Effect of Graphene Oxide on the Demulsification Process of Heavy Crude Oil Emulsion

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***Abstract*— Chemical demulsification is one of the famous method to separation of oil and water emulsion. The higher price of chemical used in the market industry create a potential study on the graphene oxide as a demulsifier. Recent study on Grapehne oxide show ability to act as efficient demulsifier. The abudance and cheap price can be problem solver to the emulsion problem. The synthesis of graphene oxide created from raw graphite that undergo strong oxidation based on Hummer method. The categorization of sample can be determine by using FTIR and XRD test. The test for the efficiency study of graphene oxide as demulsifier can be divided in two part which is bottle test and Interfacial tension. The demulsification process efficiency of added graphene oxide can yield in the range of 99.87% to 99.98%. The reason can be supported by the interfacial tension reduction with increasing concentration of graphene oxide.**

***Keywords*— Demulsification, Graphene Oxide, Heavy Cude Oil emulsion, Surface Tension**

I. Introduction

Energy in this era is one of the important thing that keep the world ticking. Oil and gas is the main source to produce enough supply of energy to the world demand. From electricity to transportation and production used petroleum. The problem arise when the production of oil cannot meet the demand. According to BP Statistical Review of World Energy 2013, the difference of oil consumption between the year 2000 and 2012 increase by 17 % with the 89773 thousand barrel of oil make up to 32 000 million barrel per year of consumption alone in 2012. Decreasing trend of supply and increasing trend of user notice oil and gas industry to taking serious this problem for before getting worse.

The most obvious method to fight this problem is increase the production of oil and gas to meet the demand. The problem is conventional oil resources will soon face decline phase. Conventional oil for all over the countries near the limit reserve set exclude five major Middle-East supplier.[1] Breaking the limit of oil resource is need to increase the production. One of the method to increase the production of oil is to implement enhanced oil recovery method. Enhanced oil recovery method artificially alter the reservoir properties to extract oil that cannot be done by natural depletion. This method will create more potential of oil and gas production. One of most commonly method used in this process is water injection which will produce stable oil and water emulsion.

Emulsion is undesired formation either in the aspect of environment, production, or economic. Many method can be used to treat crude oil emulsion like biological approach, chemical demulsification, and physical method such as electrical and mechanical. Most common method to treat emulsion in oil and gas industry are chemical demulsification. This method was widely chosen due to effectiveness and it proven record. Apart from its advantages, one main problem of chemical demulsification is regarding it cost of implementation. Experiment state that chemical demulsification very effective in the role of separation with effectiveness of 57% compared to other method however the process was used expensive chemical.[2]

The revolutionized idea that will change chemical demulsification method come in 2004. 2D materials without 3D base was consider not viable by science due to unstable state.[3] Andre Geim and Kostva Novoselov are 2010 Nobel Price winner due to their contribution in discovery of graphene. The first graphene only extracted by ordinary tape repeatedly until thin layer of graphene produced. Graphene nowadays is famous matter that sometime called super material and predict to play big role in the future. Recent study was done to apply graphene as chemical for demulsification. The graphene is modified by Hummer reaction to produce graphene oxide. Graphene oxide has amphiphilic characteristic that proven to be good demulsifier agent.

II. METHODOLOGY

A. Materials

Several chemical used in this experiment especially in the synthesis of graphene oxide. Raw Graphite powder, concentrated Sulfuric Acid (H_2SO_4), Sodium Nitrate($NaNO_3$), Sodium Hydroxide ($NaOH$), Hydrogen Peroxide (H_2O_2), Potassium Ferricyanide ($K_3Fe(CN)_6$), and Potassium Permanganate ($KMnO_4$). As for emulsion the chemical used is Sodium Nitrate ($NaNO_3$), Sodium Chloride ($NaCl$), Magnesium Chloride (KCl), Magnesium Sulphate Heptahydrate ($MgSO_4.7H_2O$), and Monopotassium Phosphate (KH_2PO_4) for synthesis of brine solution and crude oil is taken from heavy crude oil of Bertam Field.

B. Synthesis of Graphene Oxide

Graphene Oxide were synthesis from raw graphite powder by applied Hummer's Method. First step of Graphene Oxide synthesis started with addition of 400ml of concentrated Sulphuric Acid into 10g Graphite powder and 5g sodium nitrate mixture. The beaker was immerse in the ice bath to maintain temperature of the solution below 15^0. The solution was stirred for 1 hour at stirring speed of 300-400 rpm. After that 60g of $KMnO_4$ quarterly within period time of 2 hour. After all $KMnO_4$ completely dissolve in the mixture solution. The solution was mix for another 2 hour. For beaker was removed from ice bath and left to surrounding temperature. The solution than heat to $70C^0$ and 100 ml distilled water was added slowly within period of 2 hour for oxidation process. After that, the solution was continue heat to $90C^0$ and 100ml distilled water was added slowly within period of 1 hour. The solution was left overnight. Concentrated Hydrochloric Acid was diluted to 5% concentration by using distilled water. The solution was undergo acid washing by adding 1500ml of diluted HCL to the solution beaker. The mixture was left for 2 days at room temperature. After that the acid was solution was removed from sediment in the beaker. The sediment was added with 1500ml of distilled water for continuous washing for another 2 days. The solution was left overnight. Distilled water was removed from beaker to let the sediment settle down. The sediment solution centrifuge until it reach neutral pH. The centrifuge was set at $15C^0$ and 20000rpm.

C. *Synthetic Brine Solution*

Synthesis of brine solution was produce from addition of 1L distilled water with 10g NaCl, 0.29g KCL, 0.42g $MgSO4.7H_2O$, 0.83g KH_2PO_4, 0.42g $NaNO_3$. The mixture then stir for another 1 hour to allow the chemical dissolve completely in the Distilled water.

D. *Oil in Water emulsion*

Table 1: Oil properties table for Bertam crude oil.

Properties	**Value**
Oil density (g/cm^3)	0.9
kinematic Viscosity (50^{0}c,cP)	17751
saturate (%wt)	3
aromatic (%wt)	63.4
resin (%wt)	12.9
asphaltene (%wt)	20.7

Heavy crude oil emulsion sample was retrieve from Bertam field with API^0 11. The heavy crude oil was diluted first using toluene by adding 20% by volume of toluene into the heavy crude oil. The emulsion was synthesis by combining the ratio of synthetic brine water and diluted crude oil. The 100ml of diluted crude oil was added to 400ml of synthetic brine solution to produce 20:80 water cut of emulsion. The mixture was stirred with low rotation which is 500-600 rpm for about 10 minute and then continuous stirred for high speed rotation around 1500-1800 rpm.

E. *Demulsification Bottle Test*

The Demulsification with different concentration was done to observe and calculate the efficiency of demulsification process affected by Graphene Oxide. The emulsion with 20:80 was immediately put into 5 different centrifuge with volume of 45ml. Graphene Oxide was added into each of centrifuge tube with different concentration of Graphene Oxide by ppm which is 40, 80, 120, 160, and 200. The centrifuge tube was immerse in the water bath with $60C^0$. The time was set to 30 min to let the Graphene Oxide effect the demulsification process. The picture was taken for observation before and after demulsification process. The separate water sample was taken using separating funnel. The sample then analyze using UV-VIS Spectrometer with 340nm wavelength.

F. *Goniometer Interfacial surface tension*

Pendant drop shape technique used as method to determine interfacial surface tension between oil and water surface. Goniometer VCA 3000 liquid surface analysis used with syringe volume of 100 microlight. The pendant drop shape taken for every concentration of graphene oxide. The Surface tension was automatically calculated using Goniometer equipment.

III. RESULTS AND DISCUSSION

A. *Categorization of Graphene oxide.*

Figure 1 show FTIR result of Graphene Oxide. The spectrum show varies peak within the range of 800-4000 cm^{-}. The visible peak at 3220.35 cm^{-} was indication of hydroxyl group (-OH). The broad type peak support the indication of hydroxyl group. The sequence small peak between 1716.58 and 1622.91 were stretching effect of carbonyl group (–C=O). Another peak show at 1048 cm^{-} was assigned to alkoxy group (O-C-O). So overall the spectrum show several major functional group in this sample which is carbonyl, hydroxyl and alkoxyl presence in the graphene oxide powder. The functional group stated above presence due to oxidation process during Hummer method. Parades study on graphene oxide also produce close identical spectra of FTIR.[4]

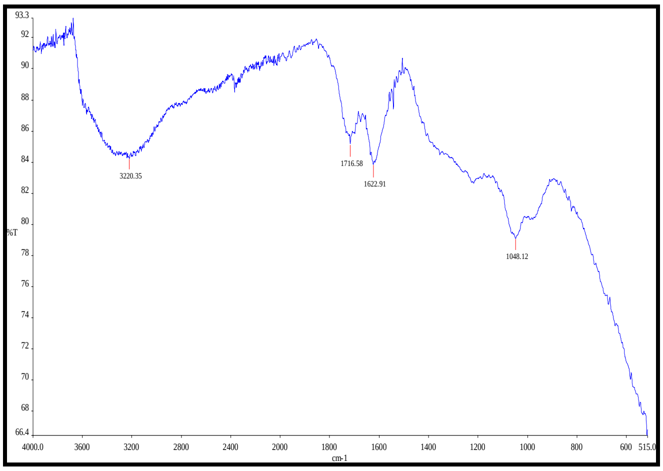

Fig. 1: Fourier transformation Infrared spectrum of Graphene Oxide several during during 800-4000 cm^{-} wavelength.

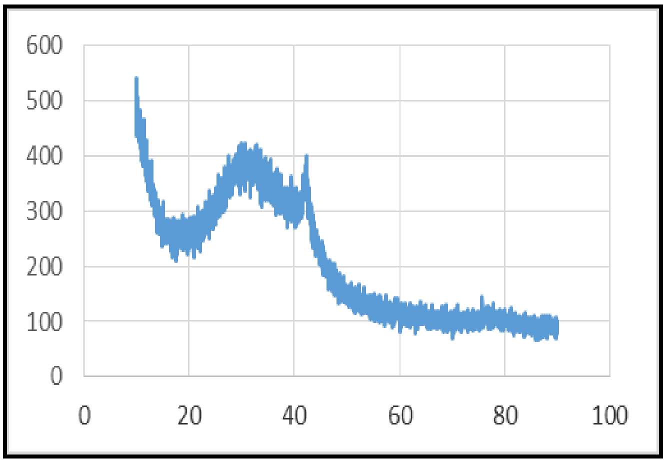

Fig. 2: Xray diffraction peak of Graphene Oxide from angle 10 to 100.

Another test method for categorization of graphene oxide is X-Ray diffraction. The method calculate using peak of sample at different angle. The sample was calculate from angle 10 to angle 100. The highest peak at 10.26 degree show that presence of

Graphene Oxide in the sample. Recent study show that peak of graphene oxide is in between angle 9.5 to 11.5. Based on Kuila study confirmed that upon oxidation of graphite, the reflection peak shifts to a lower angle at 2theta = 11.2^0.[5] The other small peak come around 20 degree show that there is still presence of graphite powder in the sample. The peak at 20 degree show low concentration compared to graphene oxide. This can be due to impurities of graphite in the synthesis of graphene oxide. This impurities can be removed by further washing the sample and centrifuge until all graphite powder eliminate.

B. *Demulsification Bottle Test*

The demulsification can be observe from figure 3 as the bottle test analysis whereas when given time the separate part of oil and water will be visible. The observation of the crude oil emulsion separation after 30 minutes can be seen more clearly in 20:80 water cut and more cloudy in the 50:50 water cut oil concentration. The cloudiness of 50:50 crude oil emulsion occur due to the concentration of oil that contain in the synthetic brine solution. The retention time was not sufficiently to completely separate oil from water. One of the factor that added to the cloudiness of separation is heavy crude oil properties that viscous tend to stick on the wall of centrifuge tube. Based on the observation of demulsification bottle test can be stated that, separation of heavy crude oil in the given time is due to gravity factor which density difference between oil and gas is main contributor toward separation process.

C. *UV-VIS Spectrometer Analysis.*

UV-VIS spectrometer one of the method used to analyze concentration of substance in the given sample. To detail the efficiency analysis the concentration of oil in the separate water was taken by UV-VIS with 340nm wavelength. The efficiency can be taken from the formula of:

$$C = (M_o / V_w) \times 10^3 \quad (1)$$

Concentration represent in the node C calculate based on mass of oil (M_o) contain in the volume of sample (V_w). C in this formula calculated in the unit of mg/ml.[6]

$$E = (C_o - C_i) / C_0 \quad (2)$$

The efficiency calculated by taken in consideration of initial oil concentration in water sample and the residual oil content in separated water sample.

Table 2: C_o for each of water cut emulsion

Water cut	M_o (mg)	V_w (ml)	C_o (mg/ml)
20:80	5988	30	199600
30:70	8982	30	299400
50:50	14970	30	499000

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Based on the calculation C value for each of the concentration is 199600, 299400, and 499000.The calibration curve is made using dilution known sample from 10 ppm to 1000 ppm. Summary on table 2 show result of complete value of concentration oil initial (C_o). Figure 4 show concentration of 20:80 water cut resulting the separation efficiency in between 99.95% to 99.97%, 30:70 water cut also show good separation where in between 99.87% to 99.91%. The last concentration given was 50:50 water cut and yield separation at value of 99.91% to 99.96%.

Effect of concentration of graphene oxide also study by varies the emulsion sample with different concentration of demulsifier. Effect of graphene oxide concentration at low concentration of 50:50 water cut much more dominant compare to other concentration of oil concentration. In the 50:50 water cut, the the different between efficiency yield up to 0.05%. whereas at 30:70 water cut, the effective difference lie between 0.04%. For 20:80 water cut the difference rate of efficiency can be varies up to 0.02%. Based on the trend can be stated that effect graphene oxide much more significant in higher concentration of oil initial.

For all the case the best suited graphene Oxide concentration is 80ppm. It also can be stated that higher value of GO concentration can increase efficiency until it reach certain optimum value the efficiency will decreasing due to dispersion of excess graphene oxide in the separated water sample.[7]

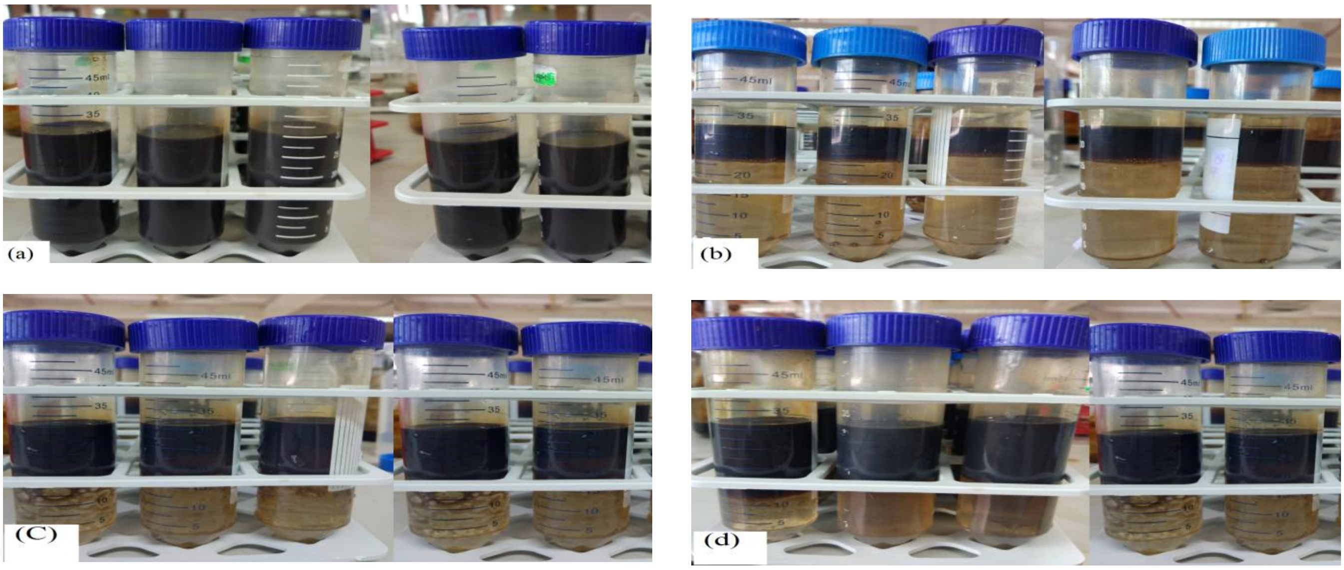
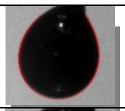
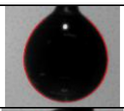
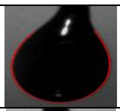
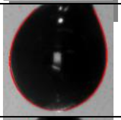
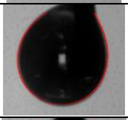
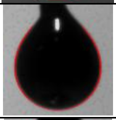
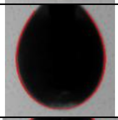
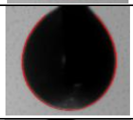
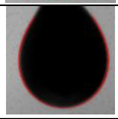
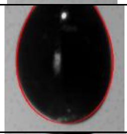
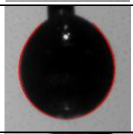
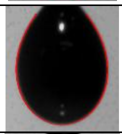
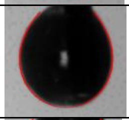
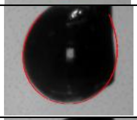
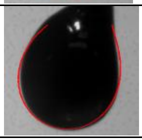
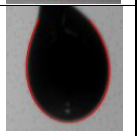


Fig.3: Demulsification bottle test (a) before separation, (b) 20:80 water cut emulsion, (c) 30:70 water cut emulsion, (d) 50:50 water cut emulsion after separation with addition of 40, 80, 120, 160, and 200 ppm graphene oxide from left tube to right tube.

. ***Table 3: Pendant shape of emulsion sample with addition GO.***

Water cut GO Conc	20:80	30:70	50:50
0			
40			
80			
120			
160			
200			

D. Effect on Interfacial Tension

The Interfacial surface tension related directly to demulsification process. Interfacial surface tension can be stated as how much pressure needed to break the link between two liquid. Higher value of interfacial surface tension mean the mixture of two solution hard to be separate and stable. One of the good criteria of demulsifier is reduction of interfacial surface tension between emulsion film.

Goniometer result can be shown figure 4 as all the concentration of oil emulsion reduce interfacial surface tension value when graphene oxide is added. The highest change happen at concentration of oil 30:70 by water cut which is up to 16.992% from its initial without demulsifier. Another two concentration record different about 8.16% and 5.230% for 20:80 and 50:50 concentration by water cut.

The reason reduction of interfacial surface tension is due to graphene oxide mechanism that partially replace the emulsifier in the oil film and reduce the stability of the emulsion hence increase the efficiency of emulsion.[8]

IV. Conclusion

The categorization test indicate that the sample was graphene oxide by synthesis due to viable peak that support the presence of oxide. The result of bottle test analysis also proved graphene oxide can act as effective demulsifier with diluted heavy crude oil emulsion with efficiency from 99.87% to 99.98% within 30 minute of retention time given. The rapid demulsification process by adding graphene oxide support by the decrease of interfacial tension value of emulsion with increasing value of grpahene oxide concentration. It can be conclude that graphene oxide can break the film between oil and water to ease the emulsion to separate.

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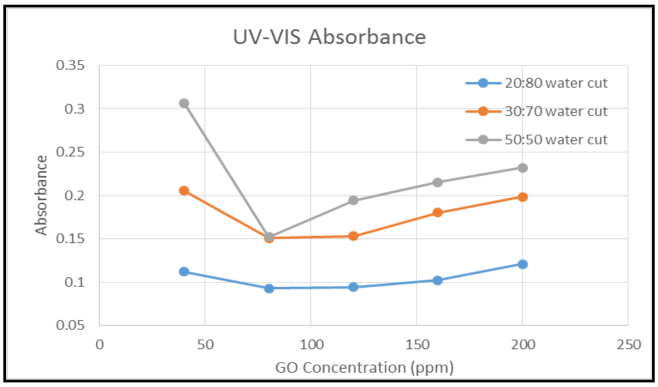

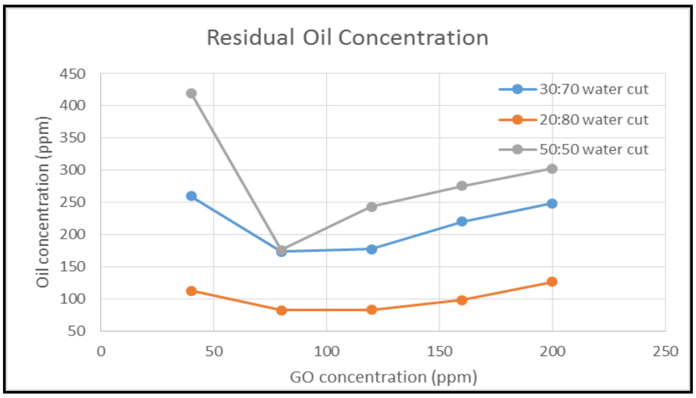

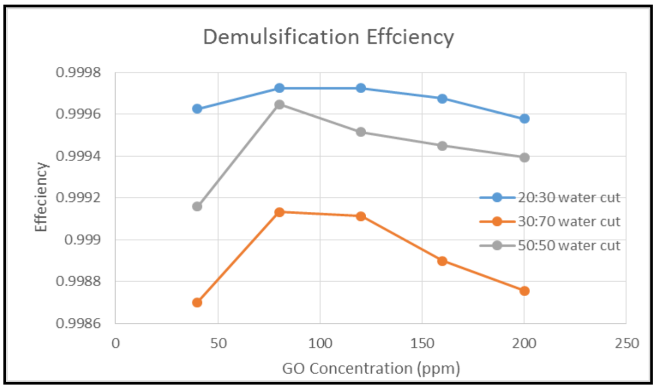

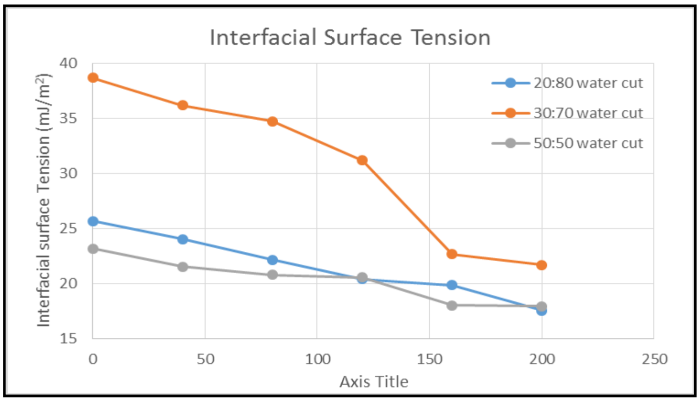

Fig.4: analysis graph of demulsification bottle test UV-VIS and interfacial tension of emulsion with different concentration of graphene oxide.

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