Application of Magnetic Molybdenum Disulphide (MoS_2) on Heavy Oil: Effect on Asphaltene Precipitation and Wax Deposition

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Abstract. The application of nanoparticles has been widely used in the oil and gas industry research activities. In this study, the magnetic molybdenum disulphide (MoS_2) was synthesized from molybdenum disulphide. The magnetic MoS_2 were then characterized by FTIR, XRD, BET and particle size analyzer. Then, rheometer was used to determine the changes of viscosity with the effect on asphaltene deposition. For wax deposition, cold experiment was done with different concentration of magnetic MoS_2 to determine the amount of wax deposited. The results showed that increasing the concentration of MoS_2 will reduce the asphaltene precipitation and wax deposition of heavy oil.

Keywords: Asphaltene, Heavy Crude Oil, Nanoparticle, Wax Deposition.

1.0 Introduction

Nanotechnology is defined by development and techniques used to investigate physical phenomena thus constructing the physical size range of 1-100 nm. It is worth mentioning the size of nanotechnology sometimes differs from various international organizations. The invention of nanotechnology created one of the essential materials called nanoparticles [1]. The various types of nanoparticles can be found and at the same time provide numerous advantages towards variety of sectors. The most notable facts about nanoparticles are their unique properties which can be manipulated based on different applications. The changes in size when compared to bulk materials used in nanotechnology eventually lead to an increase in the volume of contact area to volume ratio which greatly benefits all sectors. The significant changes of nanoparticles will be their enhanced properties which are high reactivity, strength, surface area, stability and sensitivity which are mainly caused by reduction of size or in simpler terms, small size [2]. The various types of existing nanoparticles also promote numbers of methods in term of synthesizing different type of nanoparticles. Various methods are required after taking account for commercial use such chemical, physical, and mechanical processes exist to ensure the nanoparticles can be synthesis accordingly to the demand of nanoparticles across the globe.

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Aromatics, resins, waxes, asphaltenes, and naphthenic make up crude oil, which is a very complex mixture of hydrocarbons. Among these components, wax precipitation is one problem as it can decrease production rates. Wax has high molecular weight paraffin in crude oil. For asphaltene, it is one of the components in crude oil that caused many problems during transportation and production of oil from reservoir. It has different structures and molecular makeup making it complex in the components of oil. Asphaltene deposition is a significant problem in many parts of the world. Following an initial production rate of up to 3,000 BPD, the wells in the Prinos field [3] in the north Aegean Sea would have to be completely shut down in a matter of days. This is a major problem, as the cost of fixing the well workover might be as much as a quarter of a million dollars. Besides the problem of asphaltene deposition, crude oil also has a problem of wax precipitation. Crude oil comprises of naphthenic, asphaltenes, resins, waxes, and aromatics, as it is composed of a complex blend of hydrocarbons. By disregarding wax precipitation, significant problems such as lower production rates, increased power consumption, and facility failure will follow.

In this study, two experimental procedures will be carried out to achieve the objectives of the research study which are to synthesize and characterize the magnetic molybdenum disulphide (MoS_2) and the effect of asphaltene precipitation and wax deposition on heavy crude oil.

2.0 Methodology

2.1 Materials and Apparatus

Iron (II) chloride tetrahydrate and iron (III) chloride hexahydrate are used for the process of magnetizing the MoS_2. Ammonia solution (30%) is used to control the pH to 7 as the solution cannot be too acidic. Ultrasonic cleaner is used to exfoliate the MoS2 through sonification process. Heating mantle used for stirring and heating purposes. Pure water solution and deionized water is used to ensure the mixture will not have any by- product chemicals. Nitrogen gas tank is to supply constant nitrogen gas and fume hood to avoid smell of the chemicals from spreading. Finally, drying oven is to remove any moisture from the sample. The properties of Bertam heavy oil are presented in Table 1.

Table 1. Chemical and physical properties of Bertam heavy oil.

Properties	Value
Oil density (g/cm3)	0.988
Kinematic viscosity, (50 °C, cP)	17,751
Saturate (% wt.)	3.0
Aromatic (% wt.)	63.4
Resin (% wt.)	12.9
Asphaltene (% wt.)	20.7

2.2 Preparation of Magnetic Disulphide (MoS_2)

Firstly, the MoS_2 will be exfoliated for 1 hour. After MoS_2 mixed with 250mL water, the mixture will be undergoing sonification in ultrasonic cleaner. Sonification process is to convert carboxylic acid groups into carboxylate anions. Next, iron (II) chloride tetrahydrate ($FeCl_2$,$4H_20$) and iron (III) chloride hexahydrate ($FeCl_3$,$6H_2O$) will be dissolved into a 200 mL pure water solution with weight of 6.25g and 16.25g respectively. The solution of iron (II) chloride tetrahydrate ($FeCl_2$,$4H_20$) and iron (III) chloride hexahydrate (FeCl3,6H2O) will be added dropwise into the MoS_2 solution which is inside the round bottom flask. The temperature is room temperature and undergoes stirring with constant supply of nitrogen flow (40 mL/min). Next, 30% ammonia solution will be added to change the mixture of the solution to pH of 10. Next, the mixture will be heated to 90°C for 2 hours. Next, the mixture will undergo cooling and aging for 12-24 hours without stirring. The precipitate will gather at the bottom of the round flask. After that, the precipitate will be collected and washed with deionized water to neutralize the pH of 10 to 7. Finally, the precipitate will be dried in the oven with temperature of 60°C for 24-48 hours and grinded with mortar to make the sample into solid powder form. The sample was sent for characterization through XRD, BET, FTIR spectroscopy, and Particle Size Analyzer which help to define the properties of sample.

2.3 Performance study of MoS_2 on Asphaltene Precipitation and Wax Deposition of Heavy Crude Oil

For the effect of magnetic molybdenum disulphide (MoS_2) on asphaltene precipitation of heavy oil, the $MoS_2$is mix with heavy oil in at continuous 500 rpm for 30 minutes at room temperature. The concentrations are mixed with crude oil at 5 wt%, 10 wt% and 15 wt%. The mixture will be tested in a rheometer for rheological measurements to determine the changes in viscosity. The shear rate is set to between 0 and 500 s–1 at 30°C. The shear rate and apparent viscosity values were obtained for every 10 sec, which will result in 28 points. The degree of viscosity reduction was calculated by using Equation 1.

$$DVR\% = \frac{\mu_{ho} - \mu_{np}}{\mu_{ho}} \qquad (1)$$

where DVR% is degree of viscosity reduction percent, μho is viscosity of heavy oil before addition of MoS_2, and μnp is viscosity of heavy oil after addition of MoS_2.

For the performance study of magnetic molybdenum disulphide on heavy oil wax deposition, 5 wt% and 15 wt% MoS_2 were chosen for the investigation of wax deposition. For 24 hours, crude oil samples with and without MoS_2nanoparticles were subjected to a cold finger experiment to determine the amount of wax deposited. 400 rpm was maintained for the impeller speed. After that, the amount of solid deposited were scrapped and weighed. Paraffin inhibition efficiency (PIE %) was calculated using Equation 2.

$$PIE\% = \frac{W_f - W_t}{W_f} \quad (2)$$

where PIE % is paraffin inhibition efficiency, W_f is amount of wax deposition without addition of MoS_2, and W_t is amount of wax deposition with addition of MoS_2 treatment in grams.

3.0 Findings

3.1 Characterization of Magnetic Molybdenum (MoS2)

3.1.1 XRD. The peak (cps) from the XRD report of the magnetic MoS_2. The highest peak gain for the sample were recorded at value of 71 a.u. The parameters set for XRD are the scan speed is 2.0°, the voltage and current are 40 kV and 40 mA respectively. The XRD will be divided into two graph which are the first graph is to ensure the MoS_2 is genuine. The graph of the bulk powder MoS_2 shown as below (Figure 1).

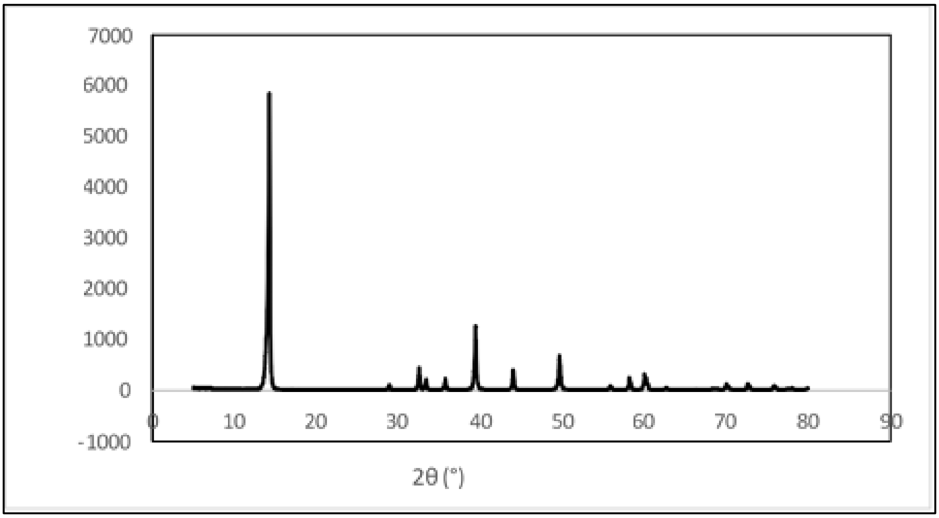

Fig. 1. RD pattern for MoS_2 (bulk powder).

The result for this graph XRD patterns were clearly obtained, the results are 2θ= 14.35° (5856), 2θ= 39.05° (1168), 2θ= 49.76° (587) and 2θ= 58.28° (259). The graph was compared with other articles and journal which showed only slight difference between the graphs [4]. Figure 2 is the graph for XRD patterns for magnetic MoS_2.

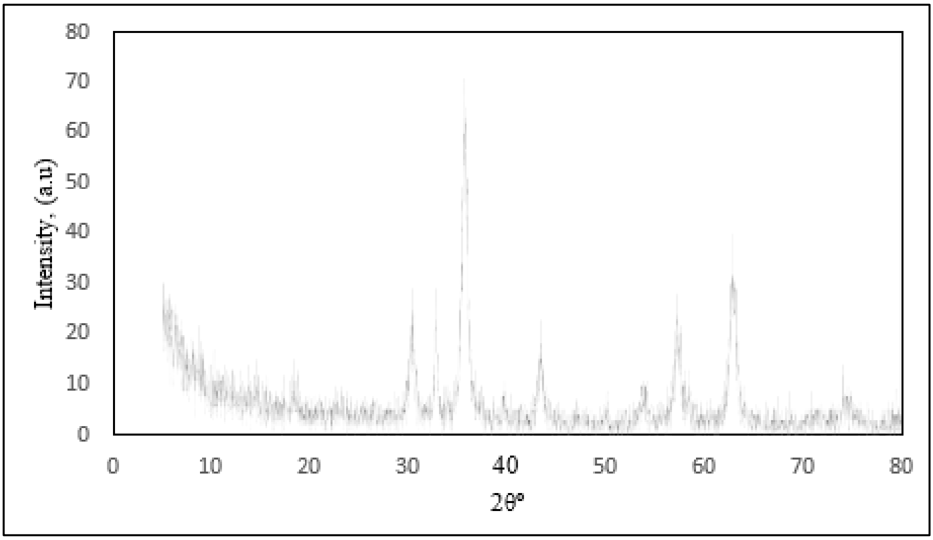

Fig. 2. XRD patterns for magnetic MoS_2.

The result is 2θ= 32.80° (29), 2θ= 35.59° (71), 2θ= 43.44 (23), 2θ= 58.54 (28) and 2θ= 63.67° (40). The comparison between both graphs were made thus showed difference in the pattern due to structural changes of the second graph which was mainly caused by ultrasonic exfoliation. The exfoliation process was highly responsible in producing fewer layer of graphene like MoS_2 [5].

3.1.2 FTIR. The FTIR was crucial to ensure that the type of functional group bending or stretching can be identified as it is important before implementing the application on the heavy crude oil. The characterization of Magnetic MoS_2 can be performed by analysis all the available adsorption peaks in the graph [6, 7]. Figure 3 below shows the FTIR Spectra for magnetic MoS_2.

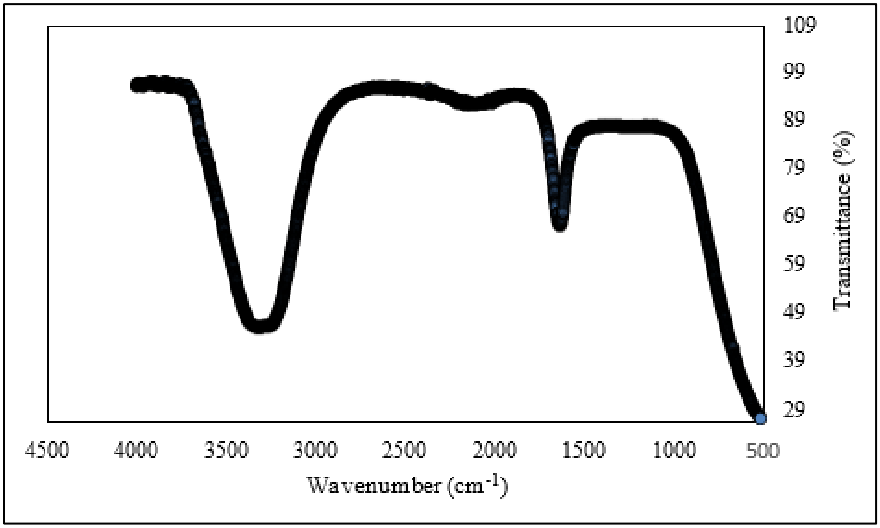

Fig. 3. FTIR spectra for magnetic MoS_2.

The group shows that the magnetic MoS_2 has a frequency range of 4000–515 cm-1. The characterization of magnetic MoS_2, will be performed on the peaks result. The absorption peaks show at 3320.74 cm^{-1}, 2145.29 cm^{-1}, and 1534.2 cm^{-1}. From Fig.3 magnetic MoS_2 revealed that the sample had an O-H stretch from the alcohol group (3320.14 cm^{-1}) and C≡H stretch for wavelength of (2145.2 cm^{-1}) [8]. At (1534.2 cm^{-1}), the final wavelength, C=C bending was clearly visible (Aromatic group).

3.1.3 BET. The surface area of the magnetic MoS_2 is measured using the BET, which falls under the category of nanoparticles. It is also capable of determining the adsorption of magnetic and maximum pore volume MoS_2 as well as other properties. Mesoporous and type IV isothermal samples were previously thought to be present in both iron oxide and magnetic MoS_2 nanoparticles [9]. Pore diameters between 2 and 50 nm are considered mesoporous, which is defined by the presence of pores [10]. The adsorption graph for magnetic MoS_2 was obtained and used to determine the amount of gas adsorbed by the sample sent to show the quantity adsorbed (mmol/g) against relative pressure (p/p°). Figure 4 below shows the Isotherm Linear Plot.

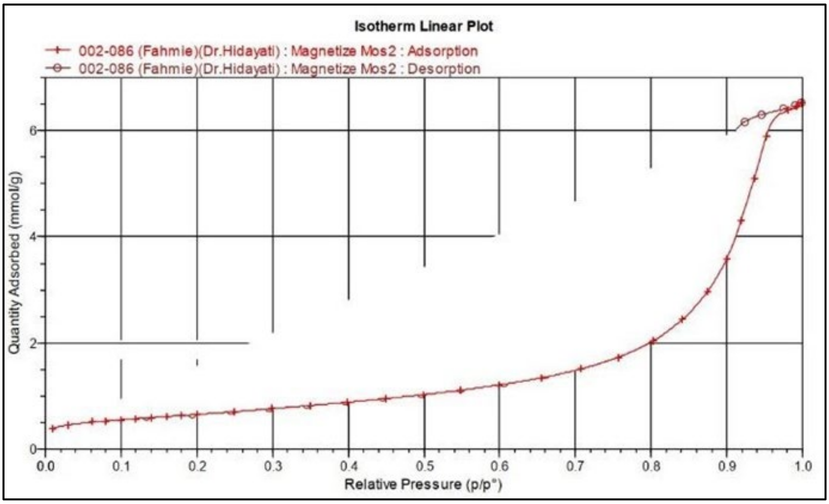

Fig. 4. Isotherm linear plot for magnetic MoS_2.

According to the BET summary report, the sample had a surface area of 60.00 m^2/g, which was confirmed by the magnetic MoS_2. The maximum pore volume of the sample was estimated at the value of 0.22 cm^3/g which then compared with previous study which have 0.27 cm^3/g maximum pore volumes [11]. Because the pore size of 136 Angstrom was converted to 13.6 nm, it was classified as mesoporous, falling within the range of nano porous, which was 2-50 nm [12].

3.1.4 Particle Size Analysis. Particle Size Analyzer used to determine the particle size of magnetic MoS_2. The refractive index used for the sample will be 4.000 [13] and the sample was added till the obscuration of the equipment reached at least 10% which was required to ensure the compliance Standard Operation Procedure (SOP) of the equipment. From figure below, the size is average around 73 nm which is in the range of nanoparticle between 1 to 100 nm [14].

4.0 Discussion

4.1 Asphaltene Precipitation

Figure 5 shows the viscosity of heavy oil when magnetic MoS_2 is added at different concentrations of 5 wt%, 10 wt% and 15 wt%. The figure below shows that different concentration of nanoparticle sizes reduce viscosity. The viscosity decreases as the concentration of nanoparticles decreases [15]. In comparison to the other concentrations, a viscosity reduction of 5 wt% of nanoparticles is clearly visible. When crude oil and magnetic MoS_2 mixed, nanoparticles can increase the contact area between asphaltene and nanoparticles by increasing the interaction between asphaltene and nanoparticle [16]. The viscosity of heavy oil is decreasing because of heavy oil fragmentation and internal redistribution [17].

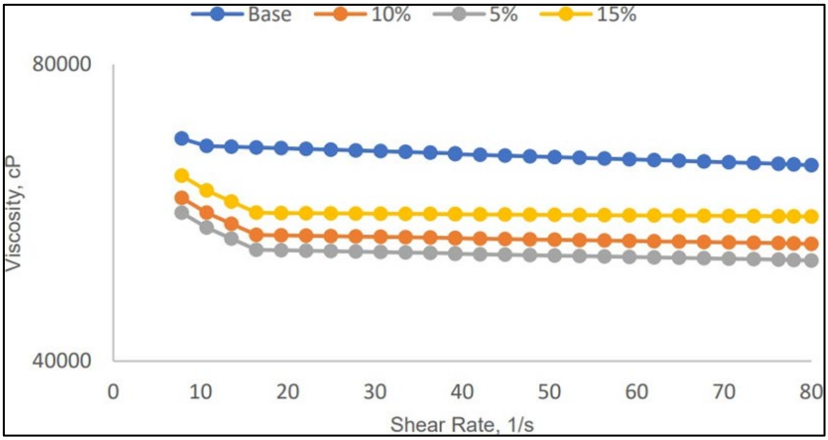

Fig. 5. Rheological measurement of crude oil with MoS_2 nanoparticle of different wt% at 30ºC and shear rate between 0-80 s^{-1}.

Calculating viscosity reduction (DVR%) can be done using the equation 1 where, µHO and µnp are the crude oil before and after-nanoparticle- inclusion viscosity values, respectively. The DVR% is measured at shear rate between 0-80 s^{-1}. On Figure 6, the biggest reduction in viscosity was observed at 5wt% nanoparticle content, according to the graph. An important part of the reason for this reduction in viscosity [20] is due to interactions between its internal structure and that of the fluid.

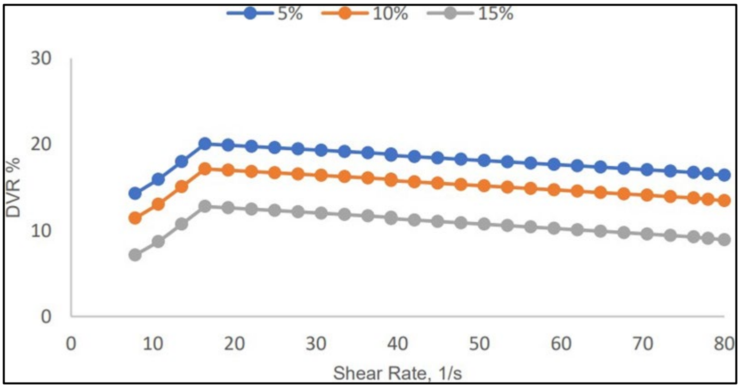

Fig. 6. Degree of viscosity reduction of heavy oil with magnetic MoS_2 nanoparticles of different wt% at 30 ºC and shear rate between 0-80 s^{-1}.

4.2 Wax Deposition

The comparison results between crude mixed with 5wt% and 15wt% of magnetic MoS2 nanoparticles is shown in Figure 7. Crude oil with no chemical treatment served as the foundation for two different wt% categories that may have the ability to reduce wax and may even be the best reduction of wax in their respective categories. In comparison to the original wax deposit, 5 wt% exhibits a tendency to reduce the wax by as much as 12 g, while 15 wt% exhibits a tendency to reduce the wax by about 8 g. This occurs because of the strong intermolecular force that exists between the nanoparticle and the wax [19]. The figure below shows comparison of deposition of wax for 5 wt% and 15 wt% of nanoparticles.

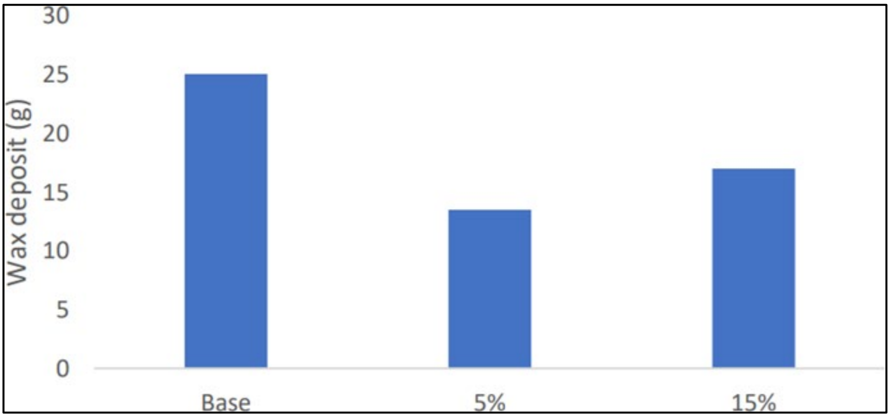

Fig. 7. Deposition of wax for 5 wt% and 15 wt% of nanoparticles.

The table shows the percentage inhibition efficiency (PIE%), which was calculated to determine the efficiency of nanoparticle in terms of wax reduction. The 5 %wt have higher Percentage inhibition efficiency (PIE%) than 15 %wt. These findings demonstrate that magnetic MoS_2 nanoparticles can reduce the amount of wax produced by separating from individual molecules because the nanoparticles cause less favorable interaction between the molecules [19].

Table 2. Percentage of inhibition efficiency.

Concentration of MoS_2	Percentage of Inhibition Efficiency (PIE)
Heavy oil + 5 wt%	32%
Heavy oil + 15 wt%	46%

5.0 Conclusion and Recommendation

As a conclusion, the study shows that increasing the concentration of MoS_2 results in low asphaltene precipitation and wax deposition. For XRD characterization, the XRD for both bulk powder and magnetic MoS_2, the result was analyzed with the highest intensity of 71 for $2\theta = 35.59°$ for the magnetic MoS_2. Both XRD patterns were compared with past studies to ensure the material used is genuine. The magnetization of nanoparticles is also a success. For FTIR characterization, bending or stretching of the functional group were O-H stretching (Alcohol), CH_3 stretch and CH_2 bend which belong to aromatic functional group Next, the surface area of the magnetic MoS2 is measured using the BET, which falls under the category of nanoparticles. It is also capable of determining the adsorption of magnetic and maximum pore volume MoS2 as well as other properties, the sample had a surface area of 60.00 m^2/g. Because the pore size of 136 Angstrom was converted to 13.6 nm, it was classified as mesoporous, falling within the range of nano porous. For particle size analysis is to determine whether magnetic MoS_2 possess the similar particle size as nanoparticles such as MGO. The size is average around 73 nm which is in the range of nanoparticle between 1 to 100 nm. For performance studies, the asphaltene deposition was a success in reducing viscosity when mixed with nanoparticle and the wax precipitation is also a success when mixed with nanoparticle as the number of waxes collected decreased.

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