Synthesis of ZnO for Wax Deposition Control and Oil Upgrading: Effect of pH

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Abstract – **Waxes and asphaltene depositions are one of the major problem happened during oil and gas operation. Deposition of asphaltene in pipes and pipelines may cause damages to the equipment and increase the maintenance cost. To overcome this problem, several methods are invented in the industries. One of the methods is by using nanoparticles as an agent in controlling wax deposition in crude oil because of their applicable characteristics. At some point, to maximize the outcome of the method, an optimum pH of nanoparticles is vital because the higher the pH, nano-size of nanoparticles become smaller. To get the best viscosity reduction and wax deposition control, uses nanoparticles at optimum pH is important. So, objectives of this study are to synthesize and characterize zinc oxide, ZnO nanoparticles by using sol – gel method in the effect of pH and to run performance study of zinc oxide in-situ addition to heavy crude oil. Firstly, heavy crude oil is characterized to obtain physical properties and rheology characteristics. Secondly, synthesis of ZnO nanoparticles by using sol-gel method in variations of pH values (pH 2, pH 3, pH 4 and pH 5). Thirdly, the ZnO nanoparticles is characterized using X-ray diffraction (XRD) to analyze crystal structure and crystallite size of ZnO nanoparticle. Energy Dispersive X-ray (EDX) and Field Emission Scanning Electron Microscope (FE-SEM) also used to observe morphology and final composition of ZnO nanoparticles. Lastly, performance studies of in-situ addition of ZnO nanoparticle to heavy crude oil by using Electronic Rheometer and cold finger method. The result showed that high pH values will produce smaller crystallites size of ZnO nanoparticles when checked by using X-ray diffraction (XRD). Performance study result showed that optimum pH for wax deposition control is at pH 2. On the other hand, pH 4 ZnO nanoparticle give the best result for viscosity reduction of the heavy crude oil. When shear rate increases, the viscosity reduction decreases. In conclusion, this study will provide the best option of pH for ZnO nanoparticle that can be used to overcome the wax and asphaltene problems and oil upgrading in industries.**

Keywords— **ZnO; nanoparticles; sol gel; pH; XRD**

I. INTRODUCTION

Nowadays, oil and gas industry is a very important source of economic incomes for many countries all over the world. According to US Energy Information Administration, it is almost 100 countries that already have their own reserves of oil in all over the world. That is including their hydrocarbon exploration, production and processing facilities equipped with advanced technologies and expertise such as unconventional drilling, seismic logging systems, hydraulic fracturing systems and others.

As rising of these upstream or downstream activities all over the world, many problems arise that faced by the operators. Most of the problems cause in delaying progress of operations as well as decreased productions and increase costs for maintenance and spare parts. One of the problems are wax and asphaltene depositions in boreholes, piping and transportation pipelines.

Waxes and asphaltenes are the most important elements of the crude oil as they influence the oil properties. Waxes are complex mixture of solid hydrocarbons which consist of paraffin with a small amount of naphthenic and aromatic hydrocarbon at ambient temperature[1].

Current development of technologies has resulted in some new solutions that can be used in oil and gas industries to overcome wax deposition problems in the operations. According to Thota & Onyeanuna, 2016, there are three categories for wax remediation techniques which are thermal, chemical and mechanical techniques. Thermal technique is using high temperature to heat up wax until they are melted. Hot fluid are pumped into the well until its contact oil in the reservoir or production routes. Examples of thermal techniques are hot oiling, hot water treatment and direct heating. These techniques are very costly. Mechanical technique is using tools to scrap the tubing mechanically. Both technique are very costly. For chemical techniques, uses of dispersants, wax crystal modifiers and surfactants. These techniques are less costly but need to use the right chemicals that suitable for the oil to prevent further reactions[2]. Nanoparticles is one of the new chemical technique developed to solve asphaltene and wax deposition problems in industries. Nanoparticles are inorganic particles which are very small and range of the size is 1-100 nanometer (nm).

In this research, zinc oxide, ZnO nanoparticles are chosen as sample to study the effect of nanoparticles on the wax deposition problem and oil upgrading. This is because zinc oxide have large surface area and high catalytic activity for any reaction efficiently compare to other nanoparticles which make it the most suitable nanoparticle to study on[3].

II. METHODOLOGY

A. *Chemicals and Materials*

For ZnO synthesis by using sol-gel method, 100g of zinc acetate dehydrate, $Zn(CH_3COO)_2.2H_2O$, 100 g of oxalic acid $C_2H_4O_4.2H_2O$, 100 ml of ethanol (C_2H_5OH, 95%) and 10 ml distilled water. The chemicals were obtained from Vchem Laboratory. For pH alteration; hydrochloric acid

(HCl, 37%) fuming and ammonium hydroxide. The chemicals were purchased from DAEJUNG Company.

Material used in this experiments was heavy crude oil with 11˚ API obtained from Kemaman Bitumen Company in Terengganu.

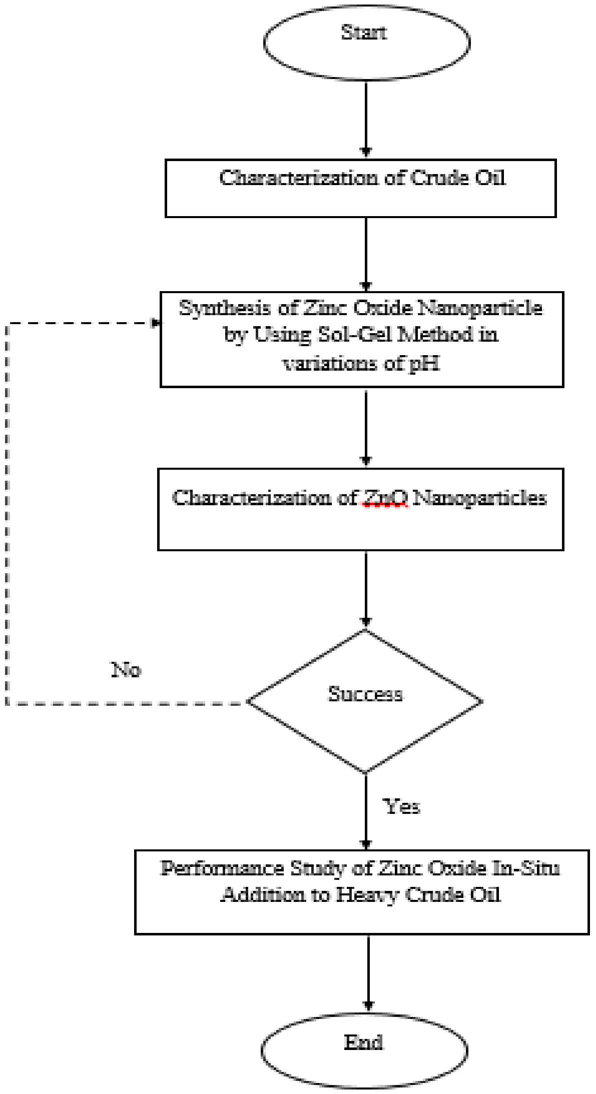

Figure 1 Flowchart of the methodology

B. Characterization of crude oil

Table 1 shows physical and chemical properties of heavy crude oil sample

Physical properties	Crude oil sample
Density, kg/m^3	993
Specific Gravity	0.993
˚API	11
Color	black
Cloud point, ˚C	12
Chemical properties	**wt (%)**
Saturate	3
Aromatic	63.4
Resin	12.9
Asphaltene	20.7

Table 1 showed the physical and chemical characteristics of heavy crude oil. Viscosity of the crude oil was checked using the electronic rheometer at shear rate at 0 – 500 s^{-1} and 45˚C [4]. For density and specific gravity of crude oil, equations[5] below was used with the reference of API Gravity value that already given by the manufacturer which was API 11˚.

SG = $\rho_{oil} / \rho_{water}$ …………………………………….. (1)
API˚ = (141.5/SG) - 131.5 …………….…….……….. (2)

C. Synthesis of ZnO

ZnO nanoparticle was synthesized using sol – gel method. Zinc acetate and oxalic acid was prepared I solution of molar ratio of 1:2 where it is the optimum molar ratio for the mixtures [6]. 3.28g of oxalic acid was mixed with ethanol and stirred with magnetic stirrer at temperature ranging between 45°C to 50°C for 30 min. Next, 4g of zinc acetate was mixed with 200 ml ethanol and distilled water (10% volume of ethanol). The solution was heated using hot plate at temperature between 65°C to 70°C for 30 min. Oxalic acid solution was slowly dropped dropwise into zinc acetate solution under vigorous stirring to obtain gel-like structure. When gel appeared, the mixture was continuously stirred until white precipitations fully formed. Initial pH value of zinc oxide solution was checked by using Mettler Toledo Seven Multi Bencthop Meter. An amount of 37% hydrochloric acid (HCl) fuming and ammonium hydroxide was added to adjust the pH value according to desired values which were pH 2, pH 3, pH 4, and pH 5 [7]. Then, white gel formed were filtered by using vacuum pump and 90mm diameter filter paper. The sample was collected from the filter paper and dried in the oven at 80°C for 2 hours to remove moisture of the sample [7]. Lastly, the sample was calcined using furnace at 400°C for 2 hours to form firm crystal structure of ZnO nanoparticles [6].

D. Characterization of ZnO

The ZnO nanoparticles crystal structure and crystallite size were determined using the powder X-ray Diffractometer (Panalytical, model: EXPERT Pro). The average crystallite sizes, d were determined using Scherer's equation (3):

$$d=k\lambda/\beta\cos\Theta \quad (3)$$

Where k=0.94, x-ray wavelength, λ = 1.54056 Å. β was the full width of half maximum (FWHM) of the peaks in the pattern. Final compositions of ZnO was analyzed using Energy Dispersive X-ray (EDX) (Bruker, UK). Lastly, Field Emission Scanning Electron Microscope (FE-SEM) (Zeiss, Model: SUPRA 40VP) was used to analyze the morphology of ZnO nanoparticles.

E. Performance study

(a) Effect of Size of Nanoparticle on Wax Deposition

The performance were conducted to find out changes of wax deposition before and after addition of ZnO nanoparticles. The experiment was conducted using cold finger (Wisebath, UK) method. ZnO at pH 2, pH 3 and a blank heavy crude oil as base were used in this experiment to observe effect of sizes of the nanoparticles toward wax deposition. Percentage of Efficiency of ZnO was calculated by using equation (4)[2].

$$\text{Efficiency (\%)} = [(W_{oil} - W_{np}) / W_{oil}] \times 100 \quad \text{……………. (4)}$$

(b) Effect of size (pH) of Nanoparticles on Viscosity Changes of heavy crude oil

This experiment was to find the optimum pH value that will give the best viscosity changes of heavy crude oil. Concentrations of ZnO nanoparticles was kept constant at 1000 mg/L and the shear rate was set from 0 s^{-1} to 80 s^{-1} [4]. The best result will be selected and run for viscosity reduction with the effect of temperature and shear rates.

(c) Effect of Temperatures and Shear Rate on Viscosity Reduction of heavy crude oil

Effect of temperatures and shear rate on viscosity reduction were analyzed by using MCR 300 Modular Compact rheometer. The temperature variations in this experiment were 30˚C, 45˚C and 60˚C and the shear rates range from 0 – 500 s^{-1} [4]. Degree of viscosity reduction (DVR) were calculated by using equation (5).

$$\text{DVR\%} = [(\mu_{oil} - \mu_{np}) / \mu_{oil}] \times 100 \quad \text{………………….. (5)}$$

III. RESULTS AND DISCUSSION

A. Synthesis of ZnO

Table 2 the conditions for pH alteration

pH (wanted)	pH (initial)	Conditions (added into the ZnO solution)
2	2.63	0.5 ml of Hydro Chloric acid (HCl)
3	2.24	2 drops of ammonium hydroxide
4	2.74	0.2 ml of ammonium hydroxide
5	2.89	0.57 ml of ammonium hydroxide

Based on the synthesis process that have been done in preparing zinc oxide nanoparticle by using sol-gel method, there were several chemical reactions that take places. Zinc acetate dehydrate undergoes hydrolysis process when mixed with water and ethanol with the presence of heat. They will form zinc ions and acetate ions[7]. Further complete hydrolysis will form zinc hydroxide acetate as the intermediate product. The mixture of oxalic acid which was strong acid in ethanoic solution with the solution will form ZnO colloid[7]. Oxalic acid solution was dropped slowly into the zinc acetate solution slowly to ensure that the formation of ZnO colloid to be uniform[6]. Further heating process at higher temperature will easily form stable ZnO nanoparticle.

Based on the conditions in **Table 2**, the pH was adjusted according to the initial pH of the zinc colloid solution. If the wanted pH was more than initial pH, ammonium hydroxide (alkaline) was added. However, if wanted pH was lower than the initial pH, HCl was added into the solution. This due to the number of pH will increase from acids to alkaline[8].

B. Characterization of ZnO

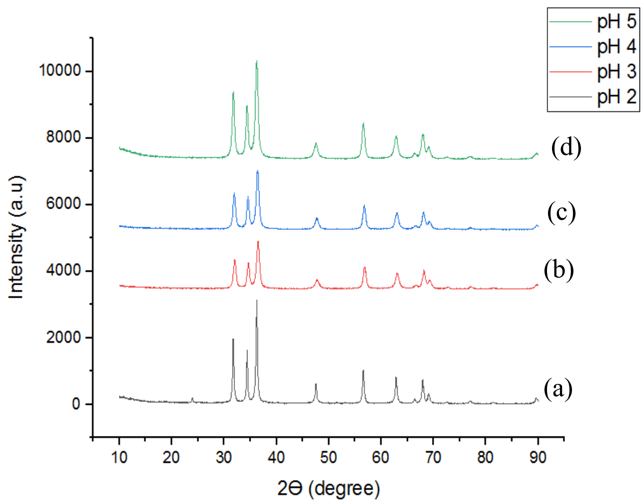

Figure 2 shows compilation of peak patterns of ZnO nanoparticles at (a) pH 2, (b) pH 3, (c) pH 4 and (d) pH 5

In this experiment, XRD was used to observe and justify the structure and peaks of zinc oxide nanoparticles that present in the sample. All the peaks patterns of different pH values were compiled using Origin Pro 2018 software. **Figure 2(a)** shows the various XRD peak patterns of ZnO nanoparticles in the fraction angel, 2Θ, range 20˚ to 80˚ at pH 2. All the peaks in the figure showed the crystallinity of the nanoparticle in nature. The diffraction peaks were at 31.7345˚, 34.3505˚, 36.2153˚, 47.5209˚, 56.5891˚, 62.8435˚, and 67.8734˚. All these peak were originated from (100), (002), (101), (102), (110), (103) and (112) planes. The crystallites sizes calculated was 10.87 nm.

Figure 2(b) shows the various XRD peak patterns of ZnO nanoparticles in the fraction angel range 20˚ to 80˚ at pH 3. The diffraction peaks were at 32.0198˚, 34.6254˚, 36.4909˚, 47.7928˚, 56.8341˚, 63.0585˚, and 68.1599˚. All these peak were originated from (100), (002), (101), (102), (110), (103) and (112) planes. The crystallites sizes calculated was 16.31 nm.

Figure 2(c) shows the various XRD peak patterns of ZnO nanoparticles in the fraction angel range 20˚ to 80˚ at pH 4. The diffraction peaks were at 31.9310˚, 34.5333˚, 36.41 ˚, 47.6856˚, 56.7718˚, 63.0032˚, and 68.0995˚. All these peak were originated from (100), (002), (101), (102), (110), (103) and (112) planes. The crystallites sizes calculated was 13.05 nm.

Figure 2(d) shows the various XRD peak patterns of ZnO nanoparticles in the fraction angel range 20˚ to 80˚ at pH 5. The diffraction peaks were at 31.7614˚, 34.3737˚, 36.2349˚, 47.5377˚, 56.6073˚, 62.8494˚ and 67.9451˚. All these peak were originated from (100), (002), (101), (102), (110), (103) and (112) planes. The crystallites sizes calculated was 13.04 nm.

Based on the discussion above, all the peaks were found to match with to wurtzite structure of ZnO in the standard JCPDS (Card No. 36-1451) [9]. The sample was justified as zinc oxide nanoparticles successfully.

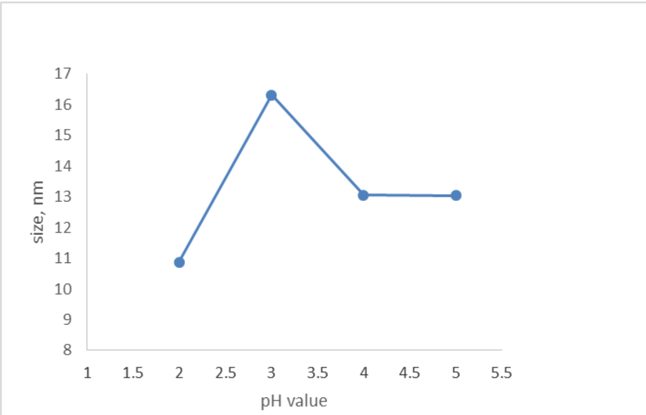

Figure 3 shows effects of pH on the crystallite sizes of ZnO nanoparticles

Crystallite sizes of ZnO nanoparticles were calculated using Scherer's equation. From pH 2 to pH 3, the graph showed the increment in crystallite size. This was because the additional of ammonium hydroxide into the solution, increased the concentration of OH− ions caused the rapid growth of nanoparticles [6]. From pH 3 to pH 5, the crystallite sizes was decreasing as further additional of ammonium hydroxide produce stable Zn2+ complex with ammonia which stabilized the growth of the ZnO particle [6].

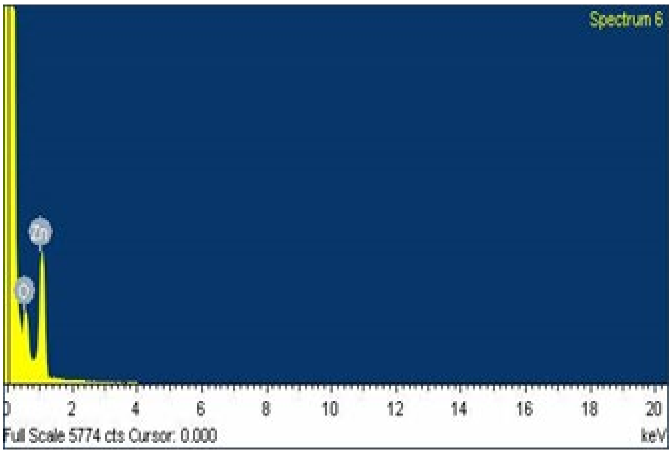

Figure 4 EDX pattern of ZnO at pH 3

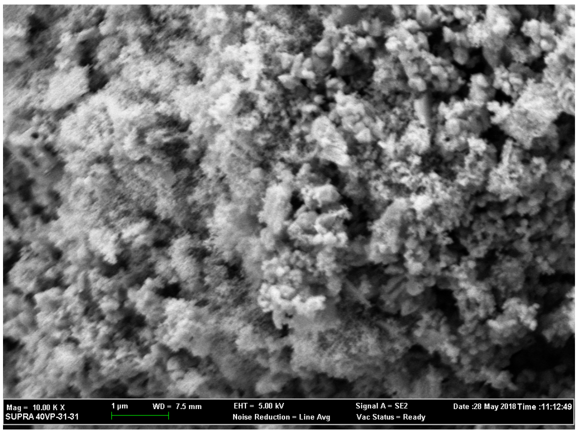

Figure 5 shows the image of morphology of pH 3 ZnO nanoparticle under FE-SEM

Figure 4 showed the pattern of Energy Dispersive X-ray (EDX) of pH 3 ZnO nanoparticles. From that, the final compositions of ZnO nanoparticles were tabulated in **Table 3**. From the FESEM image in **Figure 5**, we observed the nanoparticles that we produced have irregular in shapes.

Table 3 shows the final composition of ZnO nanoparticle by using EDX

Element	*Weight%*	*Atomic%*
O K	22.59	54.39
Zn L	77.41	45.61
Totals	100.00	

C. Performance study

(a) Effect of Size of Nanoparticle on Wax Deposition

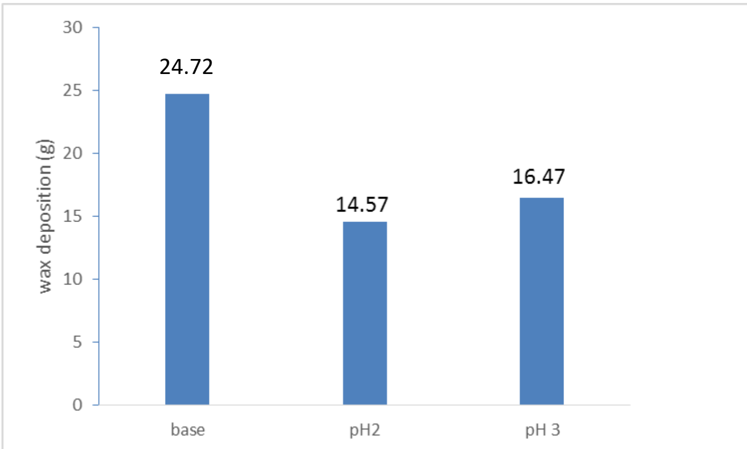

Figure 6 shows wax deposition of crude oil

Based on the **Figure 6**, the experiment was conducted to observe the changes of wax deposition amount after added ZnO nanoparticle. pH 2 ZnO shows the lowest wax deposition which was 14.57g compare to pH 3 which was 16.47g. This was because pH 2 ZnO has smaller crystallite size which was 10.87 nm compare to pH 3 ZnO. Low crystallite size have high surface area. Nashaat N. Nassar [10] concluded that surface are of nanoparticles can effect absorption rate of asphaltene. pH 2 ZnO has high surface area, so it was easy to adsorb asphaltene compared to pH 3. It reduces the wax deposition up to 41.06% of efficiency. Percentage of efficiency was tabulated in Table 4 below. So, this experiment can be conclude that pH 2 ZnO was the optimum pH for wax deposition control.

Table 4 shows percentage of efficiency of ZnO nanoparticle on controlling wax deposition

Nanoparticles	Efficiency (%)
pH 2 ZnO	41.06
pH 3 ZnO	33.37

(b) Effect of pH of Nanoparticles on Viscosity Changes of heavy crude oil

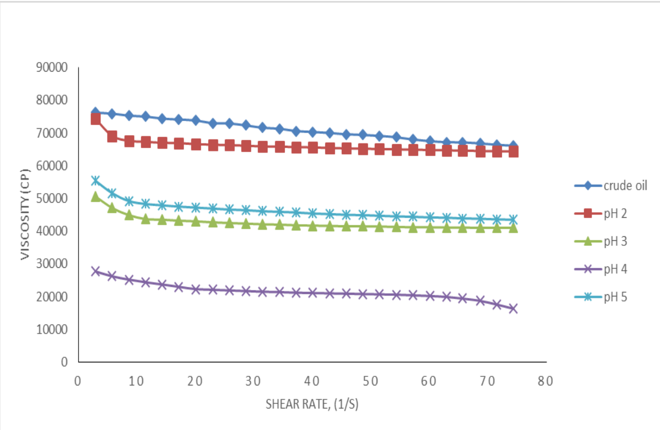

Figure 7 shows changes of viscosity of heavy crude oil in the effect of different pH at 0 - 80 s^{-1}

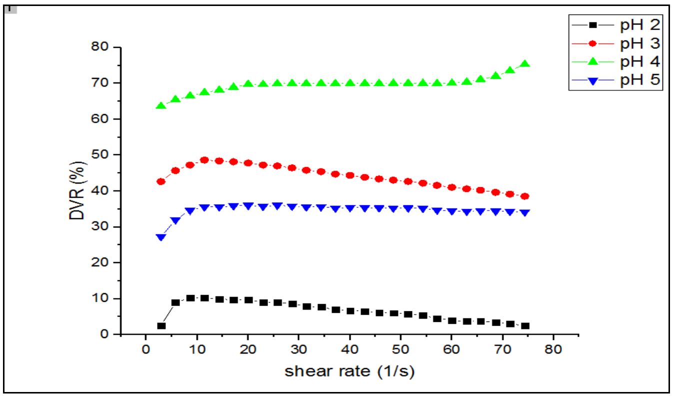

Figure 8 shows degree of viscosity reduction, DVR (%) at various pH

This experiment conducted was to find the best pH for viscosity changes of heavy crude oil sample. Based on the **Figure 7,** heavy crude oil without ZnO nanoparticles has very high viscosity. When added ZnO nanoparticle, the viscosity seems to be decreased. The optimum pH of ZnO nanoparticle for viscosity reducing was at pH 4 (size: 13.05 nm). This was because the viscosity of the crude oil when added with pH 4 ZnO nanoparticles showed the most decreasing pattern among others. This was supported with **Figure 8**, where the degree of viscosity reduction, DRV of pH 4 ZnO were 63% to 75% which was very good in viscosity reduction. The higher the DVR, the better the viscosity reduction [4].

(c) Effect of Temperatures and Shear Rate on Viscosity Reduction of heavy crude oil

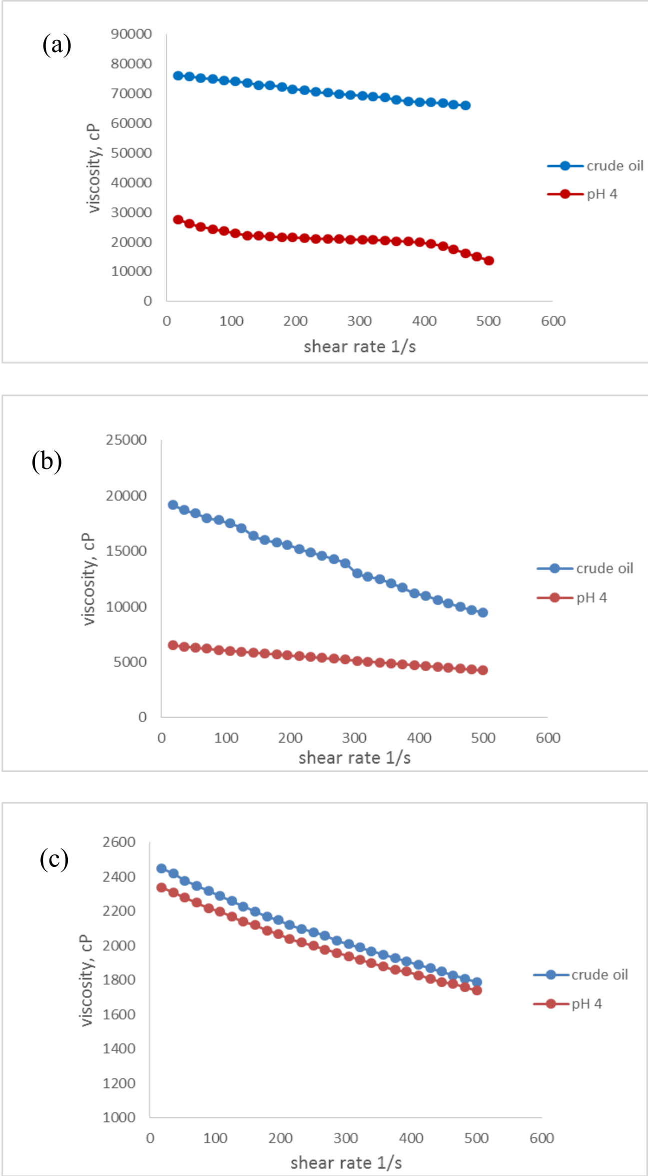

Figure 9 shows the effect of Temperatures, (a) 30˚C, (b) 45˚C and (c) 60˚C at shear rate 0 s^{-1} to 500 s^{-1} on Viscosity Reduction for pH 4 ZnO nanoparticles

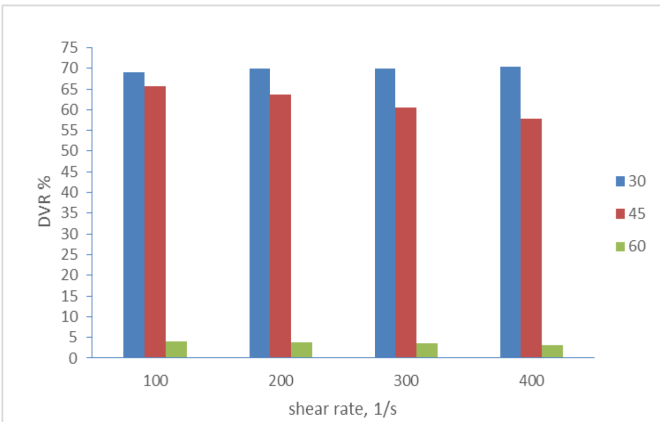

Figure 10 shows DVR (%) for pH 4 ZnO at shear rate 100s^{-1}, 200s^{-1}, 300s^{-1} and 400s^{-1}

Based on **Figure 9** above, at temperature 30˚C, 45˚C and 60˚C, with shear rate of 0 to 500s^{-1}, the most significant viscosity reduction was at temperature 30˚C and the least viscosity reduction was at temperature 60˚C. This was because at 60˚C, more heat break the bond between crude oil particles and make them very low viscosity[11].

All of the graph also showed the same pattern of viscosity decrease as shear rate increased. This was known as pseudo-plastic type shear thinning behavior[4]. The viscosity decrease as shear rate increase ere due to presence of asphaltene and its tendency to self-aggregate. Stirring condition increased, internal structure of ZnO was reorganized, produced the decreasing of viscosity when shear rate increased [4].

Based on the **Figure 10**, Degree of viscosity reduction (DVR) decreased when shear rate increased. This was due to the DVR at different temperature also decreased. The highest viscosity reduction was 70.38% at shear rate 400, temperature 30 ˚C.

IV. Conclusion

As a conclusion, two objectives for this research were achieved. First, Zinc oxide nanoparticles were synthesized using sol-gel method, controlled by variation of pH value from pH 2, pH 3, pH 4 and pH 5. It was observed that the change in structure and crystallite sizes of the nanoparticle were dependent on the pH values. Second, performance study on in-situ addition of ZnO nanoparticles into the heavy crude oil to analyzed effect of sizes of ZnO nanoparticles on asphaltene deposition. The result showed the lower the size, the lower the amount of asphaltene deposited. The optimum pH for wax control from the experiment was at pH 2. After that, for oil upgrading, viscosity changes and viscosity reduction was analyzed by the effect of sizes (pH) of nanoparticles, temperature and shear rates. The result showed that optimum Zinc oxide for viscosity reduction was pH 4 ZnO nanoparticles. As shear rate was decreased, the degree of viscosity reduction (DVR) were decreased. It was proven that, zinc oxide nanoparticle can reduce the heavy crude oil wax deposition as well as upgrading the oil.

This study supports that ZnO nanoparticles can be applied for heavy crude oil wax deposition control and oil upgrading, as they could be prepared in situ. Our study has the potential to be developed into a future technology that may have a huge effect on the industrial.

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