1. Introduction

An emulsion is likely to form between two immiscible liquids that are mixed together, where one is dispersed as droplets in the other1). The formation of an emulsion significantly affects the production facilities at the surface and the amount of oil recovery as it can cause problems to the operation activities. The size of the droplets can be of all ranges of size, from large sizes that are visible to the human eye to one sub-micron in size. There are several demulsification techniques to break the emulsion which include the application of heat, mechanical or chemical2). In this project, we focused on the chemical part only. Demulsification process can be done by reducing the interfacial energy as an emulsion is thermodynamically unstable.

2. Review of Literature

2.1. Emulsions

Emulsion can be divided into three types as shown in Fig. 1: water-in-oil (W/O) emulsion where water is the dispersed phase and oil is the continuous phase, oil-in-water (O/W) emulsion in which oil is the dispersed phase and water is the continuous phase and multiphase...
emulsion which consists of both W/O emulsion and O/W emulsion simultaneously. Mayonnaise, ice cream, soap and body lotion are examples of stable emulsions.

The three main conditions that encourage the stability of the emulsion are that the liquids involved must be immiscible, the presence of an emulsifying agent or emulsifier, and sufficient agitation. In the petroleum industry, the most common emulsifying agents found include asphaltenes, solid paraffin, resinous substances and naphthenes.

Four main factors affect the stability of the emulsion which are viscosity, specific gravity, water percentage and age of emulsion. As the viscosity of the liquid increases, the resistance of the liquid to flow will also increase and vice versa. Often, if a liquid of high viscosity is heated, the viscosity of the liquid decreases and causes the liquid to flow freely. Heavy oils with a high specific gravity and low API gravity in W/O emulsion tend to cause the water droplets to stay in suspension longer than the oil with low specific gravity and high API gravity. The relationship between specific gravity and API gravity can be illustrated by using the formula below.

\[
\text{API gravity} = \frac{141.5}{\text{Specific gravity}} - 131.5
\]

A small percentage of W/O will emulsify more thoroughly and permanently than a large water percentage. The wells that produce only small quantities of water will form a tight emulsion and this emulsion will almost completely disappear if the percentage of water is increased beyond a certain limit. The crude oil emulsions are systems that are not in stable equilibrium. The stability of the emulsions increases with age while the resistance to dehydration also increases.

2.2. Theories of Demulsification

Demulsification is a process of breaking down the emulsion by injecting chemical demulsifier into water and oil. There are four theories regarding the resolution of crude oil emulsions: rigid film, pH, electric charge and temperature. In the rigid film theory, the presence of the demulsifier is to assist in the emulsion breaking process by converting the film from a plastic or what can be assumed as a distensible envelope to a glass like which has a relatively low coefficient of expansion. As the enclosed water is undergoing the heating process, it expands and shatters the glass-like film, which breaks the emulsion. Figure 2 shows the steps involved in emulsion destabilization.

Emulsion also can be broken down through neutralization by changing the pH or loss of solubility. The efficiency of demulsification is attained at a neutral pH. Emulsifying agents are polar bodies which have negative or positive charges to function and therefore chemicals that present with opposite charges should encourage the emulsion to break. A sufficient amount of heat is needed for the state of the film to change. As the film experiences an increase of heat, the particles that form the film will collide with each other and finally the bonds between the particles will break, which breaks the emulsion. Consequently, increased temperature has been employed as a demulsification technique but heat generation is expensive and the lighter components of crude oil may be lost in the process.

2.3. Plants Selected

There are two main plant compositions that are able to break the emulsion by specific approaches: the hexane group and octadecenoic acid. Both compositions can react with surfactant to flocculate and coalesce the water droplets. There were three types of plants that were selected: green tea leaves, olive oil and coconut oil.

In the early stage, the W/O is present as small droplets. Once the demulsifier was injected into the W/O emulsion, the demulsifier traveled through the oil to reach the water droplets. The emulsifying agent was displaced by the demulsifier as the surface active character, causing lower surface tension and interfacial energy of the water droplets. The water droplets then moved toward each other and flocculation occurred. The large water droplets that resulted from the flocculation process coalesced to form larger droplets.
coalesced droplets moved downwards through the oil and finally settled out at the bottom of the treating vessel due to the gravitational effect.

2. 4. Blend Demulsifier Materials
The materials used to formulate these blend demulsifier were tapioca starch, camphor, Ca(OH)\(_2\), NaOH, paraffin wax, liquid soap and distilled water. Each of these materials had specific functions that cause the W/O emulsion to be separated. Tapioca starch and paraffin wax are important as water repellant agents. Meanwhile, Ca(OH)\(_2\) and NaOH were able to flocculate the water droplets and camphor as a solid wetting and viscosity adjuster. Liquid soap was necessary as a surfactant that created a good interface between water and oil. This blend demulsifier formulation used distilled water as the solvent.

Both NaOH and Ca(OH)\(_2\) have some important differences. Ca(OH)\(_2\), also called slaked lime, is a white powder that has two hydroxyl groups\(^9\). Meanwhile, NaOH is a colorless crystal that has one hydroxyl group. Due to this difference in structural formula, both of these chemicals were mixed in two different formulations to observe which one is the better flocculent.

3. Methodology
This project involved processes such as plant extraction process, identification of plant extracts compositions, preparation of the blend demulsifier samples, preparation of synthetic emulsion crude samples, static bottle test, dynamic bottle test, toxicity level test and performance evaluation.

3. 1. Plant Extraction Process
In this process, the plant leaves were dried first in the oven for about 12 h, where the temperature was maintained at 60 °C. The leaves were grounded until it became powder using a mortar grinder. The plant powder was extracted using Soxhlet extraction and ethanol was used as solvent. The estimated amount of ethanol that was used was 6 mL for 1 g of plants, 6 : 1. The extraction process took around 24 h. The plant extraction was then separated from ethanol by using a rotary evaporator. The parameters used by the rotary evaporator were 100 rpm at 60-70 °C. This separation process took about 30 min. The extraction underwent gas chromatography mass spectrometer (GCMS) for compositions identification. The plant extracts were named E1 for green tea extract, E2 for olive oil extract and E3 for coconut oil extract.

3. 2. Identification of Plant Extracts Compositions
The plant extract compositions were determined by using a GCMS. In this gas chromatography analysis, the temperature of the oven was maintained at 100 °C for 5 min. The temperature was increased up to 375 °C at a rate of 20 °C/min and was maintained for 5 min. The injector temperature was about 350 °C and the transfer line temperature was about 300 °C.

3. 3. Preparation of Blend Demulsifier Sample
At first, there were two different blend demulsifiers formulated that consisted of six local materials. The first formulation of blend demulsifier consisted of E3 extract, tapioca starch, camphor, flocculants Ca(OH)\(_2\), paraffin wax, liquid soap and distilled water, and named as B1. The other one was formulated using NaOH instead of using Ca(OH)\(_2\) and named as B2. These two formulations were tested with the synthetic emulsion samples. Tables 1 and 2 show the various compositions of the demulsifier blends. The formulations that gave good result were further developed by replacing the E3 extract with the other two plant extracts that gave the best result, which would be either E1 or E2 extract.

3. 4. Preparation of Synthetic W/O Emulsion Sample
Two main materials that were used to prepare this sample were crude oil and brine of 90,000 ppm (mainly NaCl) salinity. This synthetic W/O emulsion was formulated by mixing 50% of crude oil and 50% of brine water. The mixture was stirred for about 20 min. The emulsion was filled in the centrifuge tube to 25 mL for testing purposes.

3. 5. Static Bottle Test
Prior to the test, the synthetic emulsion crude sample is placed in the water bath at 60 °C for 10 min in order to simulate it with actual temperature conditions. In this test, 0.5 mL of demulsifier was injected into 25 mL of emulsion sample and labeled with the name of the demulsifier injected. The centrifuge tube was closed and was shaken manually for 100 times continuously. After shaking, the sample was kept in the water bath again. The amount of water and oil separated was recorded at 0, 10, 30, 60 and 120 min. The experiment was repeated with 1.0 mL and 1.5 mL amount of demulsifier used and also tested with different type of demulsifier. The amount of separated water was read directly from the calibrated centrifuge tube.

3. 6. Dynamic Bottle Test
In this test, 0.5 mL of demulsifier was added into the centrifuge tube that contained 25 mL of synthetic emulsion sample. The centrifuge tube was immersed in the water bath for 10 min at 60 °C operating temperature. The injected sample was then places in the bench cen.
trifuge and spun for 10 min at 2000 rpm. The column separation of water was read and recorded immediately after the bench centrifuge was stopped. The experiment was repeated with 1.0 mL and 1.5 mL of demulsifier amount and also tested with different types of demulsifier.

3.7 Toxicity Level Test

In this part, we used two techniques of toxicity level test. EC50 is a European Community-approved procedure for measuring the toxicity of various chemicals to marine life. The EC50 value is the concentration at which 50% of the species exposed to the chemical survive\(^{10,11}\). The first was by using fish in what is known as the Aquatic Toxicology Test. The second method was the pH value test. For Aquatic Toxicology Test, the test was carried out by filling a container with 100 mL of tap water and was injected with 0.5 mL of the demulsifier formulated. A fish was placed in the container and the time taken for the fish to die was recorded in minutes. The pH value test was carried out as a confirmation test for the Aquatic Toxicology Test. This test was conducted by immersing the pH paper into the water that was already injected with the demulsifier. The value of the pH test was recorded.

3.8 Performance Evaluation

There are four main parameters that were observed and evaluated at this stage: the amount of the water separated, the quality of the water separated, the separation time between water and oil, and the amount of extracts used. All these parameters also depended on the test conditions being either static or dynamic.

4. Results and Discussion

The three conventional demulsifiers used SR 1637, OFC-05-G and OFC-08-K were obtained from PETRONAS but their compositions were not released due to proprietary issues. The results obtained was divided into six parts: the static bottle test for conventional demulsifier, the static test for plant extracts, the static test for blend demulsifier, the static test for blend demulsifier by replacing the E3 extract with the best plant extract, the static test for combination of E3, and the best plant extract as well as the static test for combination of the best conventional demulsifier with the best green demulsifier formulations.

4.1 Static Bottle Test

Based on Fig. 3, SR 1637 gave the best results compared with the other two conventional demulsifiers where the amount of water separated after 120 min was around 12.5 mL of water being separated. The water quality was also excellent as it was clear compared with the other demulsifiers that were hazy. SR 1637 was selected for further testing.

Based on Fig. 4, E2 and E3 extracts gave better results compared to the E1 extract which did not show a significant effect on the emulsion. The quality of water separated was clear for E2 and E3 extracts compared with the green tea extract that produced a very hazy water quality.

In terms of the interface between oil and water, both E2 and E3 extracts were also able to give sharper interface than the green tea extract. This meant that E2 and E3 were good dehydrating agents and were selected for...
further testing. This involved using E3 to formulate the blend demulsifier and then being substituted by E2 in order to compare the dehydrating property of both extracts. Overall, E3 extract was the best plant extract.

There were two blend demulsifier formulations that have been tested: B1, which contained Ca(OH)\textsubscript{2} and B2 which contained NaOH. Based on the results obtained as shown in Fig. 5, B2 formulations gave the best results, but as the dosage was increased, the performance reduced. This was due to the incompatibility factor with the crude oil and also water content. In terms of separated water quality, the water that was separated by using B2 formulations was clearer compared with B1.

Figure 5 shows the results obtained for B3. B3 was the blend formulation where the E3 extract was replaced by E2 extract. The results were not promising compared to the blend demulsifier that contained E3 extract since the quality of water also was not clear for the dosage of 1.0 mL and 1.5 mL.

Figure 6 shows that the results for the formulations of E2 and E3 that were mixed together in order to determine whether the separation of water and oil could be enhanced further since based on the previous results, both of these extracts were very promising. Based on the results, it was not consistent since these formulations only showed the best result at a higher percentage of E2 or E3. For instance, the results are good for the formulations that contain 80-70 % of E3 and 80-70 % of E2. For the formulations that contained half of each chemicals, the results were inconclusive as these chemicals were not compatible and were not suitable to be mixed. Based on the results, FE2 which contained 70 % of E3 and 30 % of E2 gave good result and the water quality also was clear.

Figure 7 shows the formulations for the combination of the best green demulsifier, E3 with the best conventional demulsifier, SR 1637. The results obtained are almost same with the results shown in Table 3 where it was good for the formulations that contain 80-70 % of E3 and 80-70 % of SR 1637.

For the formulations that contained almost half of
each of the chemicals, the results were not good enough as both chemicals were not compatible and not suitable to be mixed together. Based on the results above, FI1, which consisted of a 4 : 1 ratio of E3 to SR 1637, gave good results and the water quality also was clear.

**Figure 8** shows the results of volume of water separated for the six best demulsifier formulations that are SR 1637, E2, E3, B2 FE2 and FI1. SR 1637 was not selected for the final formulations since it was from the industry and is highly toxic.

Based on the results, E3, FE2 and FI1 give the best results that are around 11 mL of water separated after 120 min for all dosages. These best three demulsifiers were further analyzed based on the dosages and the volume of water separated at 0, 10, 30, 60 and 120 min.

**Figure 9** shows that the volume of water separated at the respective time for demulsifier dosage of 0.5 mL. Based on the graph, at 10 min, E3 gave good performance that was around 10 mL of water separated compared with FE2 and FI1 which can separate the water for about 9 mL and 8 mL. Based on industry standards, E3 showed the best results within 10 min as it can squeeze out 90% of the water.

**Figure 10** shows the volume of water separated at the respective time for a demulsifier dosage of 1.0 mL. The result was most likely the same when compared to the previous dosage, E3 and FI1 gave good results as the water separated from both demulsifiers was 10 mL and the performance of FI2 dropped from 8 to 7 mL. This was due to the amount of the demulsifier that exceeded the point of injection amount and the excess amount will cause the demulsifier to coagulate and do not spread well throughout the emulsion. **Figure 11**

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**Table 3** Results for Demulsifier Formulations for Dynamic Bottle Test

| No. | Products  | Demulsifier dosage [mL] | Water quality |
|-----|-----------|--------------------------|--------------|
|     |           | 0.5 | 1.0 | 1.5 |               |
| 1   | SR 1637   | 8   | 11  | 11  | clear         |
| 2   | OFC-05-G  | 3   | 6   | 3   | clear         |
| 3   | OFC-08-K  | 3   | 5   | 6   | clear         |
| 4   | E1        | 1   | 3   | 1   | clear         |
| 5   | E2        | 8   | 7   | 10  | clear         |
| 6   | E3        | 10  | 11  | 11  | clear         |
| 7   | B1        | 5   | 6   | 6   | clear         |
| 8   | B2        | 8   | 7   | 5   | clear         |
| 9   | B3        | 5   | 5   | 3   | clear         |
| 10  | FE1       | 9   | 10  | 8   | clear         |
| 11  | FE2       | 9   | 10  | 10  | clear         |
| 12  | FE3       | 5   | 5   | 7   | clear         |
| 13  | FE4       | 5   | 4   | 6   | clear         |
| 14  | FE5       | 6   | 8   | 6   | clear         |
| 15  | FE6       | 3   | 5   | 7.5 | clear         |
| 16  | FE7       | 5   | 6   | 8   | clear         |
| 17  | FI1       | 8   | 10  | 10  | clear         |
| 18  | FI2       | 7   | 9   | 10  | clear         |
| 19  | FI3       | 6   | 7   | 8   | clear         |
| 20  | FI4       | 6   | 7   | 7.5 | clear         |
| 21  | FI5       | 4   | 5   | 4   | clear         |
| 22  | FI6       | 7   | 9   | 9   | clear         |
| 23  | FI7       | 7   | 7   | 7.5 | clear         |
shows the performance of the demulsifiers at 1.5 mL dosage.

Based on Fig. 12, the plot clearly shows that E3 gave the best results compared to FE2 and FI1 when the volume was maintained for all three dosages. It can be finalized that E3 individually is the best extract that can separate water and oil as it was able to act as a surfactant and also as an interface corrector.

Based on the results E3 is the most suitable demulsifier selected due to its lowest toxicity level since it is 100% organic. Meanwhile, FI1 was blended with some amount of SR 1637, which contained highly toxic compounds. The analysis of toxicity levels can be seen in the toxicity level test part.

4.2 Dynamic Bottle Test

Table 1 shows that the results of the demulsifier formulations that have been tested in a dynamic condition test by using a bench centrifuge for 10 min. Based on the table, there were six best formulations that gave good results which are SR 1637, E2, E3, B2, FE2 and FI1.

Figure 12 shows the results of the best demulsifier formulations for dynamic bottle test. Based on the bar chart, the performance of SR 1637 and E3 were the best as they were able to separate the water at almost 85 to 90%. SR 1637 was not selected in this project as it is highly toxic, so E3 formulation was selected as the best green demulsifier, the same result as the static bottle test.

4.3 Results for Plant Extract Compositions Identification

Based on the results obtained, approximately 500 volatile compounds have been identified in tea extracts. Alcohols are considered as forming in tea leaves through biosynthesis. Most of the remaining volatile constituents of black tea are formed. Coconut oil is predominantly composed of saturated fatty acids (about 94%), with a good percentage (above 62%) of medium chain fatty acids among them. The acids include Lauric acid, Myristic acid, Caprylic acid, Capric acid, Caproic acid, Palmitic acid, Oleic acid, Palmitoleic acid, Linoleic acid, Linolenic acid and Stearic acid.

Olive oil composed mainly of triacyl glycerols (triglycerides or fats) and contains small quantities of free fatty acids (FFA), glycerol, phosphatides, pigments, flavor compounds, sterols, and microscopic bits of olive.

4.4 Analysis of Toxicity Level of Best Demulsifier Formulations

Table 2 shows the result of the toxicity level test by observing the effect of the demulsifiers to the fish by monitoring the time taken for the fish to die and the pH value of the chemicals. The fishes were placed in different containers that were filled with water injected with different demulsifier.

Based on Table 2, the time taken for the fish in the containers that was injected with SR 1637 and B2 to die was very short, taking only 10 min and 8 min respectively. This shows both demulsifiers have high toxic content, either too acidic or too alkaline. Meanwhile, fish inside the container that was filled with water injected with E2 and E3 took a longer time to die. This was because the pH values of these demulsifiers were almost neutral which was around 6 to 7.

The results obtained from the pH test showed that SR 1637 has a pH value of 3, which indicates high acid content and the pH value for B2 was 12 that indicates high alkali content. Meanwhile, the pH value for both E2 and E3 are 6 that are almost neutral. High pH
levels from 9 to 14 can harm fish by denaturing cellular membranes. This is because most ammonium contained in the water is converted to toxic ammonia. Meanwhile, if the pH of the water is too low, the metals from the rock or sediments in the stream will be released rapidly and these metals can affect the fish’s metabolism and disrupt the water flow through the gills, thus killing the fish.

5. Conclusion and Recommendation

As a conclusion, this project focused on the breaking of the emulsion in crude in order to increase the oil recovery by using a demulsifier that does not harm the environment. Based on the results obtained, we concluded that E3 extract was the best extract that can separate oil and water effectively within the time range and also able to produce clear water which showed that maximum amount of water was extracted from the oil. This E3 extract cannot be added or mixed with other extracts for formulation as the effectiveness will be reduced. This is because E3 extract was not compatible enough to be tested together with other extracts or formulations as the interface that formed was not sharp and the water separation also was not at the maximum level. Future works should investigate oil sheen formation by vegetable oils and examine how it can be reduced.

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**Table 4** Toxicity Level of the Best Demulsifier Formulations

| No. | Products | SR 1637 | E2 | E3 | B2 | FE2 | FI1 |
|-----|----------|---------|----|----|----|-----|-----|
| 1   | Time for the fish to die [min] | 10      | 107| 110| 8  | 90  | 60  |
| 2   | pH value | 3       | 6  | 6  | 12 | 5   | 5   |