0

Table A.9: Triton X-100, 0.1 vol%; 50/50

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	6.60	1.02	17.0
100	6.60	2.04	34.0
150	5.80	2.96	51.0
200	6.60	4.39	68.0

Table A.11: Triton X-100, 1.5 vol%; 50/50

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	10.2	1.73	17.0
100	7.50	2.55	34.0
150	7.20	3.67	51.0

200	6.90	4.69	68.0

Table A.13: Tween 80, 0.1 vol%; 50/50

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	112.8	18.6	17.0
100	86.1	29.3	34.0
150	74.6	37.8	51.0
200	62.2	41.6	68.0

Table A.15: Tween 80, 1.5 vol%; 50/50

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	2.40	0.51	17.0
100	3.00	1.02	34.0
150	1.20	2.04	51.0
200	3.45	2.45	68.0

Table A.10: Triton X-100, 0.1 vol%; 20/80

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	171.0	29.2	17.0
100	133.2	45.3	34.0
150	119.8	61.4	51.0
200	96.3	63.9	68.0

Table A.12: Triton X-100, 1.5 vol%; 20/80

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	133.2	19.9	17.0
100	86.4	29.3	34.0
150	76.6	39.1	51.0
200	71.4	49.6	68.0

Table A.14: Tween 80, 0.1 vol%; 20/80

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	329.9	55.7	17.0
100	213.0	72.3	34.0
150	150.0	76.4	51.0
200	118.2	89.9	68.0

Table A.16: Tween 80, 1.5 vol%; 20/80

rpm	Visc., cP	SS, D/cm^2	SR, 1/sec
50	154.8	26.2	17.0
100	113.7	38.9	34.0
150	101.2	51.8	51.0
200	94.9	64.5	68.0

B Gravity Settling

All the emulsions were prepared at 800 rpm.

Table B.1: SDDS, 0.1 vol%; 50/50

Time	Water, mL	Oil, mL	Total, mL
10 mins	1	13.5	41.5
30 mins	2	14.5	41.5

1 hr	5	14.5	41.5
2 hrs	9	14.5	41.5
6 hrs	14	15.5	41.5
12 hrs	14	15.5	41.5

Table B.3: SDDS, 1.5 vol%; 50/50

Time	Water, mL	Oil, mL	Total, mL
10 mins	0	0	40
30 mins	0	0	40
1 hr	0	0	40
2 hrs	0	0	40
6 hrs	0	2.0	40
12 hrs	0.5	7.0	40

Table B.5: Span 83, 0.1 vol%; 50/50

Time	Water,mL	Oil, mL	Total, mL
10 mins	0.5	1	40
30 mins	1	1	40
1 hr	1	1	40
2 hrs	1	1	40
6 hrs	1.5	1.5	40
12 hrs	1.5	1.5	40

Table B.2: SDDS, 0.1 vol%; 20/80

Time	Water,mL	Oil, mL	Total, mL
10 mins	0	1	40.5
30 mins	0.2	1	40.5
1 hr	1.5	1	40.5
2 hrs	2	1.5	40.5
6 hrs	3	2.5	40.5
12 hrs	4	3.5	40.5

Table B.4: SDDS, 1.5 vol%; 20/80

Time	Water, mL	Oil, mL	Total, mL
10 mins	0.2	0.25	41
30 mins	1	5	41
1 hr	1.5	5	41
2 hrs	4	12	41
6 hrs	5	12	41
12 hrs	5	12	41

Table B.6: Span 83, 0.1 vol%; 20/80

Time	Water, mL	Oil, mL	Total, mL
10 mins	0	0	40.5
30 mins	0	0.5	40.5
1 hr	0	0.5	40.5
2 hrs	0	0.5	40.5
6 hrs	0	1.5	40.5
12 hrs	0	1.5	40.5

Table B.7: Span 83, 1.5 vol%; 50/50

Time	Water, mL	Oil, mL	Total, mL
10 mins	0	0	40
30 mins	0	0	40
1 hr	0	0.5	40
2 hrs	0	1.0	40
6 hrs	0	2.0	40
12 hrs	0	2.0	40

Table B.9: Triton X-100, 0.1 vol%; 50/50

Time	Water, mL	Oil, mL	Total, mL
10 mins	14.5	6	37
30 mins	17.5	6	37

1 hr	17.5	6.5	37
2 hrs	17.5	6.5	37
6 hrs	18	7	37
12 hrs	18	7.5	37

Table B.11: Triton X-100, 1.5 vol%; 50/50

Time	Water, mL	Oil, mL	Total, mL
10 mins	13.0	0	40
30 mins	14.0	0	40
1 hr	15.0	15.0	40
2 hrs	15.0	15.0	40
6 hrs	16.5	15.0	40
12 hrs	17.0	15.0	40

Table B.8: Span 83, 1.5 vol%; 20/80

Time	Water, mL	Oil, mL	Total, mL
10 mins	0	0.5	40.5
30 mins	0	2	40.5
1 hr	0.2	2	40.5
2 hrs	0.4	8.5	40.5
6 hrs	0.4	15.5	40.5
12 hrs	0.5	17.5	40.5

Table B.10: Triton X-100, 0.1 vol%; 20/80

Time	Water,mL	Oil, mL	Total, mL
10 mins	0	0	40.5
30 mins	0	0.5	40.5

1 hr	2	1	40.5
2 hrs	3.5	1.5	40.5
6 hrs	6	3.5	40.5
12 hrs	6.5	6.5	40.5

Table B.12: Triton X-100, 1.5 vol%; 20/80

Time	Water, mL	Oil, mL	Total, mL
10 mins	1.25	0	41
30 mins	1.5	0	41
1 hr	2.5	6	41
2 hrs	3	8.5	41
6 hrs	3	10	41
12 hrs	3	13	41

Table B.13: Tween 80, 0.1 vol%; 50/50

Time	Water, mL	Oil, mL	Total, mL
10 mins	0.2	4	41
30 mins	2	5	41
1 hr	3	5.5	41
2 hrs	6	8	41
6 hrs	11	8	41
12 hrs	12	10	41

Table B.15: Tween 80, 1.5 vol%; 50/50

Time	Water, mL	Oil, mL	Total, mL
10 mins	3	5	40
30 mins	3	5	40
1 hr	2.5	4	40

2 hrs	2.5	4	40
6 hrs	2.5	4	40
12 hrs	2.5	4	40

Table B.14: Tween 80, 0.1 vol%; 20/80

Time	Water, mL	Oil, mL	Total, mL
10 mins	0.2	1	41
30 mins	0.4	1	41
1 hr	0.6	1	41
2 hrs	0.7	2	41
6 hrs	3	6	41

12 hrs	3.5	8	41

Table B.16: Tween 80, 1.5 vol%; 20/80

Time	Water, mL	Oil, mL	Total, mL
10 mins	0.5	0.75	41
30 mins	1.5	1.75	41
1 hr	2	3.75	41
2 hrs	2.5	4.75	41
6 hrs	2.5	7.75	41
12 hrs	2.5	7.75	41

C Microwave Separation

All the emulsions were prepared at 800 rpm.

Table C.1: SDDS, 1.5 vol%; 50/50; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	41	42.5	94.5
30 mins	40	41	93.5
1 hr	40	40	93
2 hrs	46	45	93
6 hrs	46.5	40	93
12 hrs	46.5	44.5	93

Table C.3: SDDS, 1.5 vol%; 20/80; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	13	61.5	82.5
30 mins	14	61	82
1 hr	15	60.5	81.5
2 hrs	16	60	81
6 hrs	17	61	81
12 hrs	17.5	61	81

Table C.5: Span 83, 0.1 vol%; 50/50; 360 W

Time	Water,mL	Oil, mL	Total, mL
10 mins	0.5	0.25	89
30 mins	1.5	0.5	89
1 hr	2	1	89
2 hrs	5	2	89
6 hrs	35	16.25	88.5
12 hrs	31	25.5	88.5

Table C.2: SDDS, 1.5 vol%; 50/50; 540 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	33	28	67
30 mins	33	28	67

1 hr	33	26	66.5
2 hrs	33	26.5	66.5
6 hrs	33	25	66
12 hrs	33	25	66

Table C.4: SDDS, 1.5 vol%; 20/80; 540 W

Time gap	Water,mL	Oil, mL	Total, mL
10 mins	3.5	19	38
30 mins	2.5	18.5	37.5
1 hr	2.5	18.5	37.5
2 hrs	2.5	18	37
6 hrs	5	19	37
12 hrs	5.5	19	37

Table C.6: Span 83, 0.1 vol%; 50/50; 540 W

Time	Water,mL	Oil, mL	Total, mL
10 mins	0	1	95
30 mins	0.5	2.5	95
1 hr	1.5	5	95
2 hrs	2	10	95
6 hrs	37	21	94
12 hrs	34	27	93

Table C.7: Span 83, 1.5 vol%; 50/50; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	0	1.5	88.5
30 mins	0	2.5	88
1 hr	0.2	2.5	87.5
2 hrs	0.2	2.5	87
6 hrs	0.2	16.5	87
12 hrs	0.2	11	87

Table C.9: Span 83, 0.1 vol%; 20/80; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	2.5	3.5	93.5
30 mins	2.5	3.5	93
1 hr	3	9.5	92.5
2 hrs	2.5	10.5	92.5
6 hrs	3	18.5	92.5
12 hrs	3	18.5	92.5

Table C.11: Span 83, 1.5 vol%; 20/80; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	1	1	94
30 mins	5	23	93
1 hr	15	29.5	92.5
2 hrs	15	34	92.5
6 hrs	5	44	92
12 hrs	5	51.5	92

Table C.8: Span 83, 1.5 vol%; 50/50; 540 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	0.5	1	96
30 mins	0.75	1	96
1 hr	1	1.5	94.5
2 hrs	1	1.5	94.5
6 hrs	1	3	94
12 hrs	1	5	94

Table C.10: Span 83, 0.1 vol%; 20/80; 540 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	1	1	93
30 mins	1	6	93
1 hr	1	13	93
2 hrs	3.5	14	92.5
6 hrs	2	26	92.5
12 hrs	3	26.5	92.5

Table C.12: Span 83, 1.5 vol%; 20/80; 540 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	0.2	2	96
30 mins	5	25	95
1 hr	6.5	34	95
2 hrs	15	40.5	94.5
6 hrs	13	48.5	95
12 hrs	10	55	94

Table C.13: Triton X-100, 0.1 vol%; 50/50; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	30	19.5	94.5
30 mins	33		93.5
1 hr	35	26.5	93.5
2 hrs	37	28.5	93
6 hrs	42	32	93
12 hrs	43	33	93

Table C.15: Triton X-100, 1.5 vol%; 50/50; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	4	41.5	97
30 mins	6.5	40	96
1 hr	7.5	40	96
2 hrs	7.5	39	96
6 hrs	7.5	37	96
12 hrs	7.5	37.5	95.5

Table C.17: Triton X-100, 0.1 vol%; 20/80; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	19.5	75	95
30 mins	20	74	95
1 hr	19.5	73.5	94.5
2 hrs	19.5	73	94
6 hrs	20	73	94
12 hrs	20	73	94

Table C.14: Triton X-100, 0.1 vol%; 50/50; 540 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	10	16.5	96.5
30 mins	23	17.5	96
1 hr	32	18.5	95.5
2 hrs	39	25	95
6 hrs	42	28	95

12 hrs	43	29	95

Table C.16: Triton X-100, 1.5 vol%; 50/50; 540 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	0	43	98
30 mins	5	42	97
1 hr	5	41	97
2 hrs	5.5	40.5	96.5
6 hrs	6	39.5	96.5
12 hrs	6.5	39	96.5

Table C.18: Triton X-100, 1.5 vol%; 20/80; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	20	64.5	92
30 mins	21.5	68.5	90.5
1 hr	21.5	68.5	90.5
2 hrs	22	67.5	90
6 hrs	22	67	90
12 hrs	22.5	67	90

Table C.19: Tween 80, 0.1 vol%; 50/50; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	2	2.5	93
30 mins	2.5	3	92
1 hr	3	3.5	92
2 hrs	3.5	4	92
6 hrs	4	4.5	92

12 hrs	3.5	5	92

Table C.21: Tween 80, 1.5 vol%; 50/50; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	0	28	93
30 mins	0	33	93
1 hr	25	35.5	92.5
2 hrs	35	37	92
6 hrs	40	35	92
12 hrs	40	40.5	92

Table C.23: Tween 80, 0.1 vol%; 20/80; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	6	75	82
30 mins	8	72	81
1 hr	7	72	81
2 hrs	7.5	71.5	81
6 hrs	9	59	81
12 hrs	10	59.5	81

Table C.20: Tween 80, 0.1 vol%; 50/50; 540 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	8	9	87
30 mins	8	9	86
1 hr	9	11	86
2 hrs	14	13	86
6 hrs	17	16	85.5

12 hrs	18	18	85.5

Table C.22: Tween 80, 1.5 vol%; 50/50; 540 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	29	39.5	97.5
30 mins	29	43	97
1 hr	29	38	96
2 hrs	29	24	96
6 hrs	29	40	96
12 hrs	29	39	96

Table C.24: Tween 80, 0.1 vol%; 20/80; 540 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	12.5	78	94.5
30 mins	13	74.5	93.5
1 hr	13	74	93
2 hrs	13.5	73	93
6 hrs	9	72	93
12 hrs	15	72	93

Table C.25: Tween 80, 1.5 vol%; 20/80; 360 W

Time	Water, mL	Oil, mL	Total, mL
10 mins	23	62	92
30 mins	22.5	60	90
1 hr	22.5	65	90
2 hrs	22.5	64	90
6 hrs	22.5	64	90

12 hrs	22.5	64	90