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

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Abstract- The difficulties associated with the crude oil emulsions and produced water cause the oilfield researchers to investigate into practical demulsification methods for many decades. Surfactant is the main component in stabilizing the interfacial film surrounding the dispersed phase droplets which contribute to emulsion stability. The most efficient demulsification method is chemical demulsification which able to attain desirable separation efficiency while complying with the environmental regulations and imposing the least economic burden on the petroleum industry. A magnetic graphene oxide (MGO) was synthesized by one-step co-precipitation method from graphene oxide (GO). The properties of the MGO were characterized by XRD analysis and supported by FTIR analysis. Different concentrations of MGO used to demulsify the heavy oil emulsions of different water cut were studied. The magnetic graphene oxide (MGO) was successfully synthesized and used for separating diluted heavy oil emulsions. Demulsification tests which is bottle test indicated that MGO could separate the emulsions within a few minutes. The residual oil content in the separated water analyzed by UV-Visible spectrophotometer was as low as 20 mg/mL corresponding to a demulsification efficiency of 99.99% at an optimal dosage. The interfacial tension of the emulsions during demulsification process were also analyzed.

Keywords— Chemical Demulsification, Diluted-heavy oil emulsion, Interfacial tension, and Magnetic Graphene Oxide

I. INTRODUCTION

In oilfield industry, emulsification of crude oil with brine always occur during production phase and in processing industry. Extraction of crude oil commingled with water cause the emulsions to form. The emulsions that are always encountered are Oil-in-Water (O/W) emulsions and Water-in-Oil (W/O) emulsions. Wen et al. (2010) stated that these emulsions can be classified based on the continuous phase and the dispersed phase. It is essential to separate these two immiscible materials before processing the produced crude oil. Failure to separate these emulsions could results in several difficulties such as damage in surface separation equipment and pipeline corrosions [2]. Due to these problems, chemical demulsifier additives are mostly used in treating the emulsions.

Emulsion is a dispersion of one liquid throughout another immiscible liquid in a form of small droplets which then stabilized by emulsifying agent. Natural emulsifier such as surface-active agents or surfactants consists of hydrophilic and hydrophobic parts that each only attracted to water and oil, respectively. This molecular structure cause the surfactants to form interfacial films at the oil/water interface of the emulsions. The interfacial rheological properties, solubility, and adsorption-desorption kinetics of the surfactants determine the stability of the interfacial film [3]. Interfacial films acts as a barrier against coalescence and flocculation of the oil and water droplets. Thus, to separate these emulsions, omission, variation, or neutralization can be done towards the emulsifying agents [4].

One of the method that is widely applied to treat the emulsions is chemical demulsification. Chemical demulsifier reduced the kinetic stability of the interfacial films during demulsification process by changing the interfacial rheological properties of the emulsion. For example, one of the emulsifying materials in the crude oil is asphaltene. It have a sufficient number of functional groups which formed interfacial layer with a great mechanical strength. Demulsification process occurs when the demulsifying materials break the interfacial layer of the asphaltenes.

Nowadays, graphene-based material have been discovered as a potential adsorbents. One of it is Graphene Oxide (GO) which rich with surface-active agents, hydroxyl and carboxyl, makes it potential adsorbent. Due to the good disperse ability and high hydrophilicity of GO make it difficult to separate from aqueous solution thus, cannot use directly as an adsorbent [5]. Liu et al. (2017) had indicated that despite the contamination cause by GO to the water or oil in the refinery, GO has a fast and great separation efficiency. The contamination is because GO can stably exist in aqueous and oil phase.

Due to inability of the GO to use directly as an adsorbent, GO is introduced to the magnetic nanoparticles (MNPs). Since GO is dispersible in aqueous solution and difficult to separate, the magnetic property could aid to the post treatment separation and reuse [7]. By introducing MNPs to GO, additional functional groups can be added to the adsorbent, enhancing its adsorption capacity. MNP capable for magnetic separation, environmental remediation, and many others application in most fields catch the interest of the researchers on the subject. Magnetic graphene oxide (MGO) nanocomposite possesses high adsorption capacity and can easily separate oil from water phase when an external magnetic field is introduced. Separation process using MGO requires less energy compared to other separation method such as filtration and centrifugation [5].

The chemical demulsification process will be carried out in this research to treat diluted heavy oil emulsions. It is a process where the effect of MGO on the acceleration of the emulsion breaking process is studied. The rheological properties and efficiency of demulsification at different concentration of MGO on the different water cut of diluted heavy oil emulsions were investigated.

II. METHODOLOGY

A. Materials

Graphite powder was obtained from MERCK, sodium nitrate (NaNO₃), concentrated sulphuric acid (H₂SO₄), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂), 5% of

hydrochloric acid (HCl), acetone, ferric chloride (FeCl₃), ferrous chloride (FeCl₂) and 28% ammonia solution, .Bertam heavy crude oil samples, sodium chloride (NaCl), potassium chloride (KCl), magnesium sulphate heptahydrate (MgSO₄.7H₂O), potassium dihydrogen phosphate (KH₂PO₄) and toluene were provided by faculty. Distilled water were used throughout the experiment.

Table 1: Chemical and Physical Properties of the Bertam Heavy Crude Oil

Properties	Value
Oil density (g/cm ³)	0.988
Kinematic viscosity (50°C, cP)	17,751
Saturare (%wt)	3
Aromatic (%wt)	63.4
Resin (%wt)	12.9
Asphaltene (%wt)	20.7

B. Synthesis of GO

GO was synthesized from graphite powder according to the modified Hummer's method which involved both oxidation and exfoliation of graphite. In this method, 10 g of graphite powder and 5 g of NaNO3 were added into 500 ml beaker. Then, 200 ml of concentrated H₂SO₄ was added into the mixture. The mixture was then stirred for an hour at temperature less than 15°C at speed 350 rpm in an ice bath. After that, 60 g of KMnO₄ was added quarterly into the mixture and stirred continuously within two hours at a temperature below 15°C. Later, the ice bath was removed and the mixture was kept stirred for two hours at room temperature. The mixture was then heated to 70°C. Then, 100 ml of distilled water was added slowly within two hours. The mixture was heated up to 90°C and added another 100 ml of distilled water within one hour while stirred. Then, 60 ml of H₂O₂ was added to the mixture to eliminate excess of KMnO4 and constantly stirred for an hour. The solution then was left overnight. The mixture was washed with 5% of HCl solution to remove the supernatant and followed by distilled water to obtain alkali solution with pH at 10. The above mixture was centrifuged to separate water and solid. The GO solution was then washed with acetone to produce fine particles of GO. The washed GO solution was dried in the oven at 60°C for 24 hours to produce GO [8].

C. Preparation of M-GO

MGO was prepared by chemical co-precipitation method. 1.8 g synthesized GO was dispersed in 500 mL of high purity water and ultrasonicated for 2 hours to obtain a clear dispersion of GO. Then, 32.5 g FeCl₃ and 12.7 g FeCl₂ were added slowly to 400 mL of H₂O. The mix solution was then added slowly to GO solution under nitrogen (N₂) flow at 50 mL/min with vigorous stirring. The 28% ammonia solution was added slowly to precipitate Fe²⁺ and Fe³⁺ ions for synthesis of magnetite particles until the pH solution is 10. The solution was cooled at room temperature after being rapidly stirred for 30 minutes by constant mechanical stirring. Then, the external magnetic field was applied to the dark black colored solution to separate the MGO from the solution. After that, the MGO was washed with high purity water 5 times and dried in the oven at 60°C for 24 hours to produce MGO [9].

D. Preparation of the diluted-heavy oil emulsion

Synthetic brine was prepared by mixing 10 g of NaCl, 0.29 g of KCl, 0.42 g of MgSO₄.7H₂O, 0.83 g of KH₂PO₄, and 0.42 g of NaNO₃ into 1 L of distilled water [10]. Heavy crude oil was obtained from Bertam Oil field with properties of 11 ° API. The crude oil was then diluted with 20% by volume of toluene to reduces the oil viscosity [11]. Diluted heavy oil emulsions were prepared by dispersing the oil phase into the water phase. The emulsions were prepared in a 500 mL beaker. Synthetic brine was

used as the continuous phase while crude oil was used as the dispersion phase. These two phase were vigorously stirred at room temperature until they became completely homogenous. The emulsions were prepared at different percentage ratio of water to crude oil at 80:20, 70:30, and 50:50 (%, v/v).

E. Demulsification test

The bottle test was used to estimate the efficiency of the MGO towards diluted-heavy oil emulsions. The MGO was dissolved in the distilled water (1 g/L) and then added into the test tube at 20 mg/L of MGO suspension in 30 mL of the previously prepared emulsions. Then, the mixture was shaken vigorously for 1 minute. The test tubes were then placed in the water bath for 10 to 15 minutes at 60°C. Oil/water separation were observed for half an hour. The separated water were then subsequently removed from the newly formed oil phase and collected carefully from each separation bottle carefully by using separatory funnel.

The demulsification efficiency of MGO was determined by measuring the residual oil content in the separated water sample. The samples were collected from each bottle sample analyzed by UV-Visible spectrophotometer at a wavelength of 350 nm of a 1 cm path length. The initial oil concentration can be calculated by the following equation:

$$C_{o} = (m_{o} / V_{w}) \times 10^{3}$$
(1)

where C_o (mg/L) is the oil concentration, m_o (mg) is the corresponding mass of oil in the standard sample and the V_w (mL) is the water volume. The demusification efficiency was calculated from the measured residual oil content by equation:

$$E = (C_{o} - C_{i}) / C_{o}$$
(2)

where C_o and C_i are the initial and residual oil content concentration in the separation water, respectively. The residual oil content concentration for each sample were obtained from standard curve. The demulsification efficiency value is in percentage. The value shows that the percentage of the diluted-heavy oil removed from the emulsions. Liu et al. (2017) stated that, the higher the efficiency is, the better the demulsification performance will be.

The rheological measurements of the emulsions were performed using a pendant drop method using Goniometer instrument. The pendant drop is a drop of liquid suspended from a needle. The shape of the drop results from the relationship between the interfacial tension and the gravity. The drop shape was captured to retain the permanent visual image. With a good image and lighting, the software directly calculated the interfacial tension of the pendant drop using drop shape analysis.

III. RESULTS AND DISCUSSION

A. Characterization of M-GO

There are numerous methods can be used to determine the properties of MGO including Fourier-transform Infrared (FTIR) Spectroscopy and X-Ray Diffraction (XRD) analysis.

FTIR was used to determine the information on the functional groups on the surface of MGO and the binding mechanism of pollutants [5]. The FTIR spectra of all the studied compounds are shown in Figure 1. The MGO high points were located at 1634 cm⁻¹ and 589 cm⁻¹, related to epoxy groups, and indicate the symmetric stretching of the iron oxide (Fe₃O₄) nanoparticles. It proved that Fe₃O₄ nanoparticles was successfully attached onto the graphene sheets [9]. The wide band at 3197 cm⁻¹ in the FTIR spectra included the stretching vibration of the hydroxyl group and N–H bond, while the peaks at 1673 cm⁻¹ and 1018 cm⁻¹ were attributed to C=O of the –NH=C=O bond stretching, and the C–OH bond stretching, respectively.



Figure 1: FTIR spectra of graphite, graphene oxide (GO), and magnetic graphene oxide (MGO)

XRD measurements were performed to obtain the crystalline structural information for the magnetic composites of the MGO. It is an effective technique to determine the phase and structure of the MGO by providing data about the physical as well as chemical forms of MGO nanocomposites. XRD spectrograms of GO and MGO are presented in Figure 2. The pattern of MGO in the Figure 2 shows the several well-defined diffraction peaks of five major peaks. It is similar with iron oxide indicating its dominance in the binary. The several well-defined diffraction peaks were clearly observed at 20 value of 30.10° , 35.49° , 43.39° , 57.25° , and 62.98° , which can be indexed as the 449, 704, 424, 456, and 481 of plane reflections of magnetic nanoparticles.

B. Demulsification performance of MGO demulsifier

The demulsification of the prepared emulsions can be visually observed through bottle test method. It is the simple and intuitive method to evaluate the performance of MGO as a demulsifier in. Demulsification process driven by MGO nanoparticles were shown on the Figure 3 below. The different concentration of MGO were



Figure 2: X-ray diffraction (XRD) spectrograms of GO and MGO

added into 30 mL of diluted-heavy oil emulsion placed inside the test tube and observed for 30 minutes. In Figure 3(a), the picture shown the initial condition of the emulsions before different concentration of MGO demulsifier were added into the test tube. The emulsions were prepared with three different ratios of oil to water which were 20:80 v/v% in Figure 3(b), 30:70 v/v% in Figure 3(c), and 50:50 v/v% in Figure 3(d). The separation of diluted-heavy oil from water by various MGO demulsifiers concentration can be seen clearly from the bottle test method. It was found that the color of the separated water after demulsification by various concentration of MGO nanoparticles. The cloudiness of the separation water were also due to the diluted-heavy oil tend to stick to the wall of the plastic test tube.

The demulsification efficiency of the emulsions were determined by the residual oil concentration in the separated water. The residual oil concentration in separated water were obtained by UV-Vis analysis. As shown in Figure 4(a) of emulsions with 80% water cut, the residual oil concentration in the separated water reduced to 398.8 mg/mL corresponding to a demulsification



Figure 3: Visual observation of the demulsification after the MGO is introduced with from the right at 40 ppm, 80 ppm, 120 ppm, 160 ppm, and 200 ppm (a) initial condition of emulsion before adding the MGO (b) emulsion at 20% of oil (c) emulsion at 30% of oil (d) emulsion at 50% of oil

efficiency of about 99.7% with 40 ppm MGO concentration. It was greatly decreased with increasing the MGO concentration. It was found that the best demulsification performance was acquired at concentration of about 80 ppm to 200 ppm with the demulsification efficiency could attain about 99.97% to 99.99%. Emulsions with 70% and 50% water cut were shown in Figure 4(b) and Figure 4(c), respectively. The residual oil concentration were decreased with increasing the MGO concentrations. The best demulsification efficiency attain for the emulsions were 99.98% to 99.99% for emulsions with 70% water cut at 80 ppm to 200 ppm of concentration MGO. For emulsions with 50% water cut, the best demulsification efficiency were at 99.91% to 99.99% at MGO concentration of about 120 ppm to 200 ppm. The results indicate that MGO nanoparticles could be used as an effective demulsifier for breaking the emulsions.

C. Interfacial rheology

The interfacial tension was determined as a function of MGO concentration. The interfacial tension of each emulsions with different concentration of demulsifier were measured using pendant drop of Goniometer instrument. The drop shape used to calculate the interfacial tension were shown in Figure 5. Wang et al. (2016) stated that the interfacial tension of emulsions were gradually decreased with the increase of the concentration of various demulsifiers in the solution. It was consistent with the value obtained from the pendant drop shape analysis. The relationship between the concentration of MGO and interfacial tension was shown in Figure 6. As shown in Figure 6, the interfacial tension of the emulsions decreased with the increase of the concentration of the MGO. This confirmed that MGO nanoparticles had excellent interfacial activity and was capable of diffusing into the oil/water interface to reduce the interfacial tension of the emulsions.

In Figure 7, the graph shows the relationship between the interfacial tensions with the demulsification efficiency. The figure shows that when the interfacial tension between the liquids in the emulsions were decreased, the demulsification efficiency also increased. For example, at emulsion of 20:80 v/v%, the efficiency



Figure 5: Pendant drop for IFT measurement



Figure 4: Effect of the MGO concentration on the residual oil concentration in the separated water and the corresponding demulsification efficiency at (a) 80% water cut, (b) 70% water cut, and (c) 50% water cut



Figure 6: Effect of various MGO demulsifiers on the interfacial tension of the emulsions with different water cut

of demulsification is at 99.97% to 99.99% when the interfacial tension decreased from 33.22 mN/m to 18.37 mN/m. Therefore, it is believed that reducing the interfacial tension of oil/water is an important factor contributing to the demulsification process.

IV. CONCLUSION

Magnetic demulsifier of MGO was prepared and determined to be a rapid and high-efficiency demulsifier to separate the dilutedheavy oil emulsions. It was found that the stability of the emulsions were greatly destroyed by adding MGO and the demulsification process could be finished within several minutes. MGO also able to decrease the interfacial tension of the emulsions, implying that MGO nanoparticles was interfacially active. Such excellent demulsification performance was attributed to the fact that the MGO can be separated from separated water by applying an external magnetic field. Small oil floccules combined with the MGO suspending in the separated water can be eliminated by an external magnetic field. The MGO then can be reused until it functions deteriorate. Future researcher are recommended to study on the efficiency of recyclable MGO demulsifier towards emulsions. The contact angle of the demulsification process can also be observed to know the wettability of the emulsions when subjected to recyclable MGO demulsifier.

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Figure 7: Relationship between interfacial tension and demulsification efficiency

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