DEMULSIFICATION OF CRUDE OIL EMULSION USING LOCAL DEMULSIFIERS

BY

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CERTIFICATION

This is to certify that this work "Demulsification of crude oil emulsion using local demulsifiers" was carried out by **Okereke Uchechukwu Justice (Reg. No.: 20164254168)** in partial fulfillment for the award of the doctor of philosophy degree, Ph.D. in Petroleum Engineering in the Department of Petroleum Engineering of the Federal University of Technology, Owerri.

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DEDICATION

To my family, family members and good friends

ACKNOWLEDGMENTS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

This work is based on formulation of crude oil demulsifiers (emulsion breakers) from materials locally sourced. Laboratory experimental investigation was carried out to ascertain its effectiveness and efficiency in breaking crude oil emulsion. Materials used included locally made palm oil, potassium hydroxide (KOH), lemons, glycerin, for sample A (ALPHA), locally made liquid soap, starch, camphor, alum, castor oil, and distilled water for sample B (BETA), and the combination of sample A and B make up sample C (MEGA), demulsifier. 10ml volume of water and 10ml volume of oil were mixed together to produce 20ml volume of emulsion. Separation of water and oil called demulsification started at dose of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0ml concentration. Maximum 3.0ml concentration of both locally produced and commercially available demulsifiers were used to obtain maximum demulsificaion result. The three different demulsifier formulations made were tested on a crude oil emulsion sample from a Niger Delta oil field and subjected to a temperature of 30°C, 50°C and 70°C. A commercially available demulsifier (CAD) of the same quantity and under the same laboratory experimental condition, served as a basis for comparison (validation). The composition of the separated products consist of 20ml volume of crude oil emulsion: 10ml water and 10ml oil content. After demulsification, 8.2ml (82%), 9.5ml (95%) and 9.6 (96%) of the water content was separated leaving 11.8ml, 10.5ml, and 10.4 of remaining solution as a result of using maximum concentration of 3.0ml of the produced demulsifiers; ALPHA, BETA and MEGA, temperature of 70°C, and 10mins settling time. At an increase temperature of 30°C, 50°C, and 70°C, the demulsification efficiency recorded 65%, 76%, 82% water separation of ALPHA, 75%, 91% 95% of BETA, and 79%, 95% 96% of MEGA.

The result of the treatment was a successful separation of oil and water using the sample, ALPHA, BETA and MEGA formulated demulsifier. The maximum separated water volume by the local demulsifier was 96%, at 70°C temperature and 1000rpm while that separated by CAD was 68% at the same condition. This showed that the locally formulated demulsifiers had better water separation capability than the commercially available (imported) demulsifier.

Key words: Local, Emulsion, Temperature. Concentration, Demulsfers, Niger Delta.

CHAPTER ONE

INTRODUCTION

1.1 Background of Information

Definition of emulsion as a system in which one liquid is relatively distributed or dispersed, in the form of droplets, in another substantially immiscible liquid has been established. Emulsions practical interest has long observed due to their widespread occurrence in everyday life which occurs due to reliance of the behaviour of the emulsion on the magnitude and range of the surface interaction. They may be little content of emulsion in important areas such as food, cosmetics, pulp and paper, biological fluids, pharmaceutical, agricultural industry, and petroleum industry. The common encountered emulsion types are water droplet dispersed in the oil phase and termed as water-in-oil emulsion (W/O) and if the oil is the dispersed phase, it is termed oil-in-water (O/W) emulsion in production and flow assurance. When there is dispersion (droplets) of one liquid in another immiscible liquid is called emulsion. The phase that is present in the form of droplets is the dispersed or internal phase, and the phase in which the droplets are suspended is called the continuous or external phase. For produced oilfield emulsions, one of the liquids is aqueous and the other is crude oil. The amount of water that emulsifies with crude oil varies widely from facility to facility. It can be less than 1% and sometimes greater than 80%.

In a true emulsion, either the drop size must be small enough that forces from thermal collisions with molecules of the continuous phase produce Brownian motion that prevents settling, or the characteristics of the interfacial surfaces must be modified by surfactants, suspended solids, or another semi soluble material that renders the surface free energy low enough to preclude its acting as a driving force for coalescence.

1.2 Problem Statement

When crude oil is produced from oil fields including heavy oil, there is always production of water-in-oil emulsions which can either be controlled or avoided. This emulsion results in an increase in viscosity which can seriously affect the production of oil from sandface up to flow line. Unable to separate the oil and water mixture called emulsion, efficiently and effectively could result in problems such as overloading of surface separation equipment, cost of pumping wet crude increases, and corrosion problems. It will equally result to low specification of the crude oil as a result of high BS&W. Because of inadequacy, water separation incapabilities and high cost of the conventional demulsifier; (commercially available imported demulsifiers) the research to formulate and apply local demulsifier to separate water in oil crude oil emulsion was proposed. Commercially available (imported) demulsifiers CAD are very expensive with low efficiency and effectiveness on crude oil emulsion separation and with environmental hazards. Formulation of local demulsifiers from local materials is an alternative option and also in alignment with a local content policy and initiative. This research is focused on formulation and application of locally produced demulsifier for the demulsification of crude oil emulsion.

1.3 Objectives of Study

The main objective of this study is to formulate and apply local demulsifier from locally sourced raw materials to break water-in-oil emulsion. The specific objectives are as listed:

i. Formulation of local demulsifier using local materials
ii. Laboratory characterization of local materials
iii. FTIR test on produced demulsifiers and commercially available (imported) demulsifiers
iv. Application of local demulsifiers and commercially available demulsifier on the crude oil emulsion.
v. Comparison and validation of the efficiency and effectiveness on the rate of separation of crude oil emulsion by the formulated local demulsifiers and commercially available (imported) demulsifier.

1.4 Justification of the Study

Water-in-Oil crude oil (tight) emulsion problem has grown in the Petroleum industry. Using local materials of palm oil group and local liquid soup group to formulate three different local demulsifiers is a new invention and academic research carried out in this work. The formulated local demulsifiers for demulsification of crude oil emulsion addresses the limitations of the existing commercially imported demulsifiers in the following ways:

1. High cost implication, downtime (retention time), environmental adverse effect and many other disadvantages of the commercially available imported demulsifiers
2. Very low efficiency and effectiveness of commercially available imported demulsifiers for a better water separation capability
3. Local use of indigenous products to reduce importation of commercially available demulsifiers is in line with Federal government of Nigeria policy for local production of raw materials used in the industries.
4. Locally formulated demulsifier contained no organic chloride, bromides, iodides, or lead thereby not going to cause any refining problems
5. The application of these local produced demulsifiers in the production process will relief the petroleum industry of the menace of water-in-oil emulsion.
6. The use of these demulsifiers produced from this work will improve crude oil quality by reducing the water content.

1.5 Scope

The research was focused on formulating local demulsifiers using Nigerian local raw materials and the formulated local demulsifiers was tested on crude oil emulsion specifications of low (minutes), medium (hours) and tight (days) emulsions to ascertain its water separation capability. The rate of water separation efficiency and effectiveness was compared and validated with the existing commercially imported demulsifier in determination of one with higher water separation efficiency and effectiveness.

CHAPTER TWO

LITERATURE REVIEW

2.1 Formation of Emulsion

Encountering water-in-oil emulsions at all stages in the petroleum production and in processing industry is common. With presence of water, it is typically become not only unvalued but can result in high pumping costs, pipeline corrosions and increase in the cost of transportation (Hanapi, Ariffin, Aizan, & Siti, 2006). Reduced throughput is needed to introduce special handling equipment, contribute to plugging of gravel pack at the sand face (Espinoza & Kleinitz, 2003) and affect oil spill cleanup (Fingas & Fieldhouse, 2003).

Emulsion problem also involved during enhanced oil recovery (EOR) process, despite its success in recovery process. (Efeovbokhan, Akinola, & Hymore (2010) observed that physical factors that enhance oil recovery can also greatly contribute to the formation of very stable emulsions because EOR-induced emulsions are established by surfactant/polymer (SP) and alkaline/surfactant/polymer (ASP) processes which makes breaking of emulsion different from naturally occurring emulsions which are stabilized by asphaltenes and resins (Efeovbokhan et al., 2010). Traditional demulsifiers are often not effective on emulsions created by chemical floods; therefore, the performance of demulsifier in surfactant/polymer–flooding-induced emulsion depends on the selection of the best demulsifier with respect to the system under consideration (Nguyen & Sadeghi, 2011). In breaking of surfactant/polymer-flooding-induced emulsion with the use of surfactant, (Oseghale, Akpabio, & Udottong (2012) worked on separation of oil-water emulsions expected during chemical enhanced recovery operations using crude oil from a field in Niger delta during surfactant/polymer flooding operation. Surfactant N-octyltrimethyammonium bromide (C8TAB) was used as the demulsifier and a dosage between 200 and 300ppm was the optimum dose that yielded oil and water phases with oil content reduction from 550 to 70 ppm after 4 h. Microscopy test confirmed that addition of N-octyltrimethyammonium bromide (C8TAB) produced significant coalescence shortly after it was added to the emulsion, which is in agreement with an increase of the oil droplet size in the presence of the demulsifier. Their

findings show that this investigation worked with the principles of using cationic surfactants as demulsifier (Oseghale et al., 2012).

Early petroleum industry operators used condensed chemicals such as sulphuric acid, sulphated castor oil, polyamines and polyhydric alcohols directly as demulsifier (Auflem, 2002). Later in the early 1940, the alkoxylated polymer group derivatives such as ethylene-, propylene-, and butylene-oxides were used (Chandran, 2014). A decade after, as a result of a large scale production of ethylene and prophylene oxide, a new classes of non-atomic detergents developed through condensed polyether were used as demulsifiers (Mosayebi & Abedini, 2013).

Presently, a polymer based hydrophilic and hydrophobic surfactants are used as demulsifiers this is to enable the demulsifier to permeate and destabilize the interfacial barrier between the crude oil and water in the emulsion. Hence it is expedient for the designed demulsifier to contain both oil soluble (hydrophobic) and water soluble (hydrophilic) solvents. (Daaou & Bendedouch, 2012) in their study on the effect of pH on Algerian crude oil emulsion, confirmed the fact that neutral medium is more efficient in stabilizing the emulsions compared to the acidic and basic solutions.

The surfactants used in the petroleum industry can be grouped into four groups namely, the amines, polymeric compounds, alcohols and polyhydric alcohols (Chandran, 2014). While oil soluble demulsifiers such as polymeric demulsifier give outstanding performance for water in oil emulsion, water soluble demulsifiers such as amine group, alcohol and polyhydric alcohol based demulsifiers are prefer for oil in water emulsion (Nurainia, Abdurahmanab, & Kholijaha, 2011).

Amines are surface active with high solubility in the continuous water phase. However, the amine group demulsifier has an ability to alter the pH or salinity of the aqueous phase of the emulsion thereby stabilizing the emulsion (Nurainia et al., 2011).

2.2 Emulsion identification and Characterization

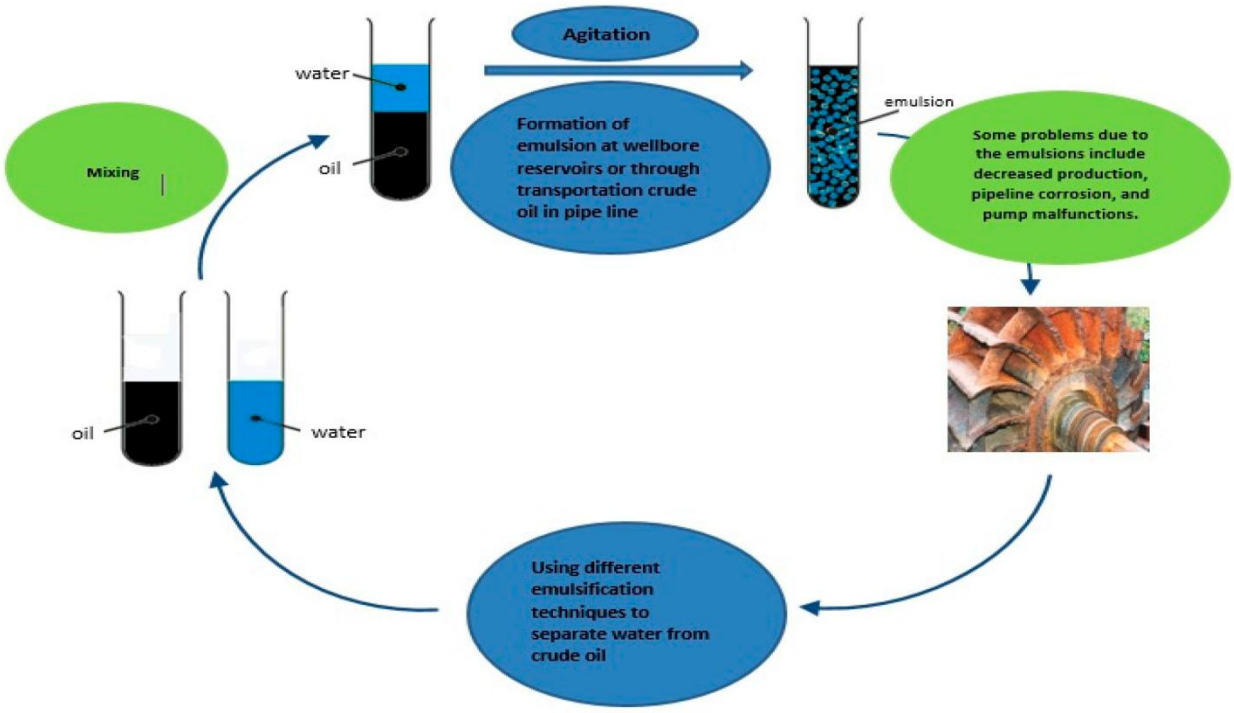


Figure 2.1 Cycle of emulsion (Okereke and Chijoke 2022)

Figure 2.1 cycle of emulsion is the complete phase of emulsion formulation to emulsion demulsification.

The separation of water and other foreign materials from produced crude oil is the most obligation of any oil production facilities. Emulsions of oil and water are one of many problems directly associated with the petroleum industry, in both oil-field production and refinery environments (Grace, 1992),

Whether these emulsions are created inadvertently or are unavoidable, as in the oil-field production area, or are deliberately induced, as in refinery desalting operations, the economic necessity to eliminate emulsions or maximize oil-water separation is present. The crude oil production and transportation problem caused by emulsion requires expensive emulsion separation equipment such as water treaters, separators and coalescers. Hence, chemical demulsification is the most suitable method from both operational and economic point of view to break the crude oil emulsion (Auflem, 2002). Among chemical agents, interfacial-active

demulsifiers, which weaken the stabilizing films to enhance droplets coalescence, are preferred due to lower addition rates needed. However, these demulsifiers are costly and pose significant threat to the environment. It becomes imperative to develop cheap and environmentally friendly demulsifiers from locally source raw material.

The complexibility crude oil emulsions should be characterized as completely as possible. Droplet-size distribution, interfacial phenomena, and the nature of organic and inorganic components are important. The viscosity of the emulsion is affected by both the water content and droplet size distribution (Thompson, Taylor, & Graham, 1985). The increase in aqueous phase of the emulsion leads to an increase in viscosity of emulsion which in turn aggravates flow of emulsion in conduit either at the sand face or through the surface facilities (Espinoza & Kleinitz, 2003; Kokal, Al-Ghamdi, & Meeranpillai, 2007). Interfacial viscosity and/or elasticity modulus found in water-in-oil emulsions stability are generally high. Viscosity of crude oil emulsion was found to increase with increase in water and decreased with increase in speed of rotation of spindle when demulsifier is added (Abdurahman & Mahmood, 2012).

An emulsion's characteristics change continually from the time of formation to the instant of complete resolution. Accordingly, aged emulsions can exhibit very different characteristics from those that fresh samples do. This is because any given oil contains many types of adsorbable materials and because the adsorption rate of the emulsifier and its persistence at the interface can vary. The emulsion characteristics also change when the liquid is subjected to changes in the following:

- Temperature
- Pressure
- Degree of agitation

Color and appearance is an easy way to characterize an emulsion. The characterization becomes somewhat easy if the emulsion is transferred into a conical glass centrifuge tube. The color of the emulsion can vary widely depending on:

- Oil/water content
- Characteristics of the oil and water

The common colors of emulsions are dark reddish brown, gray, or blackish brown; however, any color can occur depending on the type of oil and water at a particular facility. Emulsion brightness is sometimes used to characterize an emulsion. An emulsion generally looks murky and opaque because of light scattering at the oil/water interface. When an emulsion has small diameter droplets (large surface area), it has a light color. When an emulsion has large diameter droplets (low total interfacial surface area), it generally looks dark and less bright. Understanding the characteristics of an emulsion by visual observation is an art that improves with experience.

Oil and water (brine) forms crude oil emulsion when there is a contact with each other, Three conditions must be fulfilled which are; sufficient mixing, two immiscible liquid and when an emulsifying agent or emulsifier is present. Proper mixing, agitation and the presence of emulsifier are inevitable for the emulsion to form. During crude oil production, there are several sources of mixing, often referred to as the amount of shear, including: Flow through reservoir rock, Bottomhole perforations/pump, Flow through tubing, flow lines, and production headers, Valves, fittings, and chokes, Surface equipment, Gas bubbles released because of phase change. The amount of mixing depends on several factors and is difficult to avoid. In general, the greater the mixing, the smaller the droplets of water dispersed in the oil and the tighter the emulsion. Emulsion studies have shown that the water droplets can vary in size from less than 1 μm to more than 1000 μm. The second factor important in emulsion formation is the presence of an emulsifier. The presence, amount, and nature of the emulsifier determines, to a large extent, the type and "tightness" of an emulsion. The heavy fraction accommodates the natural emulsifier in crude oil. Because there are different types of crudes and because these crudes have different amounts of heavy components, the emulsifying tendencies vary widely. Crude with a small amount of emulsifier forms a less stable emulsion and separates relatively easily. Other crudes contain the right type and amount of emulsifier, which lead to very stable or tight emulsions. Emulsions may be encountered at all stages in the petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions)

Emulsion viscosity can be substantially greater than the viscosity of either the oil or the water because emulsions show non-Newtonian behavior. This behavior is a result of droplet crowding or structural viscosity. A fluid is considered non-Newtonian when its viscosity is a function of shear rate. A closely related and very important property, especially for demulsification, is the

interfacial viscosity, or the viscosity of the fluid at the oil/water interface. As mentioned water-in-oil emulsions form rigid interfacial films encapsulating the water droplets. These interfacial films stabilize an emulsion by lowering IFT and increasing interfacial viscosity. These films retard the rate of oil-film drainage during the coalescence of water droplets, thereby greatly reducing the rate of emulsion breakdown. The oil-drainage rate depends on the interfacial shear viscosity. High interfacial viscosities significantly slow the liquid drainage rate and thus have a stabilizing effect on the emulsion. Emulsion interfacial viscosity plays a very important role in demulsification.

Generally emulsion can be produced in the oilfield into three broad groups:

- Water-in-oil
- Oil-in-water
- Multiple or complex emulsions

Emulsions that consist water droplets in a continuous oil phase is water-in-oil emulsions, and oil-in-water emulsions consist of oil droplets in a water-continuous phase. **Figures.2. 2 and 2.3** show the two basic (water-in-oil and oil-in-water) types of emulsions. The commonest emulsion type in the oil industry is water-in-oil emulsions (most produced oilfield emulsions are of this kind); therefore, the oil-in-water emulsions are sometimes referred to as "reverse" emulsions.

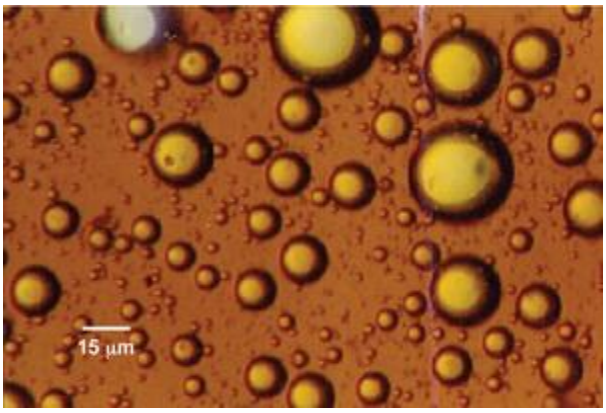


Figure*. 2.2 – Photomicrograph of water-in-oil emulsion.* *(Sjoblom et al 1993)*

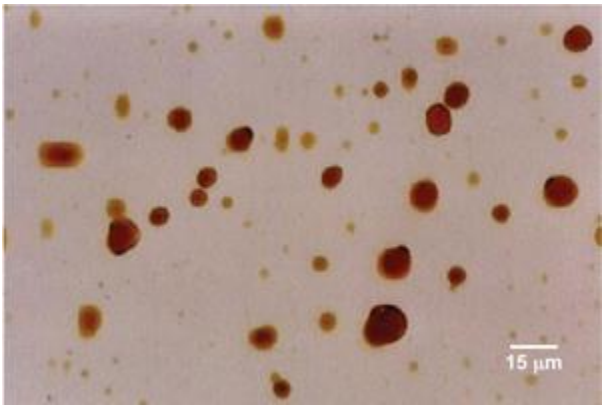


Figure. 2.3 Photomicrograph of oil-in-water emulsion. *(Daaou & bendedouch 2000)*

Multiple emulsions are more complex and consist of tiny droplets suspended in bigger droplets that are suspended in a continuous phase. For example, a water-in-oil-in-water emulsion consists of water droplets suspended in larger oil droplets that, in turn, are suspended in a continuous water phase. **Figure. 2,4** shows an example of a multiple emulsion.

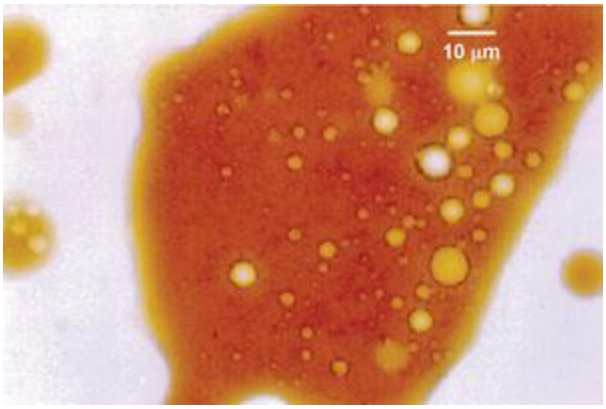


Figure.2.4 Photomicrograph of water-in-oil-in-water emulsion. *(Tombe & Sharma 1993)*

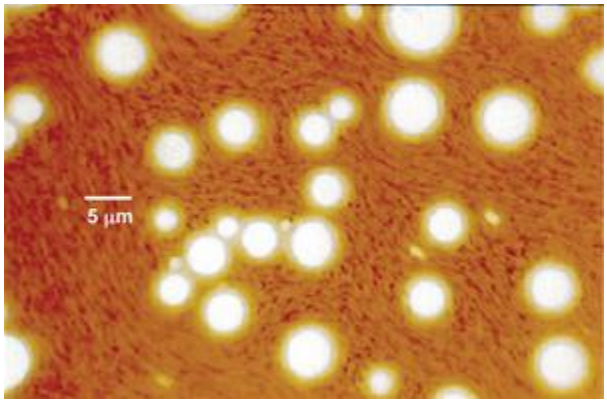


Figure. 2.5 – Photomicrograph of emulsion showing the presence of solids. *(Fingas & Fieldhouse 2003)*

Water-in-oil crude oil emulsions may be encountered at all stages in the petroleum production and in processing industry. With presence of water, they are typically undesirable and can result in high pumping costs and pipeline corrosions and increase the cost of transportation. Reduced throughput is needed to introduce special handling equipment, contribute to plugging of gravel pack at the sand phase, and affect oil spill cleanup.

2.3 Demulsification Process

A number of general rules help to form the basic philosophy of how emulsion behave within commercial emulsion breaking (Grace, 1992). Petroleum emulsions are primarily composed of immiscible liquids, which should theoretically separate based on their density differences, driven by gravity segregation. However, the settling rate of these liquids is influenced by the interfacial tension (IFT) between the droplets of the internal phase and the continuous phase. Notably, larger droplets exhibit lower IFT-to-mass ratios compared to smaller droplets, impacting the coalescence and settling behavior of the emulsion, which can be critical in processes like demulsification and dehydration of crude oil

Therefore, anything that can be done to increase the droplets size or coalescence will increase the rate of separation. Thirdly, an emulsion is stable within a given environment. Varying the environment may affect the stability of an emulsion and allow the phases separation. Finally, a

stable emulsion exists only when emulsifying agents are present. Neutralization, alteration or elimination of the emulsifying agents will allow immiscible liquids to separate.

From the above four generalizations it becomes noticeable that a number of options exist in emulsion breaking. Any single change in these areas may result in the resolution of an emulsion.

There are six factors that affect the emulsion stability such as:

i) Viscosity

Elevated oil viscosity enhances emulsion stability by suspending larger water droplets, thereby reducing the settling rate. To mitigate this, heat treatment, diluent addition, or chemical injection can be employed to reduce the oil viscosity, increasing the settling rate of water droplets and promoting mobility. This facilitates collisions and coalescence, ultimately accelerating the separation process.

ii) Density Differential

Thermal treatment of the emulsion decreases the oil's density more significantly than water's, thereby increasing the density differential between the two phases. This enhanced density difference enables faster settling of water droplets. Heavier crude oils, with densities closer to water, pose dehydration challenges due to reduced density differentials. Furthermore, freshwater tends to separate from oil at a slower rate than saltwater due to its lower density.

iii) Water Cut

The water-to-oil ratio significantly impacts emulsion stability. Emulsions exhibit maximum stability at specific water cuts, typically at low water percentages, where water droplets have a lower probability of collision and coalescence. As the water cut increases, emulsion stability decreases, rendering it more susceptible to separation. Understanding these factors enables operators to optimize conditions for effective emulsion breaking and oil-water separation.

iv) Age of emulsion

Age of emulsion is generally increasing the emulsion stability. The ratio of emulsifying agents within oil may increase because of oxidation, photolysis, evaporation of light ends, or bacterial action. This is because light ends are low molecular weight and low-density hydrocarbons such as pentane, hexane and butane that will vaporize xylene significantly over time. Breaking the

emulsion as soon as possible after the emulsion formation will reduce the effects of ageing (Grace (1992)

v) Control of emulsifying agents

Emulsifying agents or surfactants are important in the emulsion formation process. The surfactants are either natural or synthetic (Leopold, 1992). The elimination, alteration or neutralization of these materials allows the prevention or resolution of emulsions.

Elimination of emulsifying agents may include corrosion inhibition programs to reduce the amount of iron sulfide, to avoid emulsification tendencies, or elimination of incompatible crude oils from crude oil blends. Alteration of emulsifying agents are the addition of an asphaltene dispersant to "tie up" asphaltene polar sites, addition of paraffin crystal modifiers to prevent large paraffin crystals from stabilizing emulsions, or by raising the treating temperatures above the paraffin cloud point of a crude oil. Neutralization of emulsifying agents such as by neutralization of polar charges associated with the film of emulsifying agents formed around the emulsified droplets.

vi) Agitation control

Emulsion stability will be reduced by reducing or eliminating the agitation of oil-and-water mixture. The effectiveness of any demulsifier used is directly dependent on the contact between the demulsifier and the emulsion.

Therefore, the emulsion must be sufficiently agitated after the chemical demulsifier has been added. Increase of the mild agitation, is beneficial in promoting coalescence. Re-emulsification may occur if an emulsion is agitated severely once it has broken into oil and water (Leopold, 1992). The factors that influence emulsion formation and breaking show wide variation from site to site. Smart action would provide the most effective method in emulsion breaking of the producers and transporters.

2.4 Mechanisms of Demulsification Process

Chemical demulsification is a dynamic process since it is a phenomenon that occurs under non-equilibrium conditions. Coalescence of the dispersed phase often happens before the interface is at equilibrium. Therefore, it is paramount to consider dynamic and dilatational properties in the analysis of the demulsification mechanism (Krawczyk, 1990).

An important feature of dispersants is the ability to break water-in-oil emulsions that form naturally as the oil slick weathers and tosses about on the sea surface. Recent laboratory and field experience have demonstrated the ability of some dispersants to break emulsions formed at sea, particularly before the extremely viscous and stable 'mousse' stage of emulsion forms. This demulsification activity promotes coalescence of the water droplets in the emulsion, which in turn causes separation of water and lowering of viscosity. This step will slow down the dispersion process and can make effectiveness monitoring more difficult since oil releases more slowly into the water column. In addition, since a portion of the dispersant can be used up in the demulsification step, application of additional dispersant may be needed to increase the dispersion rate (Fiocco & Lewis, 1999).

Since the stability of emulsions can be traced to the presence of surfactant films at the water/oil interface, the rupture of the thin film separating droplets in a water-in-oil emulsion is affected primarily by the adsorption kinetics and interfacial rheological properties of the demulsifier. The role of the demulsifier, therefore, is the suppression of the interfacial tension gradient in addition to the lowering of interfacial shear viscosity, thus causing accelerated film drainage and coalescence.

Demulsifiers are very similar to emulsifiers because both are surfactant in nature. Consequently, the action of the demulsifier in emulsion breaking is to "unlock" the effect of the emulsifying agents present. This unlocking is accomplished in three fundamental steps, which are flocculation, coalescence and solids wetting (Leopold, 1992).

Flocculation is the first action of the demulsifier on an emulsion involves a joining together of flocculation of the small water droplets. When magnified, the flocks take on the appearance of bunches of fish eggs. If the emulsifier film surrounding the water droplets is very weak, it will break under this flocculation force and coalescence will take place without further chemical action. Bright oil is an indicator of good flocculation. The term bright oil refers to the shiny color

that is characteristic of treated oil. In most cases, however, the film remains intact, and therefore, additional treatment is required.

Coalescence is the rupturing of the emulsifier film and the uniting of water droplets. Once coalescence begins, the water droplets grow large enough to settle out. Good coalescence is characterized by a distinct water phase.

In most crude oil, solids such as iron sulfide, silt, clay, drilling mud solids, and paraffin complicate the demulsification process. Often such solids are the primary stabilizing material, and their removal is all that is necessary to achieve satisfactory treatment. To remove solids from the interface, they can either be dispersed in the oil or water-wetted and removed with water. Figure 2.6 shows the level of demulsification of water in oil emulsion (Kim, Wasan, & Breen, 1995).

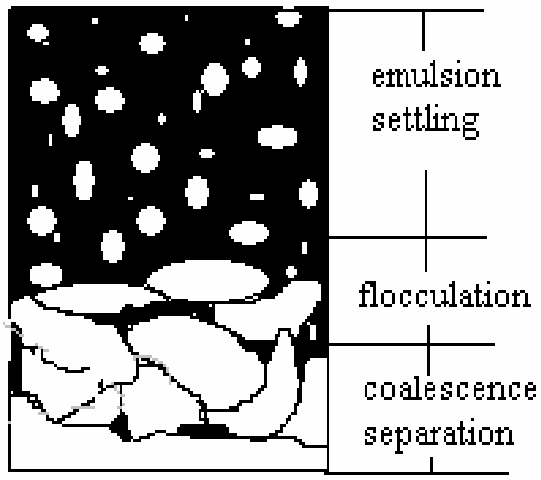


Figure 2.6: The level of demulsification process of water in oil emulsion (Ese et al, 1999)

Separation of water from water in oil emulsion by gravity force) Ese, Galet, Clausse, & Sjöblom (1999) state that the kinetics of chemical demulsification process is caused by the three main effects:

i) The displacement of the asphaltenic film from the water/oil interface by the demulsifier

ii) Flocculation

iii) Coalescence of water droplets

The demulsifiers will increase the water separation when present at low or moderate concentration, but at high concentration, the water droplets is dissolution and formed condense

liquid phase. Besides that, water separation is reduced as a result of stearic stabilization of larger water drops.

(Bhardwaj and Hartland (1998) summarized in their work that a lowering of interfacial tension and adsorption of demulsifier at the crude oil/water interface is necessary condition, but not a sufficient condition for an effective demulsifier. More important characteristics of a good demulsifier are sufficient surface pressure and good partition between the two phases. Ese et al. (1999) conclude that an effective oil soluble demulsifier will decrease the interfacial tension gradient and interfacial viscosity and caused the increasing rate of film thinning and decrease the time to reach a certain thickness.

The correlation between the rate of interfacial tension lowering and the demulsification efficiency of demulsifiers has been found. So, the kinetics of adsorption and the resulting dynamic elasticity of the interface are the main factors to consider the demulsification mechanism and performance.

Thus, most emulsion treating agents are composed of surfactants which modify the properties of the oil/water interface, by displacing, mixing with, or chemically neutralizing the naturally occurring emulsifying surfactant in the oil, thus inhibiting or destabilizing the emulsion.

2.5 Demulsifiers Development, Formulation and Performance

Historical development

Rigorous attempts have been in trying to correlate between demulsifier performance and physical properties such as molecular structure, interfacial tension, Hydrophilic-Lipophilic balance (HLB), interfacial viscosity, partition viscosity, dynamic interfacial tension and relative solubility number. A quick look on the chemical demulsifiers history reveals that prior to the knowledge of polyether condensates synthesis, chemicals such as Turkey red oil, sulphuric acid, sulphated caster oil, mahagony soaps, polyamines and polyhidric alcohols were used directly as demulsifiers (Monson, 1969).

In early 1940’s, the technology of alkylene oxide condensation started to evolve worldwide, and since then almost all demulsifier components were made up of condensation products of ethylene, propylene and butylenes oxide. Most of these are alkoxylated polymers that are mainly

etoxylated and propoxylated and sometimes both. They are macromolecules held in chains, industrially synthesized from petroleum chemicals.

After World War II, the whole branch of chemistry was opened to companies involved in surfactant (surface-active agents) technology. With the beginning of condensed polyether made possible by large-scale production of ethylene and propylene oxides (Becker, 1997), a new class of non-ionic detergents began to appear. The condensation products of the ethylene oxide were found to be water soluble and the high reactivity of the oxirane ring made it useful in a host of chemical reactions. It was found that the propylene oxide gave poly condensation products that tended to be oil soluble. The polymer most employed in the demulsification industry is surfactant that exhibits both hydrophilic and hydrophobic groups. The polymeric surfactant when added to the petroleum emulsion located itself in the interface between the water and oil molecules. The hydrophilic groups orient themselves towards water whist the hydrophobic ones orient themselves towards the oil.

The best polymeric surfactants used nowadays throughout the world are

alkoxylated material derivatives. Because they are alkoxylated, they are considered as non-ionic polymers. Sometimes mixtures of nonionic, cationic or anionic materials are used together, depending on the oil characteristics. Etoxylated nonionic surfactants are effective multi-purpose and versatile substances. Commercial products are obtained by reaction of ethylene oxide with a hydroprobe having an active hydrogen group (e.g. fatty acids, akylphenols or fatty alcohols) in the presence of suitable catalysts.

(Sjöblom, Söderlund, Lindblad, Johansen, & Skjärvö (1990) stated that a similar destabilization sequence for model and authentic crude oil emulsions can be obtained when medium-chain alcohols and fatty amines are used as destabilizers. The commercial demulsifiers that used to break up water-in-oil emulsion are oil soluble and water soluble demulsifiers. Table 2.2 shows the comparison between those demulsifiers.

Table 2.1: The development and evaluation of chemical demulsifiers

Year	Demulsifiers
1920-1930	Soap, naphtenic acid salts and alkylaryl sulphonate, sulphated caster oil
1930-1940	Petroleum sulphonates, derivatives of sulpho-acid oxidized caster oil and sulphosucinic acid ester
1940-1950	Fatty acids, fatty alcohols, alkylphenols
1950-1960	Ethylene oxide/propylene oxide copolymer, Alkoxylated cyclic palkylphenol formaldehyde resins
1960-1970	Amine alkoxylate
1970-1980	Alkoxylated cyclic p-alkylphenol formaldehyde resins
1980-1990	Polyesteramine and blends
1990-2000 2000-2010	Amine, alcohols Amine group

(Selvarajan et al., 2001)

Table 2.2: Comparison between oil soluble demulsifier and water soluble demulsifiers

No/Type	Oil soluble demulsifiers	Water soluble demulsifiers
1	Moderately 2000-50,000 molecular weight (mw). High mw are the preference.	10,000-15,000 molecular weight. Lower mw are the preference.
2	Polydispersed interfacially active polymers.	Tetrapolymer or pentapolymer
3	Mostly non-ionic block polymer with hydrophilic and hydrophobic segments.	The polymer present hydrophilic (-COOH) and hydrophobic (alkyl) groups.
4	Dangerous and expensive chemicals like ethylene and propylene oxide.	Easy handling chemicals like methyl metachrylate, butyl acrylate, acrylic acid and methacrylic acid.

(Bhattacharyya, 1992)

In water-in-oil emulsion cases, the most effective demulsifiers are oil-soluble or hydrophobic. This is because oil is the continuous phase while water is the dispersed phase. Thus, the surfactants will absorb straightly into the continuous phase without any resistance in optimum temperature.

Typically, these oil soluble demulsifiers are formulated in organic solvent alone such as toluene, xylene, tetrahydrofuran, dioxane, lower alcohols and light gasoline fractions having boiling limits of from 50 to 200°C, or in co-solvents comprising organic solvents and water where in the organic solvent are usually C3 to

C10 alkanols, ethylene diamine, diethylene triamine or ethanolamines including diethanolamine (Mercant et al., 1988).

Among the disadvantages of having organic solvents in a demulsifier formulation are increased cost, flammability, and toxicity. Therefore a demulsifier formulation, which does not include organic solvents, would represent an advance in the art of demulsification.

2.6 Demulsifier Formulation

Demulsifiers can be used singularly or in combinations of two or more.

Finding a demulsifier system that works well is often done by trial and error. (Grace (1992) stated that the selection process has historically been viewed as a "black art", which produces as many failures as successes. But the failures can be eliminated with the increasing understanding of emulsions and emulsion-breaking chemicals, the development of new test procedures and devices, and well-organized method of chemical selection.

To date, most demulsifier products are hydrophilic surfactant that is surfactants with a strong tendency to make oil-in-water emulsions from water-in-oil emulsions. These surfactants are more soluble in water than oil, and therefore have the ability to revert the water-in-oil emulsion into two separate phases. Therefore, such demulsifier products are most effective when used in a confined environment; they are likely ineffective on open water. Meso-stable emulsions, the most frequent emulsion produced at sea, are relatively easy to break and may be broken with as little as 1/100 of the same demulsifier products. Some demulsifier products are not capable of breaking these emulsions.

The best demulsifiers are one that can reduce the interfacial shear viscosity, increases the interfacial mobility and destabilizing the water-in-oil emulsion. To ensure the high quality performance, a demulsifier should posses the following characteristics (Krawczyk, 1990):

• The demulsifier should be able to partition into the water phase;

• Dissolved in the oil phase;

• The concentration of the demulsifier in the droplet must be sufficient to ensure a high enough diffusion flux to the interface;

• The interfacial activity of the demulsifier must be high enough to suppress the interfacial tension gradient, thus accelerating the rate of film drainage hence promoting coalescence.

According to (Tambe & Sharma 1993) there are three possibilities to cause the process of inversion where; if the demulsifier applied is not sufficient to convert the crude oil emulsion, the natural emulsion remains unbroken, if the demulsifier is ever sufficient, then natural emulsion will be broken, but a certain amount of crude oil will contaminate the water effluent and may caused re-emulsification of the oil in water and if the demulsifier is just sufficient, then the best separation of oil and water phase will be occurred.

There are a lot of commercial formulation published by various authors such as VX7079 Demulsifiers from ESSO, code D1 and D2 (Bhattacharyya, 1992). According to (Bhattacharyya, 1992) both D1 and D2 completely demulsified an East Texas crude oil after 10 minutes by using 10 to 15 ppm of each demulsifiers formulation.

2.7 Demulsifiers Performance

Different types of demulsifiers will give the different way in demulsificationprocess. Knowledge of formation and stability of crude oil emulsions, types of demulsifiers, demulsification mechanisms and so on are very important since it can be useful in the demulsification process of crude oil emulsions. Thus, it is frequently observed in studies of parameters that can affect the formation of stability of the crude oil emulsion. All parameters that are being identified to affect demulsifiers performance are: -

i. Temperature

The suitable temperatures considered for demulsification process for lab scale are between 50 to 70°C, which are similar to the actual refinery process (Grace, 1992). The interfacial viscosity of the internal phase will decrease to the increasing of the temperature. This is because the rate of film drainage is increased proportional to the temperature. The momentum between two water droplets will increase before coalescence is occurred. The two phases of immiscible liquids will be separated due to the different density among them.

ii. pH

(Tambe & Sharma 1993) studied that oil-in-water emulsions are preferential at low pH value ranging between 4 to 6, while water-in-oil emulsions are favored at high pH values that are between pH 8 to 10. Based on their experiments, the stability of oil-in-water emulsion formed increased as pH was increased from 4 to 6, but further increasing in pH, from 6 to 8 and finally 10 resulted in formation of relatively less stable oil-in-water emulsions and more stable water-in-oil emulsions. (Johansen et al., 1989) concluded that at very high and low pH values, the emulsions seem to be stable, while intermediate pH seems to cause instability. The optimum pH values in treating crude oil emulsions are between 5 to 12. Furthermore, the demulsifiers that are used in treating the emulsion problem are depending on the pH value.

iii. Solvents/Diluents

Solid or high viscous demulsifiers need to be dissolved in suitable solvents to increase the pour point and the solubility of demulsifiers in oil. This is because the surfactants are classified according to the polar (hydrophilic) part of the molecule (Schramm, 1992)(Schramm, 1992). As the result, the demulsification process will be completed successfully. The stability of emulsions is depends on the solubility of aromatic solvents. When the solubility parameter of the solvent decreases, for example; the oil is more aromatic, the oil forms more stable.

Gafonova (2000) stated that the influence of solvents of various aromatic and structure including benzene, toluene, xylene, ethylbenzene, tert-butyl benzene and cymene on emulsion stability. The results indicate that the more aromatic solvents (i.e. with the highest content of the aromatic carbon) are more effective in destabilizing emulsions.

iv. Salinity of oilfield brine

The presence of divalent cations in the brine decreases the optimal salinity of the surfactant formulations.(Binks (1993) studied that oil-in-water droplets are increase in size solubilizing more oil with increasing of salt concentrations, while water-in-oil droplets decrease in size. At low and high salt concentrations, the monolayer constrained to lie at the flat interface has a preferred tendency to curve and the tension becomes high. (Tambe & Sharma (1993) used some inorganic salts such as sodium chloride and calcium chloride to study the effect of emulsion stability for some pH values. They suggested that the presence of inorganic cations in the systems has an adverse effect on emulsion stability. (Calderon et al. (1993) studied that adding salts to the asphalt emulsions cause the depletion force is reduced at low salt concentrations, leading to a melting aggregates, whereas at high concentrations, rapid aggregation occurs as a consequence of van der Waals attractive force.

Aqueous-phase substrate salt differences will result the pronounced change in interfacial film behaviour. The salts ions lead to an increased relaxation of the film formed and a decrease in the resistance to press ion compared to distilled water (Jones, Neustadter, & Whittingham, 1978).

v. Natural surfactants (asphaltene and resin)

Many researchers have been trying to relate the emulsion stability to the asphaltene/resin ratio. When both asphaltenes and resins are present, the range is larger than for either resins or

asphaltenes alone. But the opposite results are pointed out by many researches that too much resins destabilizes emulsions (Gafonova, 2000). The investigation of the film formed by the adsorption of asphaltene/resin mixture indicated that resins start to predominate the film properties when their content exceeds 40% (Ese, Yang, & Sjöblom, 1998). (Sjöblom, Mingyuan, Christy, & Gu 1992) suggested that the amount of resin and asphaltene were quite decisive for the stability of the emulsion system from the interfacial tension point of view. They also suggested that the asphaltene fractions would give a higher stability than resin. The emulsion stability would decrease if the high components were mixed.

vi. Solid particles/waxes/crystals

Solid particles are often part of an emulsion formulation and they may be used to stabilize the emulsion. The key factor for the use of particles as a stabilizing agent is their wetting by the two liquids. They serve as a mechanical barrier to prevent the coalescence of the droplets.

Sjöblom et al. (1990) concluded that there is a correlation between a high content of wax particles and a high viscosity. In two specific cases, the interfacial tension exceeds the surface tension. The melting and crystallization (and recrystallization) sequence of the waxes is important for stabilizing the properties of waxes. If the melting point is exceeded, the waxes will mainly act as a component in the crude oil bulk and their activities at the oil-water interface is normally substantially reduced.

vii. Pressure

Reservoir pressure has a less significant effect on emulsion stability than temperature. Interfacial tension decreases as the pressure of the system increases.

Pressure effects probably have an indirect effect on emulsion stability because of the dependence of physical properties on pressure (S. L. Kokal, Maini, & Woo, 1992).

Chemical programs applied in commercial emulsion breaking are selected from a wide variety of emulsion-breaking chemistries and auxiliary chemicals that control very specific agents within the emulsion. These chemicals and parameters that involved in demusification process provided a measure of performance of the performance of treating chemicals with a specific crude oil and treating system.

The most common method of emulsion treatment is adding demulsifiers. The effect of chemical demulsifier in demulsification of water in oil emulsions experimentally has been studied by a few investigators (Abdurahman, Mohd, Hassan, & Yunus, 2007; Abdurahman & Nuraini, 2010).

Four groups of demulsifier with different functional groups were used namely; amines, polyhydric alcohols suphonates and polymer. The results obtained have shown the capability of chemical demulsifier in destabilization of water-in-oil emulsions. These chemicals are designed to neutralize the stabilizing effect of emulsifying agents. Demulsifiers are surface-active compounds that, when added to the emulsion, migrate to the oil/ water interface, rupture or weaken the rigid film, and enhance water droplet coalescence.

Optimum emulsion breaking with a demulsifier requires a properly selected chemical for the given emulsion; adequate quantity of this chemical; adequate mixing of the chemical in the emulsion; and sufficient retention time in separators to settle water droplets. It may also require the addition of heat, electric grids, and coalescers to facilitate or completely resolve the emulsion.

The authors (Batista, Ramalho, Fernanda, & Elizabete Lucas, 2010) investigated three different macromolecular structures of poly (ethylene oxide-b-propylene oxide) copolymers, used in formulations of commercial demulsifiers for breaking water-in-crude oil emulsions. The interfacial activity (a), the lower interfacial tension (gm), the critical micelle concentration (CMC), the interfacial concentration (I) and the molecular area (A) adsorbed at the interface of the surfactant solutions were evaluated. These results were correlated to surfactant performance in coalescing three different asphaltene model emulsions. The Poly (ethylene oxide-b-propylene oxide) PEO-b-PPO commercial demulsifiers that were capable to dewater asphaltene model emulsions, exhibited interfacial activity to the oil-water interface, reduced the interfacial tension to low values, reached the CMC at low concentration and presented low molecular area adsorbed at the interface.

Selection of the right demulsifier is crucial to emulsion breaking.

The selection process for chemicals is still viewed as an art rather than a science. However, with the increasing understanding of emulsion mechanisms, the availability of new and improved chemicals, new technology, and research, and development efforts, selection of the right chemical is becoming more scientific. Many of the failures of the past have been eliminated.

Demulsifier chemicals contain the following components: solvents, surface-active ingredients, and flocculants. Solvents, such as benzene, toluene, xylene, short-chain alcohols, and heavy aromatic naptha, are generally carriers for the active ingredients of the demulsifier. Some solvents change the solubility conditions of the natural emulsifiers (e.g., asphaltenes) that are accumulated at the oil/brine interface. These solvents dissolve the indigenous surface-active agents back into the bulk phase, affecting the properties of the interfacial film that can facilitate coalescence and water separation. Surface-active ingredients are chemicals that have surface-active properties characterized by hydrophilic-lipophilic balance (HLB) values. Flocculants are chemicals that flocculate the water droplets and facilitate coalescence.

The authors (Sjöblom et al., 1990) found that medium-chain alcohol (1-butanol and benzyl alcohol) and amines are speeding up the separation of water. The destabilization mechanisms in these two cases seem to be fundamentally different. The alcohols seem to modify the rigidity of the interfacial film by a diffusion/partitioning process while the amines show a strong and specific interaction with interfacial groups, hence hydrophilizing the whole film. Observed trends in the time dependence of the interfacial tension upon addition of alcohols and amines support these suggestions to destabilization mechanisms.

Testing procedures are available to select appropriate chemicals. These tests include bottle tests, dynamic simulators, and actual plant tests. For the demulsifier to work effectively, it must make intimate contact with the emulsion and reach the oil/water interface. The amount of chemical added is also important. Too little demulsifier will leave the emulsion unresolved. Conversely, a large dose of demulsifier (an overtreat condition) may be detrimental. Because demulsifiers are surface-active agents like the emulsifiers, excess demulsifier may produce very stable emulsions. The amount or dosage of demulsifier required is very site-specific and depends on several factors, some of which are discussed in this section of the study. On the basis of an evaluation of the literature, the demulsifier rates quoted vary from less than 10 to more than 100 ppm (based on total production rates).

To ensure good overall performance, a demulsifier should meet the following criteria.

i. Dissolve in the continuous oil phase.

ii. Have a concentration large enough to diffuse to the oil/water interface. However, it should not be higher than the critical aggregate concentration.

iii. Partition into the water phase (partition coefficient close to unity).

iv. Possess a high rate of adsorption at the interface.

v. Have an interfacial activity high enough to suppress the IFT gradient, thus accelerating the rate of film drainage and promoting coalescence

Demulsifiers are typically formulated with polymeric chains of ethylene oxides and propylene oxides of alcohols and amines, ethoxylated resins, ethoxylated phenols, polyhydric alcohols and sulphonic acids salts.

2.8 Classification of Emulsion

Crude oils, especially the heavy oils, contain large quantities of asphaltenes (high molecular weight polar components) that act as natural emulsifiers. Concentrated portion of crude oil mixes with the surface sea/production water under the influence of wind and wave action to form an emulsion (Wei, Mather, Fotheringham, & Yang, 2003). The emulsion formed can be either water in oil (w/o) or oil in water (o/w) emulsion as illustrated in Figs. above. The dispersion of water droplets into the external phase of oil is called as water in oil (w/o) emulsion, while the dispersion of oil droplets in the aqueous medium/water is called oil in water (o/w) emulsion (Cormack, 1999). Water in oil emulsions may be extremely stable because the water droplets (1-10 um diameter range) are held in a rigid structure by the components like asphaltenes, waxes, and resins (Cormack, 1999). On the other hand, oil in water emulsions is less stable because the inner droplet distance is comparatively very large and the oil droplets are relatively free to migrate (Cormack, 1999).

2.9 Stability of Emulsion

An emulsifying agent must be present to form stable water-in-crude oil emulsions (Sjöblom et al., 2002). Such agents include clay particles, added chemicals or the crude oil components like asphaltenes, waxes, resins and naphthenic acids (Sjöblom et al., 2002). In the late 1960's, Berridge and his co-workers were the first to measure several physical properties of emulsions (Fingas & Fieldhouse, 2003). They described the formation of emulsions due to the asphaltene and resin content of the oil (Fingas & Fieldhouse, 2003). (Mackay & McAuliffe 1988) also stated that the main factors affecting the stability of the emulsion is the presence of substances

like crude oil resins, asphaltenes, and natural wax. It was found that asphaltenes were a major factor in emulsion stability (Fingas & Fieldhouse, 2003). Asphaltene fraction contains the highest percentage of hetero-atoms (O, S, and N) and organometallic constituents (Ni, V, Fe) in the crude oil (Johan Sjöblom et al., 2002). These components combine with organic and/or inorganic solids producing emulsion-stabilizing films at oil-water interface, and contribute to the formation of stable emulsions (Cormack, 1999).

In their research work, (Michael, Chuai, Marble, & Marsh 2005) used bottle test method to simulate field condition of four emulsion samples (two Canadian and two Venezuelan emulsions) in order to determine the variables that affect emulsion stability. They were able to evaluate response to the different emulsion based on bottle test data by introducing thirty-six different demulsifiers to enable them to probe emulsion stability. Linear regression and partition tree analysis were used to analyze the effect of various variables on emulsion stability and were able to conclude that solid content significantly affects emulsion stability. Beside solid content crude oil properties, water chemistry and process condition also influence emulsion stability (Michael et al., 2005).

Christophe, Arla, Sinquin, Graciaa, & Bouriat (2006) evaluated and compared emulsion formed by different parts of the indigenous amphiphiles (the light, the intermediate, or the heavy ones) to determine their contribution to emulsion stability. The emulsions formed with the light and intermediate fractions separated immediately when the agitation stopped. The most stable emulsions were formed with the fraction of crude that distilled at temperature greater than 520°C, suggesting that the amphiphiles with the highest molecular weight, that is, resins and asphaltenes, play a major role in -the protection of water droplet against coalescence (Christophe et al., 2006). This is consistent with many recent findings that the presence of these components enhanced w/o emulsion stability (Ekott & Akpabio, 2011; Rondón et al., 2008). Others factors that affect emulsion stability are fine solids, temperature, size of water droplet, and brine composition (Kokal et al., 2007).

2.10 Emulsion Demulsification

With various problems encountered with the presence of emulsion in our system, there is need to find ways of controlling existence of emulsion or preventing it from forming in our system. One of the ways of controlling problems encountered by crude oil emulsion is the ability to predict crude oil behaviour both at the sand phase and during production by building a robust predictive model (Fu, 2000). Emulsion formation or break up either for oil in water or water in oil emulsion can be characterized based on the property and type of crude oil involved in the formation or break up of emulsion which can assist in formulating method of preventing formation of such emulsion (Noïk, Malot, Dalmazzone, & Mouret, 2004). (Nurainia et al. 2011) selected four groups of demulsifiers which are amine, natural, polyhydric, and alcohol demulsifier groups serving as breaking agents of stable emulsion. Their findings show that amine demulsifier group exhibited the highest efficiency to break the emulsion compared to polyhydric, alcohol, and natural groups and that demulsifier efficiency depends on two-factor solubility of demulsifier either in water or oil and molecular weight of demulsifier (Nurainia et al., 2011).

It has been established from the field and lab experience that one of the ways of breaking stable (tight) emulsion is introduction of low dose of demulsifiers. For comprehensive methods of breaking emulsion, the work of (Hanapi et al. 2006) treated that aspect. (Michael et al. 2005) used chemical demulsifiers and statistical analysis to classify emulsion. They obtained emulsion from the field and treated the emulsion with thirty-eight chemicals that serve as demulsifiers at nine different sites. The tests were tailored towards determination of water droplet, oil dryness, and oil-water interface which were analyzed using several statistical tools. A correlation was developed for water droplet, oil dryness and oil-water interface. The results show that water droplet significantly affect oil-water interface than oil dryness (Michael et al., 2005).

Crude oil emulsions are complex and should be characterized as completely as possible. Droplet-size distribution, interfacial phenomena, and the nature of organic and inorganic components are important. The viscosity of the emulsion is affected by both the water content and droplet size distribution (Taylor, 1988; Thompson et al., 1985). The increase in aqueous phase of the emulsion leads to an increase in viscosity of emulsion which in turn aggravates flow of emulsion in conduct either at the sand phase or through the surface facilities (Espinoza & Kleinitz, 2003; Jones et al., 1978). Stable water-in-oil emulsions have been generally found to exhibit high

interfacial viscosity and/or elasticity modulus. Viscosity of crude oil emulsion was found to increase with increase in water and decreased with increase in speed of rotation of spindle when demulsifier is added (Abdurahman et al., 2007). The increase of the interfacial rheological parameters has been attributed to non-Newtonian nature of emulsion (Abdurahman et al., 2007) and physical cross-links between the asphaltene particles adsorbed at the water-oil interface (McLean & Kilpatrick, 1997). Demulsification of tight emulsion proved to be a tough method of breaking emulsions but with an influence of improper selection of chemicals still unaccounted for in most of the researches; this research will study the effect of selecting and using proper chemicals to tight emulsion samples treated with chemical for three different water in oil crude emulsions (tight) collected from three different oil fields from three operators in Niger delta, Nigeria

2.9.1 Approaches

- **Destabilizing Emulsions**

Oilfield emulsions possess some kinetic stability. This stability arises from the formation of interfacial films that encapsulate the water droplets. To separate this emulsion into oil and water, the interfacial film must be destroyed and the droplets made to coalesce. Therefore, destabilizing or breaking emulsions is linked directly to the removal of this interfacial film. Factors that affect the interfacial film are discussed in Stability of oil emulsions. The factors that enhance or speed up emulsion breaking are discussed here.

- **Temperature**

Application of heat promotes oil/water separation and accelerates the treating process. An increase in temperature has the following effects.

- Reduces the viscosity of the oil.
- Increases the mobility of the water droplets.
- Increases the settling rate of water droplets.
- Increases droplet collisions and favors coalescence.

- Weakens or ruptures the film on water droplets because of water expansion and enhances film drainage and coalescence.
- Increases the difference in densities of the fluids that further enhances water-settling time and separation.

All of these factors favor emulsion destabilization and oil/water separation; however, heat by itself is not a cure-all and even has some disadvantages (e.g., loss of light ends from the crude oil). An economic analysis should be performed that takes into consideration factors such as:

- Heating costs
- Reduced treating time
- Residual water in the crude

An increase in temperature also can be achieved by burying crude-oil pipelines or by insulating them. These factors should be evaluated carefully during development, especially at facilities where emulsion problems are anticipated.

- **Agitation or Shear**

Generally, reducing agitation or shear reduces emulsion stability. Very high shear is detrimental and should be avoided. High shear causes violent mixing of oil and water and leads to smaller droplet sizes (Cormack, 1999). Smaller droplets are relatively more stable than larger droplets; therefore, measures that increase shearing of the crude oil should be avoided or minimized where possible. Such measures include (Michael et al., 2005).

- Mechanical chokes
- Valves
- Flow obstructions
- Pressure drops

However, a certain amount of shear is required for mixing the chemical demulsifier into the bulk of the emulsion.

- **Residence or Retention Time**

The duration for which the emulsion is maintained at the treating temperature is referred to as the residence time, retention time, or treating time. For conventional crude oil production, this period typically ranges from 10 to 30 minutes. However, for more stable or "tight" emulsions, a longer residence time may be required to achieve effective treatment and separation. An increase in residence time increases the separation efficiency and reduces the residual amount of water in the crude (Hanapi et al. 2006). Increasing residence time, however, comes at the expense of high separator-equipment costs.

- **Solids Removal**

The presence of solids, particularly fine particles or those exhibiting amphiphilic properties (i.e., wetted by both oil and water), can significantly stabilize emulsions. In some cases, removing the solids or addressing their source can be sufficient to mitigate or eliminate emulsion-related issues. Specifically, oil-wet solids tend to stabilize water-in-oil (W/O) emulsions, where water droplets are dispersed within a continuous oil phase. Water-wet solids can also be made oil-wet with a coating of heavy polar materials and can participate effectively in the stabilization of water-in-oil emulsions. (Sjöblom et al., 2002). The presence of **solid asphaltenes and waxes** has a definite detrimental effect on the emulsion problem, and every effort should be made to eliminate their presence in the crude oil. The solids can be removed by dispersing them into the oil or can be water-wetted and removed with the water (Michael et al., 2005).

- **Control of Emulsifying Agents**

Because emulsifying agents are necessary in the stabilization of emulsions, controlling them allows for their destabilization and resolution. Some of the ways to control emulsifiers include the following processes.

- Careful selection of chemicals that are injected during oil production. The chemicals include, for example, acids and additives during acidization, corrosion inhibitors for corrosion protection, surfactants and dispersants for organic- and inorganic-deposition control, and polymers and blocking agents for water-production control. Laboratory

compatibility testing of these chemicals should be conducted before field injection to avoid tight emulsions.

- Avoiding incompatible crude-oil blends. A crude-oil blend is incompatible if it results in the precipitation of solids (organic and inorganic). This occurs, for example, when an asphaltic crude oil is mixed with a paraffinic crude oil, resulting in the precipitation of asphaltenes. Again, laboratory testing can identify incompatible crude (Sjöblom et al., 2002)..
- Use of dispersants for controlling the precipitation of asphaltenes and the use of pour-point depressants for controlling waxes. Alternatively, emulsion stability can be controlled by raising the temperature of the crude above its cloud point (Sjöblom et al., 2002).
- Neutralizing the effect of stabilizing film encapsulating the water droplets by demulsifiers. These chemicals promote coalescence of water droplets and accelerate water separation.

➢ **Retrofitting**

Upgrading existing separation equipment can enhance water separation efficiency. However, emulsion issues often intensify over time due to factors such as field aging, rising water cuts, or design limitations. To address these challenges, additional equipment, such as free-water knockout drums and heater treaters, can be installed to facilitate emulsion breaking. Furthermore, retrofitting production-separation traps with internals, like coalescer sections, can promote water droplet coalescence and improve separation efficiency. Since each situation is unique, re-engineering and customization are typically required to optimize emulsion treatment. For more detailed information, refer to emulsion treating guidelines

➢ **Heat Approach**

Heating reduces the oil viscosity and increases the water-settling rates. Increased temperatures also result in the destabilization of the rigid films because of reduced interfacial viscosity. Furthermore, the coalescence frequency of water droplets is increased because of the higher thermal energy of the droplets. Heat accelerates emulsion breaking; however, it very rarely

resolves the emulsion problem alone (Hanapi et al. 2006). Increasing the temperature has some negative effects.

1. It costs money to heat the emulsion stream.
2. Heating can result in the loss of light ends from the crude oil, reducing its API gravity and the treated oil volume.
3. Increasing the temperature leads to an increased tendency toward some forms of scale deposition and an increased potential for corrosion in treating vessels.

The application of heat for emulsion breaking should be based on an overall economic analysis of the treatment facility. The cost-effectiveness of adding heat should be balanced against:

- Longer treatment time (larger separator)
- Loss of light ends and a resultant lower oil-product price
- Chemical costs
- The costs of electrostatic grid installation or retrofitting

➢ **Electrical Approach**

Electrostatic grids are sometimes used for emulsion treatment. When a nonconductive liquid (oil) that contains a dispersed conductive liquid (water) is subjected to an electrostatic field (Hanapi et al. 2006), one of three physical phenomena causes the conductive particles or droplets to combine:

1. The water droplets become polarized and tend to align themselves with the lines of electric force. In so doing, the positive and negative poles of the droplets are brought adjacent to each other. Electrical attraction brings the droplets together and causes them to coalesce.
2. An induced electric charge attracts the water droplets to an electrode. In a direct current (DC) field, the droplets tend to collect on the electrodes or bounce between the electrodes, forming larger and larger droplets until eventually they settle by gravity.

3. The electric field distorts and thus weakens the film of emulsifier surrounding the water droplets. Water droplets dispersed in oil that are subjected to a sinusoidal alternating-current (AC) field become elongated along the lines of force as voltage rises during the first half-cycle. As the droplets are relaxed during the low-voltage part of the cycle, the surface tension pulls them back toward a spherical shape. This effect repeats with each cycle, weakening the film so that it breaks more easily when droplets collide.

Whatever the actual mechanism, the electrical field causes the droplets to move about rapidly, which increases the probability of collision with other droplets. Droplets coalesce when they collide at the proper velocity. The greater the voltage gradient, the greater the forces that cause coalescence; however, experimental data have shown that at some voltage gradient, rather than coalescing, the water droplets can be pulled apart, tightening the emulsion. For this reason, electrostatic treaters normally are equipped with a mechanism for adjusting the voltage gradient in the field.

High-voltage electricity (electrostatic grids) is often an effective means of breaking emulsions. It is generally theorized that water droplets have an associated net charge, and when an electric field is applied, the droplets move about rapidly and collide with each other and coalesce. The electric field also disturbs the interfacial film by rearranging the polar molecules, thereby weakening the rigid film and enhancing coalescence. The electrical system consists of a transformer and electrodes that provide high-voltage alternating current. The electrodes are placed to provide an electric field that is perpendicular to the direction of flow. The distance between the electrodes is often adjustable so that the voltage can be varied to meet the requirement of the emulsion being treated.

Electrostatic dehydration generally is used with chemical and heat addition. Invariably, the use of electrostatic dehydration results in reduced heat requirements. Lower temperatures result in:

- Fuel economy
- Reduced problems with scale and corrosion formation
- Reduced light-end loss

Electrostatic grids can also lead to a reduction in the use of emulsion-breaking chemicals. The one limitation of electrostatic dehydration is shorting/arcing, which generally happens when excess water is present. Recent designs in electrostatic grids have eliminated shorting/arcing.

In oil that contains a large quantity of water, there is a tendency toward "chaining"—the formation of a chain of charged water particles—which might form links between the two electrodes, causing short-circuiting. Chaining has been observed in emulsions that contain 4% or less water. If chaining causes excess power consumption, the voltage gradient is too large (i.e., the electrical grids of the electrostatic treater are too close together or the voltage is too high) for the amount of water being handled. The breaking out of solution of small amounts of gas also can create sufficient turbulence to impede sedimentation.

- **Chemical Emulsifier/Approach**

The most widely used method for treating emulsions involves injecting demulsifiers, specialized chemicals that counteract the stabilizing effects of emulsifying agents. These surface-active compounds work by migrating to the oil-water interface, disrupting or weakening the rigid film surrounding water droplets, and promoting coalescence. Effective emulsion breaking with demulsifiers requires careful consideration of several factors, including: selecting the right chemical for the specific emulsion, ensuring adequate dosage, providing sufficient mixing, and allowing enough retention time in separators for water droplets to settle. It may also require the addition of heat, electric grids, and coalescers to facilitate or completely resolve the emulsion (Hanapi et al. 2006).

Chemical selection

Selection of the right demulsifier is crucial to emulsion breaking (Michael et al. 2005). The selection process for chemicals is still viewed as an art rather than a science. However, with the increasing understanding of emulsion mechanisms, the availability of new and improved chemicals, and new technology, research, and development efforts, selection of the right chemical is becoming more scientific. Many of the failures of the past have been eliminated.

Demulsifier chemicals contain the following components:

- Solvents
- Surface-active ingredients
- Flocculants

Solvents, such as benzene, toluene, xylene, short-chain alcohols, and heavy aromatic naphtha, are generally carriers for the active ingredients of the demulsifier. Some solvents change the solubility conditions of the natural emulsifiers (e.g., asphaltenes) that are accumulated at the oil/brine interface. These solvents dissolve the indigenous surface-active agents back into the bulk phase, affecting the properties of the interfacial film that can facilitate coalescence and water separation.

Surface-active ingredients are chemicals that have surface-active properties characterized by hydrophilic-lipophilic balance (HLB) values. For a definition and description of HLB, see the literature. The HLB scale varies from 0 to 20. A low HLB value refers to a hydrophilic or water-soluble surfactant. In general, natural emulsifiers that stabilize a water-in-oil emulsion exhibit an HLB value in the range of 3 to 8. Thus, demulsifiers with a high HLB value will destabilize these emulsions. The demulsifiers act by total or partial displacement of the indigenous stabilizing interfacial film components (polar materials) around the water droplets. This displacement also brings about a change in properties such as interfacial viscosity or elasticity of the protecting film, thus enhancing destabilization. In some cases, demulsifiers act as a wetting agent and change the wettability of the stabilizing particles, leading to a breakup of the emulsion film.

Flocculants are chemicals that flocculate the water droplets and facilitate coalescence. A detailed process for selecting the appropriate demulsifier chemicals, described in the literature, includes the following steps.

- Characterization of the crude oil and contaminants includes the API gravity of the crude oil, type and composition of oil and brine, inorganic solids, amount and type of salts, contaminant type and amounts.
- Evaluation of operational data includes production rates, treating-vessel capabilities (residence time, electrostatic grids, temperature limitations, etc.), operating pressures and

temperatures, chemical dosage equipment and injection points, sampling locations, maintenance frequency, and wash-water rates.

- Evaluation of emulsion-breaking performance: past experience and operating data including oil, water, and solids content during different tests; composition and quality of interface fluids; operating costs; and amounts of water generated and its disposal.

Testing procedures are available to select appropriate chemicals. These tests include:

- Bottle tests
- Dynamic simulators
- Actual plant tests

All test procedures have limitations. Hundreds of commercial demulsifier products are available that may be tested. Changing conditions at separation facilities result in a very slow selection process, especially at large facilities; therefore, it is important at such facilities to maintain a record of operational data and testing procedures as an ongoing activity.

Mixing/Agitation

For the demulsifier to work effectively, it must make intimate contact with the emulsion and reach the oil/water interface. Adequate mixing or agitation must be provided to thoroughly mix the chemical into the emulsion. This agitation promotes droplet coalescence; therefore, the point at which the demulsifier is added is critical (Batista, Ramalho, Fernanda, & Elizabete Lucas, 2010). Once the emulsion has broken, agitation should be kept to a minimum to prevent re-emulsification. There should be sufficient agitation in the flow stream to allow the chemical to mix thoroughly, followed by a period of gentle flow inside the separator to promote gravity separation.

Dosage

The dosage of demulsifier is critical, as under-treatment can leave the emulsion unresolved, while over-treatment can be counterproductive. Excess demulsifier can stabilize the emulsion,

replacing natural emulsifiers at the interface. Specifying standard dosage rates is challenging due to factors such as:

- The diverse range of demulsifier chemicals available
- Variations in crude oil types and properties
- Differences in separation equipment and configurations
- Changes in product quality and specifications

Additionally, demulsifier formulations can vary in concentration, with different levels of active ingredients in carrier solvents. As a result, the required dosage is highly site-specific and depends on several factors. Literature reviews indicate that demulsifier rates can range from less than 10 ppm to over 100 ppm (based on total production rates) for primary and secondary oil recovery emulsions. However, during tertiary oil recovery, particularly in surfactant or micellar flooding operations, demulsifier rates can be significantly higher, often in the hundreds of ppm or even higher in extreme cases.

2.9.2 Mechanisms

Demulsification, the separation of an emulsion into its component phases, is a two-step process. The first step is flocculation (aggregation, agglomeration, or coagulation). The second step is coalescence. Either of these steps can be the rate-determining step in emulsion breaking.

➢ **Flocculation**

The first step in demulsification is the flocculation of water droplets (Tambe & Sharma 1993). During flocculation, the droplets clump together, forming aggregates or "floccs." The droplets are close to each other, even touching at certain points, but do not lose their identity (i.e., they may not coalesce). Coalescence at this stage only takes place if the emulsifier film surrounding the water droplets is very weak. The rate of flocculation depends on the following factors. Water content in the emulsion. The rate of flocculation is higher when the water cut is higher.

- Temperature of the emulsion is high. Temperature increases the thermal energy of the droplets and increases their collision probability, thus leading to flocculation.

- Viscosity of the oil is low, which reduces the settling time and increases the flocculation rate.
- Density difference between oil and water is high, which increases the sedimentation rate.
- An electrostatic field is applied. This increases the movement of droplets toward the electrodes, where they aggregate.

➢ Coalescence

Coalescence is the second step in demulsification. During coalescence, water droplets fuse or coalesce together to form a larger drop. This is an irreversible process that leads to a decrease in the number of water droplets and eventually to complete demulsification. Coalescence is enhanced by the following factors (Batista, Ramalho, Fernanda, & Elizabete Lucas, 2010).

- High rate of flocculation increases the collision frequency between droplets (Tambe & Sharma 1993).
- The absence of mechanically strong films that stabilize emulsions.
- High interfacial tension. The system tries to reduce its interfacial free energy by coalescing.
- High water cut increases the frequency of collisions between droplets.
- Low interfacial viscosity enhances film drainage and drop coalescence.
- Chemical demulsifiers convert solid films to mobile soap films that are weak and can be ruptured easily, which promotes coalescence.
- High temperatures reduce the oil and interfacial viscosities and increase the droplet collision frequency.

➢ Sedimentation

Sedimentation is the process in which water droplets settle down in an emulsion because of their higher density. Its inverse process, creaming, is the rising of oil droplets in the water phase. Sedimentation and creaming are driven by the density difference between oil and water and may not result in the breaking of an emulsion. (Abdurahman, Mohd, Hassan, & Yunus, 2007; Abdurahman & Nuraini, 2010) Unresolved emulsion droplets accumulate at the oil/water

interface in surface equipment and form an emulsion pad or raglayer. A pad in surface equipment causes several problems including the following.

- Occupies space in the separation tank and effectively reduces the retention or separation time.
- Increases the BS&W of the treated oil.
- Increases the residual oil in the treated water.
- Increases arcing incidences or equipment upset frequency.
- Creates a barrier for water droplets and solids migrating down into the bulk water layer.

Emulsion pads are caused or exacerbated by:

- Ineffective demulsifier (unable to resolve the emulsion);
- Insufficient demulsifier (insufficient quantities to break the emulsion effectively) (Abdurahman, Mohd, Hassan, & Yunus, 2007; Abdurahman & Nuraini, 2010)
- Other chemicals that nullify the effect of the demulsifier
- Low temperatures
- The presence of accumulating solids

Limitations

Hence formulating demulsifiers from locally sourced raw materials for demulsification of crude oil (tight) emulsion thereby addressing the following limitations;

1. Not easily accessible and non-availability of the commercially available imported demulsifiers
2. Federal government of Nigeria local content policy for local production, local use of indigenous product to reduce commercially available imported demulsifier
3. Very low efficiency and effectiveness of commercially available imported demulsifiers for a better water separation capability
4. High cost implication, downtime (retention time), environmental adverse effect and many other disadvantages of the commercially available imported demulsifiers

5. Locally formulated demulsifier contained no organic chloride, bromides, iodides, or lead thereby not going to cause any refining problems
6. To ensure good overall performance a demulsifier should meet the following criteria:
    i) dissolve in the continuous oil phase,
    ii) Possess a high rate adsorption in the interface,
    iii) large concentration enough to diffuse to the oil water interface

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

3.1.1 Material Used

The local materials used in this study was sourced from the local areas and local market within Nigeria, the conventional demulsifier amine group was imported. A local demulsifier 'A' Alpha, and 'B' Beta, was formulated from the two different group of locally sourced raw material. The locally formulated demulsifiers and the imported commercially available demulsifier are both amine group and was used for the demulsification of crude oil emulsion. The bottle test method was used to determine the demulsifiers efficiency and effectiveness in breaking the crude oil emulsion.

Local Materials A:

i. Palm oil
ii. Glyserin
iii. Lemons
iv. KOH compounds

Palm oil contain hexane group and octadecenoic acid. Those compositions are two main plant components that can break the emulsion (Yaakob and Sulaimon, 2017).

Apparatus

i. Water bath
ii. Heater and stirrer,
iii. Digital scale
iv. Beakers
v. Graduated cylinder
vi. Density bottle, and stopwatch.

Local Materials B:

Table 3.1 Local material B

Content	Function	Wt/Vol
ALUM	**To facilitate** settling **of sediments**	**7.5g**
Castor Oil	**Lipophilic agent in the demulsifer**	**40ml**
Starch	**Coalescing of tiny water droplet**	**7.5g**
Liquid Soap	**Destabilization of emulsion film**	**60ml**
Camphor	**To improve the performance of the demulsifiers**	**15ml**
Distilled water	**As a solvent**	**10ml**
Paraffin wax	**Will serve as a bulking agent**	**7.5kg**
Jatropha oil	**Non edible green oil that will act as solvent for camphor and also increase the lipophilic properties of the crude oil**	**30ml**

(i) Imported Materials

Amine group Demulsifers

3.2 Method of Research

Specific Method:

1. Laboratory characterization of both local materials and commercially imported demulsifier

2. Formulation of local demulsifier using local materials

3. Laboratory FTIR test on produced local demulsifier and commercially imported demulsifier

4. Application of local demulsifiers and commercially available demulsifier on the crude oil emulsion for water separation.

5. Comparison and validation of the efficiency and effectiveness on the rate of separation of crude oil emulsion by the formulated local demulsifiers and commercially available (imported) demulsifier.

3.2.1.1 Laboratory characterization using FTIR test on local materials, produced local demulsifiers and commercially available imported demulsifier

Fourier Transform Infrared Spectroscopy, FTIR, test was done on the local materials and also on the produced local demulsifiers; Alpha, Beta, and Mega and commercially available imported demulsifier for the identification of the chemical bond of the local materials for a demulsification capacity and efficiency. The wavelength, functional group, and compound structure of all the local materials; Alum, Starch, KOH, Local soap, and Palm oil were identified and interpreted. The same objective were carried out on local produced demulsifiers (ALPHA, BETA & MEGA) and also commercially available imported demulsifier and crude oil emulsion demulsification capacity on all the materials were recorded.

3.2.1.2 Laboratory Characterization and Analysis of Local Materials

Mathematical characterization on the local materials was carried out to ascertain the water separation capacity, water solubility, and n-Hexane solubility. Two laboratory test (run1 & run 2) were done on each of the local materials samples; Alum, Starch, Local soap, KOH, and Palm oil and a result on different percentage of solubility and water separation index was achieved.

Demulsification performance capacity test was done also on the same local materials using; water separation index, gravitational force, and surface tension to determine the acting effect of the local demulsifier in breaking interfacial tension of the crude oil emulsion. Two different laboratory test (run 1 & run 2) were conducted.

3.2.2 Formulation of local demulsifier using local materials

3.2.2.1 Formulation of local demulsifier 'A'

(a) A measured 45ml of palm oil was heated to 90°C for 25mins

(b) 12g of KOH along with 20ml distilled water was heated till homogeneous

(c) Solution of (b) above was added to the solution (a) and stir it with heat at 90°C, 800rmp for 70mins

(d) 50ml distilled water was added for the last time and stir for more 5mins

(e) The formulation was observed until it become liquid after 24hrs

This is called local demulsifier 'A' ALPHA

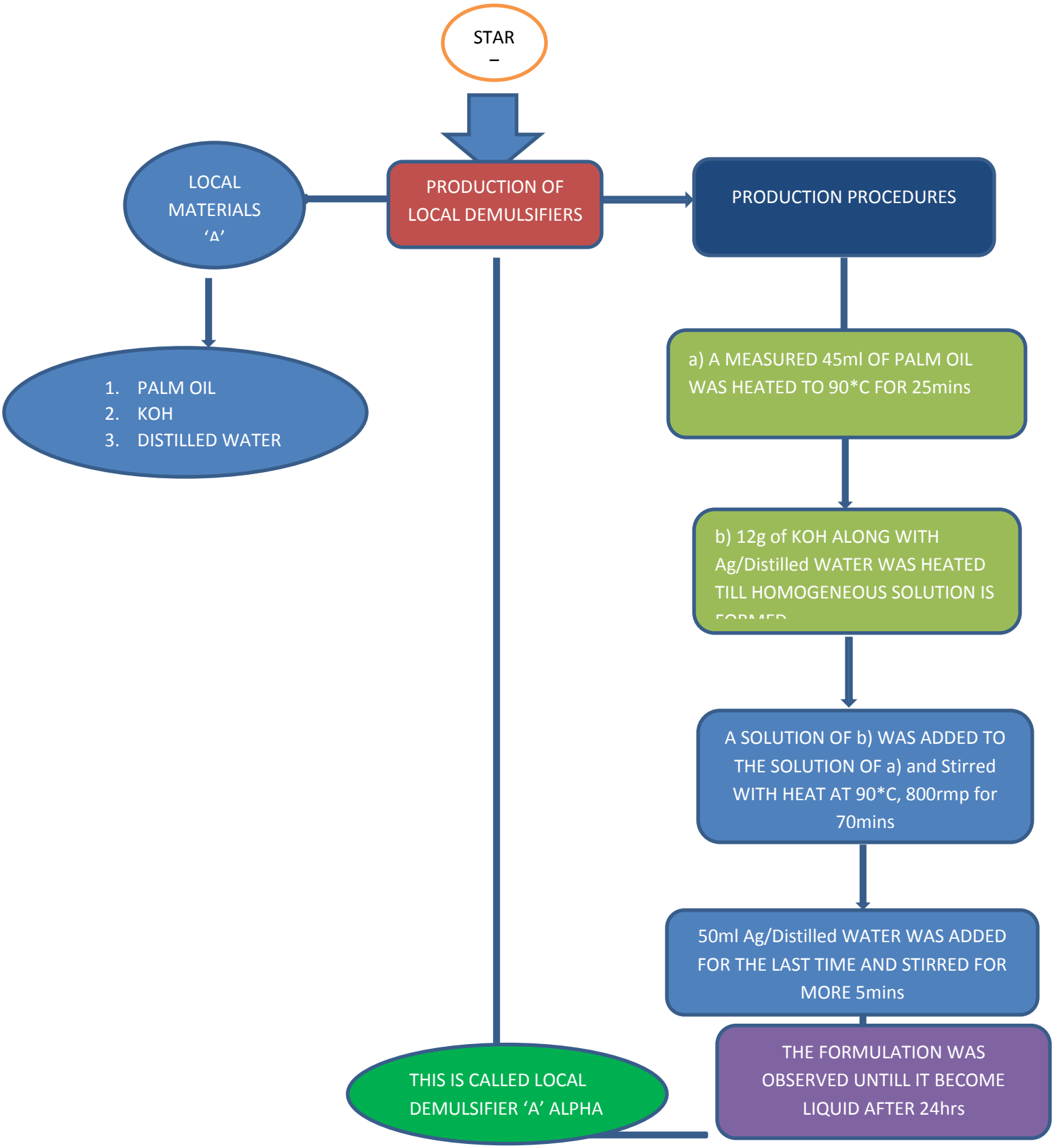


Figure 3.1 Flowchart on the production of local demulsifier 'A' ALPHA

3.2.2.2 Formulation of local demulsifier ‘B’

(a) A prepared 5ml solution of Alum was added to a mixture of 7.5g of starch and 30ml of liquid soap in a beaker

(b) A dissolved solution of 10g of camphor in 30ml of castor oil was stirred and heated to achieve homogeneity

(c) the solution (a) and (b) above were mixed, stirred and heated for 90mins 90°C, 800rmp

(d) sediments and precipitates settlement was removed after 24hrs

This is called local demulsifier ‘B’ BETA

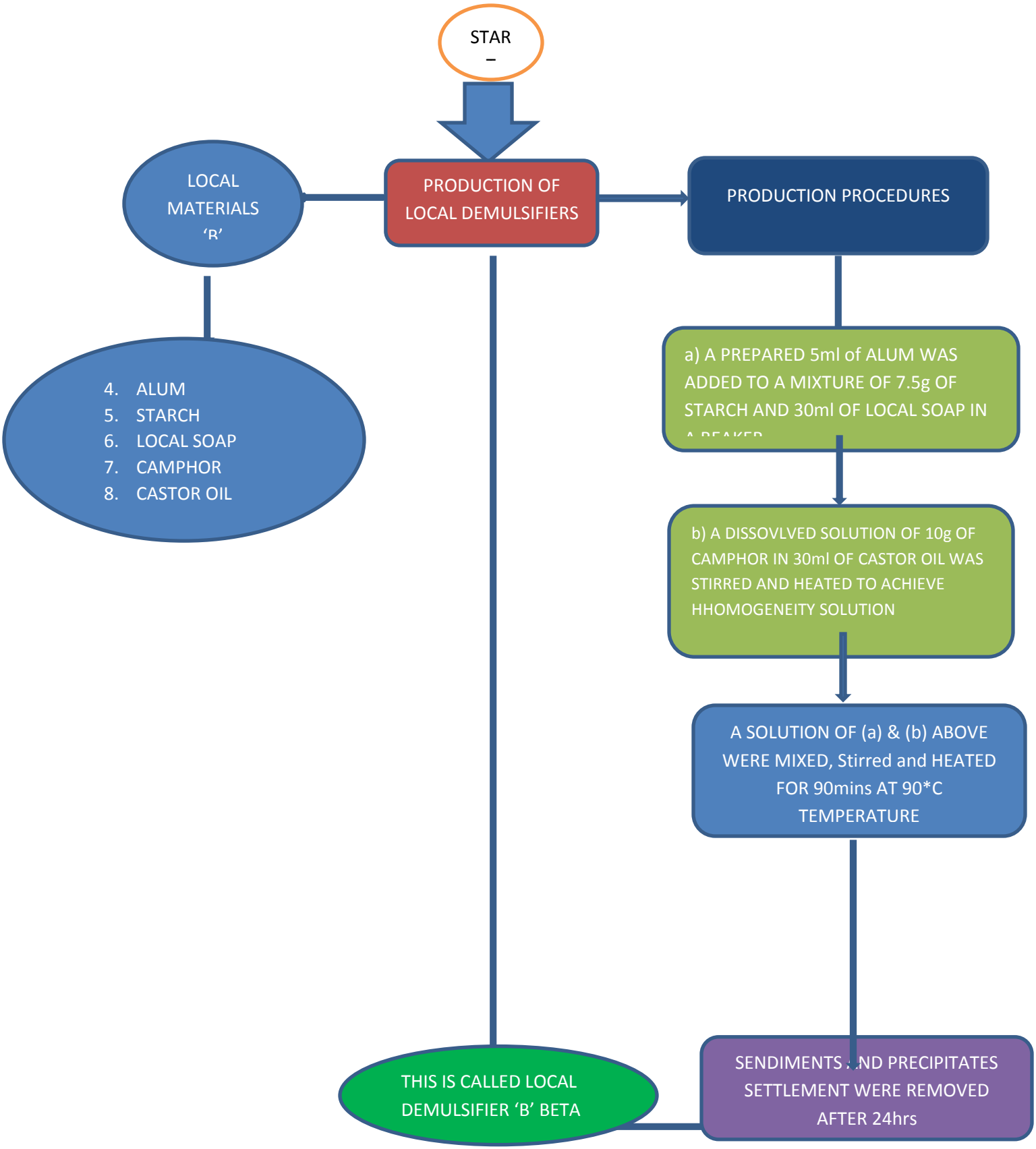


Figure 3.2 Flowchart on production of local demulsifier 'B' BETA

3.2.2.3 Formulation of local demulsifier ‘C’

(a) A mixture of produced local demulsifier ‘A’ and local demulsifer ‘B’ were stirred and slightly heated to obtain homogeneity

(b) It was observed for 72hrs for any change possible.

This is called local demulsifier ‘C’ MEGA

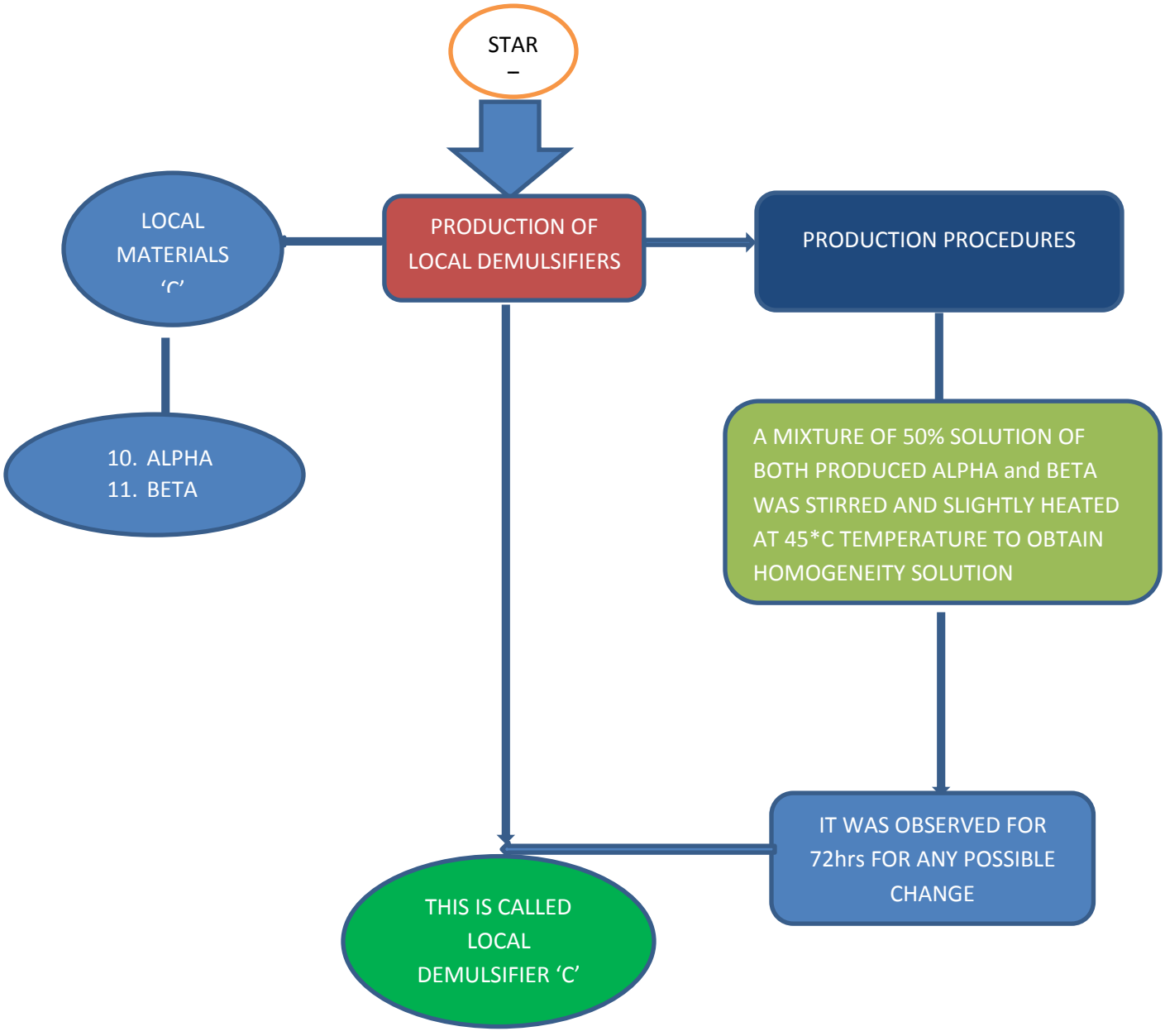


Figure 3.3 Flowchart on the production of local demulsifier ‘C’ MEGA

3.2.3 Application of local demulsifiers and commercially available demulsifier on the crude oil emulsion for water separation.

The local demulsifier formulated and commercially (imported) demulsifier were contacted with the crude oil samples in the different ratio of the crude oil emulsion samples.

i. Demulsification of crude oil emulsion using local demulsifier ‘A’
ii. Demulsification of crude oil emulsion using local demulsifier ‘B’
iii. Demulsification of crude oil emulsion using commercially available demulsifier (imported)
iv. Demulsification of crude oil emulsion (crude oil tight emulsion like tar) using the combined local demulsifier ‘A’ and ‘B’

3.2.4 Comparison and validation of the efficiency and effectiveness on the rate of separation of crude oil emulsion by the formulated local demulsifiers and commercially available (imported) demulsifier.

Comparison and validation of the efficiency of temperature, concentration of separation and the time of separation.

i. Comparison and validation of local demulsifier ‘A’ with commercially available demulsifier (imported)
ii. Comparison and validation of local demulsifier ‘B’ with commercially available demulsifier (imported)
iii. Comparison and validation of combined local demulsifier ‘A’ and ‘B’ with commercially available demulsifier (imported)

iv. Comparison and validation of local demulsifier ‘A’ with local demulsifier ‘B’

Demulsification of crude oil emulsion with formulated local demulsifiers and commercially available (imported) demulsifier

The local demulsifier formulated and commercially (imported) demulsifier shall be contacted with the crude oil samples in the different ratio of the crude oil emulsion samples.

v. Demulsification of crude oil emulsion using local demulsifier ‘A’

vi. Demulsification of crude oil emulsion using local demulsifier ‘B’

vii. Demulsification of crude oil emulsion using commercially available demulsifier (imported)

viii. Demulsification of crude oil emulsion (crude oil tight emulsion like tar) using the combined local demulsifier ‘A’ and ‘B’

Comparison and Validation of the efficiency of temperature, concentration of separation and the time of separation.

v. Comparison and validation of local demulsifier ‘A’ with commercially available demulsifier (imported)

vi. Comparison and validation of local demulsifier ‘B’ with commercially available demulsifier (imported)

vii. Comparison and validation of combined local demulsifier ‘A’ and ‘B’ with commercially available demulsifier (imported)

viii. Comparison and validation of local demulsifier ‘A’ with local demulsifier ‘B’

Apparatus

i. Digital Weigh balance

ii. Measuring Cylinder (50ml graduated)

iii. Beaker

iv. Magnetic Heat-Stirring machine

v. Filter paper

vi. Prescription bottles (200ml graduated)

vii. Thermostatic Water Bath

viii. Stop watch

ix. Syringe

x. Micro-pipette

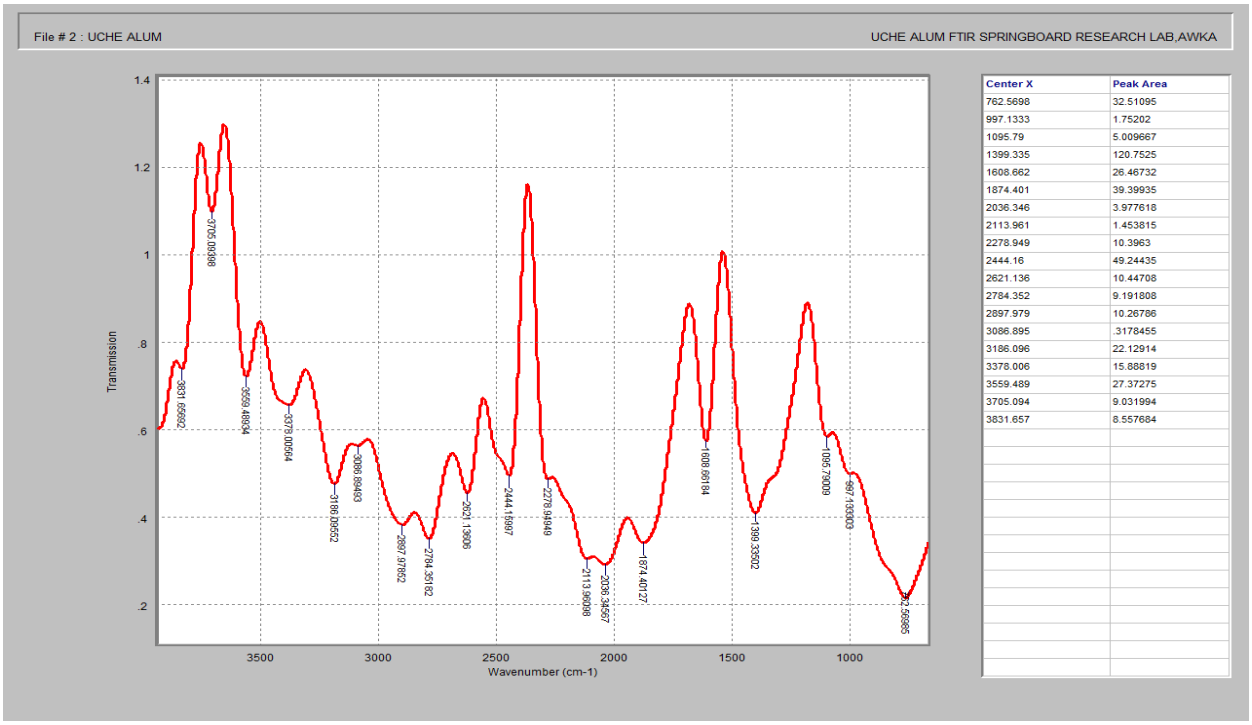
CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results

The demulsification results using the three locally formulated demulsifiers (ALPHA, BETA and MEGA) and Commercially Available Demulsifier CAD at a different treatment temperature of 30°C to 70°C and at time intervals of 1-10 minutes after heating, are summarized in tables and plots respectively. Before carrying out any analysis, all samples were drained of free water after aging for a week. This allowed the water to settle out by gravity. The Basic Sediment and Water (BS&W) and the API of a sample before and after treatment were determined.

4.1.1 The FTIR Test Result for the Four Different Samples



Center X	Peak Area
762.5698	32.51095
997.1333	1.75202
1095.79	5.009667
1399.335	120.7525
1608.662	26.46732
1874.401	39.39935
2036.346	3.977618
2113.961	1.453815
2278.949	10.3963
2444.16	49.24435
2621.136	10.44708
2784.352	9.191808
2897.979	10.26786
3086.895	.3178455
3186.096	22.12914
3378.006	15.88819
3559.489	27.37275
3705.094	9.031994
3831.657	8.557684

Figure 4.1 Characterization of the local material samples (Alum) using FTIR

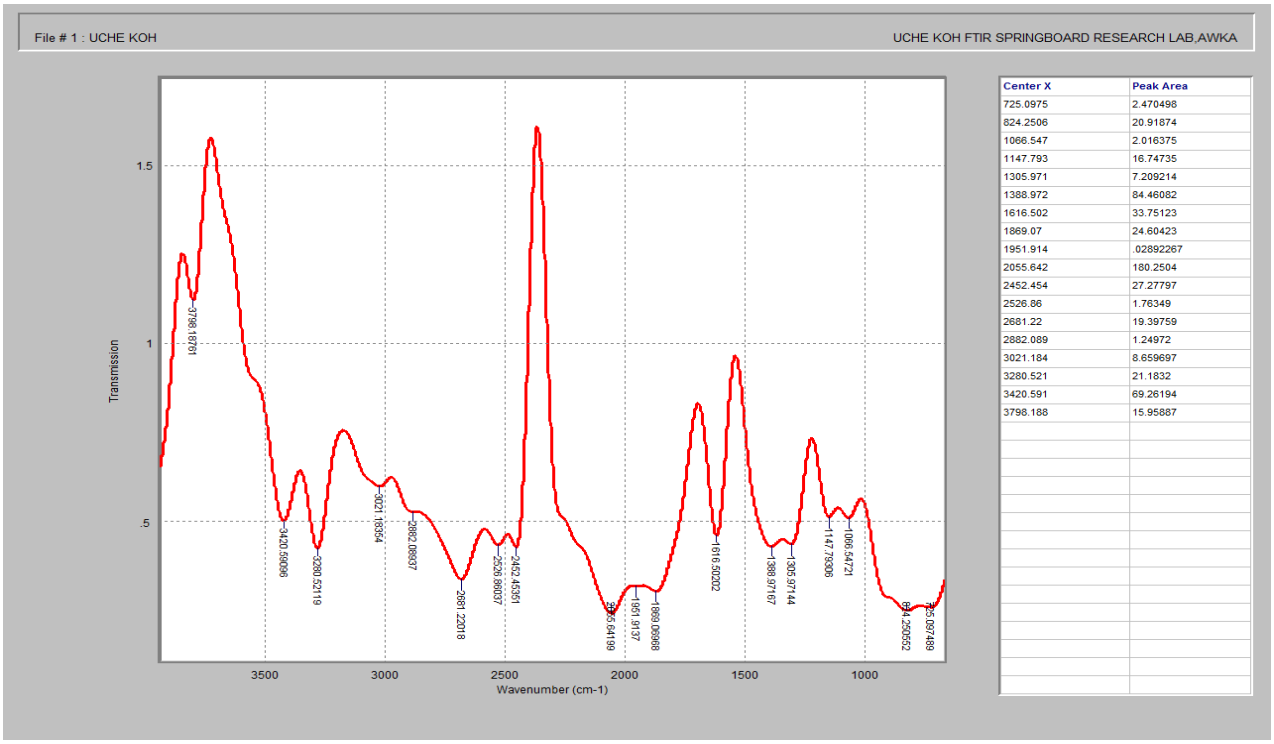
FTIR Interpretation of Alum

Table 4.1 laboratory interpretation of Alum using FTIR

Wavelength (cm^{-1})	Functional group	Compounds
762.5898	C-CI	Chloro compound C-CI stretch
997.1333	R-0-R	Ether C0 symmetric stretch
1095.790	R-0-R	Ether C0 symmetric stretch
1399.335	$H_2C=CH$	Ethene CH anti-symmetric stretch
1606.662	RNH_2	1^0 amine NH stretch
1874.401	R-0-R	Cyclic ester C0 stretch
2036.346	RC00H	Carboxylic acid C00 stretch
2113.961	RC00H	Carboxylic acid C00 stretch
2278.949	RC00H	Carboxylic acid C00 stretch
2444.160	R-C≡N	Nitriles CN antisymmetric stretch
2621.136	CH_2	Methylene C-H symmetric stretch
2784.352	CH_2	Methylene C-H symmetric stretch
2897.979	CH_2	Methylene C-H symmetric stretch
3086.695	RCH0H	1^0 alcohol 0H symmetric stretch
3186.096	RCH0H	1^0 alcohol 0H symmetric stretch
3376.006	R_2CH0H	2^0 alcohol 0H symmetric stretch
3559.489	R_3CH0H	3^0 alcohol 0H symmetric stretch
3705.094	R_3CH0H	3^0 alcohol 0H symmetric stretch
3831.657	R_3CH0H	3^0 alcohol 0H symmetric stretch

From the table of results above for **Alum,** the wavelength around 997.1333cm^{-1} and 1095.790cm^{-1} were assigned to C0 stretching vibration ether compound. The peak values around 1399.335cm^{-1} was assigned to C=C stretching vibration of alkene compound. The wavelength located at 1874.401cm^{-1} was assigned to C0 stretching vibration of ester compound. The absorbance

around 2036.346cm^{-1} , 2113.961cm^{-1} and 2278.949cm^{-1} corresponds to C00 stretching vibration carboxylic acid compounds respectively. The peak around 2444.160cm^{-1} was assigned to CN stretching vibration of nitrile compound. The weak band around 2621.136cm^{-1}, 2784.352cm^{-1} and 2897.979cm^{-1} were assigned to CH stretching vibration of methylene compound. The broad band around 3086.695cm^{-1}, 3186.096cm^{-1}, 3376.006cm^{-1}, 3559.489cm^{-1}, 3705.094cm^{-1} and 3831.657 cm^{-1} were assigned to 0H stretching vibration of 1^0 , 2^0 & 3^0 alcoholic compounds respectively.



Center X	Peak Area
725.0975	2.470498
824.2506	20.91874
1066.547	2.016375
1147.793	16.74735
1305.971	7.209214
1388.972	84.46082
1616.502	33.75123
1869.07	24.60423
1951.914	.02892267
2055.642	180.2504
2452.454	27.27797
2526.86	1.76349
2681.22	19.39759
2882.089	1.24972
3021.184	8.659697
3280.521	21.1832
3420.591	69.26194
3798.188	15.95887

Figure 4.2 Characterization of the local material samples (KOH) using FTIR

FTIR Interpretation of KOH

Table 4.2 laboratory interpretation of KOH using FTIR

Wavelength (cm^{-1})	Functional group	Compounds	
725.0978	C-CI	Chloro compound C-CI stretch	
824.2506	R-0-R	Ether C0 symmetric stretch	
1066.547	R-0-R	Ether C0 symmetric stretch	
1147.793	R-0-R	Ether C0 symmetric stretch	
1305.971	H_2C=CH	Ethene CH anti-symmetric stretch	
1388.972	H_2C=CH	Ethene CH anti-symmetric stretch	
1616.502	RNH_2	1^0 amine NH stretch	
1869.070	R-0-R	Cyclic ester C0 stretch	
1951.914	R-0-R	Cyclic ester C0 stretch	
2055.642	RC00H	Carboxylic acid C00 stretch	
2452.454	R-C≡N	Nitriles CN antisymmetric stretch	
2526.860	R-C≡N	Nitriles CN antisymmetric stretch	
2681.220	CH_2	Methylene C-H symmetric stretch	
3021.184	RCH0H	1^0 alcohol 0H symmetric stretch	
3280.521	RCH0H	1^0 alcohol 0H symmetric stretch	
3420.891		R_2NH	2^0 amine NH stretch
3798.188		R_3CH0H	3^0 alcohol 0H symmetric stretch

From the table of results above for **KOH,** the wavelength around 1305.971cm^{-1} and 1388.972cm^{-1} were assigned to C=C stretching vibration of alkene compound respectively. The wavelength located at 1616.502cm^{-1} and 3420.891cm^{-1} were assigned to NH stretching vibration of 1^0 & 2^0 amine compound respectively. The peak values around 1869.070cm^{-1} and 1951.914cm^{-1} were assigned to C0 stretching vibration of ester compound. The absorbance around 2055.642cm^{-1} was assigned to C00 stretching vibration carboxylic acid compound

whereas the peak around 2452.454cm^{-1} and 2526.860cm^{-1} were assigned to CN stretching vibration of nitrile compound respectively. The weak band around 2681.220cm^{-1} was assigned to CH stretching vibration of methylene compound. The broad band around 3021.184cm^{-1}, 3280.521cm^{-1} and 3798.188cm^{-1} were assigned to 0H stretching vibration of 1^0 & 3^0 alcoholic compounds respectively.

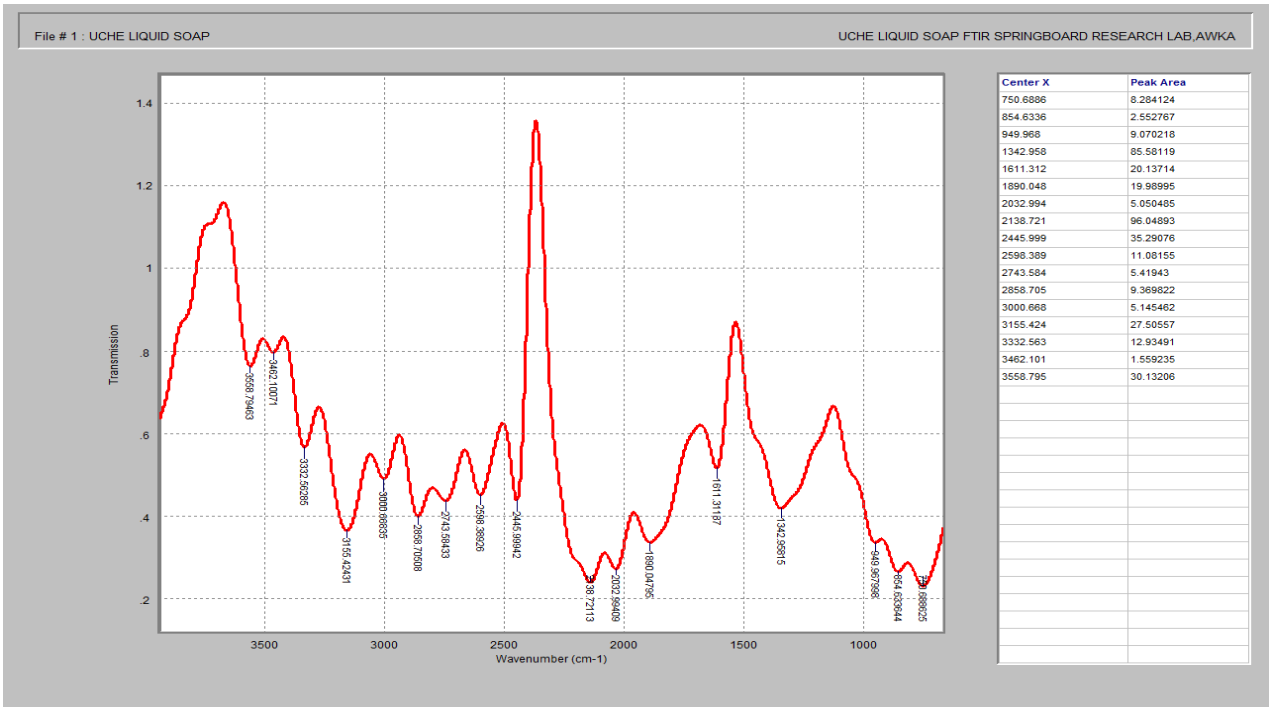


Figure 4.3 Characterization of the local material samples (local soap) using FTIR

FTIR Interpretation of Local Soap

Table 4.3 laboratory interpretation of local soap using FTIR

Wavelength (cm^{-1})	Functional group	Compounds
750.6886	C-CI	Chloro compound C-CI stretch
854.6336	R-0-R	Ether C0 symmetric stretch
949.968	R-0-R	Ether C0 symmetric stretch
1342.958	H_2C=CH	Ethene CH anti-symmetric stretch
1611.312	RNH_2	1^0 amine NH stretch
1890.048	R-0-R	Cyclic ester C0 stretch
2032.994	RC00H	Carboxylic acid C00 stretch
2138.721	RC00H	Carboxylic acid C00 stretch
2445.999	R-C≡N	Nitriles CN antisymmetric stretch
2598.389	R-C≡N	Nitriles CN antisymmetric stretch
2743.584	CH_2	Methylene C-H symmetric stretch
2858.705	CH_2	Methylene C-H symmetric stretch
3000.668	RCH0H	1^0 alcohol 0H symmetric stretch
3155.424	RCH0H	1^0 alcohol 0H symmetric stretch
3332.563	R_2CH0H	2^0 alcohol 0H symmetric stretch
3462.101	R_2NH	2^0 amine NH stretch
3558.795	R_3CH0H	3^0 alcohol 0H symmetric stretch

From the table of results above for **liquid soap,** the wavelength around 1342.958cm^{-1} was assigned to C=C stretching vibration of alkene compound. The absorbance around 1611.312cm^{-1} and 3462.101cm^{-1} were assigned to NH stretching vibration of 1^0 & 2^0 amine compound respectively. The peak values around 1890.048cm^{-1} was assigned to C0 stretching vibration of ester compound. The absorbance around 2032.994cm^{-1} and 2138.721cm^{-1} were assigned to C00

stretching vibration carboxylic acid compound respectively whereas the peak around 2445.999cm^{-1} and 2598.389cm^{-1} were assigned to CN stretching vibration of nitrile compound respectively. The weak band around 2743.584cm^{-1} and 2858.705cm^{-1} were assigned to CH stretching vibration of methylene compound respectively.

The broad band around 3000.668cm^{-1}, 3332.563cm^{-1} and 3558.795cm^{-1} were assigned to 0H stretching vibration of 1^0, 2^0 & 3^0 alcoholic compounds respectively.

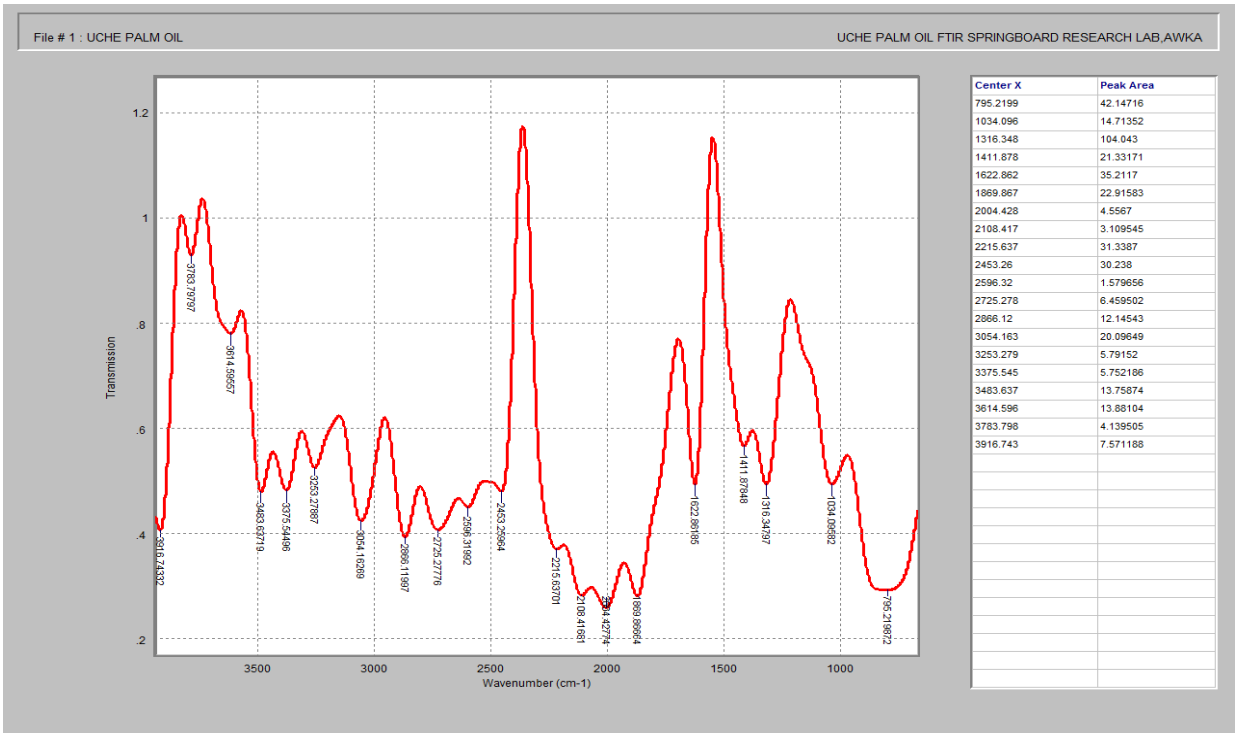


Figure 4.4 Characterization of the local material samples (palm oil) using FTIR

FTIR Interpretation of palm oil

Table 4.4 laboratory interpretation of palm oil using FTIR

Wavelength (cm^{-1})	**Functional group**	**Compounds**
795.2199	C-CI	Chloro compound C-CI stretch
1034.096	R-0-R	Ether C0 symmetric stretch
1316.348	H_2C=CH	Ethene CH anti-symmetric stretch
1411.878	H_2C=CH	Ethene CH anti-symmetric stretch
1622.862	RNH_2	1^0 amine NH stretch
1869.867	R-0-R	Cyclic ester C0 stretch
2004.428	RC00H	Carboxylic acid C00 stretch
2108.417	RC00H	Carboxylic acid C00 stretch
2215.637	RC=0	Carbonyl C0 stretching viration
2453.260	R-C≡N	Nitriles CN antisymmetric stretch
2596.320	R-C≡N	Nitriles CN antisymmetric stretch
2725.278	CH_2	Methylene C-H symmetric stretch
2866.120	CH_2	Methylene C-H symmetric stretch
3054.163	RCH0H	1^0 alcohol 0H symmetric stretch
3253.279	RCH0H	1^0 alcohol 0H symmetric stretch
3375.545	R_2CH0H	2^0 alcohol 0H symmetric stretch
3483.637	R_2NH	2^0 amine NH stretch
3614.596	R_3CH0H	3^0 alcohol 0H symmetric stretch
3783.798	R_3CH0H	3^0 alcohol 0H symmetric stretch
3916.743	R_3CH0H	3^0 alcohol 0H symmetric stretch

From the table of results above for **palm oil,** the wavelength around 1316.348cm^{-1} and 1411.878 were assigned to C=C stretching vibration of alkene compound. The absorbance

around 1622.862cm^{-1} and 3483.637cm^{-1} were due to NH stretching vibration of 1^0 & 2^0 amine compound respectively. The peak located around 1869.867cm^{-1} was assigned to C0 stretching vibration of ester compound. The absorbance around 2004.428cm^{-1}, 2108.417cm^{-1}and were assigned to C00 stretching vibration carboxylic acid whereas the peak around 2215.637cm^{-1} was due to C0 stretching vibration of carbonyl compound. The wavelength located around 2453.260cm^{-1} and 2596.320cm^{-1} were assigned to CN stretching vibration of nitrile compound respectively. The weak band around 2725.278cm^{-1} and 2866.120cm^{-1} were assigned to CH stretching vibration of methylene compound respectively. The strong band around 3054.163cm^{-1}, 3253.279cm^{-1}, 3614.596cm^{-1} , 3783.798cm^{-1} and 3916.743cm^{-1} were assigned to 0H stretching vibration of 1^0, 2^0 & 3^0 alcoholic compounds respectively.

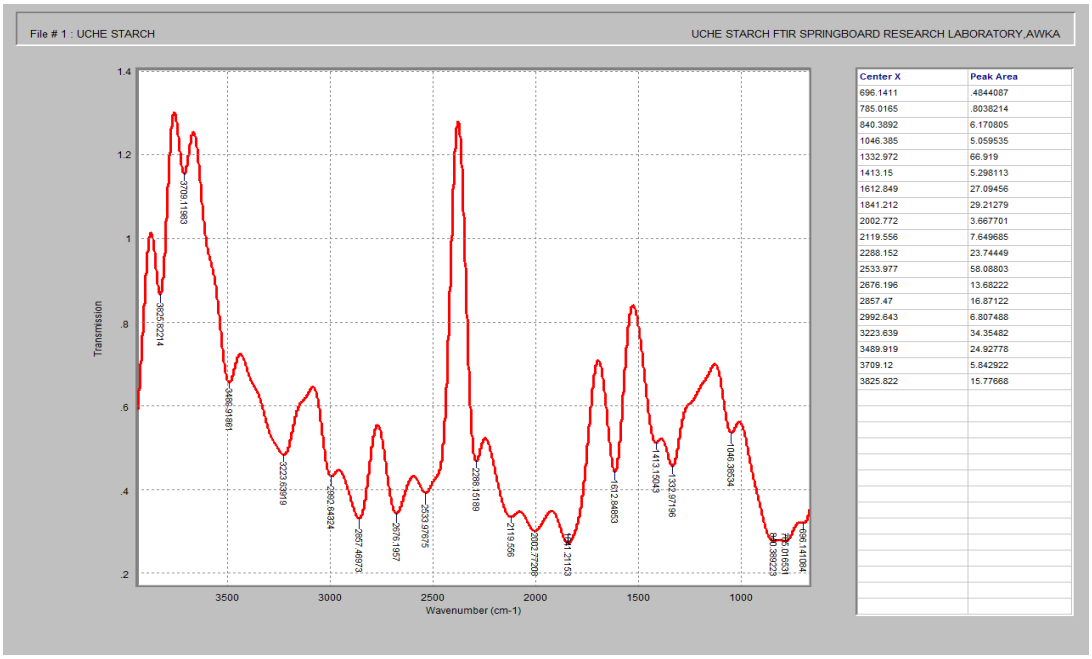


Figure 4.5 Characterization of the local material samples (starch) using FTIR

FTIR Interpretation of Starch

Table 4.5 laboratory interpretation of starch using FTIR

Wavelength (cm^{-1})	**Functional group**	**Compounds**
696.1411	C-CI	Chloro compound C-CI stretch
785.0165	R-0-R	Ether C0 symmetric stretch
840.3892	R-0-R	Ether C0 symmetric stretch
1046.385	R-0-R	Ether C0 symmetric stretch
1332.972	H_2C=CH	Ethene CH anti-symmetric stretch
1413.150	H_2C=CH	Ethene CH anti-symmetric stretch
1612.849	RNH_2	1^0 amine NH stretch
1841.212	R-0-R	Cyclic ester C0 stretch
2002.772	RC00H	Carboxylic acid C00 stretch
2119.556	RC00H	Carboxylic acid C00 stretch
2288.152	RC=0	Carbonyl C0 stretching viration
2533.977	R-C≡N	Nitriles CN antisymmetric stretch
2676.196	CH_2	Methylene C-H symmetric stretch
2857.470	CH_2	Methylene C-H symmetric stretch
2992.643	CH_2	Methylene C-H symmetric stretch
3223.639	R_2CH0H	2^0 alcohol 0H symmetric stretch
3489.919	R_2NH	2^0 amine NH stretch
3709.120	R_3CH0H	3^0 alcohol 0H symmetric stretch
3825.822	R_3CH0H	3^0 alcohol 0H symmetric stretch

From the table of results above for **Starch,** the wavelength around 1332.972cm^{-1} and 1413.150 were assigned to C=C stretching vibration of alkene compound. The absorbance around 1612.849cm^{-1} and 3489.919cm^{-1} were due to NH stretching vibration of 1^0 & 2^0 amine

compound respectively. The peak around 1841.212cm^{-1} was assigned to C0 stretching vibration of ester compound. The absorbance around 2002.772cm^{-1}, 2119.556$cm^{-1}$and 2288.152cm^{-1} were assigned to C00 stretching vibration carboxylic acid. The wavelength located around 2533.977cm^{-1} corresponds to CN stretching vibration of nitrile compound. The weak band around 2676.196cm^{-1} , 2857.470cm^{-1} and 2992.643cm^{-1} were assigned to CH stretching vibration of methylene compound respectively. The strong band around 3223.639cm^{-1}, 3709.120cm^{-1} and 3825.822cm^{-1} were due to 0H stretching vibration of 2^0 & 3^0 alcoholic compounds respectively.

4.1.2 The Laboratory Characterization Results of the Raw Materials

Laboratory characterization of both local materials and commercially available (imported) demulsifier

Table 4.6 laboratory mathematical characterization of local materials

Sample	Water Separated(SW) (%)		Water Separated Index (%)	Water Solubility 10ml		n-Hexane Solubility 10ml		pH	
	Run 1	Run 2		Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Potassium Hydroxide	0.00	0.00	0.00	15.00	15.00	20.00	20.00	14.00	14.00
Local Soap	20.00	26.67	0.05	100.00	100.00	100.00	100.00	11.90	12.00
palm oil	16.67	13.33	0.02	25.00	25.00	100.00	100.00	2.80	2.80
Alum	66.67	60.00	0.40	18.00	18.00	25.00	25.00	2.70	2.60
Starch	60.00	73.33	0.44	44.00	44.00	55.00	55.00	3.20	3.30

Table 4.7 laboratory mathematical characterization of local materials

Sample	Force (M)	Surface Tension (Nm)
Potassium Hydroxide	0.0003	0.02
Local Soap	0.0027	27.00
Palm oil	0.0023	23.00
Alum	0.0008	7.60
Starch	0.0019	19.00

WATER SOLUBILITY, %

Water solubility, % = $\frac{\text{Volume of water remaining}}{\text{Total Volume of water}} \times \frac{100}{1}$

Potassium Hydroxide

Run 1 $\frac{1.5}{10} \times \frac{100}{1}$ =15%

Run 2 $\frac{1.5}{10} \times \frac{100}{1}$ =15%

Soap

Run 1 $\frac{100}{10} \times \frac{100}{1}$ =100%

Run 2 $\frac{100}{10} \times \frac{100}{1}$ =100%

Red oil

Run 1 $\frac{2.5}{10} \times \frac{100}{1}$ =25%

Run 2 $\frac{2.5}{10} \times \frac{100}{1}$ =25%

Alum

Run 1 $\frac{1.8}{10} \times \frac{100}{1}$ =18%

Run 2 $\frac{1.8}{10} \times \frac{100}{1}$ =18%

Starch

Run 1 $\frac{4.4}{10} \times \frac{100}{1}$ =44%

Run 2 $\frac{4.4}{10} \times \frac{100}{1}$ =44%

n- HEXANE SOLUBILITY, %

$$\text{n- Hexane solubility, \%} = \frac{\text{Volume of n- Hexane + De-emulsifiers}}{\text{Total Volume of n- Hexane}} \times \frac{100}{1}$$

Potassium Hydroxide

Run 1 $\frac{2.0}{10} \times \frac{100}{1}$ =20%

Run 2 $\frac{2.0}{10} \times \frac{100}{1}$ =20%

Soap

Run 1 $\frac{100}{10} \times \frac{100}{1}$ =100%

Run 2 $\frac{100}{10} \times \frac{100}{1}$ =100%

Red oil

Run 1 $\frac{100}{10} \times \frac{100}{1}$ =100%

Run 2 $\frac{100}{10} \times \frac{100}{1}$ =100%

Alum

Run 1 $\frac{2.5}{10} \times \frac{100}{1}$ =25%

Run 2 $\frac{2.5}{10} \times \frac{100}{1}$ =25%

Starch

Run 1 $\frac{5.5}{10} \times \frac{100}{1}$ =55%

Run 2 $\frac{5.5}{10} \times \frac{100}{1}$ =55%

DEMULSIFICATION PERFORMANCE

WATER SEPARATION INDEX (WSI):

$$WSI, \% = \frac{(SW/100)^2}{N}$$

Where:

SW is the separated water (%) and

N is the number of measures of the separated water.

$$\text{Water Separated (SW), \%} = \frac{\text{Volume of water remaining}}{\text{Total Volume of water}} \times \frac{100}{1}$$

Soap Run 1 $= \frac{3.0}{15} \times \frac{100}{1} = 20.00\%$

Soap Run 2 $= \frac{4.0}{15} \times \frac{100}{1} = 26.67\%$

$$WSI, \% = \frac{(23.34/100)^2}{1} = 0.05\%$$

Red oil Run 1 $= \frac{2.5}{15} \times \frac{100}{1} = 16.67\%$

Red oil Run 2 $= \frac{2.0}{15} \times \frac{100}{1} = 13.33\%$

$$WSI, \% = \frac{(15.00/100)^2}{1} = 0.02\%$$

Alum Run 1 $= \frac{10.0}{15} \times \frac{100}{1} = 66.67\%$

Alum Run 2 $= \frac{9.0}{15} \times \frac{100}{1} = 60\%$

$$WSI, \% = \frac{(63.34/100)^2}{1} = 0.40\%$$

Starch Run 1 $= \frac{9.0}{15} \times \frac{100}{1} = 60\%$

Starch Run 2 $= \frac{11.0}{15} \times \frac{100}{1} = 73.33\%$

WSI, % $= \frac{(66.67/100)^2}{1} = 0.44\%$

FORCE, M
Force, M = M x g
Where;
M = Mass
G = Acceleration due to gravity

Potassium Hydroxide
Run 1 = 0.0355 x 0.00981 = 0.0003M

Alum
Run 1 = 0.0784 x 0.00981 = 0.0008M

Starch
Run 1 = 0.1893 x 0.00981 = 0.0019M

Local Soap
Run 1 = 0.2795 x 0.00981 = 0.0027M

Palm oil
Run 1 = 0.2352 x 0.00981 = 0.0023M

SURFACE TENSION

Surface tension (γ) = $\frac{\text{Force(F)}}{\text{2d}}$

Where;

D = Diameter in metres

50µm= 0.00005m (for starch and alum)

10mm=0.01 (for Potassium Hydroxide)

Alum

Run 1 = $\frac{0.00076}{2\text{x } 0.00005}$ =7.60nm

Starch

Run 1 = $\frac{0.0019}{2\text{x } 0.00005}$ =19.00nm

Potassium Hydroxide

Run 1 = $\frac{0.00034}{2\text{x } 0.01}$ =0.02nm

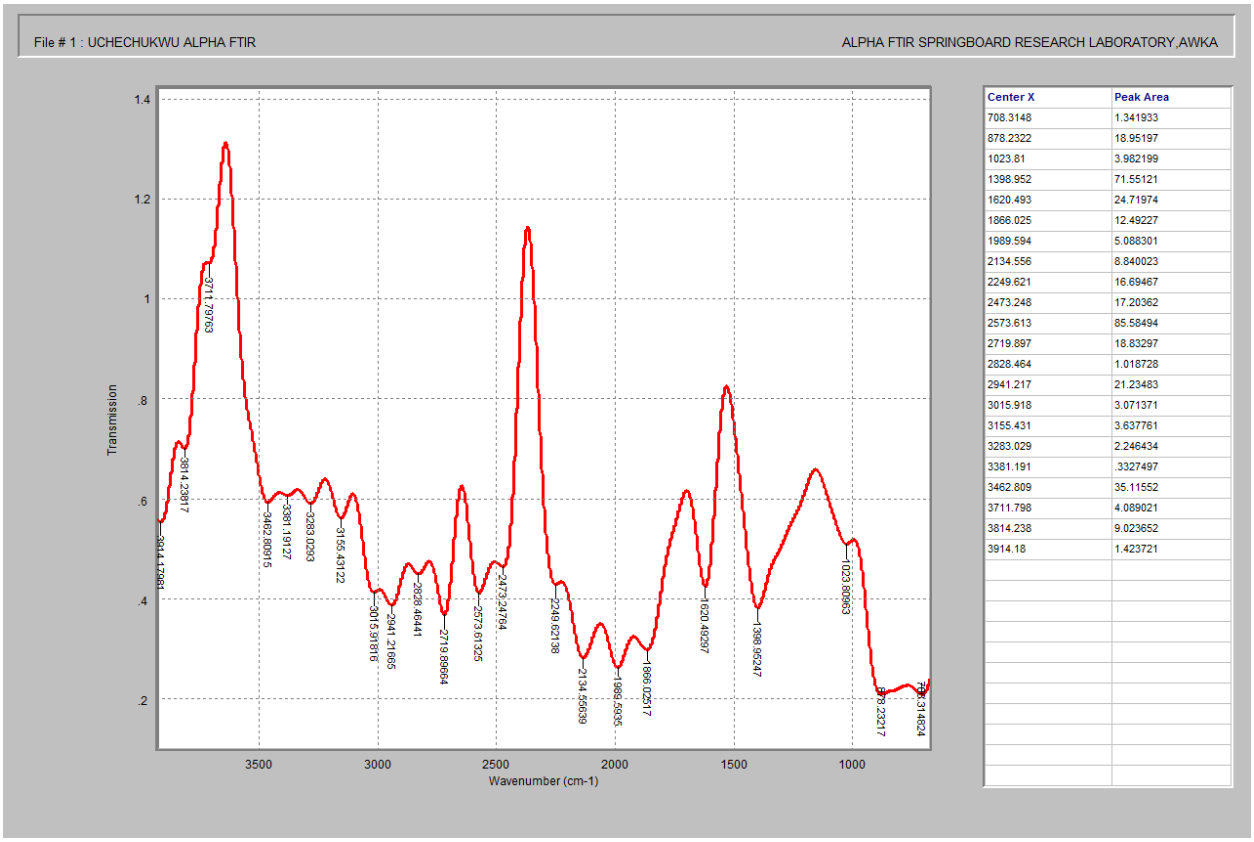
Soap

Run 1 = $\frac{0.0027}{2\text{x } 0.00005}$ =27.00nm

Red oil

Run 1 = $\frac{0.0023}{2\text{x } 0.00005}$ =23.00nm

4.1.3 The FTIR Test Result for the Local Produced Demulsifiers; ALPHA, BETA & MEGA and Commercially Available Imported Demulsifier



Center X	Peak Area
708.3148	1.341933
878.2322	18.95197
1023.81	3.982199
1398.952	71.55121
1620.493	24.71974
1866.025	12.49227
1989.594	5.088301
2134.556	8.840023
2249.621	16.69467
2473.248	17.20362
2573.613	85.58494
2719.897	18.83297
2828.464	1.018728
2941.217	21.23483
3015.918	3.071371
3155.431	3.637761
3283.029	2.246434
3381.191	.3327497
3462.809	35.11552
3711.798	4.089021
3814.238	9.023652
3914.18	1.423721

Figure 4.6 Characterization of the local produced demulsifier (ALPHA) using FTIR

FTIR Interpretation of ALPHA

Table 4.8 laboratory interpretation of local produced demulsifier (ALPHA) using FTIR

Wavelength (cm^{-1})	Functional group	Compounds
708.3148	C-Cl	Alkyl halides stretch
878.2322	C-H	Aromatics
1023.81	C-N	Aliphatic amines stretch
1398.952	C-H	Alkane bend
1620.493	C=C	Conjugated alkane stretch
1866.025	C=O	Anhydride stretch
1989.594	C=C=C	Allene stretch
2134.556	C≡N	Alkyne stretch
2249.621	C≡N	Nitrile stretch
2473.248	S-H	Thiol
2573.613	O-H	Carboxylic acid stretch
2719.897	O-H	Alcohol stretch
2828.464	N-H	Amine salt stretch
2941.217	C-H	Alkane stretch
3015.918	C-H	Alkene stretch
3155.431	O-H	Alcohol stretch
3283.029	N-H	Aliphatic primary amines stretch
3381.191	N-H	Aliphatic primary amines stretch
3462.809	N-H	Primary amines stretch
3711.798	O-H	Alcohol stretch
3814.238	O-H	Alcohol stretch
3914.18	O-H	Alcohol stretch

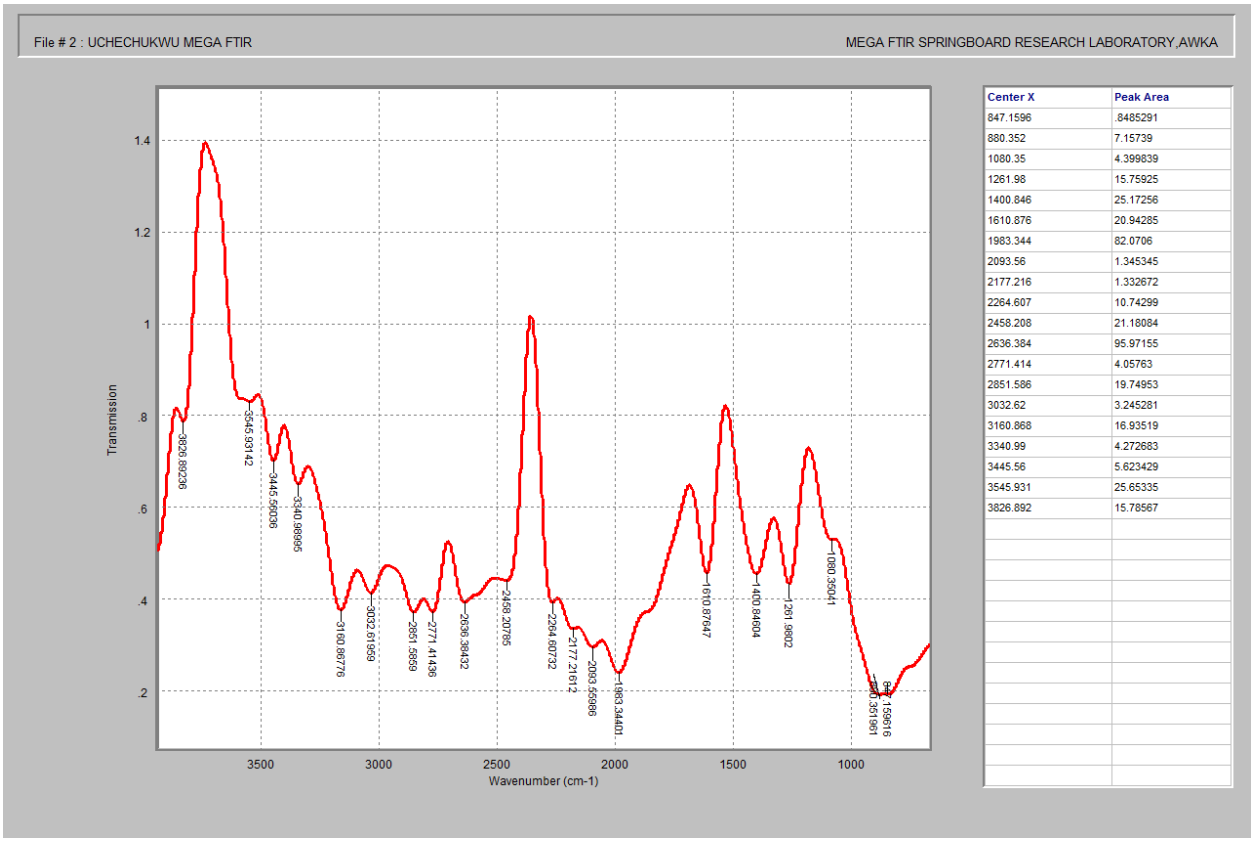
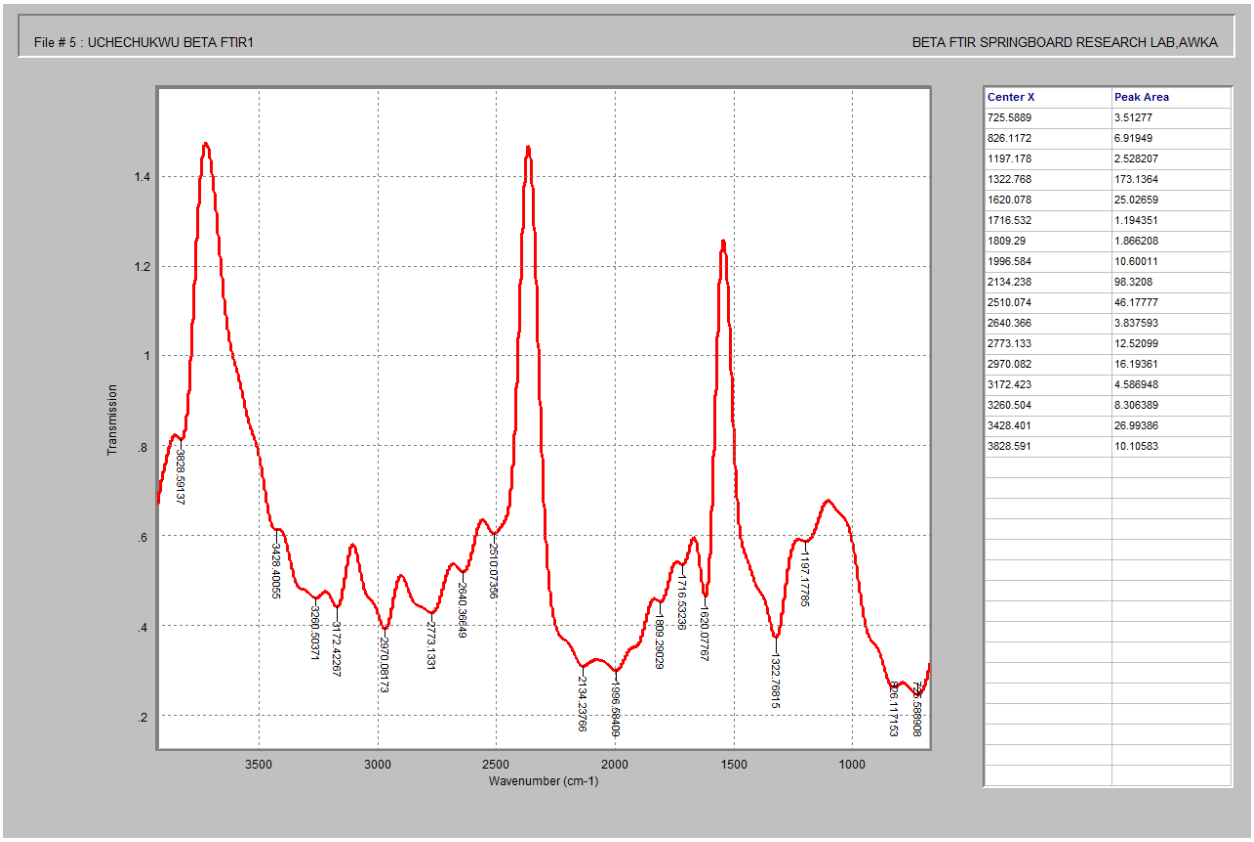


Figure 4.7 Characterization of the local produced demulsifier (BETA) using FTIR

FTIR Interpretation of BETA

Table 4.9 laboratory interpretation of local produced demulsifier (BETA) using FTIR

Wavelength (cm^{-1})	Functional group	Compounds
847.1596	C-H	Aromatics
880.352	N-H	1^0, 2^0 Amines wag
1080.35	C-N	Aliphatic amines stretch
1261.96	C-H ($-CH_2X$)	Alkyl halides
1400.846	C-C	Aromatics stretch (in ring)
1610.876	N-H	1^0 Amines bend
1983.344	C=C=C	Allene stretch
2093.56	N=C=S	Isothiocyanate stretch
2177.216	-C≡C-	Alkynes stretch
2264.607	N=C=O	Isocyanate stretch
2458.208	S-H	Thiol
2636.384	O-H	Carboxylic acid stretch
2771.414	O-H	Alcohol stretch
2851.586	N-H	Amine salt stretch
3032.62	C-H	Alkene stretch
3160.868	O-H	Alcohol stretch
3340.99	N-H	Secondary amine stretch
3445.56	N-H	Primary amine stretch
3545.931	O-H	Alcohol stretch
3826.892	O-H	Alcohol stretch



Center X	Peak Area
725.5889	3.51277
826.1172	6.91949
1197.178	2.528207
1322.768	173.1364
1620.078	25.02659
1716.532	1.194351
1809.29	1.866208
1996.584	10.60011
2134.238	98.3208
2510.074	46.17777
2640.366	3.837593
2773.133	12.52099
2970.082	16.19361
3172.423	4.586948
3260.504	8.306389
3428.401	26.99386
3828.591	10.10583

Figure 4.8 Characterization of the local produced demulsifier (MEGA) using FTIR

FTIR Interpretation of MEGA

Table 4.10 laboratory interpretation of local produced demulsifier (MEGA) using FTIR

Wavelength (cm^{-1})	Functional group	Compounds
880.5889	C-Cl	Alkyl halides
895.1172	C-H	Aromatics
1197.178	C-H ($-CH_2X$)	Alkyl halides
1322.768	C-N	Aliphatic amines stretch
1620.078	N-H	1^0 Amines bend
1716.532	C=O	α, β- Unsaturated esters stretch
1809.29	C=O	Acid halide stretch
1996.584	C=C=C	Allene stretch
2134.238	N=C=N	Carbodiimide stretch
2510.074	O-H	Carboxylic acid stretch
2640.366	O-H	Carboxylic acid stretch
2773.133	O-H	Alcohol stretch
2970.082	C-H	Alkane stretch
3172.423	O-H	Alcohol stretch
3260.504	N-H	Aliphatic primary amines stretch
3428.401	N-H	Primary amines stretch
3928.591	O-H	Alcohol stretch

FTIR Interpretation of commercially available (foreign) DEMUSIFIER

Table 4.11 laboratory mathematical characterization of commercially available demulsifier

Wavelength (cm^{-1})	**Functional group**	**Compound Name**
769.87	C-CI stretch	Alkyl halides
886.3	C-H "oop"	Aromatics
1047.94	C-N stretch	Aliphatic Amines
1157.92	C-H wag(-CH_2X)	Alkylhalides
1305.31	C-O stretch	Esters carboxylic acids
1400.41	C-C stretch Ring	Aromatics
1619.68	N-H bend	1^0 Amines
1776.38	C= O	Conjugated anhydride
2004.28	N=C=S	Isothiocyanate
2238.03	C≡N	Nitrile
2129.8	N=N=N	Azide
2466.21	O=C=O	Carbodioxide
2519.29	O-H	Carboxylic acid
2959.61	C-H	Alkane& Alkene
3099.45	C-H	Alkyne
3310.733	N-H	2^0 Amine
3429.09	N-H	1^0 Amine
3608.4	O-H	Alcohol

Parameters	**DEMUSIFIER**	
	Run1	Run2
pH	4.80	4.70
Specific gravity	0.9905	0.9911
Viscosity, mPa.s	924.60	925.00

SPECIFIC GRAVITY

Specific gravity = Density of Oil
Density of Water

$$= \frac{M_2 - M_1}{W_2 - W_1}$$

Where W_1 OR M_1 = Mass of empty specific gravity bottle
M_2 = Mass of empty specific gravity bottle + 50 ml of **demusifier**
W_2 = Mass of empty specific gravity bottle + 50 ml of water

DEMUSIFIER

Run1 = $\frac{78.0613 - 25.2653}{78.5684 - 25.2653} = 0.9905$

Run2 = $\frac{78.0966 - 25.2653}{78.5684 - 25.2653} = 0.9911$

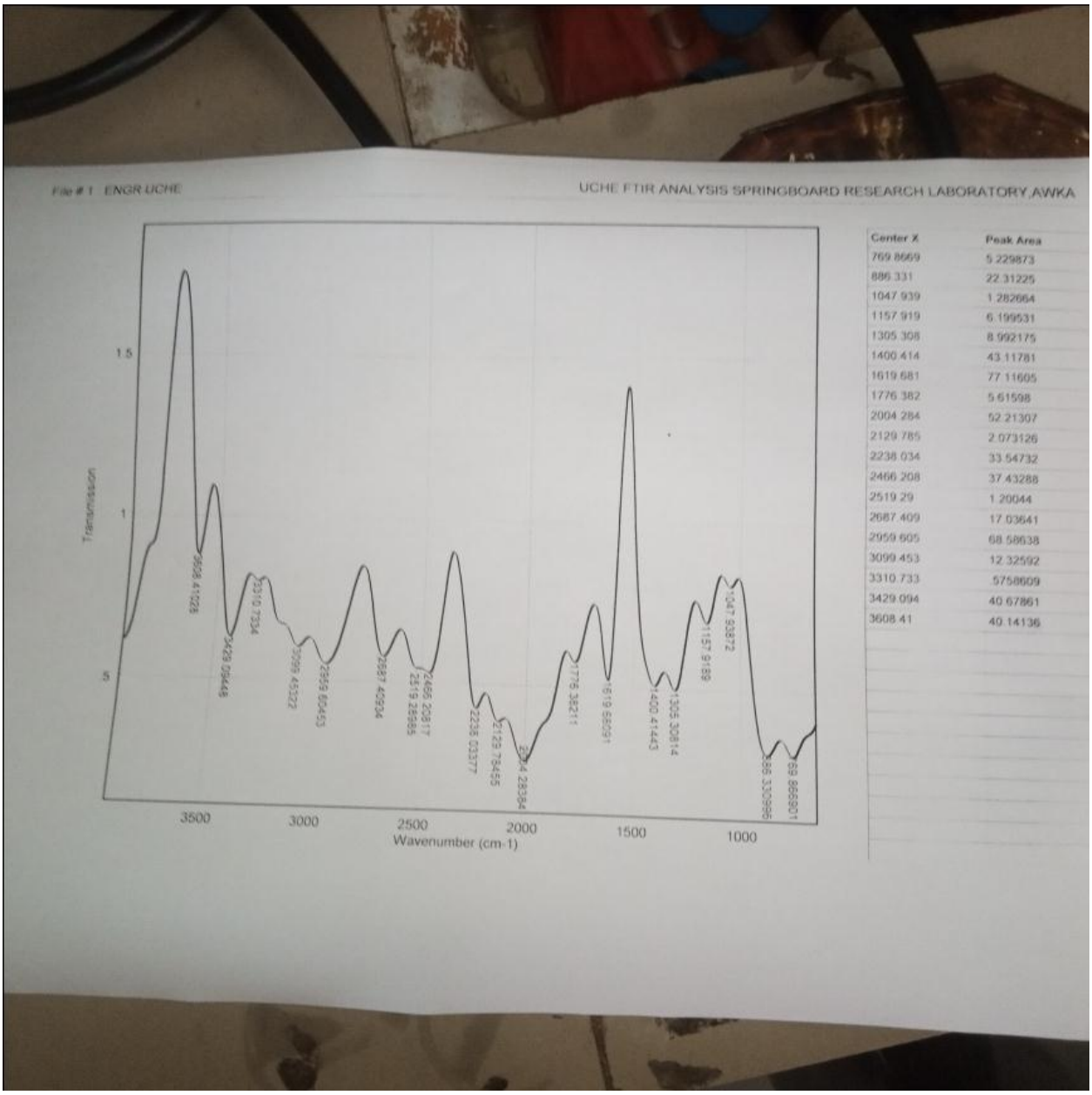


Figure 4.9 Characterization of the commercially available demulsifier using FTIR

4.1.4 The Result of the Water Separation from Crude Oil Emulsion by ALPHA, BETA, MEGA and CAD

4.1.4.1 Demulsification efficiency and effectiveness of locally formulated demulsifiers

'ALPHA', 'BETA', and 'MEGA' respectively on crude oil water emulsion demulsification was determined. A field type 10ml volume of water and 10ml volume of oil were mixed together to produce 20ml volume of crude oil water emulsion. Maximum 3.0ml concentration of both locally produced and commercially available demulsifiers were used to obtain maximum demulsificaion result

Table 4.12 demulsification result on ALPHA at Temperature 30'C (500rpm)

Vol. of demulsifier (ml) ALPHA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0.10	0.10	0.15	0.2	0.2
1.0	0.25	0.3	0.3	0.3	0.3
1.5	0.3	0.5	0.9	1.5	2.0
2.0	0.3	0.5	1.0	2.8	3.5
2.5	0.3	0.6	1.10	3.5	5.2
3.0	0.3	0.8	1.15	4.7	5.6

Table 4.13 demulsification result on ALPHA at Temperature 50'C (500rpm)

Vol. of demulsifier (ml) ALPHA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0.25	0.3	0.3	0.3	0.4
1.0	0.4	0.4	0.4	0.4	0.4
1.5	0.4	0.45	0.6	0.6	0.65
2.0	2	2.5	3	4.5	6
2.5	3	5	5	7	7.6
3.0	5.6	5.8	6.2	7.0	7.3

Table 4.14 demulsification result on ALPHA at Temperature 70'C (500rpm)

Vol. of demulsifier (ml) ALPHA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0.5	0.5	0.6	0.6	0.6
1.0	0.9	1.5	1.5	1.6	1.6
1.5	2	2.5	2.9	3	3
2.0	3	3	3.7	3.9	3.9
2.5	4.0	4.0	4.2	4.2	4.2
3.0	5.7	6.0	7.0	7.5	7.5

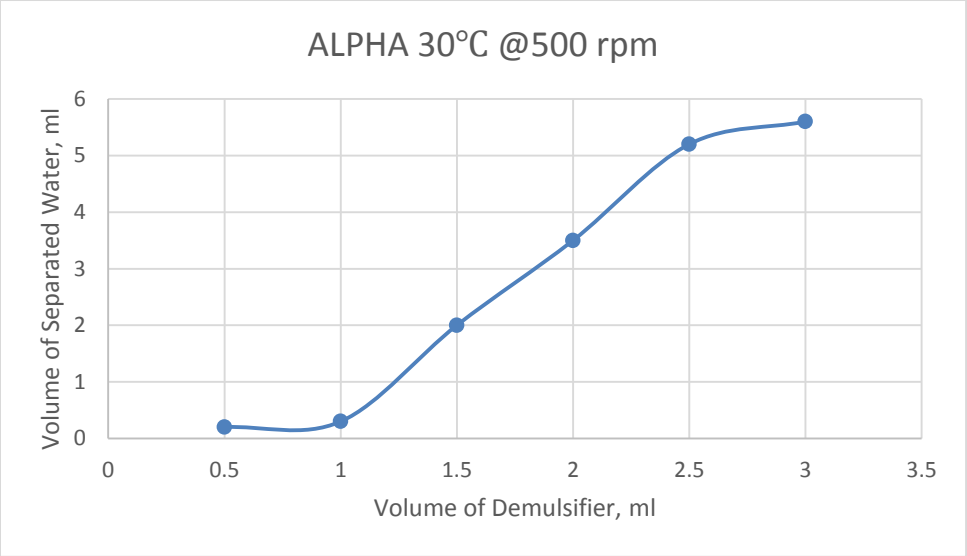


Figure 4.10 demulsification result on ALPHA at 30'C (500rpm)

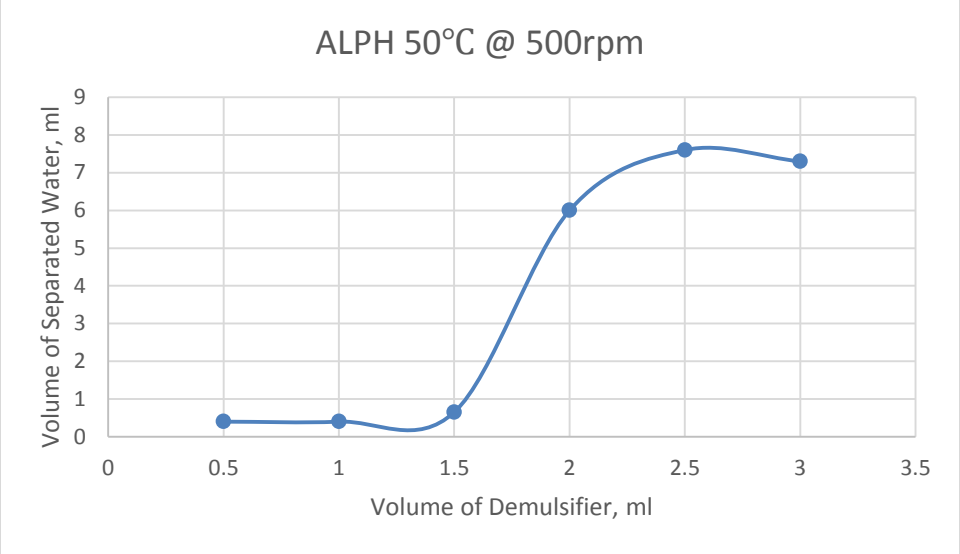


Figure 4.11 demulsification result on ALPHA at 50'C (500rpm)

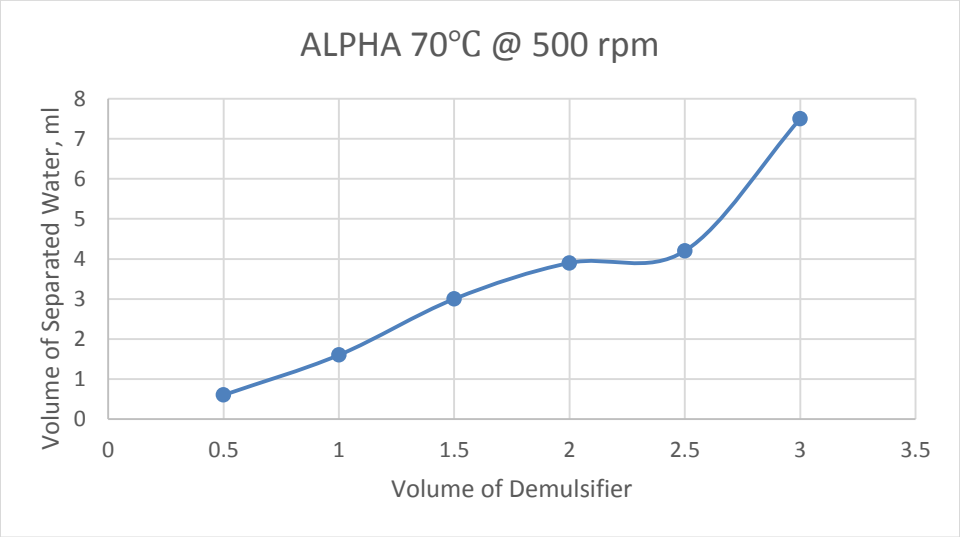


Figure 4.12 demulsification result on ALPH at 70'C (500rpm)

Figure 4.10; the produced local demulsifier Alpha resulted in separating the crude oil water emulsion with 0.5ml to 3.0ml dosage at 30°C (500rpm) with demulsification rate of 56% water separation was recorded.

Figure 4.11, the temperature of the locally produced demulsifier Alpha was increased to 50°C at the same (500rpm), 0.5 to 3.0 dosage and 73% demulsification rate was obtained.

Figure 4.12, 70°C increase in temperature (500rpm) of Alpha produced was also used for the demulsification of the same 20ml volume of crude oil water emulsion and 75% result was achieved.

Table 4.15 demulsification result on ALPHA at Temperature 30'C (1000rpm)

Vol. of demulsifier (ml) ALPHA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	1.0	1.0	1.0	1.0	1.0
1.0	1.3	1.7	1.9	2	2
1.5	2	2.3	2.5	3	3
2.0	3.5	3.7	3.8	3.9	4
2.5	4.0	4.9	4.9	5.0	5.0
3.0	5.0	5.9	6.0	6.5	6.5

Table 4.16 demulsification result on ALPHA at Temperature 50'C (1000rpm)

Vol. of demulsifier (ml) ALPHA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	1.4	1.4	1.9	1.9	1.9
1.0	2	2.3	2.8	3.5	3.5
1.5	4.0	4.3	4.3	5.0	5.0
2.0	5.0	5.2	5.5	5.5	5.5
2.5	6.0	6.0	6.2	6.5	6.5
3.0	5.0	6.8	7.2	7.6	7.6

Table 4.17 demulsification result on ALPHA at Temperature 70'C (1000rpm)

Vol. of demulsifier (ml) ALPHA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	3.5	3.5	3.5	3.5	3.5
1.0	4	4.5	5	6	6
1.5	5	5.5	6.8	6.8	6.8
2.0	6.0	7.0	7.2	7.5	7.5
2.5	6.5	7.3	7.6	7.6	7.6
3.0	6.8	7.8	8.0	8.2	8.2

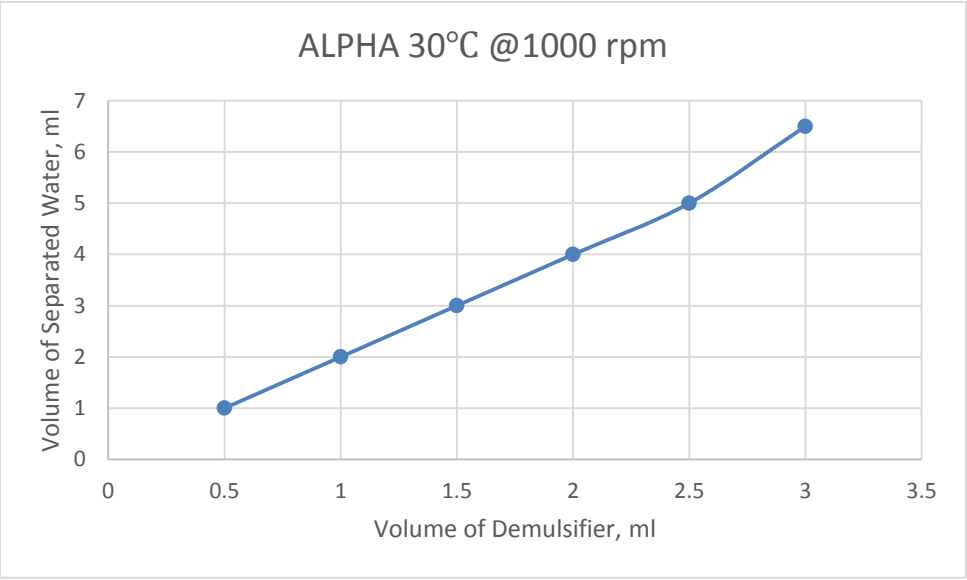


Figure 4.13 demulsification result on ALPHA at 30'C (1000rpm)

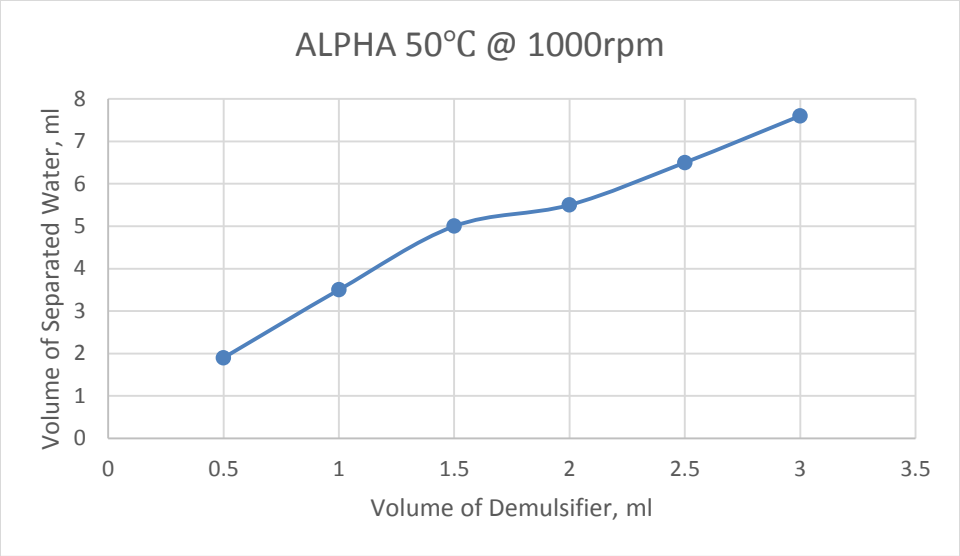


Figure 4.14 demulsification result on ALPHA at 50'C (1000rpm)

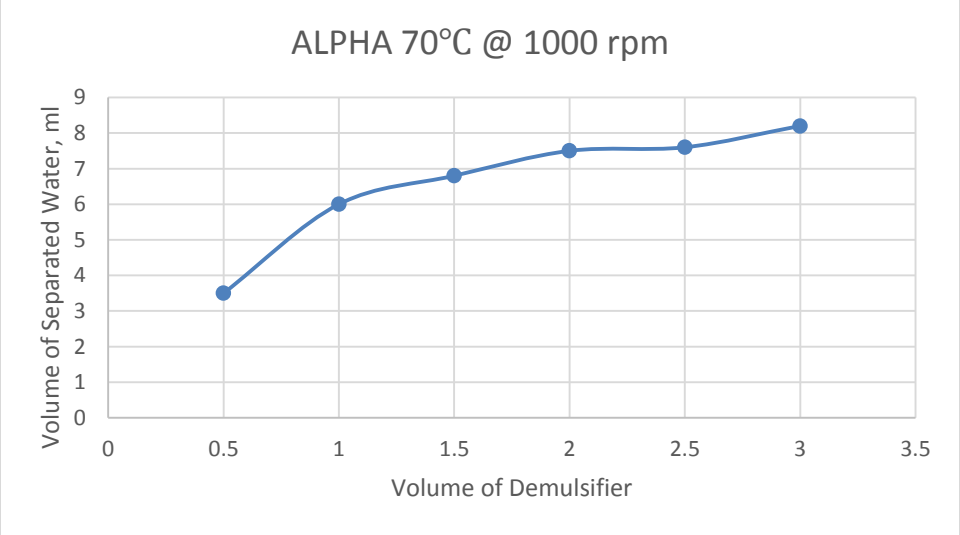


Figure 4.15 demulsification result on ALPHA at 70'C (1000rpm)

Figure 4.13; the produced local demulsifier Alpha resulted in separating the crude oil water emulsion with 0.5ml to 3.0ml dosage at 30°C (1000rpm) with demulsification rate of 65% water separation was recorded.

Figure 4.14, the temperature of the locally produced demulsifier Alpha was increased to 50°C at the same (1000rpm), 0.5 to 3.0 dosage and 76% demulsification rate was obtained.

Figure 4.15, 70°C increase in temperature (1000rpm) of Alpha produced was also used for the demulsification of the same 20ml volume of crude oil water emulsion and 82% result was achieved.

Table 4.18 demulsification result on BETA at Temperature 30'C (500rpm)

Vol. of demulsifier (ml) BETA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0.3	0.4	0.4	0.5	0.5
1.0	0.6	0.8	1	1.1	1.1
1.5	0.6	1.0	1.5	1.5	1.5
2.0	1.5	1.5	1.8	1.8	1.8
2.5	1.8	3.0	4.2	4.6	4.6
3.0	2.9	4.2	7	7	7

Table 4.19 demulsification result on BETA at Temperature 50'C (500rpm)

Vol. of demulsifier (ml) BETA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	1.0	1.2	1.5	1.6	2
1.0	1.6	2	2.5	2.5	3
1.5	2.5	3.0	3.5	3.5	3.5
2.0	3.6	3.8	4.0	4.5	4.5
2.5	5.0	5.2	6.0	6.8	7
3.0	4	6	7	8.5	8.6

Table 4.20 demulsification result on BETA at Temperature 70'C (500rpm)

Vol. of demulsifier (ml) BETA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	2.5	2.8	2.8.	3.0	3.0
1.0	3	4.9	5	6	6
1.5	3	3.5	3.6	3.8	4.0
2.0	4.0	4.2	4.5	4.6	4.6
2.5	4.6	5.0	6.2	6.7	7
3.0	6.7	6.7	7.2	8.8	8.9

The tables above, 4.18, 4.19, and 4.20 are the demulsification results of the locally produced demulsifier "BETA" at different temperature of 30°C (500rpm), 50°C (500rpm), aand 70°C (500rpm). The table indicate the volume of demulsifier applied or dosage in ml and retention time.

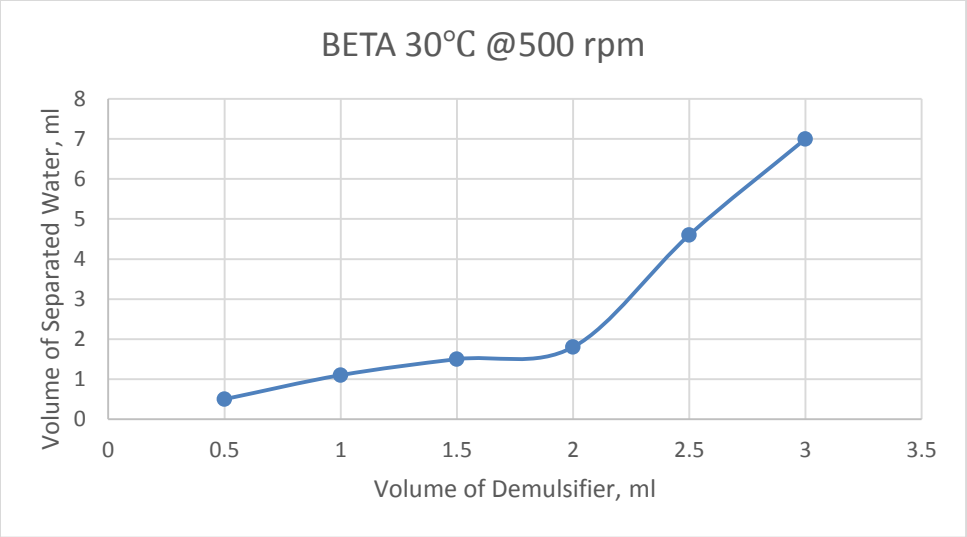


Figure 4.16 demulsification result on BETA at 30'C (500rpm)

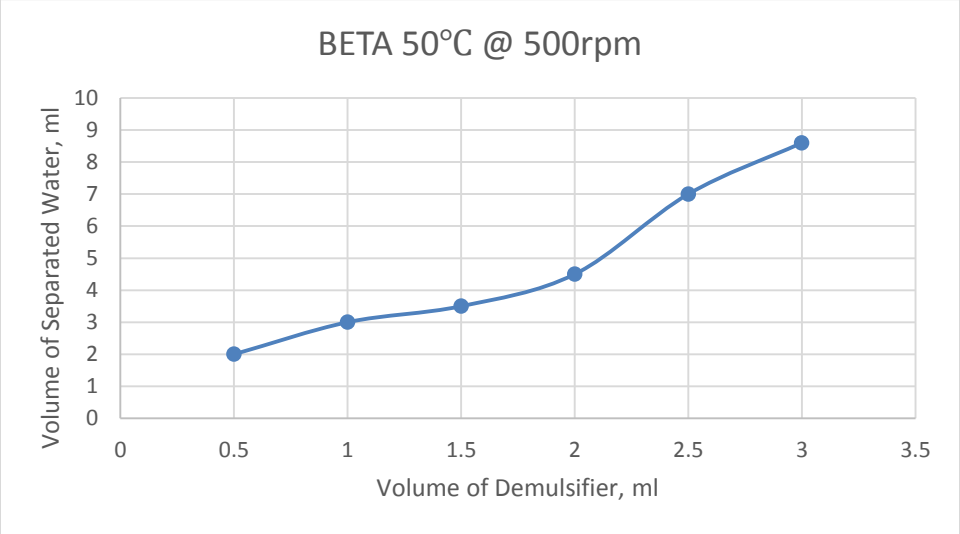


Figure 4.17 demulsification result on BETA at 50'C (500rpm)

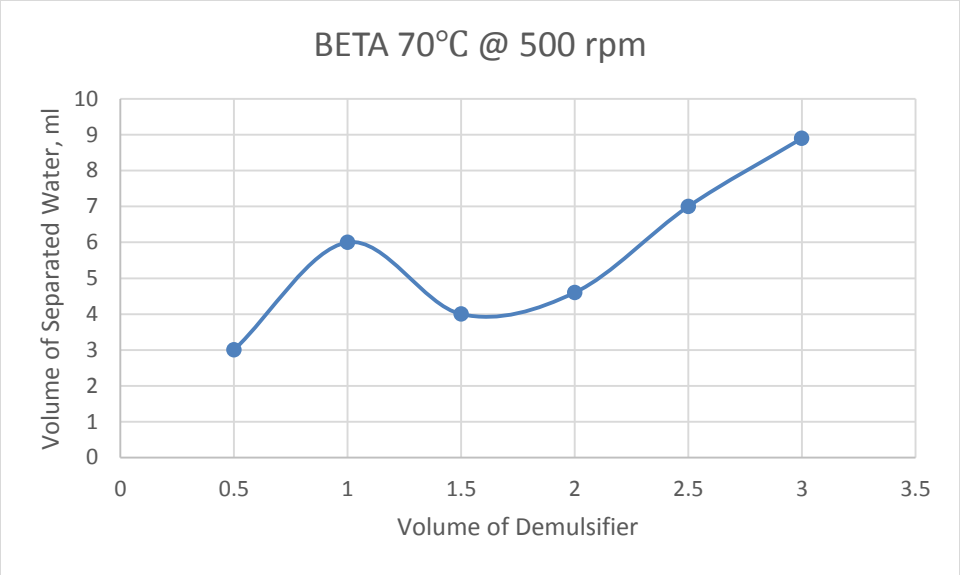


Figure 4.18 demulsification result on BETA at 70'C (500rpm)

Figure 4.16; the produced local demulsifier Beta, resulted in separating the crude oil water emulsion with 0.5ml to 3.0ml dosage at 30°C (500rpm) with demulsification rate of 70% water separation was recorded.

Figure 4.17, the temperature of the locally produced demulsifier Beta, was increased to 50°C at the same (500rpm), 0.5 to 3.0 dosage and 86% demulsification rate was obtained.

Figure 4.18, 70°C increase in temperature (500rpm) of beta, produced was also used for the demulsification of the same 20ml volume of crude oil water emulsion and 89% water separation was achieved.

Table 4.21 demulsification result on BETA at Temperature 30'C (1000rpm)

Vol. of demulsifier (ml) BETA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	3.0	3.5	4	4	4
1.0	4.1	4.5	4.8	4.8	5
1.5	5.0	5.3	5.7	5.9	5.9
2.0	5.5	5.9	6.0	6.4	6.8
2.5	6.0	6.7	7.0	7.0	7.0
3.0	6.5	6.7	7.0	7.1	7.5

Table 4.22 demulsification result on BETA at Temperature 50'C (1000rpm)

Vol. of demulsifier (ml) BETA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	3.5	3.7	4.0	4.3	4.9
1.0	5	6.8	7.0	7.2	7.5
1.5	6	7.0	7.4	7.6	7.6
2.0	7.2	7.5	7.6	7.6	7.6
2.5	7.6	8.0	8.4	8.6	8.8
3.0	8.2	8.5	9.0	9.1	9.1

Table 4.23 demulsification result on BETA at Temperature 70'C (1000rpm)

Vol. of demulsifier (ml) BETA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	6	6.6	6.8	7.0	7.0
1.0	7	7.5	7.5	7.5	7.5
1.5	7.2	7.5	7.6	7.6	7.6
2.0	8.0	8.2	8.5	8.7	8.7
2.5	9	9.1	9.2	9.2	9.2
3.0	9.2	9.2	9.4	9.5	9.5

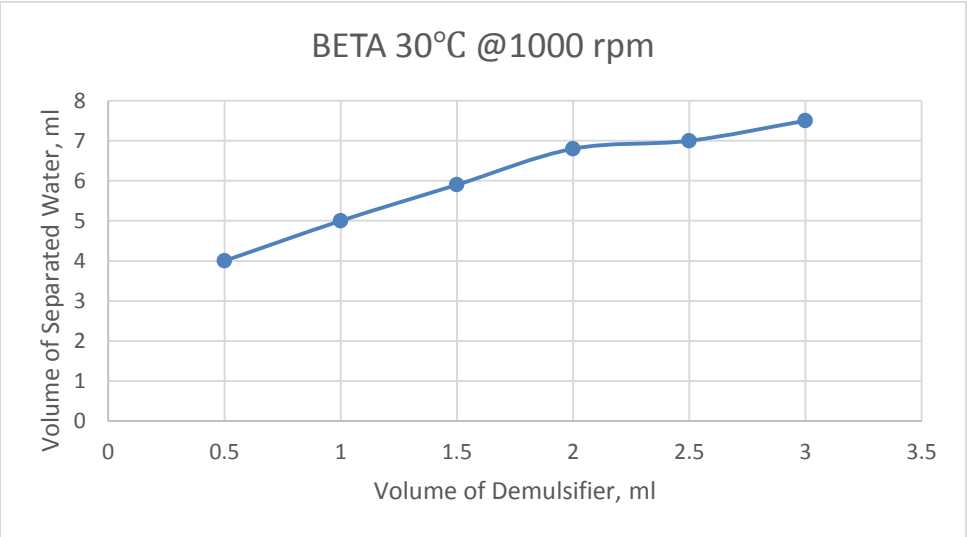


Figure 4.19 demulsification result on BETA at 30'C (1000rpm)

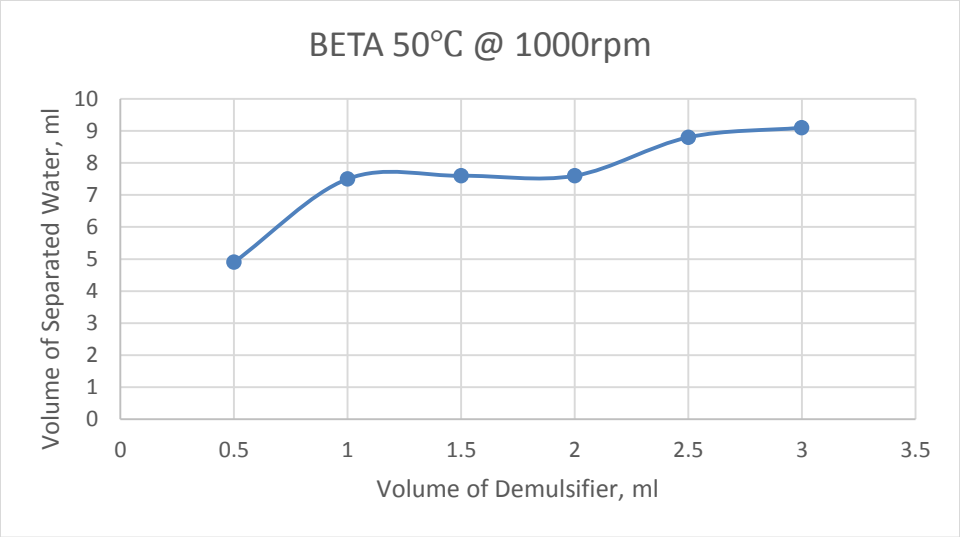


Figure 4.20 demulsification result on BETA at 50'C (1000rpm)

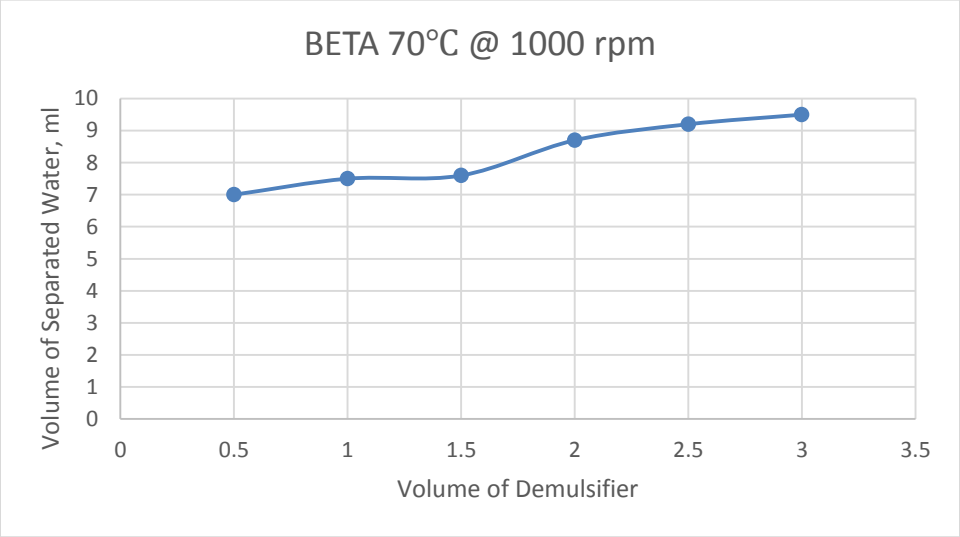


Figure 4.21 demulsification result on BETA at 70'C (1000rpm)

Figure 4.19; the produced local demulsifier Beta, resulted in separating the crude oil water emulsion with 0.5ml to 3.0ml dosage at 30°C (1000rpm) with demulsification rate of 71% water separation was recorded.

Figure 4.20, the temperature of the locally produced demulsifier Beta, was increased to 50°C at the same (1000rpm), 0.5 to 3.0 dosage and 91% demulsification rate was obtained.

Figure 4.21, 70°C increase in temperature (1000rpm) of beta, produced was also used for the demulsification of the same 20ml volume of crude oil water emulsion and 95% water separation was achieved.

Table 4.24 demulsification result on MEGA at Temperature 30'C (500rpm)

Vol. of demulsifier (ml) MEGA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0.7	0.75	0,8	0.8	0.8
1.0	0.8	0.95	1.2	1.3	1.5
1.5	2.0	2.2	2.4	2.9	3.0
2.0	2.5	2.6	2.9	3.1	3.5
2.5	3.0	3.2	4.0	4.6	5.0
3.0	2.1	3.8	6.5	7	7.2

Table 4.25 demulsification result on MEGA at Temperature 50'C (500rpm)

Vol. of demulsifier (ml) MEGA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	1.2	1.6	2.0	2.3	2.5
1.0	2.1	2.6	2.9	3.3	3.8
1.5	3.0	3.0	4.6	4.8	4.8
2.0	3.8	4.2	4.7	4.9	5.0
2.5	4.5	5.0	5.7	6.5	6.9
3.0	7.2	7.5	7.5	8.1	8.1

Table 4.26 demulsification result on MEGA at Temperature 70'C (500rpm)

Vol. of demulsifier (ml) MEGA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	2.5	2.9	3.1	3.6	4.0
1.0	3.1	4.95	5.2	6.5	7
1.5	3.3	5.0	5.3	5.8	7.6
2.0	4.1	5.4	5.8	6.6	8.0
2.5	4.2	5.8	7.0	7.3	8.5
3.0	4.4	4.4	8.1	8.5	9.5

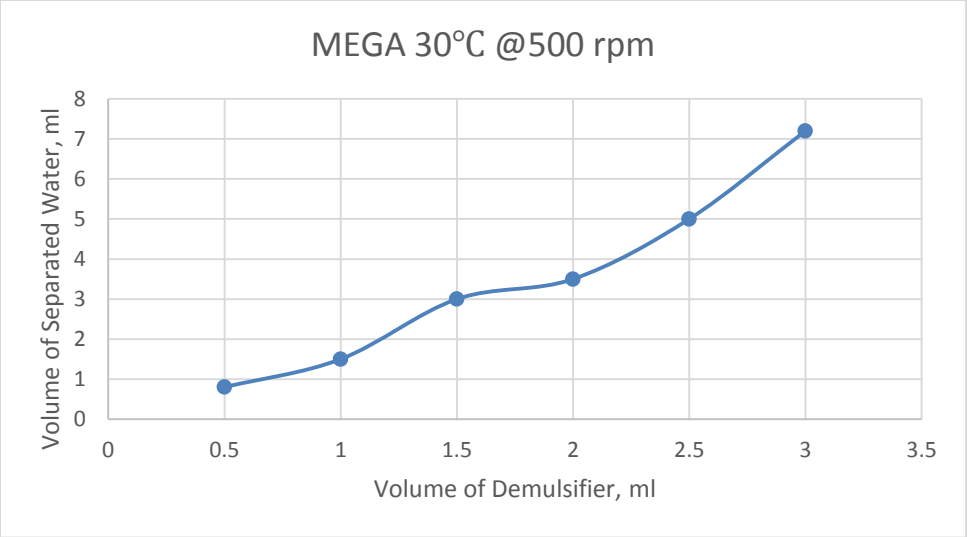


Figure 4.22 demulsification result on MEGA at 30'C (500rpm)

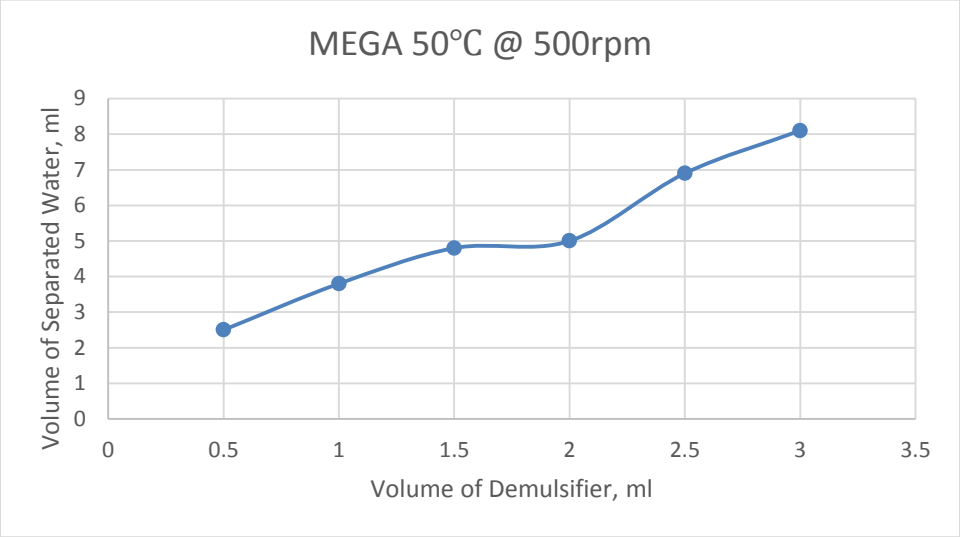


Figure 4.23 demulsification result on MEGA at 50'C (500rpm)

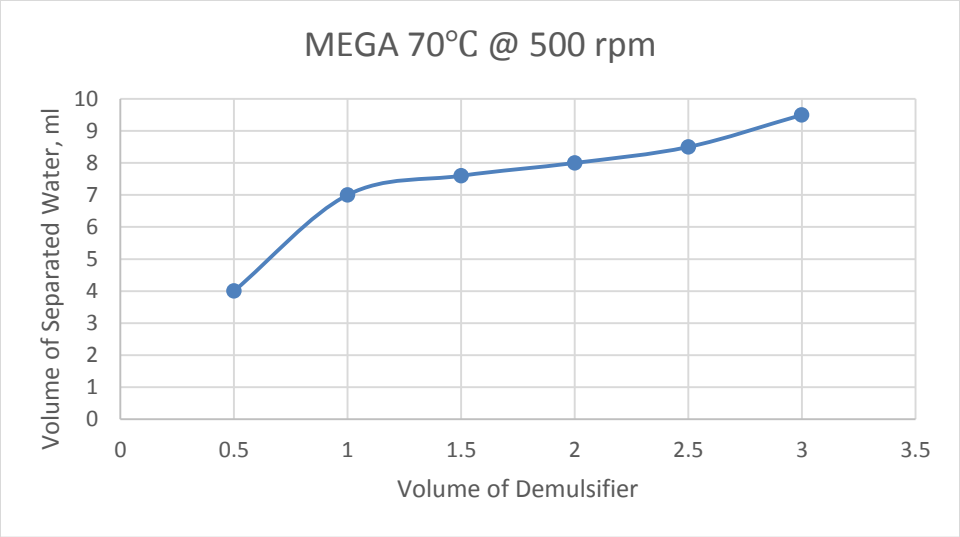


Figure 4.24 demulsification result on MEGA at 70'C (500rpm)

Figure 4.22; the produced local demulsifier Mega, resulted in separating the crude oil water emulsion with 0.5ml to 3.0ml dosage at 30°C (500rpm) with demulsification rate of 72% water separation was recorded.

Figure 4.23, the temperature of the locally produced demulsifier Mega, was increased to 50°C at the same (500rpm), 0.5 to 3.0 dosage and 81% demulsification rate was obtained.

Figure 4.24, 70°C increase in temperature (500rpm) of Mega,, produced was also used for the demulsification of the same 20ml volume of crude oil water emulsion and 95% water separation was achieved.

Table 4.27 demulsification result on MEGA at Temperature 30'C (1000rpm)

Vol. of demulsifier (ml) MEGA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	1.0	1.7	2.2	2.5	2.5
1.0	1.7	3.2	4	4.9	5.1
1.5	2.1	2.5	2.7	2.9	3.0
2.0	2.5	2.9	3.0	3.2	3.6
2.5	3.0	3.5	4.0	4.4	5.2
3.0	3.5	4.2	6.4	7.2	7.9

Table 4.28 demulsification result on MEGA at Temperature 50'C (1000rpm)

Vol. of demulsifier (ml) MEGA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	3.1	3.3	3.6	3.9	4.0
1.0	4.5	7.8	8.5	8.5	9
1.5	4.7	7.8	8.7	9	9.5
2.0	5.0	8.0	8.7	9.3	9.3
2.5	7.1	8.5	8.9	9.0	9.0
3.0	9.1	9.3	9.4	9.5	9.5

Table 4.29 demulsification result on MEGA at Temperature 70'C (1000rpm)

Vol. of demulsifier (ml) MEGA	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	4.5	4.5	4.7	8.0	8.2
1.0	6.5	7.5	7.8	8.5	8.7
1.5	7.0	7.7	7.9	8.9	8.9
2.0	7.0	8.0	8.0	8.9	9.0
2.5	7.5	8.2	8.5	9.0	9.2
3.0	8.5	9.3	9.4	9.6	9.6

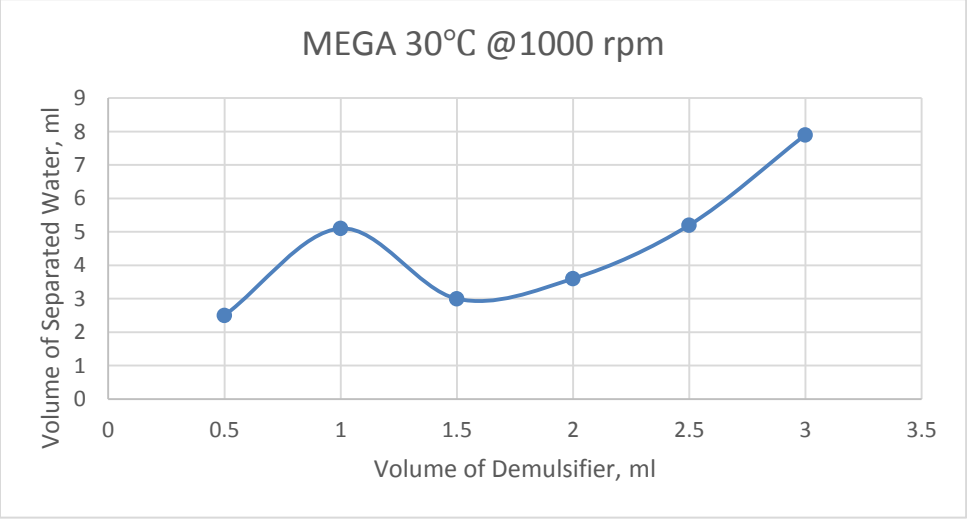


Figure 4.25 demulsification result on MEGA at 30'C (1000rpm)

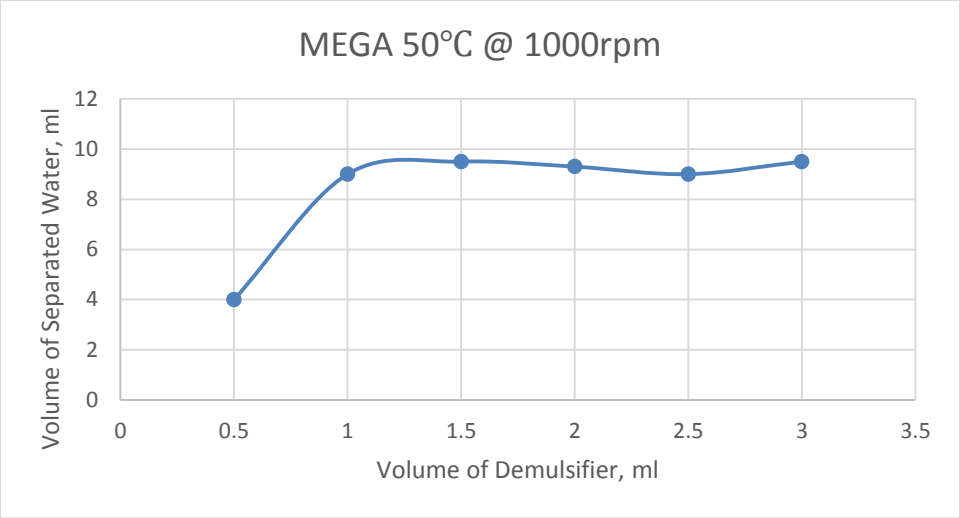


Figure 4.26 demulsification result on MEGA at 50'C (1000rpm)

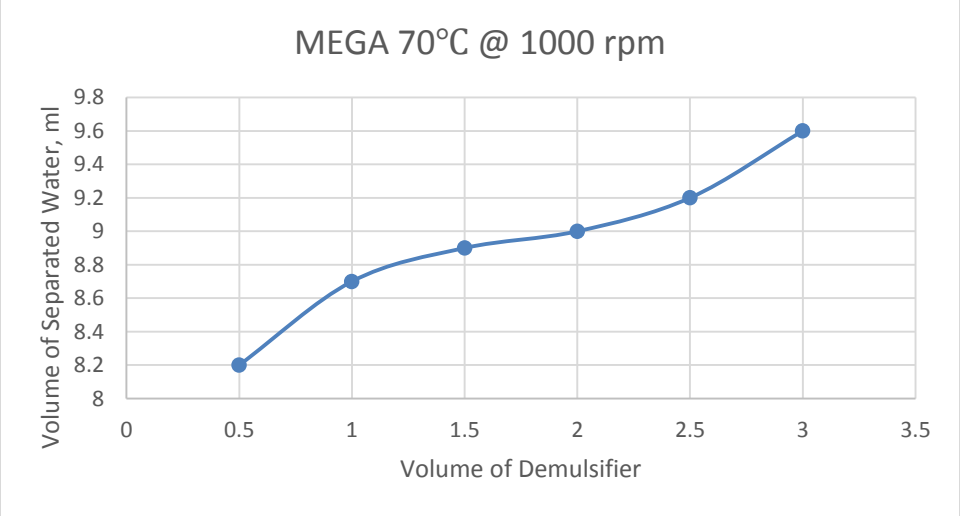


Figure 4.27 demulsification result on MEGA at 70'C (1000rpm)

Figure 4.25; the produced local demulsifier Mega, resulted in separating the crude oil water emulsion with 0.5ml to 3.0ml dosage at 30°C (1000rpm) with demulsification rate of 79% water separation was recorded.

Figure 4.26, the temperature of the locally produced demulsifier Mega, was increased to 50°C at the same (1000rpm), 0.5 to 3.0 dosage and 95% demulsification rate was obtained.

Figure 4.27, 70°C increase in temperature (1000rpm) of Mega, produced was also used for the demulsification of the same 20ml volume of crude oil water emulsion and 96% water separation was achieved.

Demulsification Efficiency and Effectiveness of Commercially Available Demulsifier CAD on Crude Oil Water Emulsion Demulsification was Determined.

Table 4.30 demulsification result on CAD at Temperature 30'C (500rpm)

Vol. of demulsifier (ml) CAD	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0	0	0	0	0
1.0	0.1	0.2	0.5	0.9	1.4
1.5	0.2	0.5	0.7	1.0	1.5
2.0	2.0	2.2	2.5	2.5	2.5
2.5	2.3	2.5	2.7	2.7	3.0
3.0	3.0	3.1	3.3	3.5	3.5

Table 4.31 demulsification result on CAD at Temperature 50'C (500rpm)

Vol. of demulsifier (ml) CAD	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0.5	0.6	0.9	1.0	1.2
1.0	1.0	1.4	1.6	1.8	1.8
1.5	1.2	1.7	1.9	2.1	2.2
2.0	2.0	2.3	2.5	2.6	2.6
2.5	2.1	2.3	2.7	2.9	3.0
3.0	2.8	3.5	4	4	4

Table 4.32 demulsification result on CAD at Temperature 70'C (500rpm)

Vol. of demulsifier (ml) CAD	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	0.5	0.55	1.4	1.7	2.0
1.0	1.50	1.55	2	2.4	2.4
1.5	2.0	2.1	2.5	2.6	2.8
2.0	2.4	2.6	2.9	3.0	3.2
2.5	3.0	3.4	4.0	4.3	4.5
3.0	4	4.2	4.5	4.5	4.5

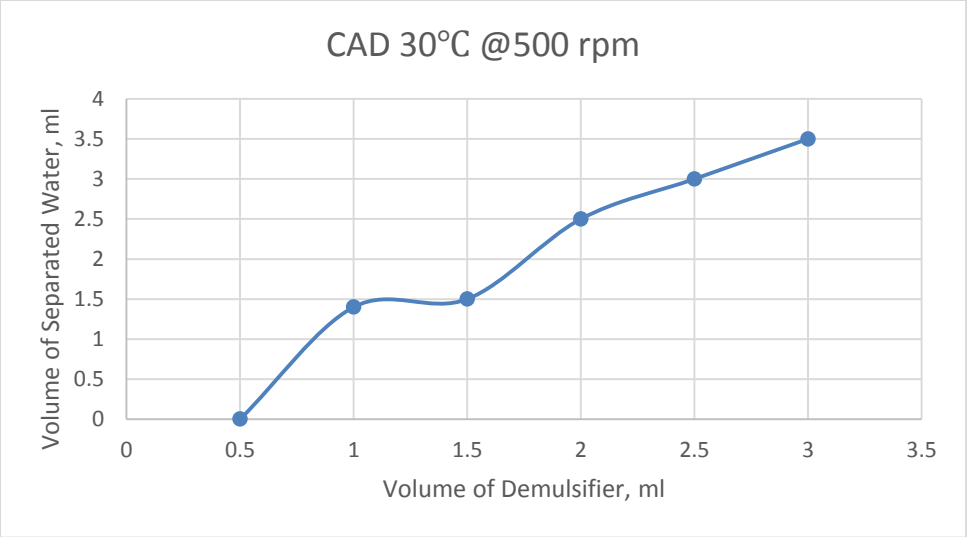


Figure 4.28 demulsification result on CAD at 30'C (500rpm)

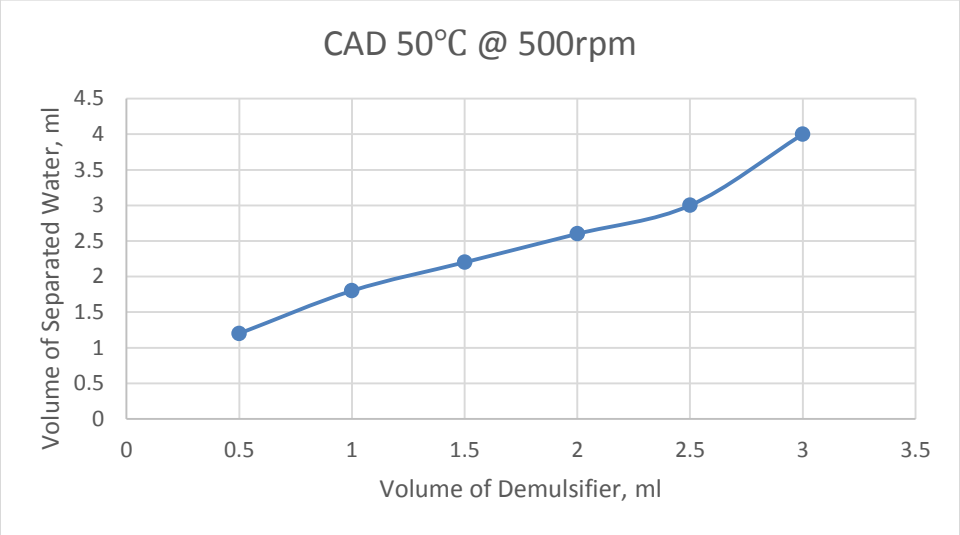


Figure 4.29 demulsification result on CAD at 50'C (500rpm)

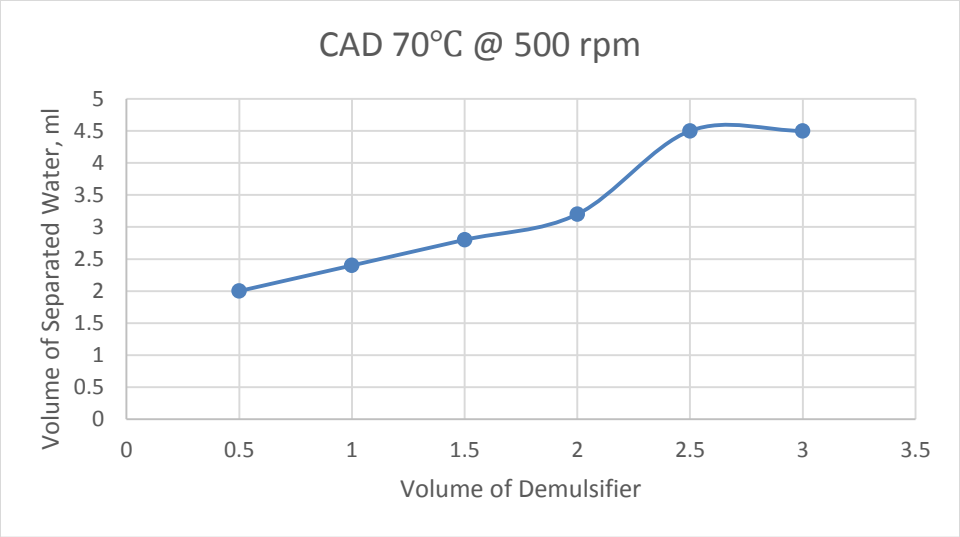


Figure 4.30 demulsification result on CAD at 70'C (500rpm)

Figure 4.28; the produced local demulsifier CAD, resulted in separating the crude oil water emulsion with 0.5ml to 3.0ml dosage at 30°C (500rpm) with demulsification rate of 35% water separation was recorded.

Figure 4.29, the temperature of the locally produced demulsifier CAD, was increased to 50°C at the same (500rpm), 0.5 to 3.0 dosage and 40% demulsification rate was obtained.

Figure 4.30, 70°C increase in temperature (500rpm) of CAD, produced was also used for the demulsification of the same 20ml volume of crude oil water emulsion and 45% water separation was achieved.

Table 4.33 demulsification result on CAD at Temperature 30'C (1000rpm)

Vol. of demulsifier (ml) CAD	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	1.4	1.5	1.5	1.9	2.0
1.0	2.45	2.65	2.5	2.7	3.2
1.5	3.0	3.2	3.5	3.5	4.0
2.0	4.2	4.2	4.6	4.7	4.8
2.5	4.4	4.5	4.6	4.8	5.0
3.0	4.5	5.5	5.5	5.6	5.8

Table 4.34 demulsification result on CAD at Temperature 50'C (1000rpm)

Vol. of demulsifier (ml) CAD	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	2.0	2.45	3.0	3.1	3.3
1.0	3.45	4.3	4.5	4.5	4.5
1.5	4.5	4.5	4.5	4.5	4.5
2.0	4.7	5.0	5.2	5.3	5.6
2.5	5.0	5.2	5.2	5.4	5.6
3.0	5.4	5.5	5.5	5.6	5.9

Table 4.35 demulsification result on CAD at Temperature 70'C (1000rpm)

Vol. of demulsifier (ml) CAD	Separated water volume in (ml)				
	1min	2min	4min	6min	10mins
0.5	3.1	3.2	3.2	3.5	3.7
1.0	4	5	6	6.2	6.4
1.5	4	5.2	6	6.3	6.5
2.0	4.5	5.5	6.2	6.4	6.5
2.5	5.0	6.0	6.4	6.5	6.5
3.0	5.5	6.0	6.6	6.7	6.8

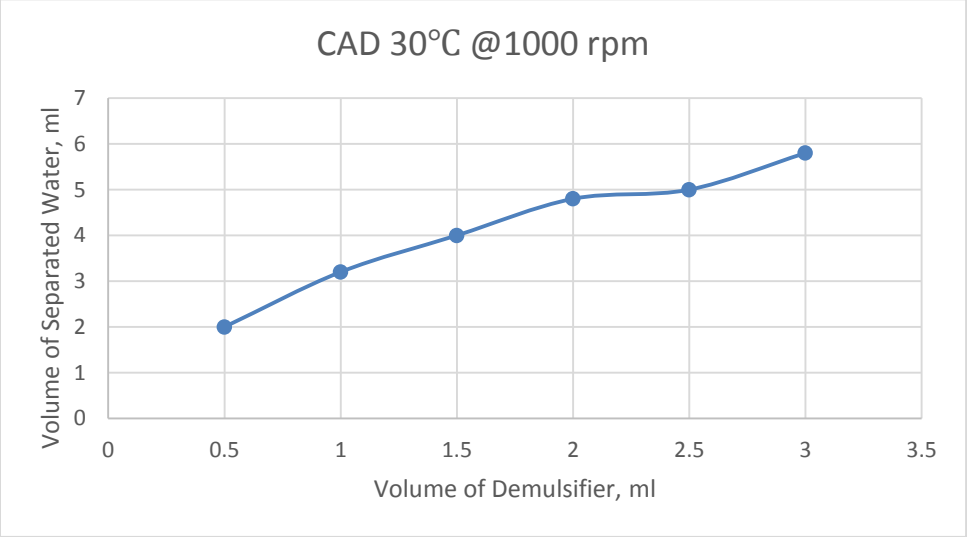


Figure 4.31 demulsification result on CAD at 30'C (1000rpm)

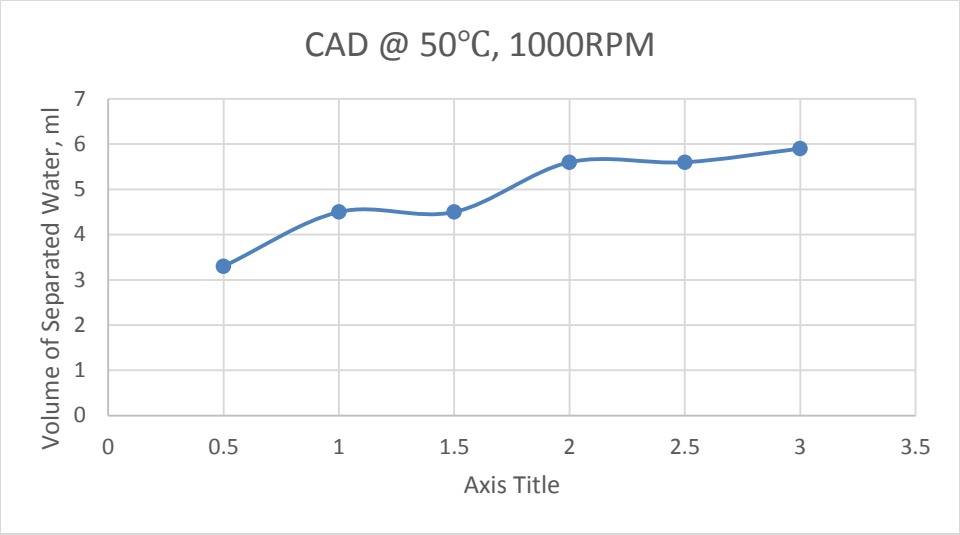


Figure 4.32 demulsification result on CAD at 50'C (1000rpm)

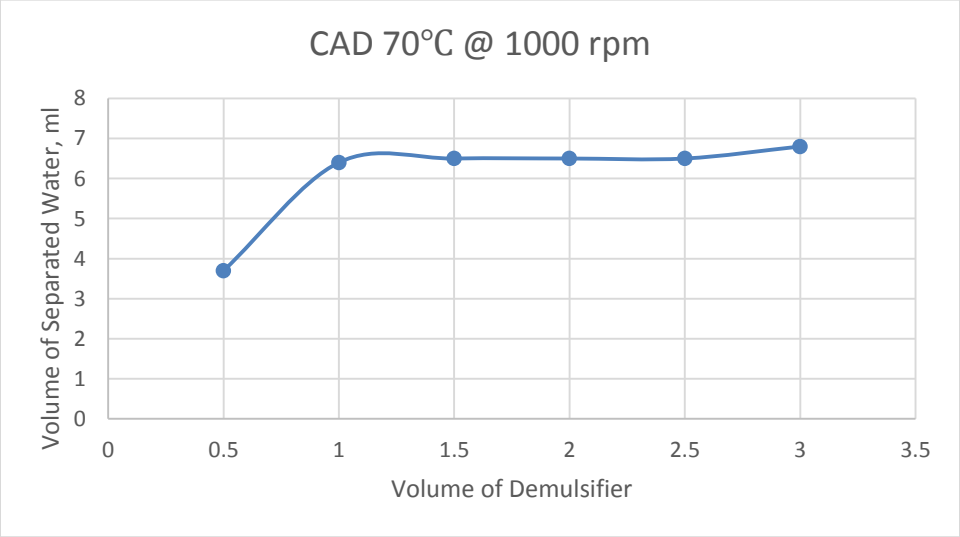


Figure 4.33 demulsification result on CAD at 70'C (1000rpm)

Figure 4.31; the produced local demulsifier CAD, resulted in separating the crude oil water emulsion with 0.5ml to 3.0ml dosage at 30°C (1000rpm) with demulsification rate of 58% water separation was recorded.

Figure 4.32, the temperature of the locally produced demulsifier CAD, was increased to 50°C at the same (1000rpm), 0.5 to 3.0 dosage and 59% demulsification rate was obtained.

Figure 4.33, 70°C increase in temperature (1000rpm) of CAD, produced was also used for the demulsification of the same 20ml volume of crude oil water emulsion and 68% water separation was achieved.

4.1.5 Comparison and Validation of Results

Comparison and validation of water crude oil emulsion rate of separation from local demulsifier 'ALPHA', 'BETA', and 'MEGA' to commercially available demulsifier CAD (imported) Result

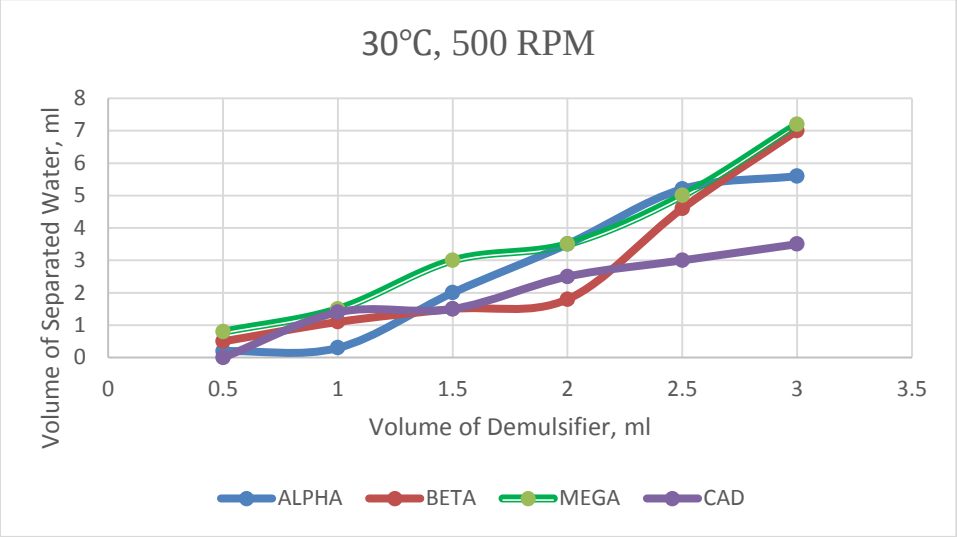


Figure 4.34 comparison demulsification result on ALPHA, BETA, MEGA & CAD at 30'C (500rpm)

Figure 4.34 is the comparison and validation of the demulsification results on the produced local demulsifiers; Alpha, Beta, Mega and the commercially available (imported) demulsifier CAD, at 30°C (500rpm) and 0.5ml to 3.0ml dosage. The rate of demulsification results of crude oil emulsion water separation are 56% Alpha, 70%Beta, 72%Mega, and 35%CAD respectively.

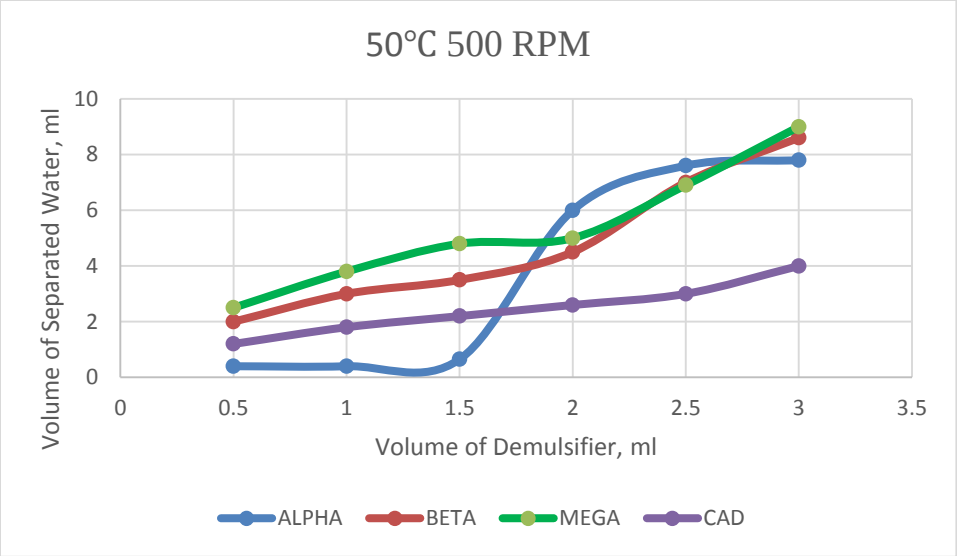


Figure 4.35 comparison demulsification result on ALPHA, BETA, MEGA & CAD at 50'C (500rpm)

Figure 4.35 is the comparison and validation of the demulsification results on the produced local demulsifiers; Alpha, Beta, Mega and the commercially available (imported) demulsifier CAD, at 50°C (500rpm) and 0.5ml to 3.0ml dosage. The rate of demulsification results of crude oil emulsion water separation are 78% Alpha, 86%Beta, 91%Mega, and 40%CAD respectively.

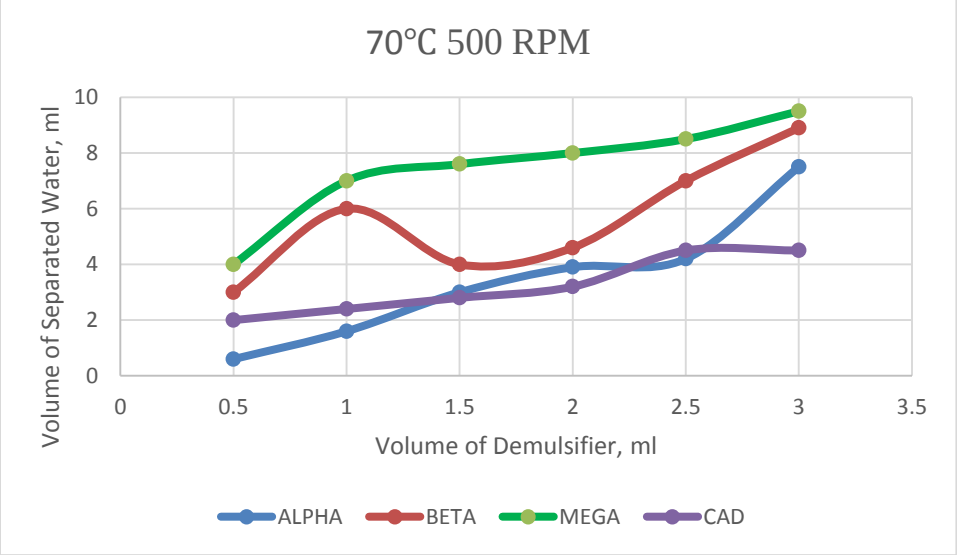


Figure 4.36 comparison demulsification result on ALPHA, BETA, MEGA & CAD at 70'C (500rpm)

Figure 4.36 is the comparison and validation of the demulsification results on the produced local demulsifiers; Alpha, Beta, Mega and the commercially available (imported) demulsifier CAD, at 70°C (500rpm) and 0.5ml to 3.0ml dosage. The rate of demulsification results of crude oil emulsion water separation are 75% Alpha, 89%Beta, 95%Mega, and 45%CAD respectively.

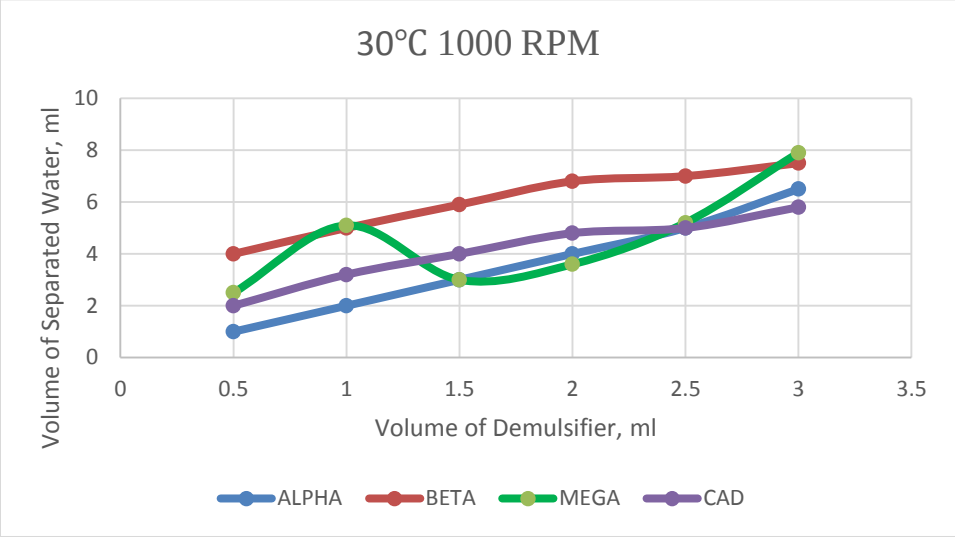


Figure 4.37 comparison demulsification result on ALPHA, BETA, MEGA & CAD at 30'C (1000rpm)

Figure 4.37 is the comparison and validation of the demulsification results on the produced local demulsifiers; Alpha, Beta, Mega and the commercially available (imported) demulsifier CAD, at 30°C (1000rpm) and 0.5ml to 3.0ml dosage. The rate of demulsification results of crude oil emulsion water separation are 65% Alpha, 75%Beta, 79%Mega, and 58%CAD respectively.

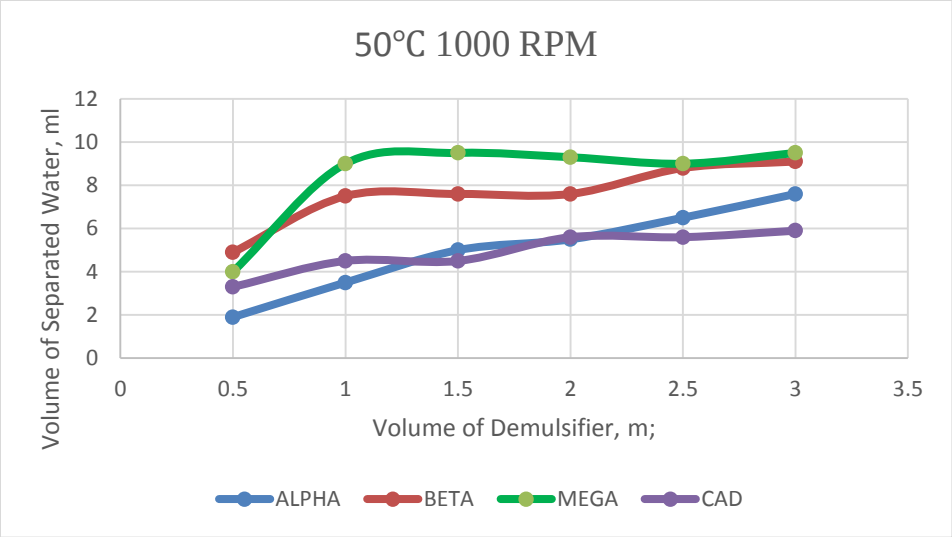


Figure 4.38 comparison demulsification result on ALPHA, BETA, MEGA & CAD at 50'C (1000rpm)

Figure 4.38 is the comparison and validation of the demulsification results on the produced local demulsifiers; Alpha, Beta, Mega and the commercially available (imported) demulsifier CAD, at 50°C (1000rpm) and 0.5ml to 3.0ml dosage. The rate of demulsification results of crude oil emulsion water separation are 76% Alpha, 91%Beta, 95%Mega, and 59%CAD respectively.

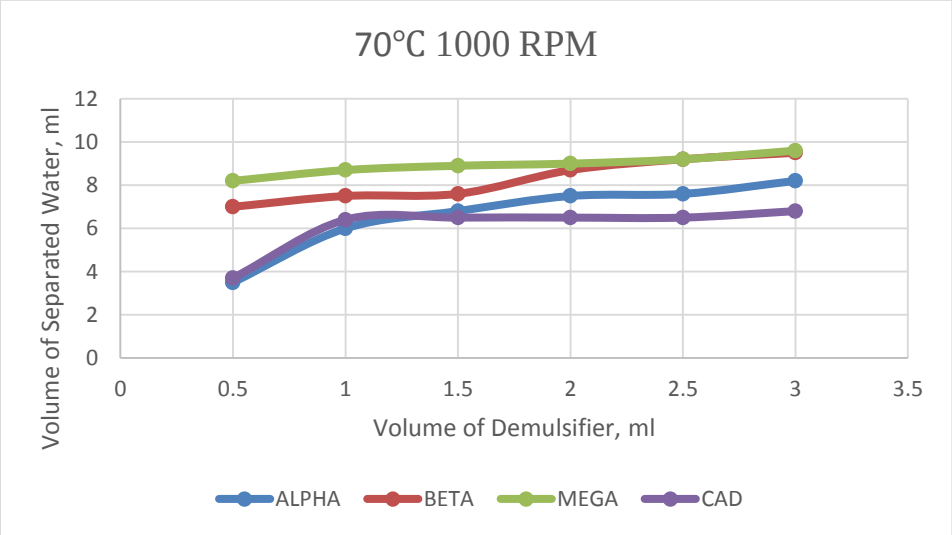


Figure 4.39 comparison demulsification result on ALPHA, BETA, MEGA & CAD at 70'C (1000rpm)

Figure 4.39 is the comparison and validation of the demulsification results on the produced local demulsifiers; Alpha, Beta, Mega and the commercially available (imported) demulsifier CAD, at 70°C (1000rpm) and 0.5ml to 3.0ml dosage. The rate of demulsification results of crude oil emulsion water separation are 82% Alpha, 95%Beta, 96%Mega, and 68%CAD respectively.

4.2 Discussion

4.2.1 The FTIR Test Result for the Four Different Samples

Fourier Transform Infrared Spectroscopy was used to identify the chemical bonds relating to the crude oil emulsion demulsification properties of local materials. The FTIR test on Alum sample has a highest wavelength of 3831.657, functional group of R_3CH0H and a compound structure of 3^0 alcohol 0H symmetric stretch that indicates crude oil emulsion demulsification capacity and properties. FTIR test was further carried out on other local materials; KOH with wavelength of 3798.188, functional group of R_3CH0H and a compound structure of 3^0 alcohol 0H symmetric stretch. Local soap with wavelength of 3558.795, functional group of R_3CH0H and a compound structure of 3^0 alcohol 0H symmetric stretch. Palm oil with wavelength 3916.743, functional group of R_3CH0H and a compound structure of 3^0 alcohol 0H symmetric stretch. Starch with wavelength of 3825.822, functional group of R_3CH0H and a compound structure of 3^0 alcohol 0H symmetric stretch. All, indicates crude oil emulsion demulsification capacity and properties using Fourier Transform Infrared Spectroscopy, FTIR.

4.2.2 The Laboratory Characterization Results of the Raw Materials

Water solubility and n-HEXANE solubility test were conducted on all the local materials; Alum, KOH, Local soap, Palm oil and Starch. 100% solubility of local soap was achieved. Other results are 25% of palm oil, 18% of alum, 44% of starch and 15%KOH solubility in water. n-HEXNE solubility; local soap and palm oil achieved 100% solubility, starch 55%, alum 25% and KOH 20% n-HEXANE solubility.

Demulsification performance; water separation index, force (gravity) and surface tension characterization technique were used to test the demulsification performance of the local

materials; Alum, Starch, Local soap, KOH, and Palm oil and its results ranges from 26% to !00% demulsification performance.

4.2.3 The FTIR Test Result for the Local Produced Demulsifiers; ALPHA, BETA & MEGA and Commercially Available Imported Demulsifier

Fourier Transform Infrared Spectroscopy test was conducted on the produced local demulsifiers; ALPHA, BETA, & MEGA and the commercially available imported demulsifier to investigate the crude oil emulsion water separating capacity. MEGA having highest wavelength indicates high water separating capacity followed with BETA and ALPHA thereby showing that commercially available imported demulsifier after the test has low crude oil emulsion water separation.

4.2.4 The Result of the Water Separation from Crude Oil Emulsion by ALPHA, BETA, MEGA and CAD

Firstly it must be a crude oil with low degree API and high specific gravity to ascertain crude oil emulsion presence and stability. A 10ml crude oil was mixed with 10ml water with a proper agitation and emulsifying agent to obtain 20ml volume of crude oil emulsion. The demulsification result was analyzed based on data from the Laboratory experiment carried out in Federal University of Technology Owerri (bottle test method). The application of local demulsifier was desalinated with the temperature range of 30℃ to 70℃ being ideal temperature for crude oil emulsion demulsification in order to not lose the lighter end of the crude and the volume range of 0.5ml to 3ml of the formulated local demulsifier with different time interval on the 20ml crude oil emulsion.

As shown on the table and figures above MEGA was the most effective demulsifier and newly ever formulated local demulsifier for treating tight emulsion despite the heavy nature of the crude. At a very minimal dosage of 0.5ml there was effect of separation of water.

The efficiency and effectiveness of the formulated local demulsifier was determined at every stage of temperature range, injected volume and time interval. At the stage that produces higher separation of water and oil was recorded and plotted.

Comparison and validation, all the local demulsifiers ALPHA, BETA, and MEGA formulated has a better water separation result than the commercially available imported demulsifier CAD as shown on the comparison demulsification result at a different temperature range and time intervals.

4.2.5 Comparison and Validation of Results

Comparison and validation of the results; the crude oil emulsion demulsification effectiveness, efficiency and performance by the local produced demulsifiers; ALPHA, BETA, and MEGA to commercially available demulsifier CAD were validated and evaluated.

At the temperature 30°C, 500rpm MEGA has the highest water separation performance of 72%, BETA 70%, ALPHA 56% and CAD with the lowest water separation of 35%. Increase in temperature to 50°C, 500rpm, CAD performance increase also to the value of 40%, ALPHA 73%, BETA 81% and MEGA 86% crude oil emulsion water separation. Further increase in temperature to 70°C, same concentration CAD improve in separation performance because the higher the temperature the tendency of losing the lighter end of the crude oil.

With 1000rpm and temperature of 30°C, 50°C and 70°C, the water separation performance of ALPHA, BETA, and MEGA to CAD were recorded with CAD having lowest crude oil emulsion

water separation performance of 58%, 59% and 68% and the MEGA with highest value of 79%, 95% and 96% showing that the formulated local demulsifier have higher crude oil emulsion water separation performance than commercially available demulsifier.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

1. Three different local demulsifiers ALPHA, BETA, MEGA were formulated and were all tested on crude oil emulsion (tight emulsion) and subjected to range of temperature, 30°C, to 70°C. The four key factors to work dependently on during crude oil emulsion demulsification are:(i) Concentration of the demulsifier, (ii) Operating Temperature, (iii) Settling/Separating Time, and (iv) Agitation.
2. Low concentration of the formulated demulsifier formed from locally sourced raw materials; ALPHA, BETA, and MEGA yielded high-demulsification efficiency with a low operating temperature employed in order not to lose the lighter end of the crude. Minimum settling/separating time was used to achieve the required BS&W needed in making a crude oil emulsion (non sellable crude) to sellable crude.

Three different local demulsifiers ALPHA, BETA, MEGA were formulated and were all tested on crude oil emulsion (tight emulsion) and subjected to range of temperature, 30°C, to 70°C

3. A successful treatment resulted in separation of the oil emulsion sample into oil and water. The separated water volume by the locally formulated demulsifiers ALPHA, BETA, & MEGA were high at different temperature range than that of commercially available imported demulsifier, CAD.

5.2 Recommendation

1. This product is highly recommended for an oil industries in Nigeria for its effectiveness and efficiency in Petroleum production performances and because of Nigeria Federal Government local content policy of using locally produced product.
2. A more low temperature should be used, likely freezing temperature
3. Local produced demulsifier could be estimated to be of low cost, a cost analysis should be included in the further works.

5.3 Contribution to Knowledge

This work has established the following

1. The three locally formulated demulsifier in this work: ALPHA, BETA and MEGA are new formulation
2. One of the formulated local demulsifiers MEGA; is a combo formular formulation demulsifier specifically for demulsification of very tight emulsion known as unable-to-break crude oil emulsion.
3. The demulsification of crude oil emulsion was achieved using the produced local demulsifiers; ALPHA, BETA, and MEGA
4. The process (demulsification of crude oil emulsion using local demulsifiers produced locally) was able to mitigate the effect of emulsion problems as stated in the problem statement.

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