SYNTHESIS ZINC OXIDE NANOPARTICLES FOR OIL UPGRADING AND WAX DEPOSITION CONTROL: EFFECT ON CALCINATION TEMPERATURE

Fatin Syahirah binti Mohamed Fuad and Siti Nurliyana bt Che Mohamed Hussein

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract—**A n*ew synthesized nano materials have massively attracted the researchers for more development of nano materials especially in the oil and gas industry to maximize the oil productivity performances. Wax deposition control measurement tests are the effective ways to recognise appropriate calcination temperature for zinc oxide nanoparticles in crude oil performance. In this study zinc oxide nanoparticles were synthesized using sol-gel method for oil upgrading and wax deposition control. The synthesized zinc oxide nanoparticles were used to measure viscosity and wax deposition in the heavy crude oil and to investigate the effectiveness of the nanoparticles in reduction of viscosity and wax deposition control of the heavy crude oil. Therefore this study is proposed to investigate the effect of calcination temperature of zinc oxide nanoparticles towards oil upgrading, viscosity reduction and wax deposition control. ZnO nanoparticles were calcined at different temperature ranging from 300°C to 900°C. Basically the calcined ZnO nanoparticles were characterized using X-ray diffraction (XRD), Field Emission Scanning Electron microscope (FESEM), and Energy-dispersive X-ray spectroscopy (EDX) in order to comprehend its structure, size, shape and morphology. The characterization results reveal the hexagonal structure of ZnO nanoparticles which is hexagonal wurtzite structure. Practically the physical properties and rheology of heavy crude oil were characterized by using Electronic Rheometer and cold finger method in order to understand and analyse the viscosity, shear rate and wax deposition of the heavy crude oil for performance study. Decrease in crystallite size from 15.59 nm to 12.84 nm was observed with increasing calcination temperature from 300°C to 400°C, and further increasing of calcination temperature from 400 to 900°C, the crystallite size is tend to increase from 12.84 nm to 41.58. The degree viscosity reduction (DVR %) of heavy crude oil was observed to increase by 41.7% with decreasing ZnO nanoparticles size from 30.11 nm to 12.84 nm. The optimum calcination temperature was 400°C. Wax deposition decrease by 32.40% after addition of ZnO nanoparticles into heavy crude oil.***

Keywords— ZnO, Nanoparticles, Calcination, wax content, viscosity reduction

I. INTRODUCTION

Wax deposition in heavy crude oil always becomes a major impact to the petroleum industry such as in transportation and production section. There is various effect of wax deposition in heavy crude oil that we should concern, for example leads to non-Newtonian flow characteristics of the fluid, increased pumping power, decreased flow rate or even to the total blockage of the pipeline. Wax precipitation induced viscosity of heavy crude oil to increase which can cause of high flow line pressure drop that can lead to low flow rates. In turn, this make conditions for wax deposition in the pipes more favorable. Serious wax deposition in heavy crude oil needs extra attention since it may cause harm not only to the transportation and production section, but also to the petroleum economy as well. There are many advanced technology and chemicals for wax prevention and removal such as wax crystal modifiers and dispersants, but these method have disadvantages such as costly and limited to one well. Zinc oxide nanotechnology introduced the more effective solution for petroleum industry as it provided simple and cheaper technology. Hence, it has become a major interest nowadays to reduce wax deposition from the heavy crude oil, to avoid its bad effect on petroleum industry as well as environment.

Wax deposition in pipelines commonly caused by several factors such as temperature, flow rate, oil composition and shear rate. Generally, wax precipitation and deposition has relationship with wax content of heavy crude oil. As temperature increase, the viscosity of the crude oil decrease. In oil composition, API gravity plays an important role in the petroleum industry as it has relationship with the wax deposition. The author of [1] stated that high API gravity shows that the crude oil have low wax content. API gravity that greater than 10 indicates the light crude oil whereas API gravity less than 10 indicates heavy crude oil. Basically, the heavier the crude oil, the higher wax content.

In this study, focus will be given on the heavy crude oil from the petroleum industry such as in transportation and production. It is well known that this heavy crude oil release higher significant deposition of wax content. The wax that present in the heavy crude oil primarily consists of paraffin hydrocarbons (C18-C36) known as paraffin wax and naphthenic hydrocarbons (C30 – C60). The factor that leads wax deposition problems is depends on type of oil and the molecular composition of the wax molecules. The waxes in crude oils are often more difficult to control because the alkane chains are often longer in the crude oil [2].

Currently, there are various conventional methods that have been used to remove the wax precipitate in heavy crude oil such as thermal techniques, chemical techniques, mechanical techniques, and thermo-chemical packages. However, these conventional methods have some downside with their process in removing or preventing the wax precipitate from heavy crude oil. For example, electric heater can cause increase maintenance costs and the availability of the electrical power is limited. For chemical techniques such as dispersant however could lead to harmful erosion.

Numerous transition metals were used in many applications such as Iron and Zinc because of its good in heat and electric conductivity. In addition, this group of metal commonly as catalytic agent due to its ability to change state or absorb other substances on their surface and active them in the process.

There are numerous methods that described in research to synthesize zinc oxide nanoparticles such as sol-gel method, co-precipitation and spray pyrolysis [3]. However, in this study sol-gel method was more preferred than the other methods because its low cost and simple method [4].

II. METHODOLOGY

A. *Characterization of crude oil*

The sample of crude oil that studied in this work was obtained from Kemaman Bitumen Company (KBC) Sdn Bhd. Table 1 show the composition of crude oil and the weight percentage (%) of the sample crude oil that obtained from KBC. Density of crude oil was determined by using Eq. 1 and Eq.2 where SG is specific gravity, ρoil is oil density and ρwater was water density at 60°F. The API gravity of crude oil refers to the density of the fluid at 60°F after gas has been liberated from the fluid at ambient pressure and reservoir temperature [5]. Crude oil gained from the KBC was considered heavy crude oil because of API and density value of mostly heavy oil ranging between 10° to 22° and 920 to 1000 kg/m^3 [6]

Table 1: Physical properties of crude oil

Physical properties	
Density (kg/m^3)	999
Specific gravity, SG	0.999
°API	11
Viscosity at 40°C (cP)	17,751
Colour	Black
Cloud Point (°C)	12

Table 2: Crude oil composition and weight percentage (%) of crude oil

Composition	
Saturates	3.0
Aromatic	63.4
Resin	12.9
Asphaltenes	20.7

$$API° = 141.5/SG - 131.5 \quad (1)$$

$$SG = \rho oil/\rho H2O \quad (2)$$

B. *Synthesis of Zinc oxide nanoparticles*

Zinc oxide nanoparticles were prepared under constant processing condition of pH, zinc acetate: oxalic acid ratio and drying temperature by using sol gel method. Zinc acetate [Zn(CH3COOH)2.2H2O], oxalic acid [C2H2O4] and ethanol [CH3CH2OH] were used as precursor materials for the preparation of ZnO nanoparticles [3][7]. In addition, the effect of calcination temperature were studied during synthesis of ZnO nanoparticles by varies it temperature from 300°C to 900°C [8][9]. For preparation of ZnO nanoparticles with molar ratios of 1:2 of zinc acetate and oxalic acid, 2 g of zinc acetate was added to the 100 ml of ethanol solution (+ 10% volume of water) in 500 ml glass beaker in a water bath at 65°C under reflux condition for 30 minutes. An amount of 1.64 g of oxalic acid powder was added to the 100 ml of ethanol solution in 500 ml glass beaker at 45°C under 700 rpm speed for 30 minutes. Then, oxalic acid solution were slowly added by using burette to the zinc acetate solution in 500 ml glass beaker under vigorous stirring at 1000 rpm[10][3]. Keep the final pH of the reactant mixture at 3 by adding required amount of hydrochloric acid [HCL] and ammonia solution [NH3] respectively. Then, keep the solution undisturbed for a while till white precipitates are seen in the solution and filter the precipitate by using vacuum pump. Dry the precipitates at 80°C for 2 hours in sintering boat in drying oven and calcined the precipitate at 300°C for 2 hours in sintering boat in the furnace to obtain smoother powder [4]. Repeat calcination of the ZnO precipitates at different calcination temperature between 400°C to 900°C.

C. *Characterization of ZnO nanoparticles*

The X-Ray diffraction was carried out for synthesized ZnO nanoparticles by using a High Resolution X-ray Diffractometer (PANalytical X'Pert PRO MRD) with Cu Kα radiation (λ = 1.54060 Å) over the angle 2θ range of 10-90°[3] . X-Ray diffraction was techniques that used to analyse the zinc oxide nanoparticles's character. The result from XRD analysis will show various profiles of peak and diffraction angle. This various profiles of peak of XRD indicate the formation of crystal structure [11]. The diffraction angle used for ZnO nanoparticles sample was from 10° to 90°. In this study, the intensity peaks and diffraction angle of calcined ZnO at 300°C to 900°C were investigate to study the effect of calcination temperature on crystallite size of ZnO nanoparticles.

Others than XRD, field emission scanning electron microscope (FESEM) and energy dispersive X-ray (EDX) were also used to study the characterization of this nanoparticles by analyzed their morphological structure and composition element of the ZnO nanoparticles. The morphological structure of ZnO nanoparticles were determined by using high resolution scanning electron (Zeiss, Supra40VP) with magnification of 10,000.

D. *Rheological measurements*

0.4 g of ZnO nanoparticles was added to the heavy crude oil. The rheological measurement was carried out using a Rheometer Paar Physica MCR300. The tests were performed at different temperature ranging between 30°C, 45°C and 60°C. This experimental was run in controlled condition: shear rate between 0 and $500s^{-1}$ at 24.85°C. Shear rate and apparent viscosity values were obtained every 10 seconds, resulting in 28 points respectively. For performance study, the effect of ZnO nanoparticle's size and the effect on temperature at higher shear rate on the viscosity reduction of heavy crude oil were investigated by using this equipment. The highest value of viscosity reduction will further experimental for cold finger method.

E. *Wax deposition determination*

To determine the wax deposition content in the heavy crude oil, cold finger method was used. Figure 1 shows the schematic component of the cold finger equipment. Each device involves of two or four cold finger, which connected to the circulating water bath. The regulated flow rate of the circulating water bath used to control the temperature of each cold finger. Other than circulating water bath, thermocouples inside the cold fingers also help to control the temperature of inlet and outlet of water bath.

In this study, the temperature of circulating water bath was set at 5°C while the temperature of water bath was set at 50°C. The heavy crude oil is placed into the cold finger jar in the annular space around the cold finger. The jar is then placed into water bath. Then, crude oil in the jar is stirred at normal operational speed at 400 rpm for 24 hours. After this time, the cold finger was removed from the water bath and jar. The wax deposit was then scrapped from the finger and weighed [12].

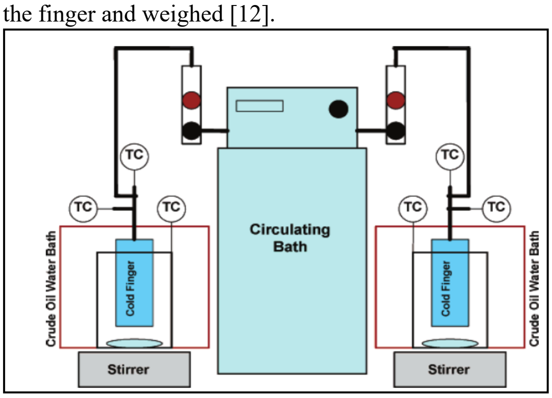

Figure 1. Schematic diagram of the cold finger apparatus[12]

III. RESULTS AND DISCUSSION

A. Characterization of Synthesized Zinc Oxide Nanoparticles

(a) X-ray diffraction (XRD)

In this investigation of synthesis zinc oxide nanoparticles, XRD was used to characterize the crystalline nature of the zinc oxide nanoparticles. Figure 2 show XRD graphs of ZnO nanoparticles at different calcined temperature ranging between 300°C to 900°C. From the graph shows on the Figure 2, presence of high intensity peaks (100), (002), and (101) gives a clear proof of the formation of the hexagonal wurtzite structure of zinc oxide nanoparticles. Figure 3 shows the standard peaks of zinc oxide powder diffraction (JCPDS 36-1451) that perfectly matches with the peaks gained in this study. All the diffraction peaks of Zinc oxide nanoparticles at different calcination temperature were observed at angle2θ: 31.95°,34.7°, 36.4°, 47.8°, 56.9°, 63.1°, 66.5°, 68.1°, and 69.3° equivalent well to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) crystal planes of hexagonal Zinc oxide powder.

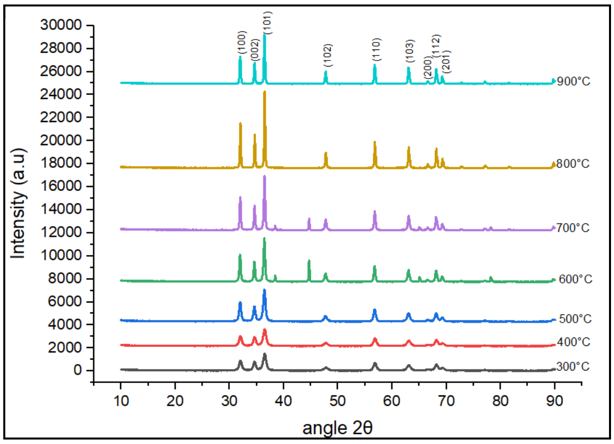

Figure 2: XRD graph of ZnO nanoparticles calcined at 300°C,400°C, 500°C, 600°C, 700°C, 800°C, and 900°C.

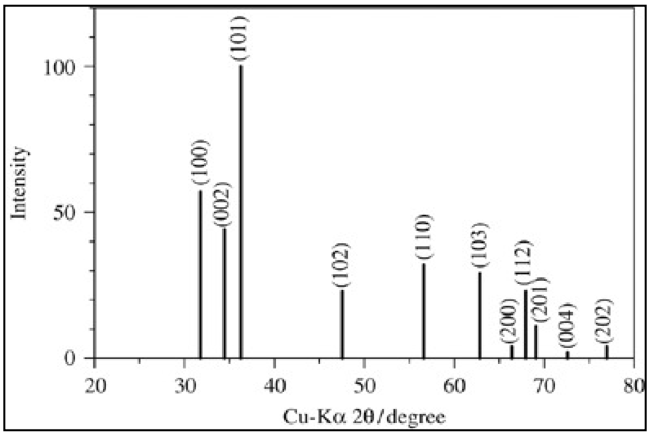

Figure 3: The standard XRD pattern of hexagonal ZnO (JCPDS 36-1451) is shown for reference.

From Figure 2, with increase in calcination temperature, the intensity of diffraction peaks increases, which indicates strengthening of ZnO phase [4]. Crystallite size for Zinc oxide nanoparticles was analyzed using the Debye-Scherer formula given in Eq. 3 where 0.89 is Scherer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle and B is the full width at half-maximum (FWHM) of the diffraction peak [13].

$$D=0.89\lambda/(B\cos\theta) \quad (3)$$

The results obtained were tabulated in the Table 3. Decrease in crystallite size from 15.59 nm to 12.84 nm was observed with increase in calcination temperature from 300°C to 400°C. However, further increase of calcination temperature from 400°C to 800°C, the crystallite size continue to increase from 12.84 nm to 41.58 nm. The average crystallite size of Zinc oxide nanoparticles was found to be 25.42 nm respectively. Based on the studied [4], decrease in crystallite size at low temperature was indicative of restructuring process whereas increase of calcination temperature with increase of crystallite size was indicative of strengthening of zinc oxide nanoparticles phase. In addition, by referring to Figure 2, the spectrum became sharper and diffraction peak became narrow with increasing in the temperature from 400°C to 800°C, indicating that the crystallite ZnO nanoparticles formation has been established [14][9].

Table 3: XRD analysis of ZnO nanoparticles: Full width at half-maximum (B) and size (nm) for each degree.

Temperature (°C)	Position (2θ) degree	Full width at half-maximum (B)	Size (nm)
300	36.4	0.56	15.59
400	36.4	0.68	12.84
500	36.4	0.47	18.58
600	36.4	0.34	25.68
700	36.4	0.29	30.11
800	36.4	0.21	41.58
900	36.4	0.26	33.58

(b) Energy Dispersive X-ray Spectroscopy (EDX)

EDX was used in this study to verified the elemental composition of nanoparticles sample which synthesized by using sol-gel method. Figure 4 shows the EDX graph that displays the peaks of Zn and O at calcination temperature 400°C.Table 4 shows results obtained from the EDX characterization suggested that the ZnO powder has good purity. Therefore, the experimental synthesis of zinc oxide nanoparticles sample was successful due to the present of zinc and oxygen element respectively.

This result showed that the final product was pure ZnO nanoparticles. According to [14] that using zinc nitrate as a precursor, the atomic percentages of Zn and O were approximately 50.13% and 49.87%. From this comparison, it showed that precursor of zinc acetate produce higher atomic percentages of Zn than precursor zinc nitrate. However, the value of atomic percentage of Zn and O between both precursor do not create huge different.

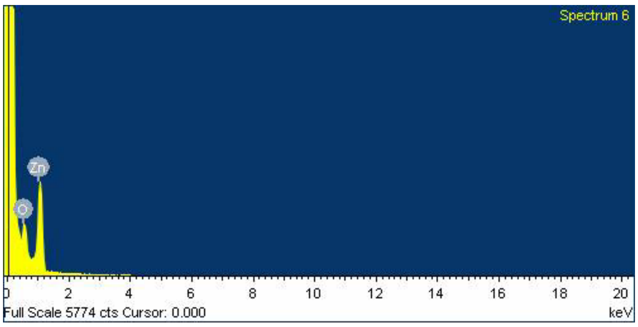

Figure 4: EDX graph of ZnO nanoparticles using zinc acetate as a precursor

Table 4: Weight and atomic percentage of EDX of ZnO element

Element	Wt%	Atomic %
O	22.59	45.61
Zn	77.41	54.39

B. Effect of calcination temperature on Zinc oxide nanoparticles

Figure 5 shows the graph of variation in crystallite size of ZnO with calcination temperature ranging between 300°C to

900°C. Based on the Figure 5, as calcination temperature increase from 300°C to 400°C, the crystallite size of ZnO was decrease. Decrease in crystallite size of ZnO from 15.59 nm to 12.84 nm was due to structural rearrangement which indicative of restructuring process [4][3].However, the crystallite size of ZnO tends increase from 12.84 nm to 41.58 nm with increasing calcination temperature from 400°C to 800°C which implying the strengthening of ZnO phase. This was because of increment of the crystallite volume to surface ratio[14][4]. The minimum crystallite size of ZnO that achieved in this study was 400°C whereas the maximum crystallite size of ZnO that can be achieved was 800°C.

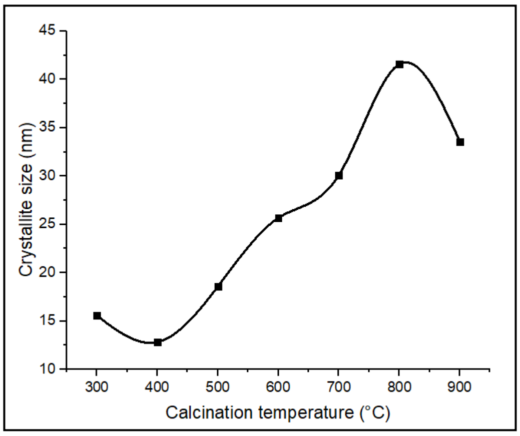

Figure 5: Variation in crystallite size with calcination temperature

C. Effect of calcination temperature on nanoparticle's morphology structure

The surface morphology of ZnO nanoparticles were determined using Field Emission scanning electron microscopy (FESEM). Figure 6, shows FESEM images of ZnO nanoparticles and the calcination temperature's effect. Figure 6(a) reveals that the synthesized sample has nanoparticles appearance with a rod-like morphology structure at lower temperature. However, Figure 6(b) shows that the length of structure was reduced with the increment of calcination temperature. This result are agreement with the previously research which stated that ZnO nanoparticles product gradually started to crumble and overlapped in a proportional relation with the increase of calcination temperature[15][14].

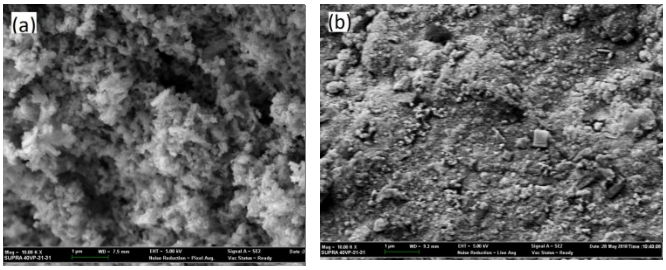

Figure 6: FESEM images of ZnO nanoparticles at calcination temperature of (a) 400°C and (b) 500°C

D. Effect of nanoparticle size towards viscosity reduction

To further investigate the effect calcination temperature of zinc oxide nanoparticles on the heavy crude oil, reduction of viscosity of heavy crude oil was carried out. Figure 7 shows the viscosity of heavy crude oil in the presence of ZnO nanoparticles at different nanoparticles size at 30°C and shear rate between 0 and 80s^{-1}. This indicates that additional of zinc oxide nanoparticles into the heavy crude oil will reduced the viscosity of the heavy crude oil. The nanoparticles size evaluated in this study were 12.84, 18.58, 25.68, 30.11, 33.58 and 41.58 nm. It was observed that viscosity of heavy crude oil was decrease with decreasing of nanoparticles size. The highest viscosity reduction of heavy crude oil happens at 12.84 nm. As particles size increases, a decrease in performance was notice (Taborda, 2017).

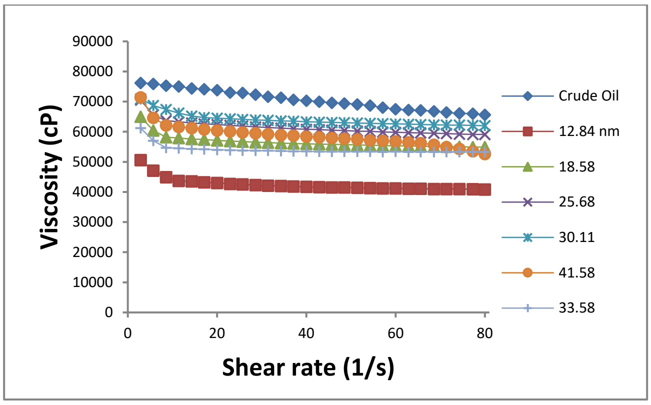

Figure 7: Viscosity of heavy crude oil in the presence of ZnO nanoparticles at different nanoparticles size at 30°C and shear rate between 0 and 80s^{-1}

The degree of viscosity reduction (DVR) was defined and calculated by Eq.4 below where μ_{HO} and μ_{np} was the crude oil before and after additional nanoparticles values, measured at shear rate between 0 and 80s^{-1}, respectively. Figure 8 indicates the degree of viscosity reduction of heavy crude oil on zinc oxide nanoparticles of different sizes presence, at 30°C and shear rate between 0 and 80s^{-1}. The values of DVR display that the optimal nanoparticles size at which the highest change in viscosity happens was 12.84 nm for all shear rates. The lowest degree of viscosity reduction was 5.5 % which occurs at 30.11 nm while the highest degree of viscosity reduction was 41.7% which happen at 12.84 nm. However, increasing in shear rate from 10 to 80s^{-1}shows the little reduced in DVR.

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

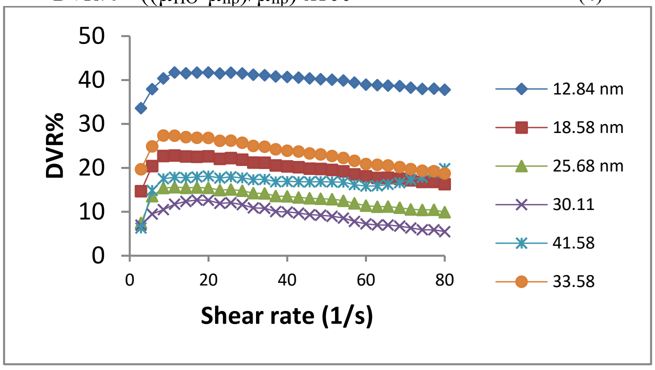

Figure 8: The degree of viscosity reduction of heavy crude oil on zinc oxide nanoparticles of different sizes presence, at 30°C and shear rate between 0 and 80s^{-1}.

E. Effect of temperature and high shear rate on heavy crude oil

Temperature plays important roles in viscosity control of heavy crude oil as higher the temperature will reduce the viscosity of oil. From previous analysis at Figure 8, indicate that ZnO nanoparticles at 12.84 nm exhibit the best performances due to higher percentage in viscosity reduction. Therefore, in this analysis of temperature and high shear rate effect, nanoparticles size at 12.84 nm was chosen to evaluate three different temperatures at high shear rates. Temperature at 30, 45 and 60°C were evaluated respectively, for shear rates between 0 and 500s^{-1}. In the Figure 9 displays the rheological responses for heavy crude oil with and without additional of zinc oxide nanoparticles at 30, 45 and 60°C, and at shear rates between 0 and 500s^{-1}. The DVR for 30, 45 and 60°C, and at shear rates between 0 and 500s^{-1}was presented.

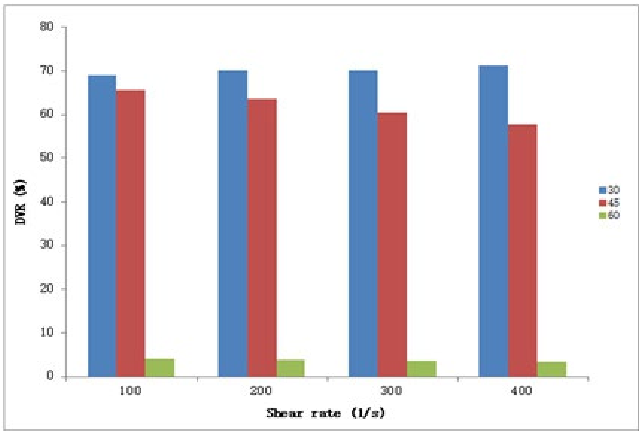

Figure 9: Rheological behaviour of heavy oil in the presence of 12.84 nm of ZnO nanoparticles and their absence at 30, 45, and 60°C, and the degree of viscosity reduction at shear rates between 0 and 500s^{-1}.

The rheological responses of heavy crude oil with additional ZnO nanoparticles at 30, 45, and 60°C shows the reduction viscosity of heavy crude oil where the highest DVR was 71%. Therefore, increasing in shear rate from 0 to 500s^{-1} with increasing of temperature at 30, 45, and 60°C will decrease the DVR. Rheological behavior of heavy crude oil at 60°C shows the minor changes in viscosity values between presence and absence of ZnO nanoparticles. Figure 9 indicated that at temperature 30°C, the DVR tend to increase up to 71% with increasing shear rate from 100 to 400s^{-1}. However, at temperature 45 and 60°C, the DVR tends to reduce with increasing shear rate from 100 to 400s^{-1}. From this statement, it can conclude that the optimum temperature of this performance was at 45°C where with further increasing in the temperature, the DVR was reduced nearly to 0%. As the temperature increase, so does the rate of reaction of ZnO nanoparticles toward heavy crude oil. But very high temperature can denature the ZnO nanoparticles and can change the chemical and physical properties of ZnO nanoparticles.

F. Potential of Zinc Oxide Nanoparticles to Reduce Wax Deposition from Heavy Crude Oil

Table 4 shows the weight of wax deposited in the heavy crude oil before and after additional of ZnO nanoparticles. This result display that the reduction of the weight of wax about 32.40%. The optimum calcination temperature obtained from the previous study of effect on particles size and effect on temperature and high shear rate on heavy crude oil was observed at 400°C which have 12.84 nm crystallite sizes. The smaller size of ZnO nanoparticles gives the higher surface area. This higher surface area will increase the absorption rate of ZnO toward heavy crude oil, so that reduced in weight of wax of heavy crude oil[16][17].

Table 4: Weight of wax with presence and absence of ZnO nanoparticles in heavy oil

Weight of wax of HO (g)	Weight of wax of present ZnO np in HO (g)
24.72	16.71

IV. CONCLUSION

Zinc oxide nanoparticles were successfully synthesized by using sol-gel method at different calcination temperature from 300°C to 900°C. Effect of calcination temperature on the structural and crystallite size of ZnO nanoparticles at different temperatures from 300°C to 900°C was study by using XRD, FESEM and EDX. The XRD results approved the presence of formation hexagonal wurtzite structure of ZnO nanoparticles with increased crystallinity. The effect of calcination temperatures on the crystallite size of ZnO nanoparticles were successfully determined when the crystallite size was reduce with increasing of calcination temperature from 300°C to 400°C (15.59 nm-12.84 nm). Further increasing calcination temperature from 400°C to 800°C, resulted in increased crystallite size from 12.84 nm to 41.58 nm. The synthesized sample then proceeds used for viscosity reduction for oil upgrading and it shows that nanoparticles size at 12.84 nm gave the best performances for viscosity reduction compared than others.

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