Synthesis of Zinc Oxide Nanoparticles for Wax Deposition Control and Oil Upgrading: Effect of Drying Temperature

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Abstract— **Wax deposition becomes a major problem in the transportation of crude oil. During the transportation and production also they encounter problem due to the characteristic of the crude oil which was high specific gravity and high viscosity. Therefore, to encounter the problems occurred, nanotechnology had been introduced by performing synthesis of zinc oxide (ZnO) nanoparticles using sol-gel method. To obtain an efficient result in overcome the problems, an optimum drying temperature during the synthesized was investigated since it gave different sizes of nanoparticles. Hence, synthesized of ZnO nanoparticles using sol-gel method were performed and the drying temperature was varied from 80ºC to 200ºC to identify which temperature gave smaller size of nanoparticles as the smaller size gave better reduction in viscosity. By varying the drying temperature during the synthesized of ZnO nanoparticles also can show its effect to the surface morphology. Then, the crystalline phase and size of the ZnO nanoparticles were determined using X-ray Diffraction (XRD) and the surface morphology by using Field Emission Scanning Electron Microscopy (FE-SEM). While for the elemental composition determined using energy dispersive X-ray spectroscopy (EDX) shows that the nanoparticles contain Zinc (Zn) and Oxygen (O) only. As for the oil upgrading, the ZnO nanoparticles had been used as the viscosity reducer at different sizes, different shear rate and temperature using electronic rheometer and it shows that the smaller size of nanoparticles which is 10.87nm gave the highest viscosity reduction with range 50%. Also, for wax deposition, the smaller size of ZnO nanoparticles gave the higher percentage of ZnO efficiency and reduces more wax compared to bigger size with efficiency 78%. Therefore, the oil upgrading can be done by the addition of ZnO nanoparticles and the 200ºC of drying temperature gave the greatest effect.**

Keywords*— *Wax, viscosity, ZnO nanoparticles, sol-gel method, drying temperature, crude oil.

I. INTRODUCTION

Crude oil is a complex mixture of hydrocarbons which consist of asphaltenes, waxes, resins, aromatics and naphthenics. Out of these mixtures, one of them which is wax deposition is a major problem in oil productions and transportations facilities where give many problems towards the production such as decrease the production rates [1]. According to the statistical analysis, 59 out of 69 different oil fields show that wax deposition problem is a serious matter and the paraffinic waxes tend to precipitate when the temperature is below wax appearance temperature (WAT) during the crude oil production, transportation and storage [2]. These wax precipitation will increase fluid viscosity and prevent the fluid from flowing through equipment and pipelines, thus reduce the effective flow cross-section of pipeline, increase delivery pressure and also cause the plugging [2]. Therefore, different prevention and removing wax methods have been approach to improve the situation and divided into three categories such as thermal, chemical, and mechanical treatment techniques [3]. For the thermal technique, hot oiling is the most popular methods where hot oil heated to a temperature above melting point for wax and then pumped into the well which normally through annular space [3].

However, this technique cannot be used in subsea flow lines because of extremely high cost of heating the oil and can cause permeability damage if the melted wax flow into the formation [3]. While for chemical technique, the use of chemical inhibitors has being in demand due to number of chemicals with paraffin inhibition properties [4]. Despite the inhibition properties, the inhibitors are not showing the same effectiveness in all wells and it is unsuccessful to perform correctly even in the same basin [4]. For the mechanical technique, it is usually include manual works such as pigging. The pigging technology is the most suitable for foams, waxy crude and wax deposit removal and also widely used in pipelines with high wax content [3]. However, the pigging activity would usually range from 2-3 days to 3-4 months which will delay the operation [5].

Taborda (2017) [6] states that heavy crude oil at current state also represent some of the percentage of the current and future oil production as the reserves duplicate those light crudes and because of this, the oil industry had encounter with some operational and production challenges. The management related to the heavy crude oil had encounter the problems due to their highly viscous characteristics and the study of their rheology had been done to approach another way to optimize the production and transportation of the crude. According to Taborda et al. [6] many researchers had used both transient and steady rheology to characterize heavy crude oils in order to optimize their mobility and transportation. Pierre (2004) [7] recently had conducted a study of effect of asphaltenes on the viscosity of a Venezuelan heavy crude oil and it was found that the viscosity increase as the asphaltene content increase.

Due to the disadvantage that existing methods had, another method for controlling the wax deposition and enable viscosity reduction has been approach which is by using nanotechnology where it will be added into the crude oil [6]. Nanotechnology had been chosen because of their characteristics such as large surface area, high dispersibility, small particle size and able to adsorb asphaltene and exhibit their self-association [6]. Nanotechnology also have showed that it will effect several parameters such as oil viscosity reduction and from an experiment there is a good proof where viscosity reduction can be achieved by adding metal particles [8]. As for that, there are three categories of nanoparticles which are metal oxide, organic and inorganic particles [9]. Among the categories, metal oxide nanoparticles will be used due to its main properties such as low ionization potential, low electronegativity, high melting point and high density which will make them very reactive and unstable elements [9]. Out of various metal nanoparticles such as aluminium oxide, iron oxide, nickel oxide, magnesium oxide that have in the industry, zinc oxide has received more attention due to its special and unique characteristics such as has low electrons conductivity, ultraviolet filtering and excellent heat resistance [10], [11]. Zinc oxide also has been chosen as the metal particles because of its catalytic properties and its larger surface area [12].

The synthesis of zinc oxide nanoparticles will use sol-gel method over other methods because of its easy method for creating large variety of metal oxides at low temperature and ambient conditions [13]. This method also preferable because of its low cost, ease fabrication and also the advantage of having highly pure and uniform structured zinc oxide [14]–[16]. As the synthesis of zinc oxide nanoparticles performed, the drying temperature will be varied during the synthesis to determine its effect on the size which then will give the best wax deposition control and viscosity reduction to improve the crude oil transportation in the future.

II. METHODOLOGY

A. Material and chemicals

Crude oil obtained from Kemaman Bitumen Company Sdn. Bhd. (KBC) was used as received for characterization and rheological test to know its properties. Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), oxalic acid ($C_2H_4O_4.2H_2O$) and ethanol (C_2H_5OH) 95% AR Grade obtained from Vchem Laboratory Chemcials, ammonia solution acquired from Daejung Chemicals. Other than that, the other chemicals such as hydrochloric acid (HCl), methanol (CH_3OH), n-heptane (C_7H_{16}) and toluene (C_7H_8) also obtained from the Vchem Laboratory Chemicals.

B. Properties of crude oil

Crude oil obtained from KBC was further investigated to know its physical and chemical properties such as density, ºAPI and specific gravity. For the determination of density, cup of the mud balance filled up until full with 200mL of crude oil and the cup covered completely with the lid to remove the air bubble inside it. The rider adjusted at the graduated arm and ensured that the level bubble was positioned at centre. The reading of the density was taken after the graduated arm balanced and recorded. The physical properties of crude oil such as specific gravity and ºAPI were further determined by using the equation (1) and (2) below and the properties were tabulated in the Table 1 and 2:

$$SG = \rho_{oil} / \rho_{water} \quad (1)$$

$$^{o}API = (141.5 / SG) – 131.5 \quad (2)$$

Table 1: Physical properties of crude oil

Physical properties	
Density (kg/m^3)	993
Specific gravity, SG	0.993
ºAPI	11
Viscosity at 40ºC (cP)	17,751
Colour	Black
Cloud point (ºC)	12

From the properties of the crude oil in Table 1, the ºAPI of the crude oil was 11 which indicate that the crude oil was classified as the heavy crude oil and high in viscosity. It also contains a high percentage of asphaltene as shown in Table 2 which could lead to wax deposition. Therefore, it was suitable to be used in this experiment so that the viscosity reduction and wax deposition control can be seen and proved.

Table 2: Chemical properties of crude oil

Chemical properties	Weightage (%)
Saturates	3.0
Aromatics	63.4
Resins	12.9
Asphaltenes	20.7

C. Preparation of zinc oxide (ZnO) nanoparticles

Zinc oxide nanoparticles were synthesized using sol-gel method where zinc acetate dihydrate and oxalic acid were used as the starting materials. 2 grams of zinc acetate dihydrate and 1.64 grams of oxalic acid were mixed with 100mL volume of ethanol respectively in a beaker. Oxalic acid stirred with magnetic stirrer at temperature 45ºC for 30 minutes at 700rpm. While for zinc acetate dihydrate, it is mixed with ethanol and 10% water and heated at temperature 65ºC for 30 minutes. After 30 minutes, the oxalic acid solution was added dropwise to zinc acetate dihydrate slowly under vigorous stirring of 1100rpm [17]. When the oxalic acid completely dropped into zinc acetate, the final pH was kept at 3 by adding required amount of hydrochloric acid (HCl) and ammonia solution respectively. Then, keep the solution undisturbed till white precipitate is seen and filtered using 110mm Whatmann filter paper. The precipitate then dried at 80ºC, 100ºC, 150ºC and 200ºC for two hours in drying oven to evaporate the solvents [18]. Then, it was calcined at 400ºC for two hours in furnace to obtain the powder.

D. Characterizations of ZnO nanoparticles

The crystalline phase of the zinc oxide nanoparticles were determined by using X-ray diffraction, XRD (Pananalytical, model: Expert PRO) in the 2θ scan range of 10-90º with CuKα radiation (1.5406 Å). The surface morphology of the nanoparticles were checked using field emission scanning electron microscopy (FE-SEM, Zeiss; SUPRA 40VP) and the elemental composition determined by energy dispersive X-ray spectroscopy (EDX; model Bruker). The average crystal size of the ZnO then further calculated from the XRD patterns, using Scherer's equation (3) [17]:

$$D = K\lambda / \beta \cos \theta \quad (3)$$

Where K is the Scherer constant (K=0.89), λ is the X-ray wavelength of CuKα, β is the Full Width at Half Maximum (FWHM) and θ is the half diffraction angle.

E. Effect of ZnO nanoparticle sizes on viscosity of heavy crude oil

Rheological measurements were taken by using electronic rheometer (Physica Anton Paar; model MCR300) to analyze the changes in viscosity of the crude oil before and after the addition of ZnO nanoparticles. To see the reduction in viscosity, crude oil without nanoparticles were evaluated first at shear rate values between 0-80s^{-1} at temperature 30ºC. Then, the nanoparticles with different size were added to the heavy crude oil and evaluated at the same parameter to know how much reduction in term of viscosity can be made and the degree of viscosity reduction (DVR) were calculated for each size of nanoparticles by using equation (4) [6]:

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

Where μ_{HO} and μ_{np} are the value of heavy crude oil viscosity before and after addition of nanoparticles respectively.

F. Effect of temperature and high shear rate on viscosity

After that, the optimal size of ZnO nanoparticles that gave the highest reduction in viscosity were selected and further evaluated by varying the temperature and shear rate at 30ºC, 45ºC, 60ºC and

0-500s^{-1} respectively.

G. *Effect of ZnO nanoparticle sizes on wax deposition*

The amount of wax deposited from crude oil performed by using the cold finger method equipment (model; Wisebath). About 100 mL of crude oil placed inside the cold finger equipment at 50ºC fixed temperature for crude oil and 5ºC for cold finger. The other samples of crude oil with addition of ZnO nanoparticles size 10.87nm and 16.31nm also were placed in the other fingers. The samples then were left for 24 hours to let the wax deposited. The wax deposited at the cold finger then was scrapped and placed in petri dish to be weighted by using weighing balance. The ZnO percentage efficiency then calculated by using equation (5) [19].

$$\text{Efficiency (\%)} = [(W_f - W_t) / W_f] \times 100 \qquad (5)$$

Where Wf is the reference amount of wax deposition without ZnO nanoparticles in grams and Wt is the amount of wax deposition with ZnO nanoparticles in grams.

III. RESULTS AND DISCUSSION

A. *Characteristic of zinc oxide (ZnO) nanoparticles*

From the synthesis, the XRD patterns of zinc oxide (ZnO) nanoparticles at different drying temperature shown as in the Figure 1. It was observed that the patterns clearly show the same diffraction peak corresponds to the Joint Committee on Powder Diffraction Standards (JCPDS no 36-1451) data of standard ZnO diffraction pattern where the diffraction peaks 2θ corresponds to (1 0 0), (0 0 2), (1 0 1) and (1 1 0) plane respectively [17]. It was also indicating that it was a good crystalline with sharp and intense diffraction peaks [20]. The diffraction peaks also indicated that the nanoparticles have a hexagonal phase with wurtzite structure of ZnO at all drying temperature with the same peaks [17].

The effect of drying temperature also were investigated by varying the temperature from 80ºC to 200ºC during the synthesis of ZnO nanoparticles and the results show no changes in diffraction peaks at correspond plane except for the intensity for each temperature. As the temperature increased, the intensity of the diffraction peaks would increase as shown in Figure 1 and becomes sharper indicating that the crystalline structure tend to had more integrity [20]. The size of ZnO nanoparticles also influence by the temperature and it was calculated by using the equation (3). The calculated crystal sizes were tabulated in Table 3.

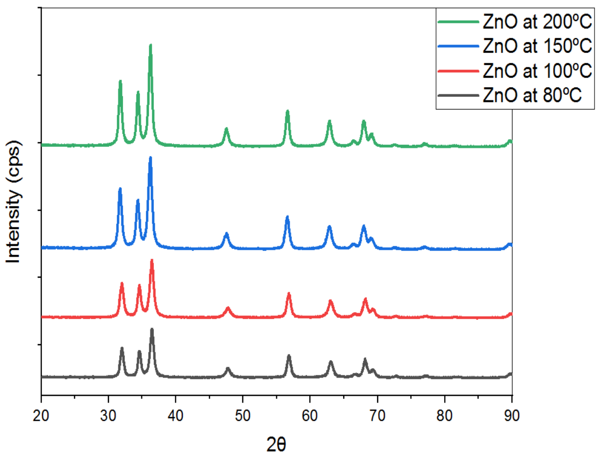


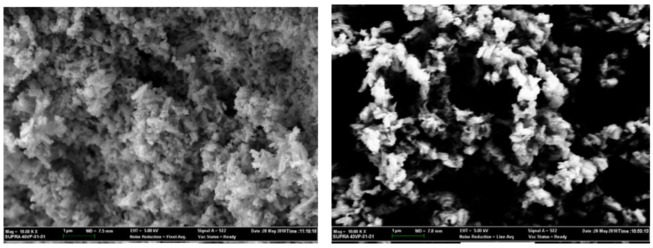
Figure 1: XRD analysis of ZnO nanoparticles at different drying temperature

Table 3: Average crystal size of ZnO nanoparticles at different drying temperature

Drying temperature (ºC)	Average crystal size (nm)
80	16.31
100	16.3
150	13.05
200	10.87

It can be seen that as the drying temperature were increased, the crystal size would decrease. According to Preethi et al. (2016) [20] the decrease in crystal size when drying temperature increase may be due to the different growth rate for the different crystallographic planes and also the abrupt vaporization of the solvents that disturbed the crystal growth [18].

Other than that, the surface morphology of ZnO nanoparticles shown from FE-SEM images in Figure 2 indicated that the ZnO were in nearly spherical shaped. The final composition of ZnO nanoparticles also determined using the EDX. From the Figure 3 and Table 4, it shows that only Zinc (Zn) and Oxygen (O) were found in the nanoparticles and no other impurities detected as indicated by the peak with large concentration in the sample [20]. The elemental composition of ZnO nanoparticles with two major peaks was found to contain weight percentage of 22.59 of Oxygen and 77.41 of Zinc. The atomic percentage also consists of 54.39 of Oxygen and 45.61 of Zinc as shown in Table 4. Therefore, it is confirmed that the nanoparticles synthesized was ZnO as the final product.



(a) (b)

Figure 2: FE-SEM images of ZnO nanoparticles at different drying temperature (a) 80ºC (b) 200ºC

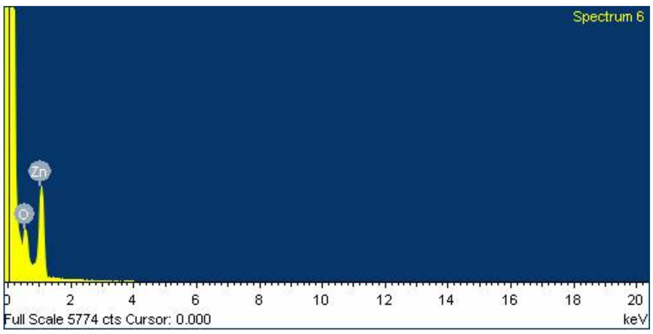


Figure 3: EDX of ZnO nanoparticles at drying temperature 80ºC

Table 4: The weight % and atomic % of ZnO nanoparticles at 80ºC

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

B. *Effect of ZnO nanoparticle sizes on the viscosity of heavy crude oil*

The rheology measurements were taken before and after the addition of ZnO nanoparticles in the crude oil to see the changes in viscosity for each nanoparticle added. Figure 4 shows the viscosity of crude oil before the addition of ZnO nanoparticles and the presence of ZnO nanoparticles with different size ranging from 10.87 nm to 16.31 nm at temperature 30ºC. From the Figure 4, it shows that the viscosity of the crude oil reduced as the ZnO nanoparticles were added but it does not alter the non-Newtonian character of the fluid and the fluid still shows a continuous pseudo-plastic behavior [6]. As the nanoparticles size decrease, the viscosity reduction will increase due to a large number of nanoparticles interacting with asphaltene aggregate, which then will increase the contact area and tends to further fragmentation of these heavy hydrocarbons. Consequently, the viscosity changes that occurred may be due to the internal redistribution with smaller aggregates [21].

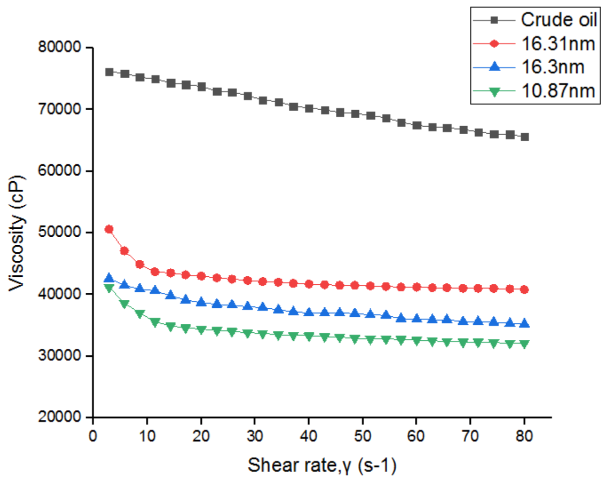


Figure 4: Viscosity of heavy curde oil before and after addition of ZnO nanoparticles with different sizes at 30ºC

In order to determine the size of nanoparticles that gave the highest viscosity reduction, the degree of viscosity reduction (DVR) was calculated by using equation (4). From the calculated values, the degree of viscosity reduction, DVR were plotted in the Figure 5 and it shows that 10.87 nm size of ZnO nanoparticle gave the highest changes in viscosity with range 50-53%. The degree of viscosity reduction reduced as the shear rate increased because of the partial breakdown of the internal structure and despite the latter, the nanoparticles remain effective [22].

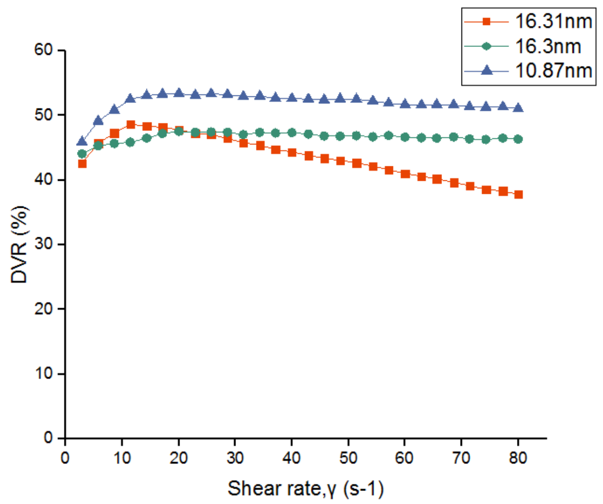


Figure 5: The degree of viscosity reduction (DVR) for different sizes of ZnO nanoparticles at 30ºC

C. *Effect of temperature and high shear rate*

From Figure 5, a ZnO nanoparticle with size 10.87 nm gave the highest DVR and was further investigated at different temperatures, 30ºC, 45ºC and 60ºC with high shear rate between 0 – 500s^{-1}. From Figure 6, it is observed that as the shear rate increase, the viscosity would decrease regardless the temperature and it is widely reported that the fluid that exhibits this behavior are called pseudo-plastic materials or shear-thinning for heavy crude oil [6], [23]. Based on the explanation by Al-Zahrani [23], this shear thinning behavior as a result of the internal structure will breaks down as the shear applied in the fluid. Other than that, Figure 6 also shows that the viscosity decrease as the temperature increase which indicate a behavior typical of liquids as reported by Taborda et al. [23].

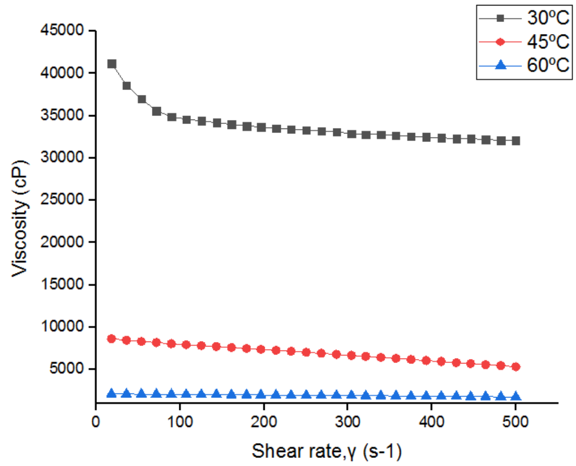


Figure 6: Viscosity of heavy crude oil upon addition of 10.87nm ZnO nanoparticles at different temperature and shear rate

As for the reduction in viscosity at 45ºC and 60ºC, the attractive binding energy is reduced because of the reduction in the cohesive forces of the molecular components of crude oil [23]. While at the lower temperature (30ºC), the viscosity is slightly higher compared at higher temperatures because at the low temperature, some of the crude oil components behave as solids and the system viscosity would depend on their breakage or alignment [23]. Figure 7 show the degree of viscosity reduction (DVR) at all temperatures that evaluated. From the results, it showed that the best performance of 10.87nm ZnO nanoparticles gave the greatest change in viscosity occur at 30ºC with DVR average of 55%. While for the highest temperature tested (60ºC), the average viscosity reduction gave roughly at 10%. This is because of the natural changes in the reference value (viscosity of heavy crude oil without nanoparticles), as the DVR calculated in percentage and it is expected that the viscosity change is greater at lower temperature compared to higher temperatures [6]. As for increasing shear rate, the DVR benefit will be slightly decrease due to the internal structure change of the fluid that causes a decrease in viscosity [6].

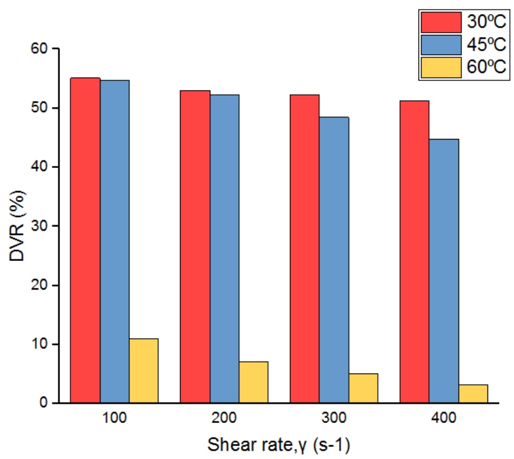


Figure 7: Degree of viscosity reduction for crude oil at shear rate 0-500s^{-1}

D. Effect of ZnO nanoparticle sizes on wax deposition

Table 5 below show the result of amount of wax deposited when different size of ZnO nanoparticles added into the heavy crude oil. From the table, it also shows the percentage of ZnO efficiency that calculated by using equation (5) to know how much the wax had been decrease when different size of ZnO nanoparticles were added. The results show that the ZnO efficiency for smaller size of ZnO nanoparticles higher compared to the bigger size which means that the wax had been reduced more when using smaller size of ZnO nanoparticles. This is due to the characteristics of nanoparticle itself that give larger surface area to volume ratio and their smaller size that lead to easier movement in porous media [24]. The ZnO nanoparticles able to adsorb asphaltene and reduce asphaltene deposition which lead to low amount of wax because of the kind of interaction force between asphaltene and nanoparticles [25].

Table 5: Amount of wax deposited

Samples	Weight wax deposited (g)	ZnO efficiency (%)
Blank heavy crude oil	24.72	-
10.87nm of ZnO nanoparticle + crude oil	6.22	74.84
16.31nm of ZnO nanoparticle + crude oil	16.71	32.40

IV. CONCLUSION

ZnO nanoparticles were synthesized by sol-gel method at different drying temperature 80ºC, 100ºC, 150ºC and 200ºC to be used for the performance study which is for wax deposition control and oil upgrading. From the characterization of ZnO nanoparticles, it was found that the XRD patterns show the ZnO nanoparticles had crystalline phase with wurtzire structure and give different size of nanoparticles ranging from 10.87nm to 16.31nm as the drying temperature increase. The increased in temperature had given the decrease in size as the diffraction peaks were highest at drying temperature 200ºC and give a size of 10.87nm. The ZnO nanoparticles then further used for viscosity reduction in order to do the oil upgrading and it shows that nanoparticles with 10.87nm size gave the highest changes in viscosity reduction compared to others. Other than that, two different size of ZnO nanoparticles which is the smallest and largest one were tested for wax deposition and it shows that the smaller size give a higher wax deposition control. As a conclusion for this study, the nanoparticles can be used to achieve viscosity reduction and wax deposition control and opens a better direction for application in optimizing the production and transportation of the crude oil and also cost-effective technology.

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