

**FORMULATION OF SYNTHETIC DEMULSIFIER FOR WATER-
IN-OIL EMULSION USING LOCAL RAW MATERIALS**

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A dissertation report submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

SEPTEMBER 2013

Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

FAIZ HAZIM BIN MOHD NORDIN

ABSTRACT

There is an increasing need to limit the use of chemical treating agents especially demulsifiers during oil and gas production and to search safer formulation and cost effective mainly due to environmental constraints. Therefore, the use and performance of demulsifiers have to be improved from the application as well as from the environmental issues. This means that the new demulsifiers formulations must be less toxic and efficient compared to the conventional demulsifiers. This thesis are focusing on two main objectives which are to identify and chose suitable local raw materials to be synthetic demulsifier focuses on 'green' demulsifier for water-in-oil emulsion and to determine the most effective 'green' demulsifier by selecting based on the faster time for water separate from crude oil and the highest volume of water separated from crude oil.

This project is conducted based on experiment and testing. An understanding about the extraction method for local raw materials specifically plants, choosing several blend as demulsifier chemical from several material, and method for creating water-in-oil emulsion is needed for completion this project successfully. The demulsifier that created for this project namely Extract Betel Leaf, Extract Cashew Leaf, Blend A, Blend B, Blend C, Blend D and Blend E. There are two testing for this project which is static test and dynamic test. Static test is by using bottle test techniques and determine water separation with time where else for dynamic test is determine water separation by using Bench Centrifuge within specified parameters. All the testing and experiment are conducted in the UTP laboratory.

The result for this project is analysis by using table and graph method. The result for static test is analyses focuses on the performance based on type of demulsifier which are Extract Betel Leaf, Extract Cashew Leaf, Blend A, Blend B, Blend C, Blend D, Blend E and performance based on demulsifier dosage which are 1ml, 2ml and 3ml. The result for dynamic test is analyses focuses on using 3ml dosage of demulsifier. Thus, based on

the analysis, Blend A and Blend E show the best performance compare to other Blend and Extract materials.

Therefore, Blend A and Blend E is chosen as the most effective demulsifiers for separating water-in-oil emulsion. It is based on the highest volume of water separated from crude oil and the faster time for water separate from crude oil which can be determine from the static test and dynamic test. It also shows that Blend materials are more effective as demulsifier compare to Extract materials. This project is relevant as demulsifiers is an important chemical used widely in the oil industry to prevent the formation of emulsion. This project also relevant because focusing on the 'green' demulsifier which will be environmental friendly and cheaper than conventional demulsifiers. The author believes that this study will have significant contribution to the oil and gas industry especially in Malaysia.

ACKNOWLEDGEMENT

The author would like to express his sincere gratitude and deep appreciation to the following people for their support, patience and guidance. Without them, this thesis would not have successfully been made. For them, I owe my deepest gratitude.

- Dr. Sulaimon Aliyu Adebayo, FYP Supervisor for his constant assistance, advice, encouragement, constructive criticism and excellent guidance throughout this research project.
- UTP technician, Core Analysis Lab (Mr Shahrul and Mr Saiful) and Environmental Lab (Mr Daniel) for their assistance and guidance on the proper method and procedure to handle and using laboratory equipment and tools.
- Momentive Performance Asia Pacific, Singapore, supplier demulsifier samples that provided for author to be used as a benchmark and comparison with new created demulsifiers in term of performance specifically water separation with oil.

Finally, above all, the author also would like to thank to lecturers of Petroleum Engineering and Geosciences Department, author's family, friends and people who are indirectly involve in this project for their assistance to complete this thesis.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Oil is produced from reservoirs in association with natural formation water or mixed formation water / injection water. This mixture is in the form of an oil and water emulsion. The separation of water from crude is critically important to the process operation. The process of separating water from crude oil is commonly called demulsification or dehydration and generally involves the resolution of a water-in-oil emulsion (w/o). Demulsifier chemicals account for approximately 40 % of the world oilfield production chemicals market. They are deployed at virtually every crude oil processing station worldwide.

An emulsion is a combination of two immiscible liquids or liquids that do not mix together under normal conditions. One of the liquids is spread out or dispersed throughout the other in the form of small droplets. The droplets are termed the dispersed or internal phase whilst the liquid surrounding the droplet is termed the continuous or external phase. Droplets can be of all sizes, from fairly large (visible) to sub-micron in size. The majority of emulsions are not thermodynamically stable. There are tendency for the system to separate, reduce interfacial area and reduce the overall interfacial energy. Emulsion however has some kinetic stability. The change of emulsion characteristic over period of time is important when dealing with process plant that has fixed fluids residence time. Ultimately the stability of an emulsion relates to the ease with which the dispersed particles are able to move and interact with each other and interact with the continuous phase.

An interface is that portion of a surface of a liquid or a solid that is in contact with another solid or gas. This interface between a liquid and gas or a solid and a gas is

usually describe as a surface. At the interface between oil and water there is an equal distribution of molecular forces, the net sum of which can be considered as the interfacial tension. The interfacial tension for any two liquids will always be less than the sum of the surface tensions of the separated liquids. When oil and water are mixed without additive chemicals will cause a simple emulsion is formed, there is a large increase in surface area and a large increase in the total interfacial tension. This is unstable. If a chemical is added that has surface activity, it will reduce the interfacial tension and therefore act to stabilize the system relative to the simple emulsion. If surface active chemicals are present and adsorbed at the boundary between oil and water then this is an interfacial film.

Emulsion stability is strongly field dependent and will vary in character as the field matures. In addition to emulsified water, there will be free, uncombined water, the proportion of which will usually increase as the water content increases. Failure to dehydrate or separate the water / oil mixture efficiently can result in a number of problems, including;

- i. Risk of corrosion in export lines, including subsea pipelines and at refinery.
- ii. Overloading of surface separation equipment.
- iii. Increased in cost of pumping crude which contains significant emulsions.
- iv. Significant flowline or tubing pressure resulting from high viscosity emulsions.
- v. High level of basic sediment, water and salt are delivered to the refinery.

Typically the desired maximum water content will be in the range 0.2 to 0.5 %.

Chemical demulsifier formulations are used throughout the oil industry to improve emulsion breaking processes. The action of the demulsifier is to stabilize the emulsion. In order to do this the ordered structure of the natural surfactant or emulsion system must be disrupted allowing the disperse droplets to approach each other. Properties that are modified as a result of demulsifier addition are surfactant behavior (oil / water interface), ability to flocculate dispersed phase drops, ability to cause coalescence of dispersed phase and wettability of solids.

Surface active molecule may be classified by the hydrophile / lipophile ratio or hydrophilic / lipophilic balance (HLB). A series of compound with similar structures show two stability maxima corresponding to w/o emulsifier properties. Between these two there are stability minimum where neither hydrophilic nor hydrophobic groups dominate the interfacial region. Most demulsifier are likely to have HLB values in the region of this stability minimum. Useful products are those that absorb and partially replace the natural surfactant, then absorb again after film rupture. Performance characteristic can be varied by product molecular weight, charge reduction potential and flocculation behavior.

Commercial and conventional demulsifiers are generally polymeric surfactants such as copolymers of polyoxyethelene and polypropylene or alkylphenol-formaldehyde resins or blends of various surface-active substances. Due to more and more severe environmental constraints, there is now need in the oil production to restrict the use of chemicals and to utilize safer formulation, less toxic and as efficient as conventional demulsifiers. In term of the budget for demulsifier, it can be reduce as 'green' demulsifiers use local raw materials to be demulsifiers. There are several potential local raw materials used in this project.

1.2 Problem Statement

Stable water-in-oil emulsion can formed at many stages during the production and processing of crude oils. Presence of resin and asphalthenes as a "natural demulsifiers" as well as by wax and solids caused the formation of these emulsions. All these components can organize and form rigid film at the oil / water interfaces. To ensure the crude oil quality and low cost of the oil production, effective separation of water and oil is important. Chemical demulsification forms the most important step in breaking of water-in-oil emulsions. Conventional demulsifier are generally polymeric surfactants such as polypropylene, copolymers, polyoxyethelene or blends of various surface-active substances. Due to more and more severe environmental constraints, there is need in the

oil production to restrict the use of the chemicals and to utilize safer formulations which are less toxic but at least as efficient and have same function as conventional demulsifiers. In this paper, the author will study about synthetic demulsifier mostly on 'green' demulsifier which is focus on local raw materials to be as demulsifiers and comparison with silicone demulsifier in term of their effectiveness.

1.3 Objectives of Project and Scope of Study

1.3.1 Objectives of Project

There are two main purposes for this project to be conduct which are:

- i. To identify several local raw materials and blends to be synthetic demulsifier focuses on 'green' demulsifier for water-in-oil emulsion.
- ii. To determine the most effective 'green' demulsifier by selecting based on the highest volume of water separated from crude oil and the faster time for water separate from crude oil.

Based on the objectives above, the new 'green' demulsifier can be used in the future as alternatives to the conventional demulsifier. The 'green' demulsifier also produce with environmental friendly as it will be less toxic and not pollute the environment.

1.3.2 Scope of Study

This project needed the author to understand about the concept of water-in-oil emulsion, synthetic demulsifier, 'green' demulsifier, materials needed to be 'green' demulsifier and materials needed to be blend demulsifier. For water-in-oil emulsion there are several steps to produce water-in-oil emulsion to be used in this project. Whereas deeply understanding on how the demulsifier works when injecting to water-in-oil emulsion is strongly needed. This project also needed the author to be involved in experiment which is Soxlet extraction, creating blend demulsifier, creating water-in-oil emulsion, static test

and dynamic test. For static test, it involve bottle test whereas for dynamic test using Bench Centrifuge. Soxhlet extraction method is for extracting plant to be as demulsifier.

1.4 Project Relevance and Feasibility

1.4.1 Relevance

- i. Demulsifier is widely used to treat water-in-oil emulsion in oil and gas industry and to make sure the quality of oil is based on the spec to be sold.
- ii. 'Green' demulsifier is more environmental friendly as it less toxic compare to the conventional demulsifier.
- iii. Creating demulsifier that is low cost to produce it as it is using local raw materials.
- iv. The efficiency of using 'green' demulsifier is at least have same efficiency as conventional demulsifier.

1.4.2 Feasibility

- i. The project can be finished within timeframe of FYP 1 and FYP 2.
- ii. The experiment can be done in UTP laboratory.

CHAPTER 2

LITERATURE REVIEW

2.1 Water-in-Oil Emulsion

The water-in-oil emulsion consists of water droplets in a continuous oil phase and oil-in-water emulsions consist of oil droplets in a continuous water phase. In the oil industry, water-in-oil emulsion are more common as most produced oilfield emulsion are of this kind and therefore the oil-in-water are referred to as 'reverse' emulsions. Multiple emulsions are more complex and consist of tiny droplets suspended in bigger droplets that are suspended in a continuous phase (Kokal, 2002). Furthermore, an emulsion is a combination of two immiscible liquids in which one of the liquids is dispersed as a small droplet into second liquid. The phase that is dispersed is called internal phase whereas the liquid into which it is dispersed is called the external phase (Champion, 2003).

Kokal (2012) and Schramm (1992) state that crude oil is rarely produced alone. Generally it is produced with water that will cause many problems during oil production. Water-in-crude oil emulsion is the most common emulsion in the oil field. Their formation is usually caused by high shear rates and zones of turbulence encountered at different points of production facilities, especially at the wellhead in the choke valve (Van der Zande, 2000). Produced water occurs in two ways which are some of the water may be produced as free water for example water that will settle out fairly rapidly and some of the water that may be produced in the form of emulsions.

Emulsions are difficult to treat and cause a number of operational problems such as production of off-specification crude oil, tripping of separation equipment in gas/oil separating plants (GOSPs) and creating high pressure drops in flowlines (Kokal, 2002). These emulsions have to be treated in order to remove the dispersed water and associated inorganics salt to meet crude specification for transportation, storage and

export to reduce corrosion and catalyst poisoning in downstream-processing facilities. Emulsion can be encountered in almost all phases of oil production and processing: inside the reservoirs, wellbores, well heads and wet crude handling facilities; transportation through pipelines and crude storage and during petroleum processing (Kokal, 2002).

Emulsifying agents are dual nature molecules. They consist of a hydrophobic end which is dislike water and a hydrophilic end which is likes water. These properties cause the agents to concentrate where the oil and water meet and form a barrier around the water droplet. Over time, more emulsifying agents will migrate to the oil-water interface and the emulsion usually becomes more stable and difficult to break. The layer that forms at the interface is called a rag layer (Clariant, 2007).

According to Kokal (2002) and Graham (1982) emulsion can be very stable due to the presence of polar compound such as asphaltene and resins that play the role of “natural emulsifier” and also because of the occurrences of many types of fine solid such as crystallized waxes, clays and scales that strongly participate in the formation of resistance films at the crude oil/water interface. These stable emulsion tend to concentrate at the oil/water interface where they form interfacial films (Kokal, 2002). This generally leads to a reduction of interfacial tension (IFT) and promotes dispersion and emulsification of the droplets. Asphaltenes and resins are believed to be the main constituents of interfacial films, which form around water droplets in an oilfield emulsions (Schramm, 2000).

Water-in-oil emulsions can affect production operations in two general ways which are cause oil to be unstable and slow the flow of production fluids. The first case is caused by water-in-oil emulsion. Only a specified percentage of water can be contained in oil for it to be “in spec” for transport in a pipeline. If oil exceeds this specification, it either cannot be transported in the pipeline or it has to be sold at less than top price. Oil that is “out of spec” because of its water content is called wet oil. If a well is producing wet oil, it is typically stored in a large tank to be demulsified and then transferred to pipeline

(Champion, 2003). Unfortunately, these tanks have only a limited capacity. Although most emulsion will break on their own over time, if they did not break before the tank is full then production must stop. Besides, making the oil unstable, emulsions cause the flow of production to reduce or slow. Emulsions are characteristically very viscous, making them thicker than base production fluids. This can cause the production flow to slow excessively because the fluid is so thick it cannot flow properly (Champion, 2003).

Schubert and Ambruster (1992), three main criteria that are necessary for formation of crude oil emulsion are: two immiscible liquids must be brought in contact, surface active component must be present as the emulsifying agent and sufficient mixing or agitating effect must be provided in order to disperse one liquid into another as droplets. Whereas, according to Champion (2003) also stated that emulsions are created when a thin film surrounds the internal phase (water), entrapping it in the oil so that it cannot readily break free. According to Champion (2003), there are certain conditions that must exist for an emulsion to be able to form which are: two immiscible liquids, an emulsifying agent and agitation.

During emulsion formed, the deformation of droplet is opposed by the pressure gradient between the external (convex) and the internal (concave) side of an interface. The pressure gradient or velocity gradient required for emulsion formation is mostly supplied by agitation. The large excess energy required to produce emulsion of small droplets can only be supplied by very intense agitation with much energy. A suitable surface active component or surface can be added to the system in order to reduce the agitation energy needed to produce a certain droplet size (Oriji, 2012). The formation of surfactant film around the droplet facilitates the process of emulsification and a reduction in agitation energy by factor of 10 or more (Becher, 2001). Stability is the persistence of an emulsion in the environment and has been identified as an important characteristic of water-in-oil emulsion. Some emulsions quickly decompose into separated oil and water phase once removed from the surface, whereas more stable emulsion can persist for days to years (Becher, 2001). Viscosity of an emulsion is correlation with its stability. Therefore viscosity is a consequence of the small droplet size and the presence of an

interfacial film on the droplets in emulsions which make stable dispersion. That is the suspended droplets do not settle out or float rapidly and the droplets do not coalesce quickly but can come together in very different ways such as sedimentation, aggregation and coalescence (Schramm, et al., 2007).

2.2 Demulsifier

Chemical demulsifier formulations are used throughout the world to improve emulsion breaking processes. While the first commercial was a solution of soap and the first demulsifier were based on sulphonated castor oil and nowadays demulsifiers are blends of highly sophisticated organic compound with surface active characteristics (Clariant, 2007). Table 1.1 is a brief listing of the chemicals used to demulsify crude oil emulsion since the beginning of the century. The industrial availability of ethylene oxide (EO) in the 1940's allowed the production of fatty acid, fatty alcohol and alkylphenol ethoxylates. This was the first time that nonionics used for this purpose (Dalmazzone, 2001).

The action of a demulsifier is to destabilize the emulsion. In order to do this the ordered structure of the natural surfactant / emulsion system must be disrupted allowing the disperse droplets to approach each other. According to Clariant (2007), the properties that are modified as a result of demulsifier addition are :

- i. Surfactant behavior (oil / water interface)
- ii. Ability to flocculate dispersed phase drops
- iii. Ability to cause coalescence of dispersed phase
- iv. Wettability of solids

Table 2.1 : Demulsifier history

Period	Rates Required (ppm)	Chemistry
1920's	1000	Soaps, salts of naphthenic acids; aromatic and alkylaromatics sulfonate; "Turkish red oil" and sulfated castor oil.
1930's	1000	Petroleum sulfonates, "mahogany soaps", oxidizer castor oil and sulfosuccinic acid esters.
Since 1935	500 to 100	Ethoxylates of fatty acids, fatty alcohols and alkylphenols.
Since 1950	100	EO/PO copolymers, p-alkylphenol formaldehyde resins + EO/PO and modifications.
Since 1965	30 to 50	Amine oxalkylates.
Since 1976	10 to 30	Oxalkylated, cyclic p-alkylphenol formaldehyde resins and complex modifications.
Since 1986	5 to 20	Polyesteramines and blends.

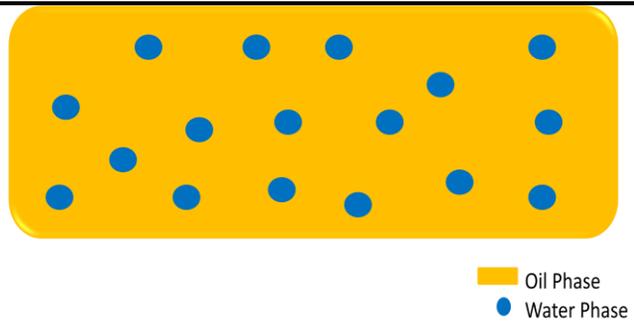
Individual demulsifiers may operate by one or more several mechanisms that are proposed to explain their efficiency when treat water-in-oil emulsion which is effective demulsifiers overcome the stabilizing effect by adsorbing at position vacant as the interfacial film is stretched (Clariant, 2007). Mobility and strong partitioning behavior of the demulsifier to the interface are the important factors. Coalescence is the result of rupture of the treated film causing formation of larger droplets. Besides, by preferentially adsorbing they also displace the pre-existing stabilizing emulsifiers from the interface. This remove the steric barrier. Interfacial tension and rheology studies confirm that this mechanism does operate. Furthermore, modern demulsifier bases have very limited solubility in crude and initial coat the interface of only the small portion of the water droplets. Demulsifier spreading then is possible by hetero-droplet interaction. This account for the spontaneous nature of the action of demulsifiers that causing rapid coalescence of water droplets. Moreover, solids such as asphalts, fine silt, iron oxides or sulphides collect at the interface. The wetting of these solids by demulsifiers will cause

them to be moved into either the oil or the water phases. It is generally more desirable to move inorganics contaminants to the water phase and this can be achieved by suitable wetting agent.

In a nutshell, the process of demulsification or demulsifier work by weakening film formed around the water by the emulsifying agents. According to Champion (2003), it is a process that occurs in four stages, as illustrated in the figure below:

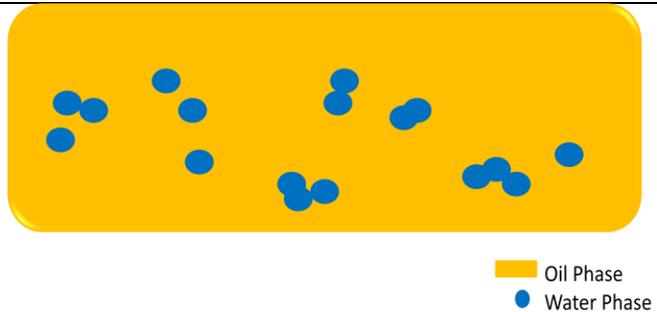
Stage 1: Small water droplets

The demulsifier chemical travels through the oil to reach the water droplet. Because the chemicals are surface active, they will displace or disrupt the emulsifying agent on the surface of the droplet, ultimately lowering the surface tension of the water droplet



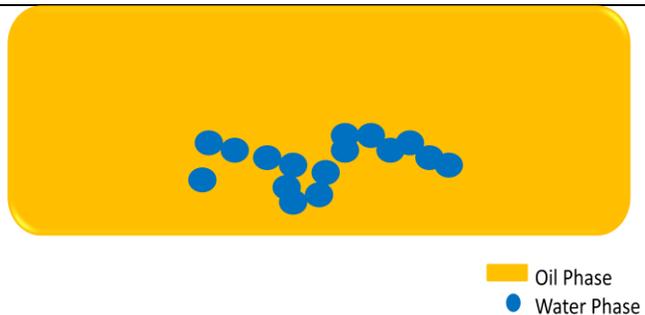
Stage 2: Flocculation

The surface of the droplets has an affinity for each other and will flocculate, or move toward each other.



Stage 3: Coalescence

Once the droplets are close together they coalesce (combine) to form larger droplets.



Stage 4: Large droplets settle out

As the droplets coalesce and grow larger they become heavy enough to fall through the oil and settle in the bottom (water section) of the treating vessel.



Figure 2.1 : Process of demulsification

Demulsifiers are generally polymeric surfactants such as copolymers ethylene oxide, polymeric chain of EO/PO of alcohols, propylene oxide, ethoxylated phenols, nonylphenols, alcohols, amines, resins and sulphonic acid salts (Dalmazzone, et al., 2005). According to Kokal (2002) and Taylor (1992) commercial demulsifier are formulated in solvents such as short-chain alcohols, aromatics or heavy aromatics naphtha and can contain a mixture of several active matters. It is believed that most of these products are not safe from an environment point of view, even if their toxicity or mutagenic effects have not been clearly demonstrated from a scientific point of view. The increase of environmental constraint make necessity to development the safer formulations in order to replace toxic chemicals such as nonyphenols (Dalmazzone, et al., 2005).

In a previous study, a large screening of commercial demulsifiers was performed by classical bottle test in the laboratory (Dalmazzone, et al., 2001). Then nontoxic polysiloxane surfactant were selected. These molecules were tested here on two types of crude oil in order to characterize their efficiency and to select high performance blends. Best products were also tested in a dynamic dispersion rig that allows reconstituting crude oil emulsion in more realistic conditions under temperature and pressure. Finally, dynamic interfacial measurement were performed with the Langmuir trough and the drop-volume techniques in order to determine the dynamic and viscoelastic properties of the crude-oil/water interface in the presence of these types of demulsifiers.

A wide range of chemical demulsifier are available in order to effect the water-in-oil emulsion separation. In principle, a complete chemical and physical characterization of both demulsifier and the emulsion to be separated would allow one to develop a fundamental understanding of the demulsification mechanism and therefore to optimize the demulsifier selection or allow synthesis of tailored demulsifiers for separation of particular emulsions (MacConnachita, etal., 1993).

2.3 Local Raw Materials

These are the list of local raw materials which is originally from plant and earth crust that were used in this project as table below:

Table 2.2 : Local Raw Materials which are from Plant and Earth Crust as Demulsifiers

Materials / Plants	Contain	Sources
Betel Leaf (Piper betle)	Polyphenols	Arambewela, L. (2005). "Studies on Piper Betle of Sri Lanka". Industrial Technology Institute, 363, Bauddhaloka Mawatha, Colombo 7.
Cashew Leaf (Anacardium occidentale)	Polyphenols	Shukri, M., Alan, C. (2011). "Polyphenols and Antioxidant Activities of Selected Traditional Vegetables". J, Trop, Agric and Fd, Sc.
Silicone		Dalmazzone, C, Noik. C. "Development of New 'Green' Demulsifier for Oil Production", paper SPE 65041 presented at the 2001 SPE International Symposium on Oilfield Chemistry, Houstan, 13-16 February.

Besides, the others local raw material used is made up from various sources. According to Emuchay, et al. (2013), there is specified function for these materials that used as demulsifier as follow:

Table 2.3 : Local Raw Materials which are from Various Sources.

Materials	Function
Coconut oil	Have dehydrating property and gives good interface control.
Liquid soap	Surfactant that gives good interface and sediment resolution.
Starch	As a water repellent.
Camphor	As a solid wetting and viscosity adjuster.
Calcium hydroxide	As a flocculants and pit booster.
Paraffin wax	As a water repellent

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

Research methodology is important as it act as guideline for completion this project. It shows the flow from the start until the end for this project. The Figure 3.1 shows the research methodology for this project.

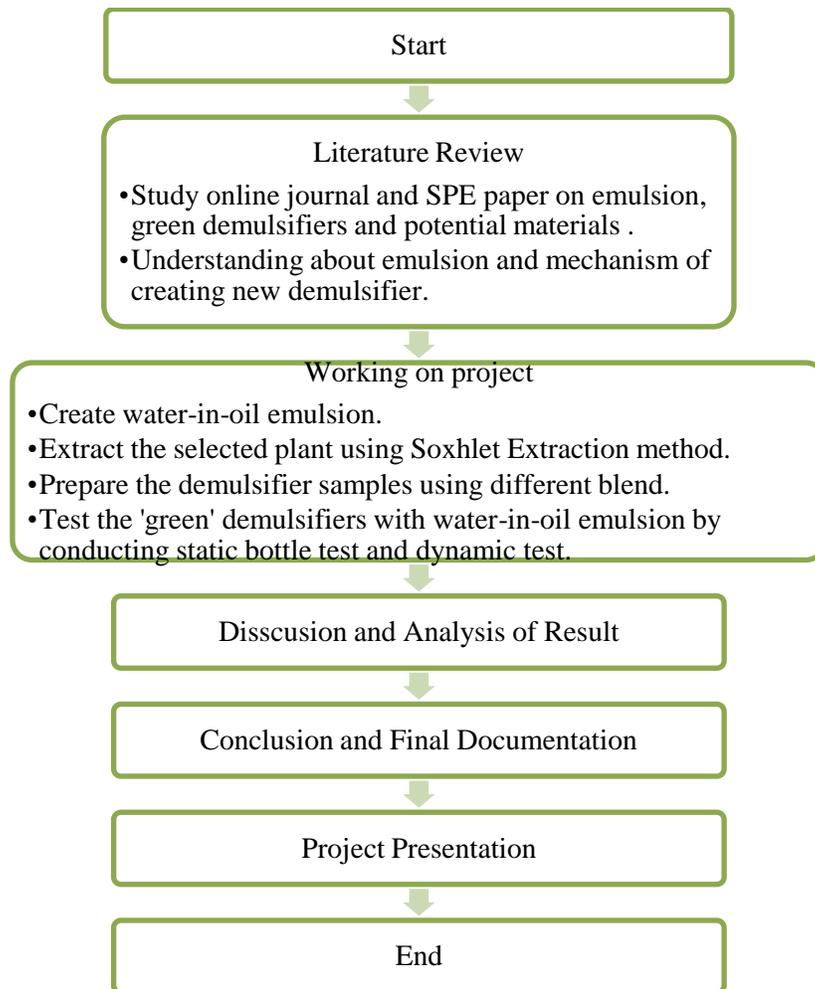


Figure 3.1 : Research Methodology of Project

3.2 Project Activities

In this project, there are three samples are prepared and two experiment conducted to determine which demulsifier is effective to separate the highest volume of water in certain time. Figure 3.2 show the illustration on overall experimental flow to result and discussion analysis.

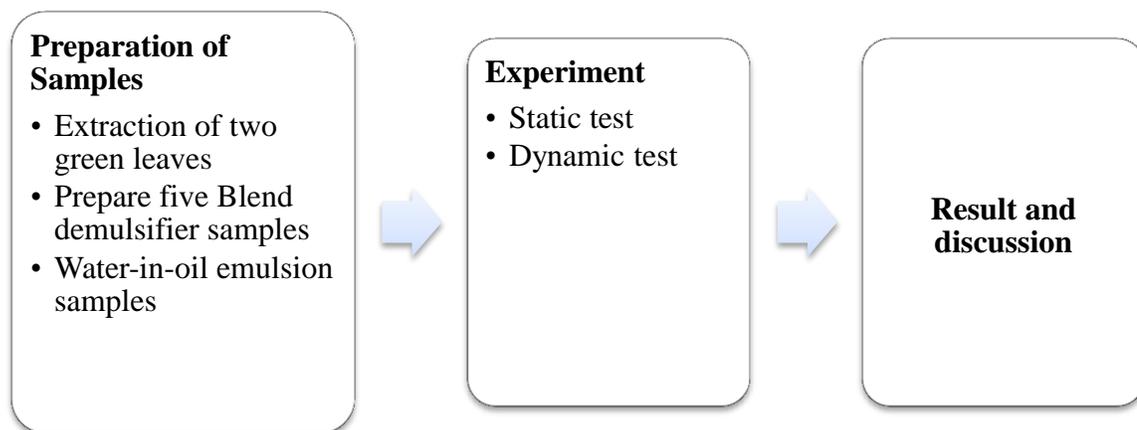


Figure 3.2 : Overall Experimental Flow

3.2.1 Extraction of Green Leaves

Green leaves that are extract are Piper Betle and Anacardium Occidentale. These two green leaves are extracted to get the polyphenols. There are several steps to extract polyphenols of these green leaves as shown in Figure 3.3.

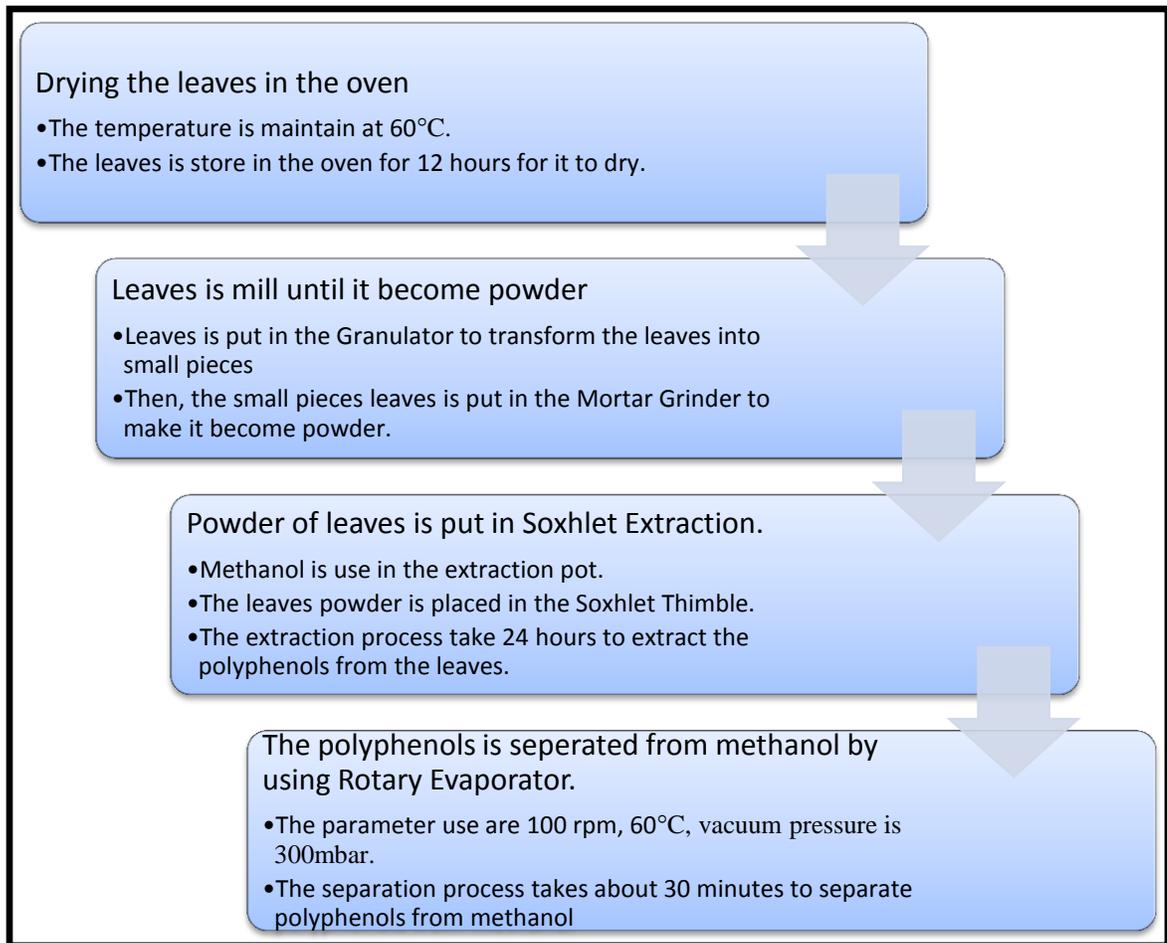


Figure 3.3 : Steps in Extracting the Green Leaves

In Figure 3.4 and Figure 3.5 show that the finish product extraction of Piper Betle and Anacardium Ocidantale.

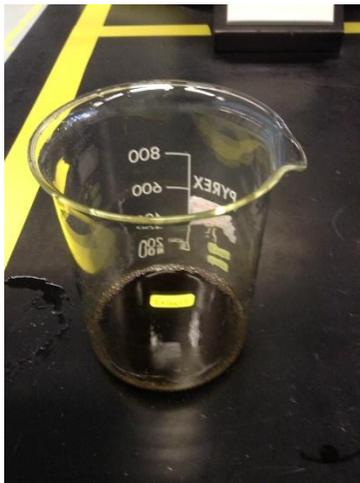


Figure 3.4 : Extract A

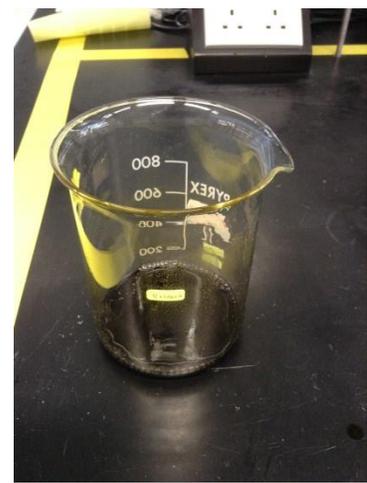


Figure 3.5 : Extract B

3.2.2 Preparation Blend Demulsifier Samples

Blend demulsifier are made from the mixture of coconut oil, liquid soap, starch, camphor, calcium hydroxide and petroleum wax. The author have prepare five different blend of demulsifier. The figure below show the steps in prepare the five blend of demulsifier.

	Blend A <ul style="list-style-type: none">•5g of camphor was melted in 15ml coconut oil and 20ml of liquid soap. 15ml of distilled water was mixed with measured starch of 25g to form a viscous paste and 5g of petroleum wax was added. The paste was thoroughly mixed with the liquid soap and 3g of calcium hydroxide was added to form a homogenous blend.
	Blend B <ul style="list-style-type: none">•10g of camphor was melted in 30ml of liquid soap and 30ml of distilled water was mixed to form a viscous paste, then 15ml of coconut oil was added. The paste was thoroughly mixed with the liquid soap and camphor to form a homogenous blend.
	Blend C <ul style="list-style-type: none">•20 g of starch was mixed with 20ml of distilled water. The viscous starch was mixed with 10ml of coconut oil respectively with the aid of the stirrer. 5g of calcium hydroxide was added and 40ml of liquid soap was added and stirred.
	Blend D <ul style="list-style-type: none">•10g of petroleum wax was melted in 20ml of coconut oil. This cause viscous paste after cooling. 80ml of liquid soap was used to dissolve the viscous paste and mixed it thoroughly, then 6g of calcium hydroxide was added to the homogenous paste.
	Blend E <ul style="list-style-type: none">•10g of camphor and 6g of petroleum wax was melted in 20ml of coconut oil. The mixture was thoroughly mixed with 80ml of liquid soap and 10g of calcium hydroxide was added. The mixture was stirred until it formed homogenous mixture.

Figure 3.6 : Steps in Prepare Five Blend of Demulsifier

Basically the various blends are mixture as follow:

Table 3.1 : Blend Mixtures

Blend	Material
A	- 25g Starch
	- 5g Camphor
	- 5g Petroleum wax
	- 20ml Liquid soap
	- 15ml Coconut oil
	- 15ml Distilled water
B	- 10g Camphor
	- 30ml Liquid Soap
	- 30ml Distilled Water
	- 15ml Coconut Oil
C	- 20g Starch
	- 5g Calcium Hydroxide
	- 40ml Liquid Soap
	- 20ml Distilled Water
- 10ml Coconut Oil	
D	- 6g Calcium Hydroxide
	- 80ml Liquid Soap
	- 20ml Coconut Oil
	- 10ml Petroleum Wax
E	- 10g Camphor
	- 10g Calcium Hydroxide
	- 6g Petroleum Wax
	- 80ml Liquid Soap
	- 20ml Coconut Oil

3.2.3 Preparation of Water-in-Oil Emulsion Samples

This samples are prepared to be used to test the various demulsifier prepared. This Figure 3.7, show the schematic diagram of how it is prepare.

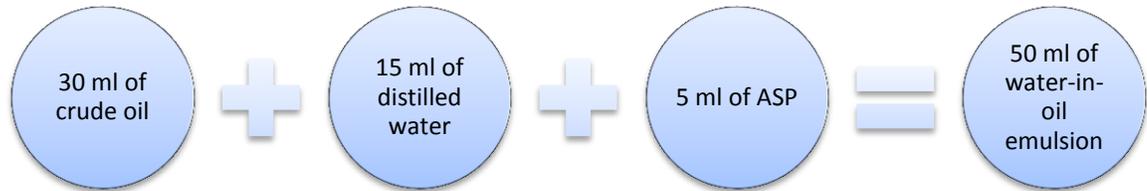


Figure 3.7 : Steps Preparation for Water-in-Oil Emulsion Samples

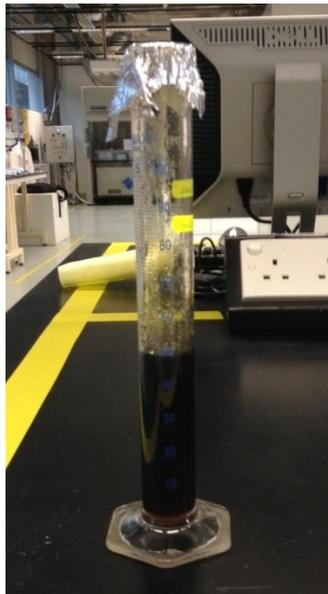


Figure 3.8 : Samples of Water-in-Oil Emulsion

The procedure below shows the steps to create water-in-oil emulsion as shown in Figure 3.7

- i. 30 ml of crude oil is mixed with 15 ml of distilled water in the 100 ml graduated cylinder.
- ii. Add 5 ml of alkaline, surfactant and polymer solution (ASP) into the 100ml graduated cylinder.
- iii. The mixture is shaken manually 100 times to make sure it mixed properly.
- iv. The mixture is keep in the oven for 10 minutes to maintain the temperature at 55°C.
- v. Repeat the step i and iv for creating 3 emulsion samples label with B1, B2 and B3 to complete for one type of demulsifier testing.

3.2.4 Static Bottle Test

- i. The demulsifier is injected into 3 different emulsion samples label with B1, B2 and B3 with different volume of demulsifier which are 1 ml, 2 ml and 3 ml.
- ii. The 100 ml graduated cylinder closed by aluminium wrapping paper is shaken manually for 50 times continuously.
- iii. After mixing the water-in-oil emulsion and demulsifier, the sample were keep in the oven at temperature maintain at 55°C.
- iv. The volume for crude oil, water and emulsion separation is measured at 10 min, 30 min, 60 min and 120 min.
- v. The result for water separation is recorded in table.
- vi. The experiment were repeated with different type of demulsifier.

3.2.5 Dynamic Test

- i. Centrifuges tube is filled with 30 ml of crude, 15 ml of distilled water and 5 ml of alkaline, surfactant and polymer (ASP) solution.
- ii. The centrifuge tube is shaken for 50 times to mix the solution.
- iii. The crude oil is maintained at 55°C by putting in the oven before the experiment started.

- iv. The 3 ml of demulsifier sample is added to the centrifuge tube.
- v. Immerse the centrifuge tubes in the water bath for 10 minutes at 55°C.
- vi. Place the centrifuge tube in the trunnion cup on opposite sides to establish a balanced condition.
- vii. Spin the centrifuge tube in Bench Centrifuge for 10 minutes with 2000 rpm.
- viii. Immediately after the Bench Centrifuge comes to the rest read and record the column or volume separation of water from the crude.
- ix. Repeat the steps i to viii by using different samples of demulsifier.

3.3 Key Milestones

Table 3.2: Project Key Milestones

Milestones	Week
Early Research Development	
<ul style="list-style-type: none"> • Research background • Scope of studies and assumptions • Information gathering • Identify tools and materials needed 	1-9
Middle Research Development	
<ul style="list-style-type: none"> • Detailed research • Developing the procedure • Data gathering • Conducting the experiment and testing 	10-19
Final Research	
<ul style="list-style-type: none"> • Analyzing the result of experiment and testing • Finalizing the result • Completing the documentation 	20-26

3.4 Gantt Chart and Milestone

Table 3.3 : Project Gantt Chart and Milestones

Project Activities	Week																													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28		
Selection of FYP title																														
Literature review and theory				Literature review on emulsion, demulsifier and other related information																										
Extended proposal submission																														
Experiment procedure development																														
Sample preparation																														
Proposal defense																														
Interim report submission																														
Lab experiment																														
Analysis the findings and result																														
Documentation																														
Final report submission																														

	progress
	suggested milestones

3.5 Tools Required

Different tool are using in the different experiments and testing as illustrate in Table 3.4. There are total five experiments and testing in this project.

The local raw materials and materials that will be used in this project are:

- i. Betel leaf (Piper betle)
- ii. Cashew leaf (Anacardium occidentale)
- iii. Silicone
- iv. Coconut oil
- v. Starch
- vi. Calcium Hydroxide
- vii. Camphor
- viii. Liquid soap
- ix. Petroleum wax or paraffin wax

Table 3.4 : Tools Required in Completing this Project

Experiment / Testing	Tools Required
Extraction of Green Leaves	<ul style="list-style-type: none"> • Still pot (extraction pot) • Soxhlet thimble • Extraction solid • Syphon arm inlet • Condenser • Methanol • Granulator • Mortal grinder • Rotary evaporator
Preparation of Blend Demulsifier Samples	<ul style="list-style-type: none"> • 100 Graduated cylinder • 50 ml Graduated cylinder • Weigher • Beaker
Creating Water-in-Oil Emulsion	<ul style="list-style-type: none"> • Magnetic stirrer • Droplet • Pipette • Water bath / Oven • Beaker • Volumetric cylinder
Static bottle test	<ul style="list-style-type: none"> • Oven • Hamilton syringe • Rotary agitator • 100 ml Graduated cylinder • Beaker
Dynamic test	<ul style="list-style-type: none"> • Bench centrifuge • Centrifuge tube • Oven

CHAPTER 4

RESULT AND DISCUSSION

4.1 Static Test

Static test is conducted using bottle test. It is to determine the volume separation of water in milliliter with time in minutes. There are nine types of demulsifier that have been test with water-in-oil emulsion which are two from the industry; Sillbreak 322 and Sillbreak 400, two demulsifier from the extraction from plant; Extract Betel Leaf (Piper Betle) and Extract Cashew Leaf (Anacardium Ocidentale) and five demulsifier which are blend from specific materials and chemicals; Blend A, Blend B, Blend C, Blend D and Blend E.

Based on the Table 4.1, the demulsifier dosage used are 1ml, 2ml and 3ml where else the volume separation of water is observed at 0 min, 10 min, 30 min, 60 min and 120 min. For the first time, 0ml demulsifier dosage injected means that no demulsifier injected. It is to know the stability of the water-in-oil emulsion that has been prepared. All these testing were conducted in 55°C as it is the optimum operating temperature of the crude oil that have been used. These are the result from the static test as in the Table 4.1 below:

Table 4.1 : Summary of Static Test Result

Product	Demulsifier Dosage (ml)	Volume Separation of Water (ml)				
		0 min	10 min	30 min	60 min	120 min
Blank	0	0	0	0	0	0
Sillbreak 322	1	0	7	7	8	8
	2	0	10	11	11	12
	3	0	10	11	11	12
Silbreak 400	1	0	6	7	9	9
	2	0	11	11	12	12
	3	0	12	12	12	12
Extract Betel Leaf	1	0	0	1	1	2
	2	0	1	3	4	4
	3	0	1	3	4	5
Extract Cashew leaf	1	0	0	1	2	2
	2	0	0	1	2	4
	3	0	1	2	3	4
Blend A	1	0	3	4	4	4
	2	0	6	6	7	7
	3	0	6	6	7	7
Blend B	1	0	1	2	2	2
	2	0	3	4	4	4
	3	0	4	5	5	5
Blend C	1	0	0	1	2	2
	2	0	0	1	3	4
	3	0	1	3	4	5
Blend D	1	0	0	1	1	2
	2	0	1	1	2	3
	3	0	1	2	3	5
Blend E	1	0	2	3	3	3
	2	0	4	6	6	7
	3	0	4	6	7	8

4.1.1 Results on Performance Based on Type of Demulsifier

4.1.1.1 Type of Demulsifier : Blank

Table 4.2 show the volume separation of water using Blank demulsifier. This testing as to show or prove that water-in-oil emulsion that used in this experiment is stable and do not break without demulsifier. It also as control for this experiment.

Table 4.2 : Volume Separation of Water using Blank

Product	Demulsifier Dosage (ml)	Volume Separation of Water (ml)				
		0 min	10 min	30 min	60 min	120 min
Blank	0	0	0	0	0	0

4.1.1.2 Type of Demulsifier : Sillbreak 322

Table 4.3 and Figure 4.1 shows the volume separation of water using Sillbreak 322. Sillbreak 322 is from the industry. Sillbreak 322 is used as the benchmark of the standard for volume separation of water for my project. Based on the Figure 10, the demulsifier dosage performance for 2 ml and 3 ml is same and also at the 120 min the volume of water separation is the highest for this demulsifier which are 12 ml. For 1ml dosage of the demulsifier, at 10 min and 30 min the volume separation of water is 7 ml and increase after 60 min to 8 ml and keep constant at 120 min. It can be conclude that the effective demulsifier dosage is 2 ml to treat water-in-oil emulsion.

Table 4.3 : Volume Separation of Water using Sillbreak 322

Product	Demulsifier Dosage (ml)	Volume Separation of Water (ml)				
		0 min	10 min	30 min	60 min	120 min
Sillbreak 322	1	0	7	7	8	8
	2	0	10	11	11	12
	3	0	10	11	11	12

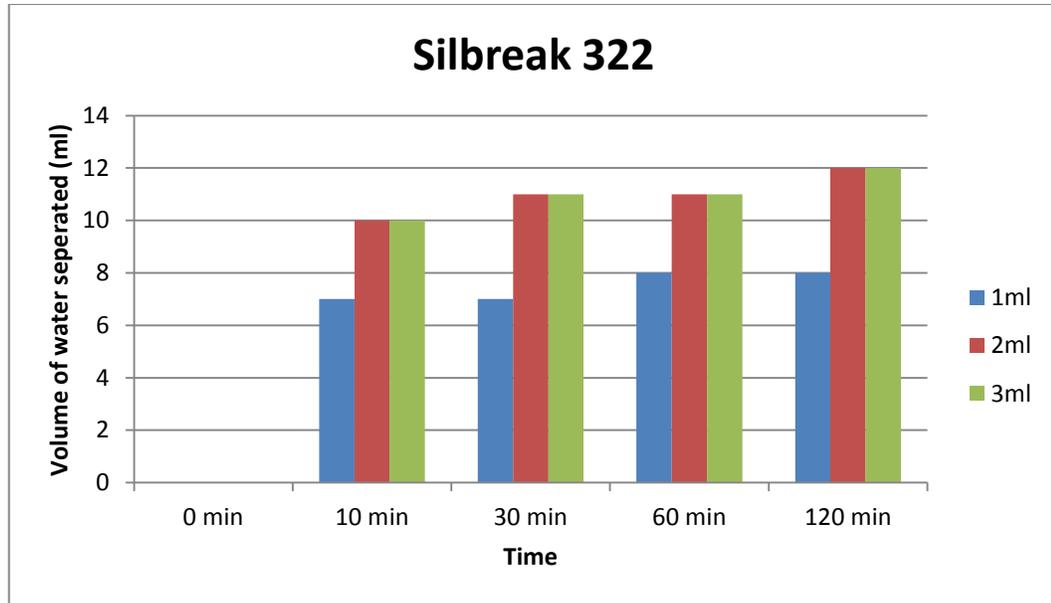


Figure 4.1 : Volume Separation of Water using Silbreak 322

4.1.1.3 Type of Demulsifier : Silbreak 400

Table 4.4 and Figure 4.2 shows the volume separation of water using Silbreak 400. Silbreak 400 is from the industry. Silbreak 400 is also used as the benchmark of the standard for volume separation of water for my project. Based on the Figure 4.2, this demulsifier is very fast in separating water as in 10 min for 3 ml, it separate 12 ml of water and maintain the same amount until 120 min. For 1 ml dosage of demulsifier, at 10 min it separate 6 ml and increase until 60 min until 9 ml and keep constant until 120 min with 9 ml of water separated. For 2 ml dosage of demulsifier, at 10 min and 30 min water separate 11 ml and increase for 60 min and 120 min to 12 ml. It can be conclude that 3 ml dosage is the most effective dosage for this demulsifier to treat water-in-oil emulsion.

Table 4.4 : Volume Separation of Water using Sillbreak 400

Product	Demulsifier Dosage (ml)	Volume Separation of Water (ml)				
		0 min	10 min	30 min	60 min	120 min
Sillbreak 400	1	0	6	7	9	9
	2	0	11	11	12	12
	3	0	12	12	12	12



Figure 4.2 : Volume Separation of Water using Sillbreak 400

4.1.1.4 Type of Demulsifier : Extract Betel Leaf

Table 4.5 and Figure 4.3 show the volume separation of water using Extract Betel Leaf. Based on the Figure 4.3, 1 ml dosage of Extract Betel Leaf is not very effective in separation of water from water-in-oil emulsion as in 120 min just 2 ml water separated. For 2 ml and 3 ml dosage of Extract Betel Leaf, within 30 min 3 ml of water separated and in 60 min 4 ml of water separated but in 120 min, 3 ml dosage of Extract Betel Leaf separated 5 ml of water while 2 ml dosage of Extract Betel Leaf keep constant with 4 ml

of water separated. Thus, it can be conclude that 3 ml dosage of Extract Betel Leaf is most effective amount for Extract Betel Leaf to treat water in oil emulsion.

Table 4.5 : Volume Separation of Water using Extract Betel Leaf

Product	Demulsifier Dosage (ml)	Volume Separation of Water (ml)				
		0 min	10 min	30 min	60 min	120 min
Extract Betel Leaf	1	0	0	1	1	2
	2	0	1	3	4	4
	3	0	1	3	4	5

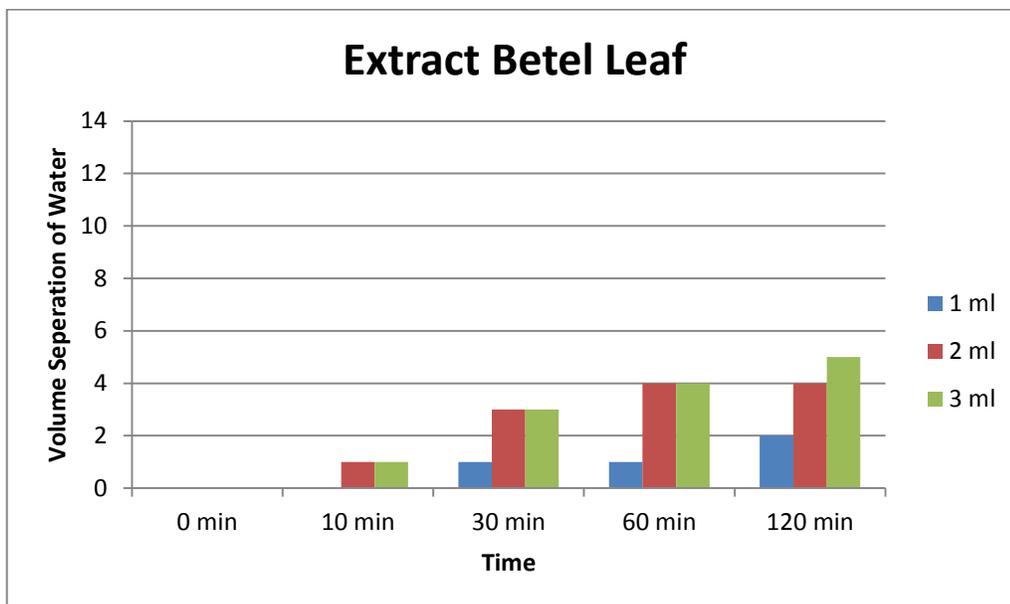


Figure 4.3 : Volume Separation of Water using Extract Betel Leaf

4.1.1.5 Type of Demulsifier : Extract Cashew Leaf

Table 4.6 and Figure 4.4 shows the volume separation of water using Extract Cashew Leaf. Based on the Figure 4.4, in 10 min just 3 ml dosage of Extract Cashew Leaf can separate water with 1 ml. At 30 min, 1 ml and 2 ml dosage of Extract Cashew Leaf can only separate 1 ml of water while for 3 ml dosage of Extract Cashew Leaf manage to separate 2 ml of water. The trend same in 60 min by increasing 1 ml for each dosage. At 120 min, for 1 ml dosage of Extract Cashew Leaf is constant as 60 min but the 2 ml and 3ml dosage of Extract Cashew Leaf separate water to 4 ml. Thus, it can be conclude that 3 ml dosage of Extract Cashew Leaf is most effective amount to treat water-in-oil emulsion.

Table 4.6 : Volume separation of water using Extract Cashew Leaf

Product	Demulsifier Dosage (ml)	Volume Separation of Water (ml)				
		0 min	10 min	30 min	60 min	120 min
Extract Cashew Leaf	1	0	0	1	2	2
	2	0	0	1	2	4
	3	0	1	2	3	4

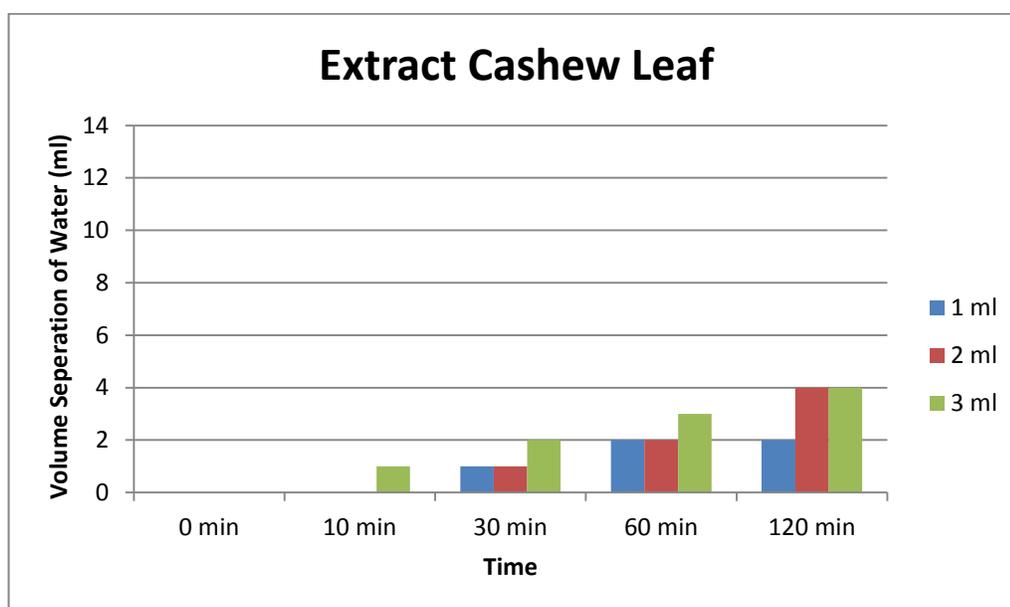


Figure 4.4 : Volume Separation of Water using Extract Cashew Leaf

4.1.1.6 Type of Demulsifier : Blend A

Table 4.7 and Figure 4.5 shows the volume separation of water using Blend A. According to the Figure 4.5 for 1 ml dosage of demulsifier, at 10 min the volume separation of water is 3 ml and it increase for 30 min till 4 ml and after that it keep constant until 120 min. Besides, for 2 ml and 3 ml dosage of demulsifier, the volume of water separation is same for both of them with at 10 min and 30 min the volume of water separation is 6 ml and at 60 min and 120 min is 7 ml. It can be conclude that, 2 ml dosage of the demulsifier for Blend A is the most effective to treat water-in-oil emulsion.

Table 4.7 : Volume Separation of Water using Blend A

Product	Demulsifier Dosage (ml)	Volume Separation of Water (ml)				
		0 min	10 min	30 min	60 min	120 min
Blend A	1	0	3	4	4	4
	2	0	6	6	7	7
	3	0	6	6	7	7

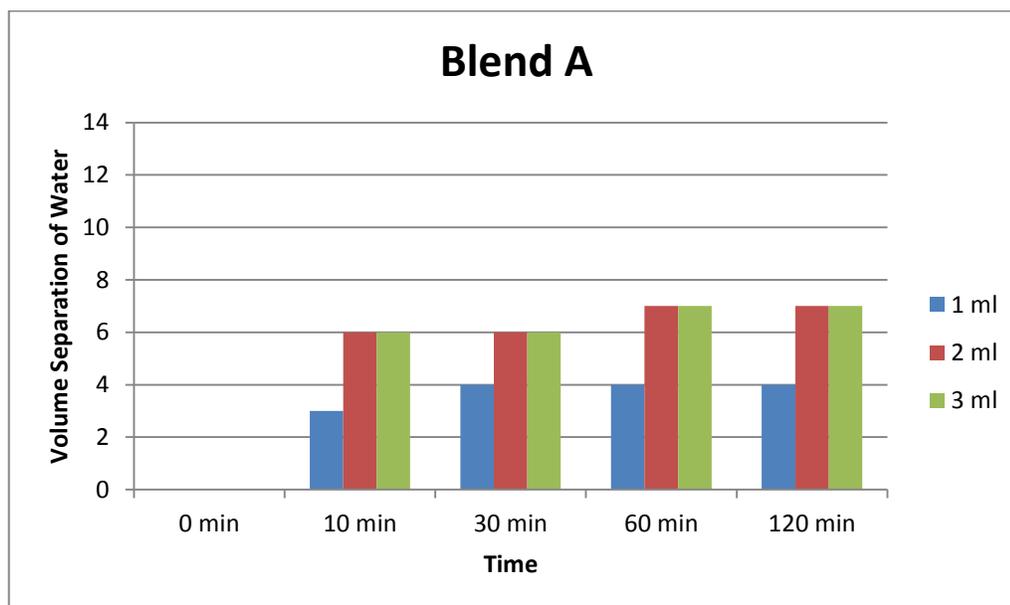


Figure 4.5 : Volume Separation of Water using Blend A

4.1.1.7 Type of Demulsifier : Blend B

Table 4.8 and Figure 4.6 shows the volume separation of water using Blend B. Based on the Figure 4.6, all dosage have low volume separation of water at initial 10 min then increase at 30 min then keep constant until 120 min. It can be conclude that, 3 ml dosage for Blend B is most effective dosage for separation of water from oil although it is low compare to Blend

Table 4.8 : Volume Separation of Water using Blend B

Product	Demulsifier Dosage (ml)	Volume Separation of Water (ml)				
		0 min	10 min	30 min	60 min	120 min
Blend B	1	0	1	2	2	2
	2	0	3	4	4	4
	3	0	4	5	5	5

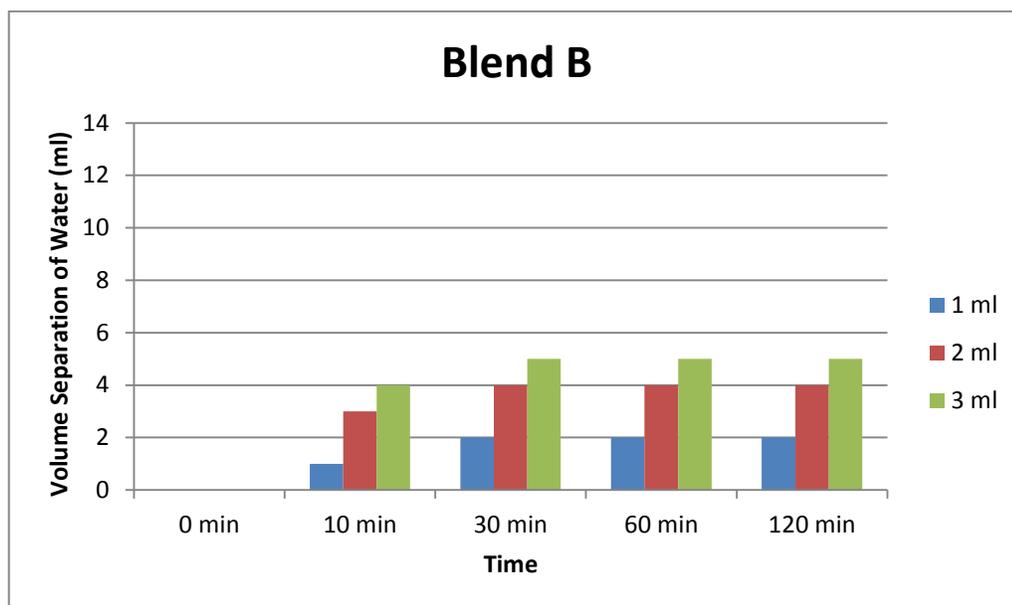


Figure 4.6 : Volume Separation of Water using Blend B

4.1.1.8 Type of Demulsifier : Blend C

Table 4.9 and Figure 4.7 shows the volume separation of water using Blend C. Based on the Figure 14, for 1 ml and 2 ml dosage of demulsifier at 10 min, there are no water separation at this time but water start to separate at 30 min for 1 ml. Then, for 1ml dosage of demulsifier, volume separation of water at 60 min is 2 ml and keep constant for 120 min whereas for 2 ml dosage of demulsifier, volume separation of water at 60 min is 3 ml and increase to 4 ml at 120 min. For blend C, 3 ml dosage of demulsifier can separate most water compare to 1 ml and 2 ml dosage of demulsifier. Clearly can be seen from the Figure 4.5, at 120 min its separated 5 ml of water.

Table 4.9 : Volume Separation of Water using Blend C

Product	Demulsifier Dosage (ml)	Volume Separation of Water (ml)				
		0 min	10 min	30 min	60 min	120 min
Blend C	1	0	0	1	2	2
	2	0	0	1	3	4
	3	0	1	3	4	5

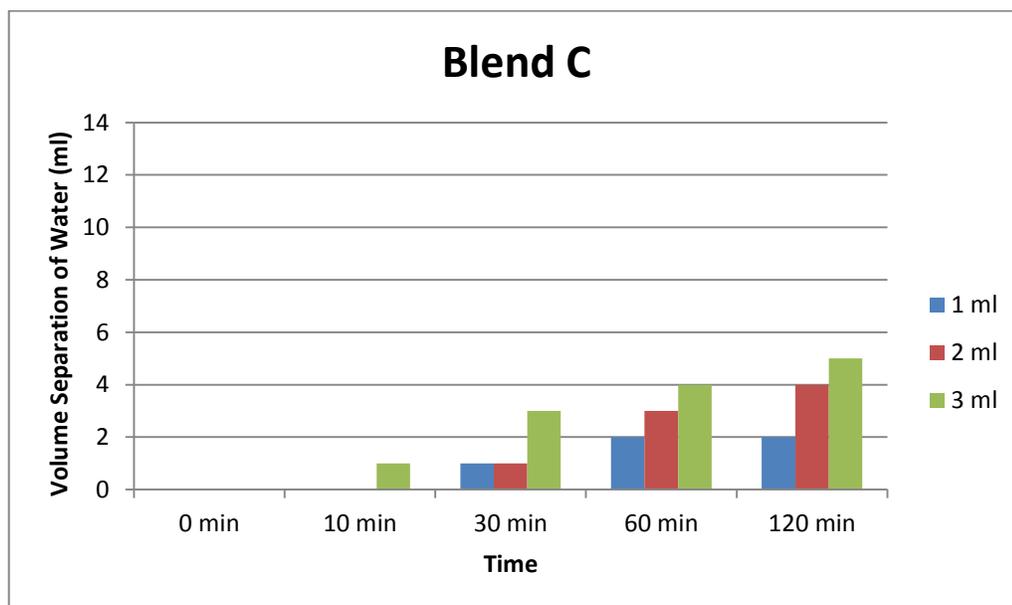


Figure 4.7 : Volume Separation of Water using Blend C

4.1.1.9 Type of Demulsifier : Blend D

Table 4.10 and Figure 4.8 shows the volume separation of water using Blend D. Based on the Figure 15, for 1 ml dosage of demulsifier, there are no separation at first 10 min but at the 30 min 1 ml water start to separate and the volume same for 60 min and slightly increase for 120 min to 2 ml. For 2 ml dosage of demulsifier, in the 30 min the volume of water separate is 1 ml and its increase to 2 ml at 60 min and keep increase until 3 ml at 120 min. 3 ml dosage of demulsifier can separate water the most for Blend D which is 5 ml at 120 min.

Table 4.10 : Volume Separation of Water using Blend D

Product	Demulsifier Dosage (ml)	Volume Separation of Water (ml)				
		0 min	10 min	30 min	60 min	120 min
Blend D	1	0	0	1	1	2
	2	0	1	1	2	3
	3	0	1	2	3	5

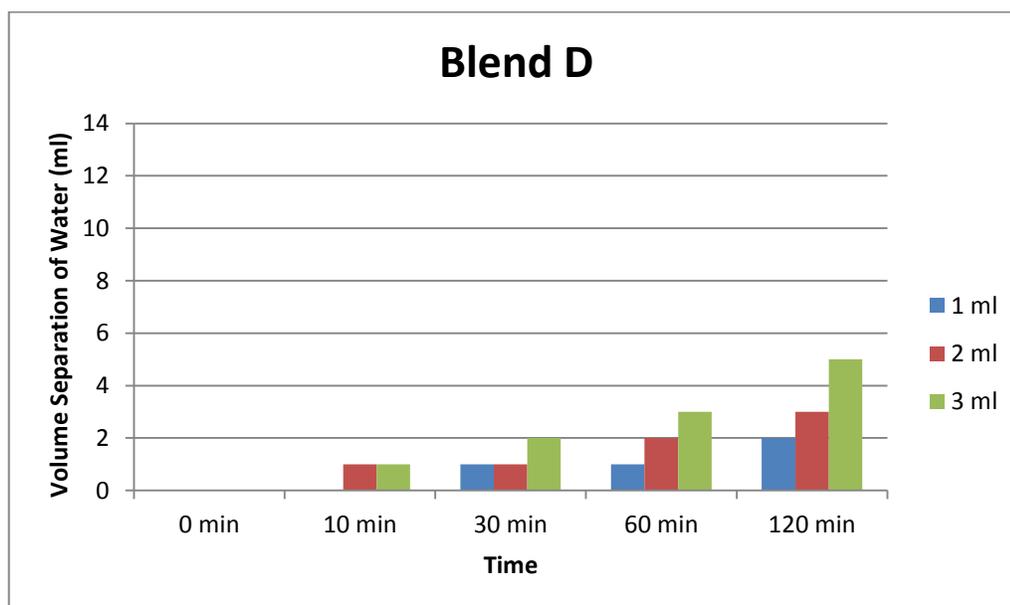


Figure 4.8 : Volume Separation of Water using Blend D

4.1.1.10 Type of Demulsifier : Blend E

Table 4.11 and Figure 4.9 shows the volume separation of water using Blend E. Based on the Figure 16, for 1 ml dosage of Blend E, at 10 min the volume separation of water is 2 ml and keep constant until 120 min. Besides, for 2 ml dosage of Blend E, at 10 min the volume separation of water is 4 ml and increase to 6 ml at 30 min and keep constant until 60 min and increase again to 7 ml at 120 min. For blend E, 3 ml dosage can separated the most volume of water which is 8 ml in 120 min. Thus, 3ml of water is the best dosage for Blend E to separate water-in-oil emulsion.

Table 4.11 : Volume Separation of Water using Blend E

Product	Demulsifier Dosage (ml)	Volume Separation of Water (ml)				
		0 min	10 min	30 min	60 min	120 min
Blend E	1	0	2	3	3	3
	2	0	4	6	6	7
	3	0	4	6	7	8

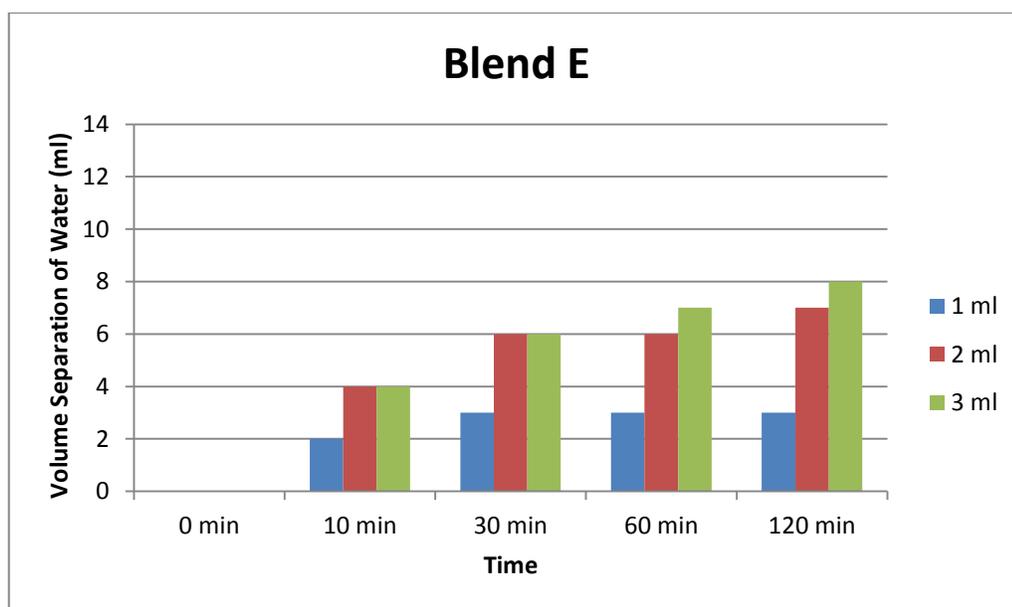


Figure 4.9 : Volume Separation of Water using Blend E

4.1.2 Result on Performance Based on Demulsifier Dosage

4.1.2.1 Dosage of Demulsifier : 1 ml

Table 4.12 show the summary of volume separation of water for 1 ml dosage for different type of demulsifier and Figure 4.10 show performance plot for 1 ml dosage for different type of demulsifier. Silbreak 322 and Silbreak 400 are from the industry and used as demulsifier benchmark to the others demulsifier. Based on the Figure 19, the highest volume separation of water for 1 ml dosage of demulsifier is Blend A followed by Blend E. The others demulsifier is not perform well. Thus, it can be conclude that for 1 ml dosage of demulsifier, Blend A and Blend E is the best in term of volume separation of water with time.

Table 4.12 : Summary of Volume Separation of Water for 1 ml Dosage for Different Type of Demulsifier

Product	Volume Separation of Water (ml)				
	0 min	10 min	30 min	60 min	120 min
Sillbreak 322	0	10	11	11	12
Sillbreak 400	0	6	7	9	9
Extract Betel Leaf	0	0	1	1	2
Extract Cashew Leaf	0	0	1	2	2
Blend A	0	3	4	4	4
Blend B	0	1	2	2	2
Blend C	0	0	1	2	2
Blend D	0	0	1	1	2
Blend E	0	2	3	3	3

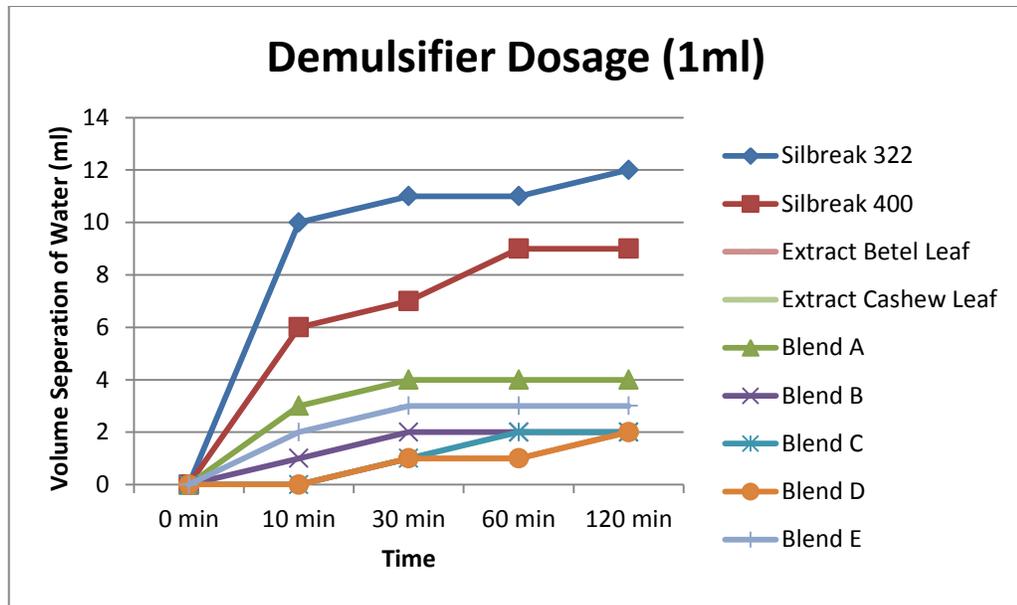


Figure 4.10 : Performance Plot for 1 ml Dosage for Different Type of Demulsifier

4.1.2.2 Dosage of Demulsifier : 2 ml

Table 4.13 show the summary of volume separation of water for 2 ml dosage for different type of demulsifier and Figure 4.11 show the performance plot for 1 ml dosage for different type of demulsifier . Silbreak 322 and Silbreak 400 are from the industry and used as demulsifier benchmark to the others demulsifier. Based on Figure 4.11, the performance of Blend A and Blend E is almost the same and the best compare to others demulsifier. At 120 min both separate 7 ml of water which is the highest compare to the others Blend and Extract. The others Blend or Extract, at 120 min the highest for water separation is only 4 ml. Thus, it can conclude that for 2 ml dosage of demulsifier, Blend A and E is the most effective demulsifier to separated water-in-oil emulsion.

Table 4.13 : Summary of Volume Separation of Water for 2 ml Dosage for Different Type of Demulsifier

Product	Volume Separation of Water (ml)				
	0 min	10 min	30 min	60 min	120 min
Silbreak 322	0	10	11	11	12
Silbreak 400	0	11	11	12	12
Extract Betel Leaf	0	1	3	4	4
Extract Cashew Leaf	0	0	1	2	4
Blend A	0	6	6	7	7
Blend B	0	3	4	4	4
Blend C	0	0	1	3	4
Blend D	0	1	1	2	3
Blend E	0	4	6	6	7

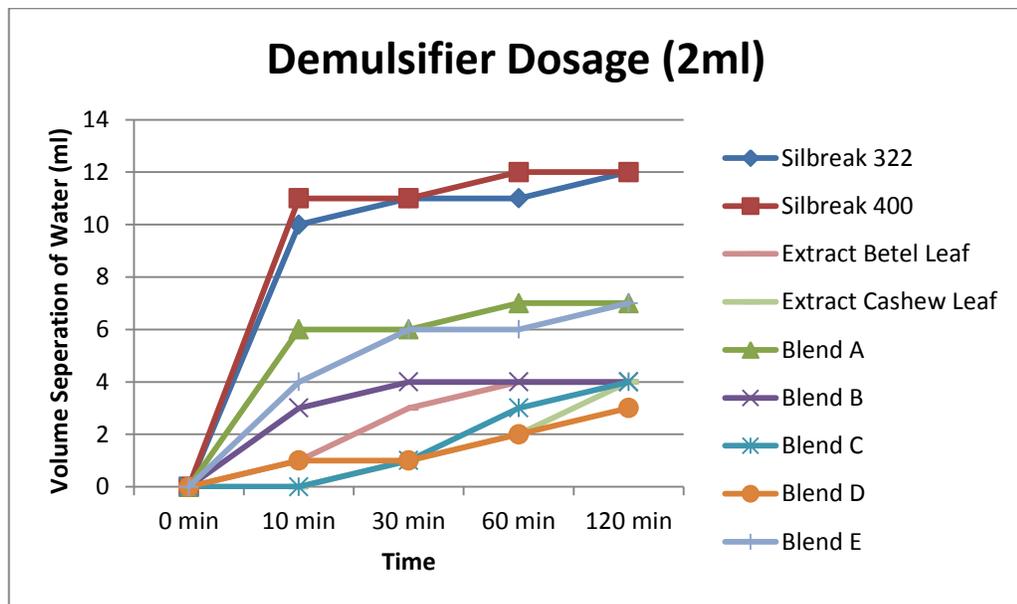


Figure 4.11 : Performance Plot for 2 ml Dosage for Different Type of Demulsifier

4.1.2.3 Dosage of Demulsifier : 3 ml

Table 4.14 show the summary of volume separation of water for 3 ml dosage for different type of demulsifier and Figure 4.12 show the comparison of volume separation of water for 2 ml dosage for different type of demulsifier. Silbreak 322 and Silbreak 400 are from the industry and used as demulsifier benchmark to the others demulsifier. Based on the Figure 4.12, at 120 min, Blend E has highest volume of water separation which is 8 ml followed by Blend A which is 7 ml and followed by the others Blend and Extract are mostly 5 ml and one of it 4 ml. Thus, it can be conclude that for 3 ml dosage of demulsifier, Blend E is the most effective to separate water and followed by Blend A.

Table 4.14 : Summary of Volume Separation of Water for 3 ml Dosage for Different Type of Demulsifier

Product	Volume Separation of Water (ml)				
	0 min	10 min	30 min	60 min	120 min
Sillbreak 322	0	10	11	11	12
Sillbreak 400	0	12	12	12	12
Extract Betel Leaf	0	1	3	4	5
Extract Cashew Leaf	0	1	2	3	4
Blend A	0	6	6	7	7
Blend B	0	4	5	5	5
Blend C	0	1	3	4	5
Blend D	0	1	2	3	5
Blend E	0	4	6	7	8

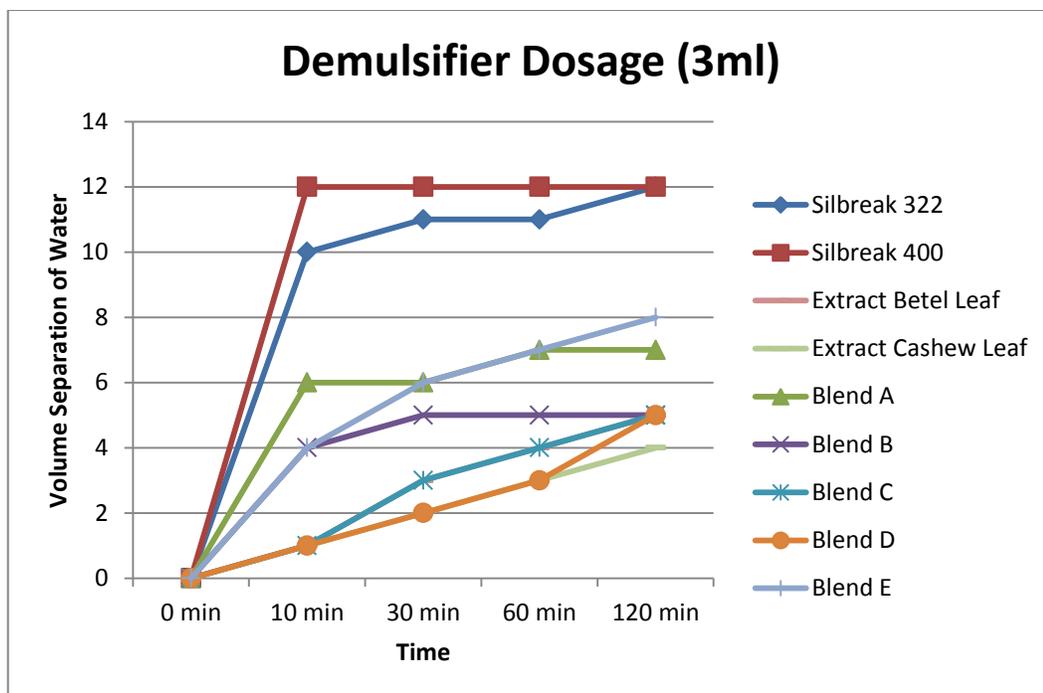


Figure 4.12 : Performance Plot for 3 ml Dosage for Different Type of Demulsifier

4.1.3 Analysis and Discussion on Static Test

According to the static bottle test, the best demulsifier based on the volume separation of water with time are Blend A and Blend E. The optimum dosage for Blend A and Blend E is 3 ml as it effectively separate water from oil compared to 1 ml and 2 ml dosage of demulsifier. The others Blend which are Blend B, Blend C and Blend D as well as Extract A and Extract B did not show good or effective performance to separate water from oil.

Errors and inaccuracies are inevitable in every experiment. Inaccuracies of measurement is the most predicted human error to be experienced in this test as lots of measuring involved such as reading the level of water separated from oil. Besides, the errors in weighing the various materials to produce Blend also effect the overall outcomes of the Blend performances.

4.2 Dynamic Test

Dynamic test is conducted using Bench Centrifuge. This method also used to separate water with oil. There are certain parameter used to conduct this testing which are 2000rpm, the duration is 10 minutes and the temperature is 55°C. There are nine types of demulsifier that have been test with water-in-oil emulsion using this test method which are two from the industry; Sillbreak 322 and Sillbreak 400, five demulsifier which are blend from specific materials and chemicals; Blend A, Blend B, Blend C, Blend D and Blend D and two demulsifier from the extraction from plant; Extract A (Piper Betle) and Extract B (Anacardium Occidentale).

Based on the Table 4.15 which is summary of dynamic test result using 3ml dosage of demulsifier and Figure 4.13 which is dynamic test result using 3ml dosage of demulsifier, the Blank dosage of demulsifier is used as control for this experiment. It shows that there are no separation of water which is indicate that the water-in-oil emulsion sample is stable. Sillbreak 322 and Sillbreak 400 show that, it separate water for 14 ml and it is as the bench mark for water separation using chemical demulsifier. Blend E show that, the highest volume separation of water which is 11 ml followed by Blend A which is 10 ml and the other chemical demulsifier do not show good performance of demulsifier which is they just separate water between 5 ml and 7 ml. Thus, the author can conclude that the best demulsifier are Blend E and Blend A compare to the others Blend and Extract. The table below shows the result from the dynamic test.

Table 4.15 : Summary of Dynamic Test Result using 3ml Dosage of Demulsifier

Product	Volume Separation of Water (ml)
Blank	0
Sillbreak 322	14
Sillbreak 400	14
Extract Betel Leaf	6
Extract Cashew Leaf	5
Blend A	10
Blend B	7
Blend C	5
Blend D	6
Blend E	11

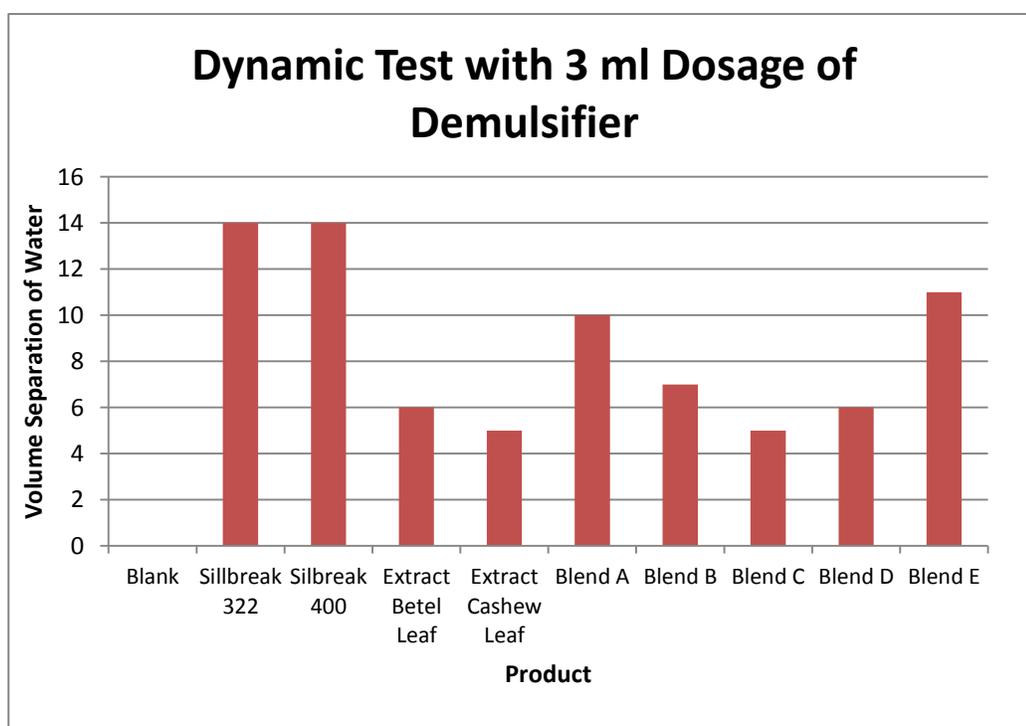


Figure 4.13 : Dynamic Test Result using 3ml Dosage of Demulsifier

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

As conclusion, based on static test and dynamic test the best demulsifier are Blend A and Blend E. It is based on the highest volume of water separated from crude oil and the faster time for water separate from crude oil which can be determine from the static test and dynamic test. It also shows that Blend materials are more effective as demulsifier compare to Extract materials. Clearly can be seen that the performance of Blend chemical demulsifier and Extract chemical demulsifier do not achieve as good as industrial demulsifier, thus the improvement must be made in the future to improve the performance of Blend demulsifier and Extract demulsifier.

In a nutshell, the author had achieved the main objectives to identify severals local raw materials and blends to be synthetic demulsifier focuses on 'green' demulsifier for water-in-oil emulsion and to determine the most effective 'green' demulsifier by selecting based on certain criteria which are the highest volume of water separated from crude oil and the faster time for water separate from crude oil. Besides, from this project the author have understanding about the concepts of water-in-oil emulsion, mechanism of demulsifiers, selecting a few potential local raw materials which are green demulsifier and other various blend materials as demulsifiers, samples preparation, conducting static test and dynamic test.

Based on the literature review, this project is relevant as demulsifiers is an important chemical used widely in the oil industry to prevent the formation of emulsion. This project also relevant because focusing on the 'green' demulsifier which will be environmental friendly and cheaper than conventional demulsifiers. The author believes

that this study will have significant contribution to the oil and gas industry especially in Malaysia.

5.2 Recommendations

Recommendations for further study about green chemical demulsifier are as below:

- More research work should be done in local raw materials formulated demulsifier as its more cost effective and more environmental friendly.
- More screening and testing of local raw materials as to get the best materials for demulsifier.
- Chemicals demulsifier should reduce used of too many chemicals as its give environmental effect.

REFERENCES

- Arambewela, L. (2005). "Studies on Piper Betle of Sri Lanka". Industrial Technology Institute, 363, Bauddhaloka Mawatha, Colombo 7.
- Becher, P. (2001). "Emulsion: Theory and Practice. 3rd Edition, Oxford University Press: New York.
- Champion. (2003). "Fundamentals of Chemical Treating", P.O. Box 450499, Houston, TX 77245.
- Clariant. (2007). Production Chemicals and Microbiology", *hts consultants*.
- Dalmazzone, C, Noik. C. "Development of New 'Green' Demulsifier for Oil Production", paper SPE 65041 presented at the 2001 SPE International Symposium on Oilfield Chemistry, Houston, 13-16 February.
- Dalmazzone. C, Noik, C, Komunjer. L. "Mechanism of Crude-Oil/Water Interface Destabilization by Silicone Demulsifiers", SPE Journal, (March 2005).
- Emuchay, D., Onyekonwu, M. O., Ogolo, N. A. and Ubani, C. (2013) "Breaking of Emulsion Using Locally Formulated Demulsifiers". Paper SPE 167528 presented at the Nigeria Annual International Conference and Exhibition, Lagos, Nigeria, 30 July – 1 August 2013.
- Graham, D.E. "Crude Oil Emulsions: Their Stability and Resolution," *Spec. Publ. R. Soc. Chem.*(1982) 61, 155.
- Kokal, S. "Crude-Oil Emulsions: A State-Of-The-Art Review," paper SPE 77497 presented at the 2002 SPE Annual Technical Conference and Exhibition, San Antonio, Texas, 29 September-2 October.

MacConnachita. C. A, Miluka. R. J, Kurucz. L, Scoular. R. J. “Correlation of Demulsifier Performance and Demulsifier Chemistry”, paper no.39 presented at the Fifth Petroleum Conference of the south Saskatchewan section, the petroleum society of CIM, Regina, 18-20 October 1993.

Oriji A.B. (2012). “Breaking of Emulsion Using Locally Formulated Demulsifiers”. Paper SPE 167528 presented at the Nigeria Annual International Conference and Exhibition, Abuja, Nigeria, 6-8 August 2012.

Oriji, A.B. “Suitability of Local Demulsifier as an Emulsion Treating Agent in Oil and Gas Production,” paper SPE 162989 presented at the 2012 SPE Nigerian Annual International Conference and Exhibition held in Abuja, Nigeria, 6-8 August 2012.

Schonfeldt, N. Grenzflächenaktive Ethlynoxidaddukte, Wissenschaft-licher Verlag. Stuttgart (1976) 804-813; Supplement (1984) 380-38.

Schramm, L.L (Ed). (1992) Emulsion: Fundamentals and Applications in the Petroleum Industry, Adv. Chem. Ser. 231, ACS, Washington DC.

Schramm. L. P., Anderez. J. and Salager. J. L. (2007). “Emulsions: Fundamentals and Application in the Petroleum Industry”. Advances in chemistry. Vol. 231, American Chemical Society, Washington DC.

Schubert and Armbruster. (1992). Emulsion stability, in Encyclopedia of emulsion technology.

Shukri, M., Alan, C. (2011). “Polyphenols and Antioxidant Activities of Selected Traditional Vegetables”. J, Trop, Agric and Fd, Sc.

Taylor, S.E. “Resolving Crude Oil Emulsions”, *Chemistry and Industry* (October 1992) 770.

Van der Zande, M.J. (2000) “Droplet break up in the turbulent oil-in-water flow through restriction”, PhD Thesis, Delft University of Technology, The Netherlands.