Synthesis of ZnO Nanoparticles for Wax Deposition Control and Oil Upgrading: Effect of Ratio of Zinc Acetate Dihydrate to Oxalic Acid Dihydrate

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***Abstract*— In the current paper, fundamental aspects of heavy oil and wax deposition problems are defined. Wax or in another term is cloud point occur when the oil starts to precipitate. When it's started to precipitate, it can cause major problem to industry of oil and gas. In this study, ZnO nanoparticles were chosen to study the effect of varying molar ratio from 1:1, 1:2, 1:3 to the morphology and size of the nanoparticle. The structures and properties were recognized with energy dispersive X-ray (EDX), field emission scanning electron microscopy (FE-SEM), and X-ray diffraction (XRD) methods. EDX and FE-SEM is to study the morphology of ZnO structure while XRD is to determine the purity and size of the nanoparticle. From the study, 1:1 ratio has the smallest size of nanoparticle with 10.37 nm while 1:2 and 1:3 give the size of 12.3 nm and 16.37 nm respectively. As the molar ratio is increases, the size of nanoparticle become bigger. The influenced of ZnO nanoparticles on rheological behaviour of model oils and the wax content is reported. From the study, the addition of ZnO nanoparticle reduced the rheology behaviour of crude oil by varying nanoparticle sizes, temperature and shear rate. ZnO nanoparticle can reduce the deposition of wax up to 50% with influenced of smaller nanoparticle size. Effect of size of nanoparticle highly impact the viscosity and wax content. This prove that, by introducing nanoparticle into crude oil, wax content can be reduced thus decrease the chance for crude to precipitate.**

Keywords*— ZnO nanoparticles, wax deposition, molar ratio, rheological behavior, effect of size

I. INTRODUCTION

The world's first energy consumption is fuel which refer to the crude oil is use almost for the industry in the world. The complication of its structure which consists of paraffins, asphaltenes, resins can cause severe problems mainly in extraction of the oil, storage, transportation and processing [1]. Wax is one of the major problems usually happened in sector of oil and gas.

Wax deposition commonly found in offshore fields due to longer range between platform and in-land facilities up to 20-60 km. Due to a long path to transport crude oil from offshore facilities to land, temperature of the crude oil can drop below its wax appearance temperature (WAT). Paraffins started to crystallize as an interlocking network which lead to increase the viscosity of the oil [2]. Wax is formation of hydrocarbon in a series of long chain of paraffins dissolved with balanced stated at high temperature[3]. Even though there is a lot of reserves of crude oil, the problems arise considering its physio-chemical properties which mainly contain resins and asphaltenes which indicate the heavy components. In result of this amount of component absence in the oil, API gravity is reducing which lead to decreasing its crude viscosity [4].

In order to solve the problems, several approaches have been done. There are a lot of published and on-going research about the techniques to reduce wax contents with its advantages and limitations. Physical and chemical approaches have been developed to counter the problems. Simple and effective physical technologies such heating processes deal with high amount of energy and time [5]. Other methods used higher amount of raw material such as pumping stations, dilution process with solvents, emulsifications and reduction of friction (annular flow). These huge amount of consumption of raw materials used increasing the cost of the process [4]. In order to cope with the situations, nanotechnology comes with various of solutions to breakdown the heavy oil and reducing the wax deposition problems. With the size of nanoparticle range between 1-100nm One of the intriguing characteristics of nanoparticles is with the small size of particle, they have a bigger surface to volume ratio due to the surface of energy [6-9]. Researcher reported that more a nano-sized particles have more than million in surface area to volume ratio when converting from millimeter scale [10]. With their unique characteristics of nanoparticles, they have the capability to hydrocracking the heavy oil to ease the transportation and meet the specific requirement of the production of oil.

Due to the scale of material in its nano form, it become demandable from the material in bulk form. Nano size material has their own multipurpose application to be applied in any type of industry because of the changes in the size of the material. With the large band gap in ZnO (3.37ev), many researchers start to interest in exploring the one-dimensional structure focused on oxide material [11]. Nanocrystalline with uniform sizes is far better from bulk material. ZnO has unique characteristics which depend on its synthesis method. Each method to synthesis ZnO nanoparticles exhibit different type of structures. Sol-gel method is chosen due to cost-friendly compared to other synthesis method and its ability to control their properties by controlling the parameters such as molar ratio, pH, drying temperature and calcination temperature [12].

The purpose of this research is to investigate the effect of changing the molar ratio between zinc acetate dihydrate to oxalic acid to observe the changes in the size and morphology of the nanoparticle. ZnO nanoparticles has been synthesized using sol-gel.

Another purpose of the study is to investigate the effect of different size of nanoparticle on the viscosity reduction of crude oil at different temperature and shear rate as well as the effect on the wax deposition.

II. METHODOLOGY

A. Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), oxalic acid ($C_2H_2O_4.2H_2O$, and ethanol 95% AR Grade were obtained from Vchem Laboratory Chemicals. Reagent chemical such as ammonium hydroxide (extra pure) was obtained from Daejung Chemicals. As a dilutions and preparations for all the samples, deionized water is used. Hydrochloric acid was obtained from Vchem Laboratory Chemicals. Crude oil sample was provided by Kemaman Bitumen Company Sdn. Bhd (KBC). and its composition mentioned in Table 1.

Table 1: Physical and chemical properties of crude oil

Chemical composition	Saturate (% wt)	3
	Aromatic (% wt)	63.4
	Resin (% wt)	12.9
	Asphaltene (% wt)	20.7
Physical composition	Density (kg/m^3)	988.433
	Specific Gravity, SG	0.993
	^{o}API	11
	Average Viscosity @ 40 ^{o}C (cP)	17,751
	Colour	Black
	Cloud Point (^{o}C)	12

B. Properties of crude oil

Physical properties such as viscosity and specific gravity was further investigated to understand it behavior of crude oil. Electronic rheometer is used to determine viscosity which the different shear rate is applied starting from 0 – 500 s^{-1} range at 40ºC. The measurement of viscosity of oil is taken before adding the nanoparticle to observe the changes before and after nanoparticle is added into the oil samples. Standard procedure to run the rheometer is applied with 40ºC as the constant parameter and 500 s^{-1} of shear rate [4].

API of the oil was calculated using equation 1 to identify the hydrocarbon type either light or heavy oil. Mud balance equipment was used to determine the density of the oil. 200 mL of crude oil is used, and the reading of the density is taken after the arm is balanced.

$$\text{API} = \frac{141.5}{SG} - 131.5 \quad (1)$$

$$SG = \frac{\rho_{oil}}{\rho_{water}} \quad (2)$$

C. Preparation of ZnO nanoparticles

Sol-gel method is the technique to obtain the ZnO nanoparticle. Oxalic acid dihydrate is fulfilled and zinc acetate is used as precursor. The function of ethanol and ammonia solution is to take care of the homogeneity and pH value of the solution which help in forming the stoichiometric solution to obtain zinc oxide nanoparticle. Firstly, mixture of zinc acetate dehydrates and oxalic acid (Z_{ac}/O_{xa}) were prepared with three different molar ratios of 1:1, 1:2, 1:3. Ethanol and oxalic acid is mixed in a beaker and stirred at 700 rpm with a magnetic stirrer about 30 minutes at temperature of 45 ± 5 ºC. After that, zinc acetate solution which is the mixture of zinc acetate dehydrate added with ethanol and 10% of volume of water is heated in a water bath at 65 ± 5 ºC at 30 min duration of time. When the solution is complete, the oxalic acid solution is added dropwise onto the zinc acetate solution under the vigorous magnetic stirring until its final drop [12]. The pH of the reactant mixture is kept between 3 ± 0.2 by the addition of hydrochloric acid (1.0M) and ammonia solution. The solution is kept undisturbed until white precipitates appeared in the solution [13]. The precipitate is then filtered using 110mm filter paper and vacuum pump to extract the white precipitate. The residue obtained is put for drying in oven at a temperature of about 80 ºC for about 2 hours. The yellowish white powder is obtained after calcination at 400 ºC for 2 hours to remove moisture and improving the impurity of the ZnO [12].

D. Characterizations of ZnO nanoparticles

1) X-ray Diffractometer

The size of ZnO nanoparticles were determined using X-ray diffraction (Pananalytical, model: Expert PRO) with CuKα radiation (1.5406 Å) in the 2θ scan range of 20–80º. Scherer's equation is used to calculate the size of the nanoparticle:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (3)$$

D is representing the size of the nanoparticle, λ is the X-ray wavelength, β is the full width of half maximum of the peak for ZnO, and θ is the maximum angle of the peak in radians.

2) Field Emission Scanning Electron Microscope (FE-SEM)

FE-SEM analysis is performed to identify the morphological study of the nanoparticle and energy dispersive X-ray spectroscopy is performed to determine the elemental composition of the nanoparticle.

3) Energy Dispersive X-ray Spectroscopy (EDX)

EDX equipment used to determine the %wt. Electron beam is scanned across a sample's surface and strike to stimulate the sample. Each element returns to its original energy state, specific x-ray wavelength was emitted on each characteristic of elements. Data shown the x-ray wavelength and intensity and plotted. Peak values determined the elements of the nanoparticle.

E. Preparation of crude oil with ZnO nanoparticles

ZnO nanoparticle was added to 100 ml of crude oil, and then stirred at 80 ºC for 3 hours.

F. Performance study of zinc oxide in-situ addition to heavy crude oil

1) Effect of nanoparticle size on viscosity reduction

Rheological measurements were performed by using Physica Anton Paar, model: MCR300 electronic rheometer to determine the changes in viscosity when nanoparticle is added, with several condition including the size of nanoparticle, temperature and shear rates. Measurement of rheology of heavy oil were taken at 30 ºC at shear rate between 0-80 s^{-1}. Nanoparticle is mix with heavy oil in at continuous 500 rpm for 30 minutes at room temperature. Degree of viscosity reduction were calculated by applying the equation 4 :

$$DVR\% = \frac{\mu_{HO} - \mu_{np}}{\mu_{HO}} \times 100 \quad (4)$$

Where μ_{HO} and μ_{np} are the viscosity of heavy oil before addition of nanoparticle and viscosity of heavy oil after the addition of nanoparticle.

ZnO nanoparticle is used as evaluation for the size effect on rheological properties. Three sample with different molar ratio of 1:1, 1:2, 1:3 of zinc acetate dihydrate to oxalic acid is used to investigate the effect of size on the rheological properties of the oil which can yields largest viscosity reduction. Positive result should be obtained from the test regarding the reduction of viscosity [4].

2) *Effect of nanoparticle size at high temperature and shear rate*

ZnO nanoparticle with size that has the optimum performance to reduce viscosity was chosen to determine the effect of temperature and shear rates to determine the viscosity reduction. 30ºC, 45ºC and 60ºC temperatures is selected with shear rate ranging from 0 – 500 s^{-1} [4].

3) *Effect of nanoparticle size on wax deposition control*

ZnO with the larger and smaller sizes were selected to investigate the deposition of wax. Cold finger experiment is carried out to determine the amount of wax deposited for 24 hours and maintained the crude oil at 50 ºC for crude oil samples with and without the presence of ZnO nanoparticles. Speed of impeller was maintained at 400 rpm. 1000 mg/L of ZnO nanoparticle is used for this performance study. The amount of solid deposited were further scrapped and weighed [14].

Parrafin inhibition efficiency (PIE %) was calculated using equation 5:

$$PIE(\%) = \frac{W_f - W_t}{W_f} \times 100 \quad (5)$$

Where W_f is the baseline amount of wax deposition which is without addition of nanoparticle treatment in grams, and W_t is the deposition of wax with treatment from nanoparticle [15].

III. RESULTS AND DISCUSSION

The result obtained from experiment test need to be analyzed in order to prove the literature review retrieved from the previous journals. In this chapter, we will discuss about the effect of ZnO nanoparticle synthesized by sol gel method in three different molar ratio which are 1:1, 1:2, and 1:3 molar ratio of zinc acetate dihydrate and oxalic acid dihydrate to study the size and morphology of the nanoparticle in different molar ratio. Another discussion will be on the effect of ZnO nanoparticle on wax deposition and viscosity reduction of heavy oil will also be discussed. 3 different conditions are set for determining the viscosity reduction on the influenced of size of nanoparticles, temperature and shear rate effect. DVR% is also plotted to see the percentage of success of nanoparticle on viscosity reduction of heavy oil.

A. *XRD analysis on ZnO nanoparticles*

Figure 1 shows the peak of XRD patterns at 1:1, 1:2 and 1:3 molar ratio respectively. All the peaks show higher intensity which indicate the ZnO crystallinity is good. The size of the nanoparticle is estimated by applying Debye-Scherer formula. From the formula, 1:1 ratio has the smallest size which is 10.37 nm compared to 1:2 and 1:3 ratio which have sizes of 12.30 nm and 16.37 nm respectively. The increasing in the molar ratio increase the average particle size of ZnO [16]. The differences of size of nanoparticle indicate there are some difference in size and morphology of the ZnO crystals.

Table 2: Average sizes of nanoparticle at different molar ratio.

Molar ratio	Average crystal size (nm)
1:1	10.37
1:2	12.30
1:3	16.37

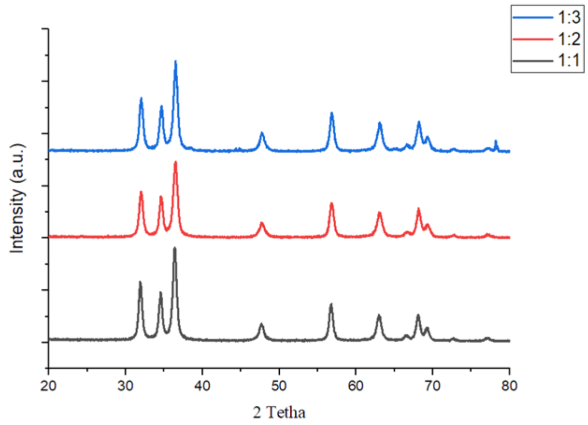

Figure 1: Comparison of XRD patterns between 1:1, 1:2, 1:3 molar ratio.

B. *Field Emission Scanning Electron Microscope (FE-SEM)*

Figure 2 shows the image taken from FE-SEM for 1:1 and 1:2 ratio. The morphology of nanoparticle can be seen from figure 2. Both images show the nearly spherical shape.

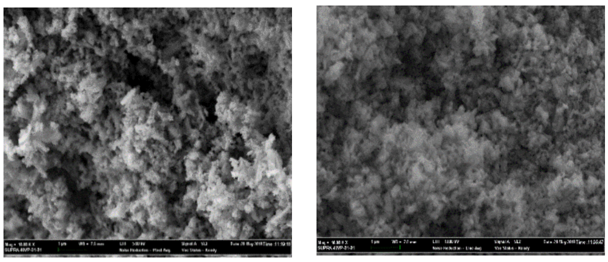

Figure 2: FESEM images of ZnO with different Zn/Ox; (left) 1:1, (right) 1:2

C. *Energy Dispersive X-ray Spectroscopy (EDX)*

Figure 3 and Table 3 shows the results from characterisation of EDX which has purity of 77.41 % of zinc content compared to oxygen content which has 22.59%. This shows the good crystallinity of ZnO nanoparticle. The theoretical value of mass per-cent between Zn and O are 80.3% and 19.7% which the result is nearly to the theoretical data [17].

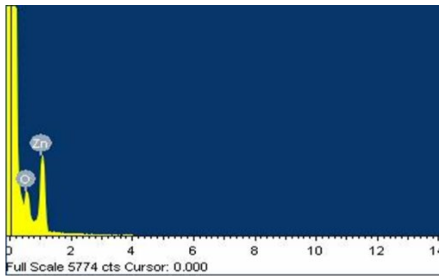

Figure 3: EDX graph of ZnO nano-powder.

Table 3: Weight % and atomic % of ZnO.

Element	Weight %	Atomic %
O K	22.59	54.39
Zn L	77.41	45.61

D. Performance study of zinc oxide in-situ addition to heavy crude oil.

1) Effect of nanoparticle size on viscosity reduction.

Figure 4 shows the viscosity of heavy oil when ZnO nanoparticle is added at different sizes of 10.37 nm, 12.3 nm, 16.37 nm. From the figure, it can be seen that different sizes of nanoparticle give different viscosity reduction. The viscosity reduces as the nanoparticle size decreases. 10.37 nm size of nanoparticle clearly shows the higher reduction of viscosity compared to the other sizes. When ZnO nanoparticle added to the heavy oil, interaction between asphaltene and nanoparticle become stronger thus increasing the contact area between the nanoparticle and asphaltene. Fragmentation and internal redistribution of heavy oil is happening thus reducing the viscosity of heavy oil [18].

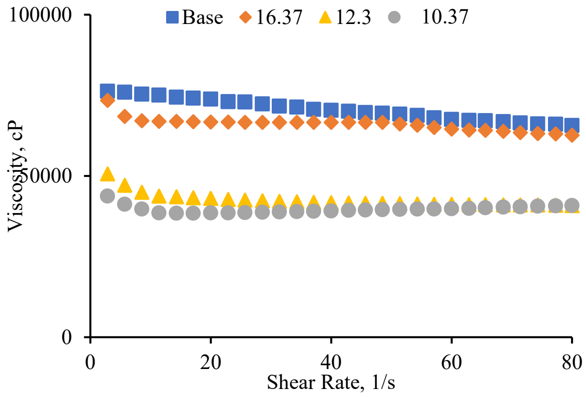

Figure 4: *Rheological measurement of crude oil with ZnO nanoparticles of different sizes at 30 ºC and shear rate between 0-80 s^{-1}.*

The degree of viscosity reduction (DVR%) can be calculated by using the equation 4 where, μ_{HO} and μ_{np} is the crude oil before and the after-nanoparticle-inclusion viscosity values, measured at shear rates between 0 and 80 s-1, respectively. From DVR%, smaller size of nanoparticle showed greatest amount of reduction up to 40% reduction of viscosity. Smallest DVR% belong to the larger size of nanoparticle which has DVR% less than 10. It considered not acceptable because a good viscosity reduction has DVR% range between 30-40%. This mainly due to interaction between internal structure of which change its structure thus promoting viscosity reduction [19]. When the size of nanoparticle is increase, the DVR% is decreasing.

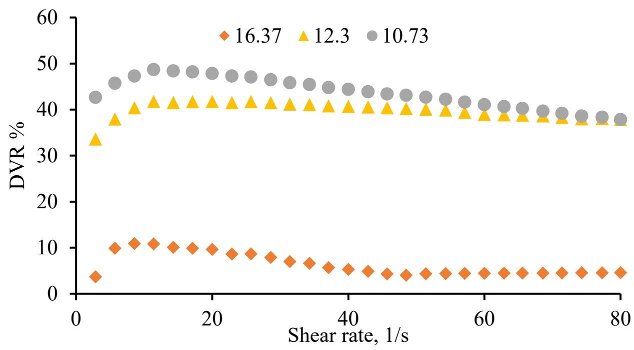

Figure 5: *Degree of viscosity reduction of heavy oil with ZnO nanoparticles of different sizes at 30ºC and shear rate between 0-80 s^{-1}.*

E. Effect of Temperature and High Shear Rate

10.37 nm of particle size clearly shown the best reduction on viscosity of heavy oil. Therefore, this size of nanoparticle has been selected to carry out further evaluation on different temperature at high shear rates. Temperature of 30, 45 and 60 ºC has been selected at 0-500 s^{-1}. Figure 6,7 and 8 demonstrate the effect of ZnO nanoparticle on heavy oil at 30, 45 and 60 ºC at shear rate between 0-500 s^{-1}. Degree of viscosity for all temperatures is also shown.

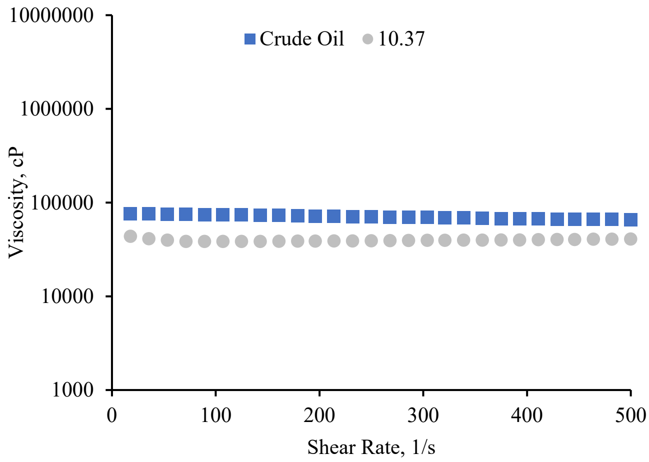

Figure 6: *Rheological behavior of heavy crude oil in the presence of 10.37 nm size of ZnO nanoparticle at 30 ºC at shear rates between 0-500 s^{-1}.*

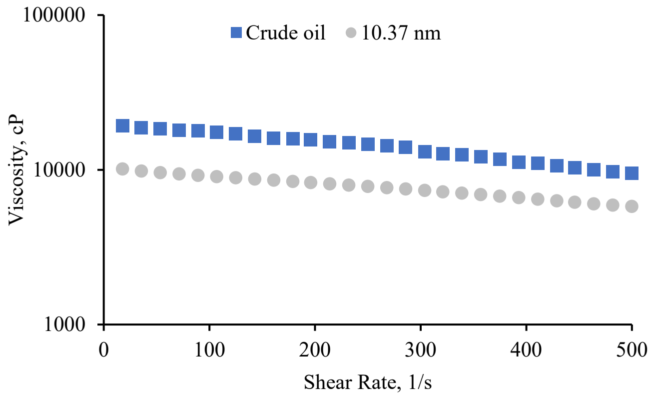

Figure 7: Rheological behavior of heavy crude oil in the presence of 10.37 nm size of ZnO nanoparticle at 45 ºC at shear rates between 0-500 s^{-1}.

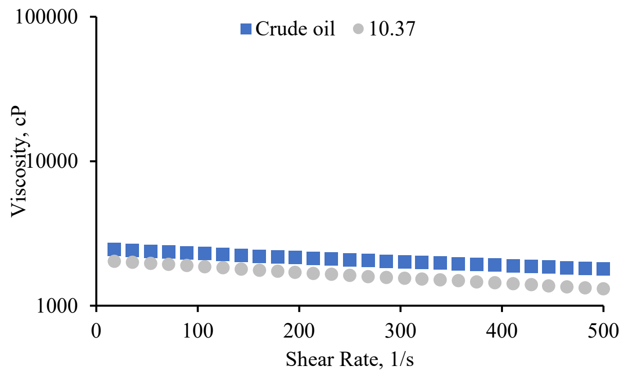

Figure 8: Rheological behavior of heavy crude oil in the presence of 10.37 nm size of ZnO nanoparticle at 60 ºC at shear rates between 0-500 s^{-1}.

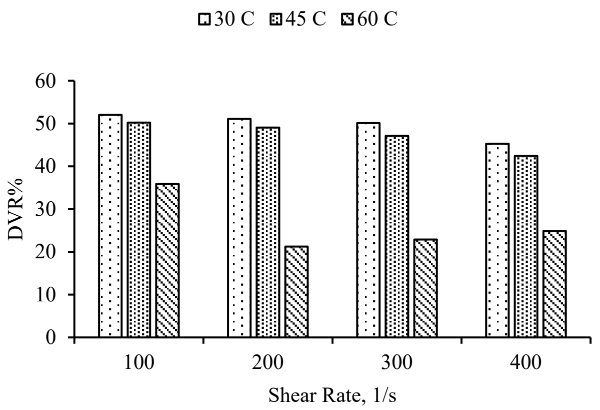

Figure 9: DVR% for ZnO nanoparticle at 30, 45, 60 ºC at different shear rates range from 0-500 s^{-1}.

At 30 ºC, pseudo-plastic type shear thinning behavior is shown for these fluids. The apparent viscosity decrease as the temperature increases from 30—60 ºC [19, 20]. Higher viscosity absence in lower shear rates due to heavy component in a crude oil such as asphaltene, wax and resins do not have the time to agglomerate and to form aggregates [19]. In figure 6, it shows the decrease in viscosity as the shear rate increases. The process happened because of the presence of asphaltene which have the tendency to self-aggregate [21, 22]. The structure of heavy oil component is reorganized when the stirring increases thus increasing shear rate will result in reduction of viscosity. When the temperature is increasing, the closer the fluids to exhibits a Newtonian behavior. Shaw's research group in their finding mentioned that as the temperature increases, the fluid have tendency to change from Non-Newtonian fluid into Newtonian fluid [20, 23]. Behavior of this process can be seen at higher shear rates (> 300 s^{-1}) due to the constant viscosity.

Recap from the evaluated scenarios, smaller size of nanoparticle exhibits a larger reduction of viscosity. Increasing in temperature shows the best performance of reduction of nanoparticle with roughly about 50%. Introducing a temperature and agitation, the dispersion of nanoparticle into the heavy oil encourage the viscosity to reduce [19]. Interaction between the heavy component of crude oil and nanoparticle increases when the dispersion increases thus increase the percentage of viscosity reduction. Based on this, it can be concluded that there are connection between nanoparticle and temperature which improve the reduction of viscosity due to interaction between asphaltene and nanoparticles [24]. Heavy oil is considered a problem to the production and transportation mainly because of its higher viscosity, thus by introducing the nanoparticle into the heavy oil is a capable technique to reduce the viscosity for better mobility of the fluid.

F. Effect of Nanoparticle on Deposition of Wax

Figure 10 shows the comparison result between the larger and smaller sizes ZnO nanoparticles. Crude oil with free chemical treatment acted as a referrence for 2 different of size categories that might have the capability to reduce the wax and potentially be the best reduction of wax. Smaller size of nanoparticle exhibit has tendency to reduce the wax up to 12.32 g while larger size of nanoparticle can only reduce the wax approximately 6.72 g compared to the original deposited of wax. This happen due to strong intermolecular force between the nanoparticle and wax [25]. Table 4 shows that the percentage inhibition efficiency (PIE%), which was calculated to determine the effeciency of nanoparticle in terms of wax reduction. From the table, it clearly shows that smaller size of nanoparticle can reduce the amount of wax deposite nearly 50% compared to bigger size of nanoparticle. These result shows that, ZnO nanoparticle can reduce amount of wax by separating from each molecules as the nanoparticle leads to less favorable interaction among the molecules [26].

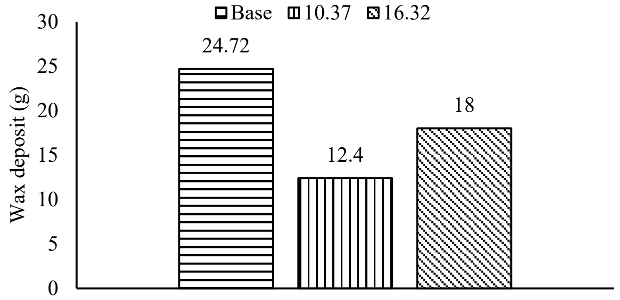

Figure 10: Comparison of deposition of wax for 10.37nm and 16.32nm, sizes of nanoparticle.

Table 4: The percentage inhibition efficiency (with and without the addition of nanoparticle at 50 ºC crude oil temperature, cold finger temperature: 5 ºC

Sample at concentration 1000 mg/L	Percentage inhibition efficency (PIE %)
Crude + 10.37 nm	49.83
Crude + 16.37 nm	27.18

IV. CONCLUSION

ZnO nanoparticles has successfully synthesized using sol-gel method by varying the molar ratio of Z_{ac}/O_{xa} starting from 1:1, 1:2, 1:3. As the molar ratio is increase, the average size of nanoparticle is increase. 1:1 ratio shows exhibit smaller particle with 10.37nm size as compared to 1:2 and 1:3 which have 12.3 nm and 16.37 nm respectively. The ZnO nanoparticle have good crystallinity as EDX result shows higher purity of ZnO (77.41%) and oxygen (22.59%). ZnO nanoparticle with different sizes were further investigated on the capability to reduce viscosity. Smaller size shows good reduction of viscosity compared to the larger size due to larger surface to volume ratio which lead to more interaction between the nanoparticle and component of crude oil. DVR% shows that reduction of viscosity for low shear rate can reduce up to 40%. As the temperature is increases, the viscosity tends to reduce as well as the increasing the shear rate. Amount of wax deposition can be reduced when nanoparticle is added. Smaller size shows higher reduction of wax with PIE% nearly 50% while larger size of nanoparticle reduced the wax content approximately 27%. Based on the result, ZnO nanoparticle can reduce the viscosity of heavy crude oil and wax content with smaller size exhibit higher reduction in viscosity and wax.

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