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# Synthesis of nano emulsion from waste cooking oil for enhanced oil recovery applications

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**Abstract.** Enhanced oil recovery (EOR) is a tertiary method to extract potential oil in a matured well. Emulsion, which is one EOR method has properties which enable it to recover oil remains in reservoir rocks of the matured well. Nano sized emulsion or nano emulsion able to recover trapped oil, by capillary force in fine pores of the reservoir rock. Nano emulsion reduces the oil-water interfacial tension and therefore changes the wettability of the reservoir rock. However, the nano emulsion is uneconomical and unstable. Therefore, this work aimed to produce nano emulsions by using low cost waste cooking oil, Tween 80 and Span 80. Ultra-sonication was used to reduce the size of the emulsion. The concentration of surfactant, power of ultra-sonication and time of sonication were varied to study the stability of the oil-in-water and size of the emulsion using the Malvern Zetasizer. The nano emulsion was then tested on a crude oil soak meligan formation sand rock to test the performance of the nano emulsion. The result show values of zeta potential and droplet size were - 15.3 mV and 262.1 d.nm respectively. The emulsion droplet sizes were about 500 nm with milky white appearance. The nano emulsion shows positive results as 63.89 % crude oil displaced from the soaked meligan formation sand rock. As a conclusion, the nano emulsion produced from waste cooking oil can potentially be used for EOR.

## 1. Introduction

As the population increases, the demand of oil production is also increasing. The petroleum industry is facing difficult challenges on the demand of oil and it needs technological innovations to overcome it. Several techniques have been used to maintain a production of crude oil at maximum level. In an oil and gas field, once the primary recovery or natural pressure of a well decreases, human intervention is needed using secondary and followed by tertiary recovery. The EOR is a tertiary recover that can efficiently extract remaining oil trapped in the reservoir rock by capillary forces [1]. This phase uses fluid that consists of several components and miscible with oil, than can therefore reduce the viscosity and improve the flow of the oil. EOR also able to extract up to 60 – 65% of the remaining oil in a well [2] therefore increase production of oil as the demand increases.

In EOR, there are several techniques can be used to increase the extraction of oil depending on the reservoir. Each reservoir has its own characteristics. Nano technology is one of the unique solution



that can be used to help and overcome this challenge due to its unique characteristics, efficient, and more environmentally sound technology. Nano emulsion also protects the layer of oil and gas to avoid permanent blockage in the oil and gas flow. Due to small droplet size, they are not subject to gravity-driven separation, but the density differences of the two phases. [3]. The nano emulsion that has been prepared is a homogeneous mixture of hydrocarbon and water with a ratio of surfactant [1].

Surfactant is a chemical substance that absorbs on or concentrated at a surface or fluid-fluid interface when present at low concentration in a system. The surfactant acts as an emulsifier to absorb the interface between water and oil medium by reducing the interfacial tension between them and prevent from conglomerate [4]. Nano emulsion is a transparent, translucent (50 – 200 nm) or milky white emulsion (about 500 nm) [5]. It is an efficient tool for EOR technique, because the emulsion has a high level of extraction efficiency by reducing oil-water interfacial tension down to <0.001 mN/m as resulted to solubilize the oil residual very efficiency which will increase the oil recovery and the completely clean up the formation [4]. However, the current nano emulsion is uneconomical and often unstable. Therefore, in this study, we proposed to produce emulsion in the size of nano scale. Focusing at formulation that can provide properties such as minimum average droplet size and minimum amount of surfactant, higher stability of nano emulsion and should be able to be used to displace oil from the pores of a rock.

## 2. Material and methods

### 2.1 Material

A filtered waste cooking oil had been obtained from a local food store. Distilled water and surfactants sorbitan monooleate (Span 80) and polyoxyethylenesorbitan monooleate (Tween 80) procured from Sigma-Aldrich Chemie GmbH, Germany and from R & M Chemical, United Kingdom respectively were used without treatment. A meligan formation sand rock sample and crude oil were used to test the potential use of the nano emulsion in EOR.

### 2.2 Experimental procedure

#### 2.2.1 Determination of concentration surfactant ratio

The combination of a high and low Hydrophilic-lipophilic balance (HLB) emulsifier is often more effective than the use of a single emulsifier. HLB is the balance of the size and the strength of the hydrophilic (water loving or polar) and the lipophilic (oil loving or non-polar) groups of the emulsifier. All emulsifier consist of a molecule that combine both hydrophilic and lipophilic groups. The value of HLB of an emulsifier is related to its solubility. Thus, an emulsifier having a low HLB will tend to be oil-soluble use for producing water-in-oil emulsions, and one having a high HLB will tend to be water-soluble (aqueous characteristics) is used for oil-in-water emulsions [6]. Figure 1 shows the HLB range.

HLB value	0		10		20
Classification	Oil-loving group		Balanced		Water-loving Group

Figure 1. HLB range.

Method for selection of surfactant as emulsifying agent is known as an HLB method by using the following equation to calculate the HLB mixed surfactant system:

$$HLB = \frac{m_A \times HLB_A + m_B \times HLB_B}{m_A + m_B} \quad (1)$$

Where  $m_A$  and  $m_B$  are the mass of surfactants A and B, respectively.  $HLB_A$  and  $HLB_B$  are the HLB number of surfactants A and B, respectively [6].

### 2.2.2 Value of surfactant ratio

A blend of a low HLB and a high HLB surfactant gives the HLB needed to form an emulsion and has better performance than a pure surfactant [6]. The HLB values for oil-in-water emulsion for this experiment, required 10 HLB for waste cooking oil (corn oil) [6]. By using,  $HLB_{Span\ 80}$  and  $HLB_{Tween\ 80}$  of 4.3 and 15.0 respectively in Equation 1 the % of Tween 80 and Span 80 obtained were 53.3 and 46.73% respectively. The ratio rounds off to 2.0 vol. Tween 80: 1.0 vol. Span 80. The most stable sample of emulsion can be formed with the formation of an emulsion system by using the mixture of Span-80 and Tween-80 surfactant in the ratio of 49/51 [7].

### 2.2.3 Preparation of nano emulsion

This experiment used high emulsification method to prepare nano emulsion. Distilled water and waste cooking oil were measured using a graduated cylinder and funnel to avoid spillage. The ratio of waste cooking oil to distilled water was set at one to four respectively [8]. As for the surfactant, pipette and measuring cylinder were used for small and higher amount of volume respectively. Volume for each material were shown in Table 1 which were filled in a 200 ml beaker. Oil and surfactant mixture was blended in a beaker and stirred mildly using a magnetic stirrer for 5 minutes. The required amount of water was simultaneously added slowly into the oil phase.

Table 1. Volume of emulsion raw material.

Exp.	Surfactant (ml)			Oil (ml)	Water (ml)	Total (ml)
	Span 80	Tween 80	Tot.			
1	1.67	3.33	5.0	30	120	155
2	3.33	6.67	10.0			160
3	5.00	10.00	15.0			165
4	6.67	13.33	20.0			170
5	8.33	16.67	25.0			175
6	10.00	20.00	30.0			180

### 2.2.4 Determination of ultrasonic intensity of the particle size of nano emulsion

The generated ultrasonic intensity from the Sonotrode horn tip was calculated using the equation 2, where,  $I$  is the intensity;  $P$  is the input power; and  $r$ , is the radius of the sonotrode horn tip [9]. The radius of Sonotrode horn tip is 2.54 cm. Based on the Equation 2, the corresponding ultrasonic intensities for power input of 150 to 750 W show in Table 2.

$$I = \frac{P}{\pi r^2} \quad (2)$$

Table 2. Conversion of power to ultrasonic intensity.

Input power (W)	Ultrasonic intensity (W/cm <sup>2</sup> )
0	0
150	7.4007
300	14.8014
375	18.5018
450	22.2022
600	29.6029
750	37.0036

### 2.2.5 Ultra-sonication process to form droplet size of particle

Emulsion material was resized by using sonication process of Ultrasonic Processors (Model no. VC 750, Sonics & Materials, Inc.). The Sonotrode horn tip of ultrasonic was adjusted in the range of 1 to 0.5 cm depth from the bottom of the surface of the beaker. As a precaution, the timer was set a pulse to have a rest around 20 second for each 50 seconds of sonication because the instrument will heat up

time to time. After sonication, the beaker needed to be cool down for 5 minutes before continuing with the Malvern Zetasizer instrument.

### 2.2.6 Measurement of droplet size

Malvern Zetasizer Nano ZS, was used to measure the particle size and zeta potential by Dynamic Light Scattering (DLS) of the nano emulsion. It is a measurement of the magnitude for electrostatic or charge repulsion/attraction between particles, which affect its stability. In general the particle with zeta potential more positive than +30mV or more negative than -30mV are normally considered stable. There are two types of cell that need to be used in the Malvern Zetasizer which were the disposable sizing cuvette and clear disposable zeta cell for measuring particle size (d.nm) and zeta potential (mV) respectively.

### 2.2.7 Determination of the performance of nano emulsion in EOR

The nano emulsion potential to be used for EOR will be determined by referring work by [5]. The nano emulsion was selected from the sample based on the smallest oil droplets and stable emulsion. A Maligan formation sand rock, which had been soaked in crude oil for a 10 day period, was immersed in the selected nano emulsion. Weight of nano emulsion and crude oil (g) and weight crude oil (g) were calculated using Equation 3 and 4 respectively

$$\text{Weight of immersed Sand Rock (Crude Oil) in nano emulsion} - \text{Weight of sand rock after immersed in emulsion (4days)} \quad (3)$$

$$\text{Weight of nano emulsion and crude oil} - \text{Weight of 200mL nano emulsion} \quad (4)$$

## 3. Result and discussion

### 3.1 Effect of surfactant concentration on particle size

To determine the effect of surfactant concentration on particle size, the amplitude and time of sonification were set at 100 % or 750 W and 15 minutes respectively. The obtained results were tabulated in Table 5. In general the droplet size decreases with the amount of surfactant. This is due to the increases in interfacial area and decreases in the interfacial tension [7].

Figure 2 shows that in general the higher amount of surfactant in the emulsion, resulted in the increase of particle size. For instance, at 14.29 vol. % of surfactant, the particle size shown the lowest value of 515.8 nm. Subsequently, the stability of the emulsion depends on the value of zeta potential. If the particles in the suspension have a large zeta potential regardless of the charges, the particles tend to repel each other and decrease the tendency for flocculation to occur. In contrast, if the particles in the suspension have a low zeta potential values, then there is no force to prevent the particles to coming together and flocculating.

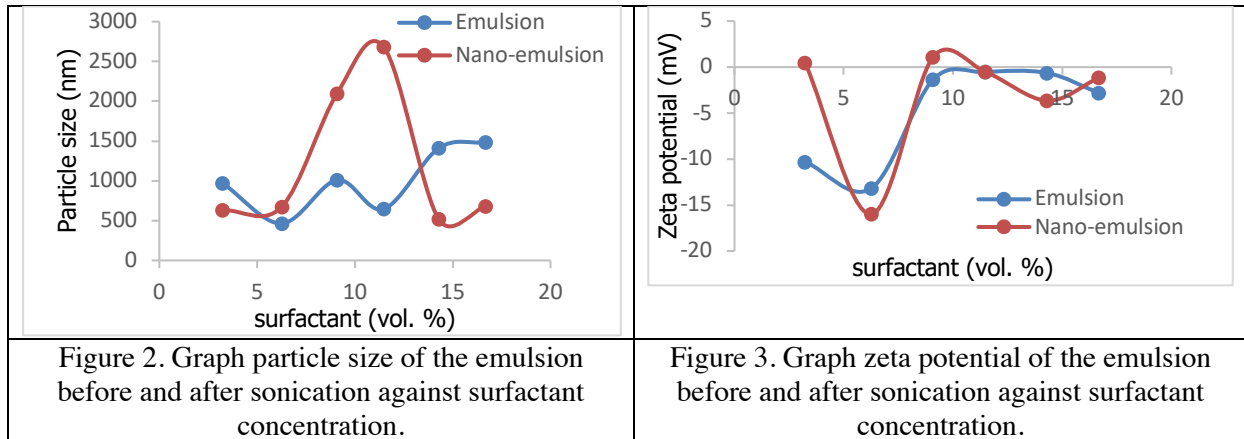
Figure 3 shows the highest value of zeta potential obtained was at surfactant concentration of 6.25 vol. %, making it the most stable emulsion compared to the others concentration at. In addition, physical observation of surfactant concentration of 6.25 vol. The % is shown in Figure 4 (b) in which, when compare with other emulsion, this emulsion does not seem to separate after a few days. Nevertheless, surfactant of 6.25 vol % was selected for the subsequent experiment instead of 14.29 vol. % to reduce costs by using the least amount of surfactant with a stable condition.

### 3.2 Effect of sonication time on particle size

The effect of sonication time on particle size was studied by fixing the amplitude of the ultrasonic at 100 % same as previous and surfactant concentration at 6.25 vol. %. The distilled water and waste cooking oil is in ratio 1 to 4 respectively.

Figure 5 shows that initially an increase in the time of sonication decreases the particle size. This indicates that it is possible to produce nano emulsion, using less energy and shorter time. At time 0, there was no sonication occurred, and after 5 minutes the particle size begins to decrease. This is

true for the time between 5 to 15 minutes. However, after 15 minutes as the sonication continues, the size of the particle increase significantly.

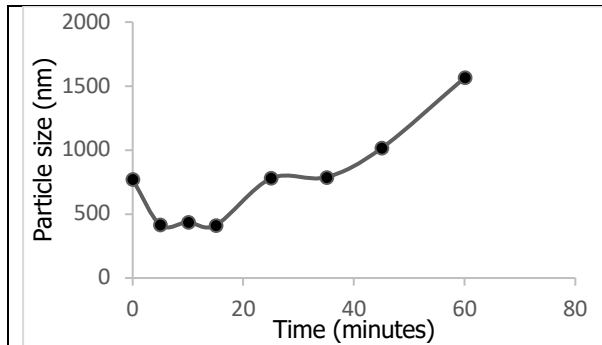


Emulsion	Nano emulsion	Emulsion	Nano emulsion	Emulsion	Nano emulsion
Particle size = 972.0 nm	Particle size = 632.3 nm	Particle size = 465.3 nm	Particle size = 672.5 nm	Particle size = 1010.3 nm	Particle size = 2100.0 nm
Zeta potential = -10.3 mV	Zeta potential = 0.49 mV	Zeta potential = -13.2 mV	Zeta potential = -16.00 mV	Zeta potential = -1.36 mV	Zeta potential = 1.09 mV
(a)		(b)		(c)	
Emulsion	Nano emulsion	Emulsion	Nano emulsion	Emulsion	Nano emulsion
Particle size = 646.5 nm	Particle size = 2684.0 nm	Particle size = 1411.0 nm	Particle size = 515.8 nm	Particle size = 1485.0 nm	Particle size = 681.4 nm
Zeta potential = -0.54 mV	Zeta potential = -0.49 mV	Zeta potential = -0.63 mV	Zeta potential = -3.65 mV	Zeta potential = -2.80 mV	Zeta potential = -1.17 mV
(d)		(e)		(f)	

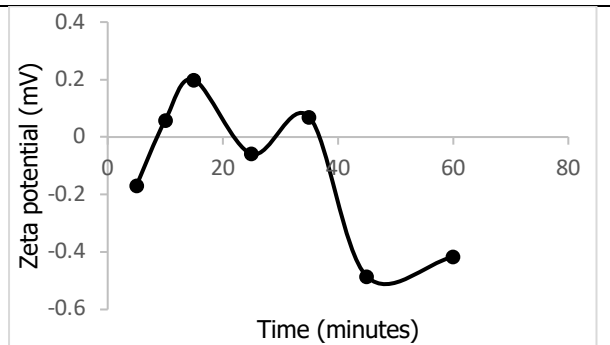
Figure 4. Concentration of surfactant (a) 3.23 vol.%; (b) 6.25 vol.%; (c) 9.09 vol.%; (d) 11.77 vol.%; (e) 14.29 vol.%; and (f) 16.67 vol.%.

Figure 6 shows the zeta potential value. As the time of sonication increases, zeta potential also increases. An emulsion at stable state should have a zeta potential value of  $\pm 30$  mV. However the highest magnitude value obtained in this experiment was at -0.485mV for 45 minutes sonication time. However, the corresponding value of particle size is bigger than the particle size of emulsion using five minutes sonication. Therefore the emulsion using the 5 minutes time of sonication was taken as the reference for the following experiment, due to a lower energy usage than the others and produces

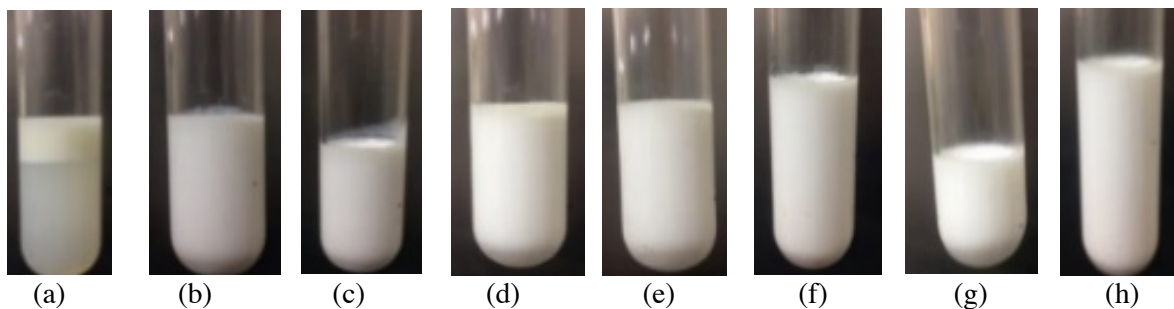
considerably small particle size. Additionally, Figure 7 (b) shown that there was no separation of the nano emulsion having 5 minutes time of sonication. The appearance shows no phase separation of oil and water, which means the emulsion is homogeneous.



**Figure 5.** Graph size droplet particle of the nano emulsion against the time of sonication.



**Figure 6.** Graph zeta potential of the nano emulsion against the time of sonication.



**Figure 7.** Time of sonication from 5 to 60 minutes (a) 0 minutes, (b) 5 minutes, (c) 10 minutes, (d) 15 minutes, (e) 25 minutes, (f) 35 minutes, (g) 45 minutes and (h) 60 minutes.

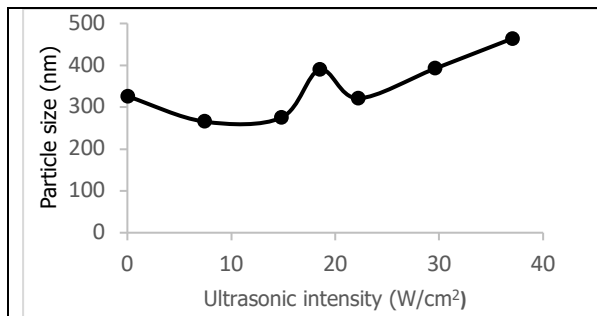
### 3.3 Effect of ultrasonic intensity on particle size

The experiment was done to investigate the role of sonication power in producing of smaller size of nano emulsion. The results obtained from previous experiment were used, which were 6.25 vol. % surfactant and 5 minutes time of sonication. The result of this experiment was plotted in Figure 8.

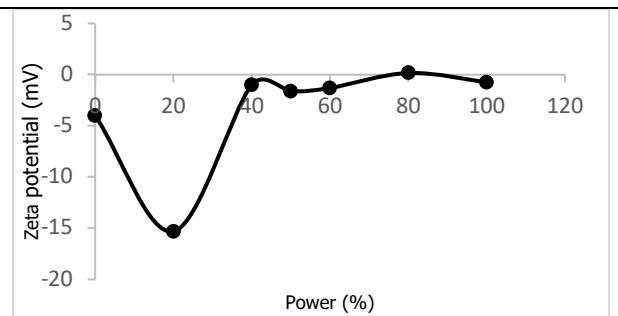
In general, at low power of 20 % the particle size is observed to reduce from 326 to 266 d.nm. However, after the 20 % power, the particle size was observed to increase with % of sonication power. This may due to the increase in shear stress in the liquid as the ultrasonic intensity increase. This shear stress can create a great number of cavitation of tiny bubbles in the liquid which then collapsed drastically to become small size droplet [9]. Subsequently, the small droplet then forms bubbles as the % of the sonication power increase.

The 20 % power of sonication shows a high value of zeta potential of - 15.3 mV nearing to a stable emulsion of  $\pm 30$  mV as shown in Figure 9. It is the highest value, compare to the other emulsions. Additionally, it uses less energy to produce the nano emulsion. However, after a few days, it does not show stability as shown in Figure 10 (a) when compared to other nano emulsion in Figure 10 (b-f) where a distinct separation of phases of the nano emulsion can be observed.

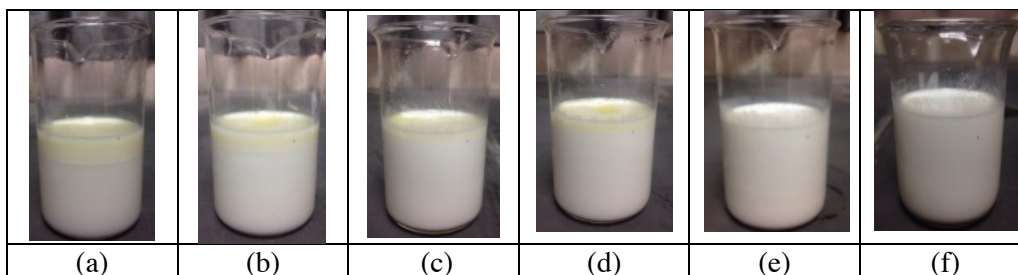
Figure 11 shows that, the highest peak of median bell graph of the size of the particle for the nano emulsion of 20% power sonication. The % intensity vs. particle size distribution curves has been shown for clarity.



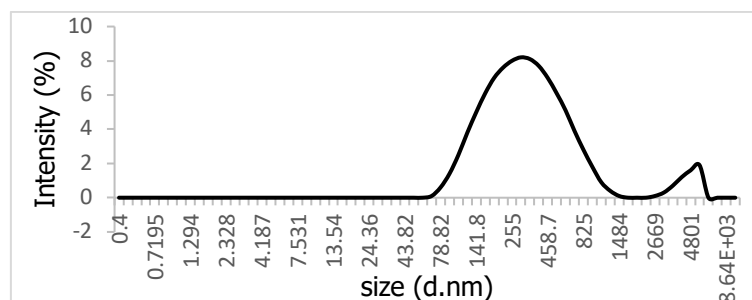
**Figure 8.** Graph size droplet particle of the nano emulsion against the ultrasonic intensity.



**Figure 9.** Graph zeta potential of the nano emulsion against the power of sonication.



**Figure 10.** Power of sonication to form nano particle size at power (a) 20 %, (b) 40 %, (c) 50 %, (d) 60%, (e) 80 and (f) 100 %.



**Figure 11.** Particle size distribution for 20% power sonication.

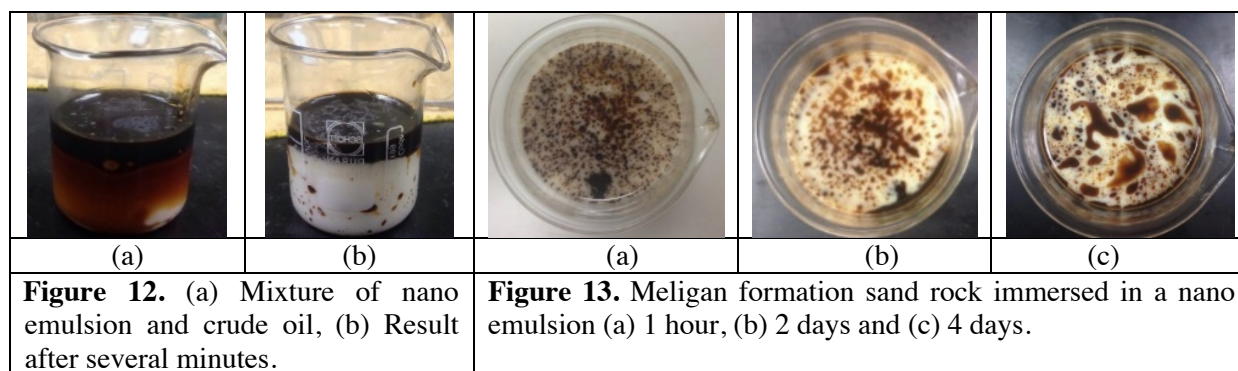
### 3.4 Use of a nano emulsion for EOR application

The nano emulsion of 20 % power sonication was selected for further investigation for EOR application. Initial investigation shows that the mixture of the nano emulsion and crude oil (Figure 12 (a)) was separated after several minutes, with crude oil on top of the mixture as seen in Figure 12 (b).

Meligan formation sand rock at an initial weight of 63.4 g were soaked with crude oil for 10 days [5]. The weight of the sand rock after the immersion was 67 g in which the rock had absorbed about 3.6 g of crude oil after 4 days. This indicates that the rock may potentially have high porosity.

Subsequently, the crude oil soaked Meligan formation sand rock was later immersed in the selected nano emulsion weigh at 184.1g (200 ml). The results were recorded in 1 hour, 2 and 4 days as shown in Figure 13. By using Equations 3 and 4, the results show about 2.3 g crude oil appear on the surface of nano emulsion after being immersed for 4 days. In which, about 63.89 % of oil was being pulled out by the nano emulsion from the sand rock.





Nano emulsions having a droplet size, which is smaller than the pores of reservoir rock shows potential to displace the crude oil trapped inside the pore of reservoir rock. The unique characteristics of nano emulsion that has been formulated with surfactant and waste cooking oil, which has smaller particle size, enable the nano emulsion to reduce the interfacial tension and provide more surface contact with the crude oil that lead to the increase of the efficiency of the displacement process [10].

#### 4. Conclusion and recommendation

In this study, a series of nano emulsion had been prepared by varying the surfactant concentrations, time and power of ultra-sonication. The result shows that, by using 6.25 vol. % surfactant and 20 % sonication power and 5 minutes of sonication time can result in the formation of a nano emulsion with reduced droplet size of 262.1 d.nm and zeta potential of -15.3 mV. The EOR application test showed that the nano emulsion able to extrate crude oil at about 63.89 %. It is an indication that the nano emulsion can be potentially used to recover residual oil, which is still trapped inside the fine pore of reservoir rocks. Further research can be carried out to investigate the type of surfactant or type of oil that can affect the nano emulsions particle size and stability since the result of this research, does not achieve a stable emulsion as indicated by zeta potential values. A study on the synthesis of nano emulsion needs consideration in every aspect, to achieve a lower cost, efficiency, stability and environmental friendly for EOR.

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