The Effect of Nanoparticles Crystallite Size on the Recovery Efficiency in Dielectric Nanofluid Flooding

Hasnah Mohd Zaid[1, a], Noorhana Yahya[1, b], Noor Rasyada Ahmad Latiff[2, c]

[1]Fundamental and Applied Sciences Department, Universiti Teknologi PETRONAS,
Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

[2]Electrical and Electronics Engineering Department, Universiti Teknologi PETRONAS,
Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

[a]hasnamz@petronas.com.my (corresponding author), [b]noorhana_yahya@petronas.com.my,
[c]syasya.latiff@gmail.com

Abstract. Application of nanotechnology in enhanced oil recovery (EOR) has been increasing in recent years. After secondary flooding, more than 60% of the original oil in place (OOIP) remains in the reservoir due to trapping of oil in the reservoir rock pores. One of the promising EOR methods is surfactant flooding, where substantial reduction in interfacial tension between oil and water could sufficiently displace oil from the reservoir. In this research, instability at the interfaces is created by dispersing 0.05 wt% ZnO nanoparticles in aqueous sodium dodecyl sulfate (SDS) solution during the core flooding experiment. The difference in the amount of particles adsorbed at the interface creates variation in the localized interfacial tension, thus induces fluid motion to reduce the stress. Four samples of different average crystallite size were used to study the effect of particle size on the spontaneous emulsification process which would in turn determine the recovery efficiency. From the study, ZnO nanofluid which consists of larger particles size gives 145% increase in the oil recovery as compared with the smaller ZnO nanoparticles. In contrast, 63% more oil was recovered by injecting Al_2O_3 nanofluid of smaller particles size as compared to the larger one. Formation of a cloudy solution was observed during the test which indicates the occurrence of an emulsification process. It can be concluded that ultralow Interfacial tension (IFT) value is not necessary to create spontaneous emulsification in dielectric nanofluid flooding.

Introduction

The usage of nanoparticles in enhanced oil recovery research has become widespread with various ways and mechanisms proposed to increase oil production. Wettability alteration of reservoir rock surfaces, emulsion and foam stabilization, interfacial tension reduction, etc. are some of the ways to use nanoparticles in enhanced oil recovery. The emulsion that is created between the two interfaces has a higher viscosity than its original components, thus adding another mechanism to oil recovery by controlling the mobility ratio between oil and water providing more force to push the trapped oil [1]. Although in high temperature and high pressure (HTHP) oil reservoirs, emulsions formed experience degradation and fail to exhibit similar performance, particles could somehow behave like a surfactant in certain condition. It was demonstrated that as particles are reduced to smaller than 6 nm, they have the tendency to be adsorbed and desorbed on a relatively fast timescale, exhibiting surfactant-like behaviour [2, 3]. Spontaneous emulsification occurs when instability exist at the interfaces, either by solute concentration or density gradient, thus mobilizing the trapped oil. A recent work by Ali Karimi *et al.* [4] has proved that zirconium oxide, ZrO_2 nanoparticles suspension can change an oil-wet carbonate system to become water-wet by changing the surface free energy as the nanoparticles being adsorbed onto the solid surfaces. Quick imbibitions of the nanofluids into the core plugs recovered about 50% OOIP in just half a day. In another study using 5 nm silica nanoparticles dispersed in aqueous solution, foam generated by co-injecting the nanofluid of 0.05 wt% concentration with CO_2 shows two to eighteen times more resistance to the flow as compared to the foam generated without nanoparticles. Silica nanoparticles act to stabilize

foam by having higher adhesion energy compared to surfactant molecules, thus once at the interfaces the particles would irreversibly adsorb [5]. Similar work was repeated but with the intention to stabilize emulsion and promising results were achieved with nanofluids concentration higher than 0.5 wt% [6]. By dispersing non-ferrous metal nanoparticles into aqueous sulphanole solution, 70-79% of reduction in oil-water interfacial tension was achieved with less than 0.01 wt% nanoparticles concentration. The tremendous IFT reduction was facilitated by the adsorption of nanoparticles onto the sand surfaces which tends to stabilize the physical and chemical adsorption process at the interfaces [7].

In this study, the effect of nanoparticles crystallite size on the recovery efficiency of dielectric nanofluid flooding was investigated by varying the size of nanoparticles suspended in an aqueous surfactant solution. Two types of materials were used; zinc oxide and aluminum oxide to compare their performance in nanofluid core flooding as well as measuring their interfacial tension with oil phase to evaluate their spontaneous emulsification process.

Methodology.

Characterization of nanoparticles. Zinc oxide, ZnO and aluminum oxide, Al_2O_3 nanoparticles were used in this research. For each type of material, the synthesized sample and purchased sample were used for size comparison. Both type of nanoparticles were synthesized by using the sol-gel method and annealed at a temperature of 300°C for ZnO and 1100°C for Al_2O_3, labeled as ZnO-SG-300 and Al_2O_3-SG-1100, respectively. For another batch of samples, both of them were purchased from R&M Chemicals, labeled as ZnO-RM and Al_2O_3-RM. Microstructural characterization and crystallographic studies were conducted via Variable Pressure-Field Emission Scanning Electron Microscope (FESEM), Energy Dispersive X-Ray Spectrometer (EDX) and X-Ray Diffraction (XRD).

Nanofluid preparation. Nanoparticles in the form of powder were mechanically mixed in deionized water to form a suspension and stabilized by a small amount of an anionic surfactant, sodium dodecyl sulphate (SDS). The amount of nanoparticles to be dispersed in the base fluid was fixed to 0.05 wt% for all samples. The nanoparticles suspensions were further agitated in an ultrasonic bath for 1 hour to reduce nanoparticles agglomeration and ensure longer dispersion of powder particles in aqueous solution. Two types of nanomaterials present in this research, namely zinc oxide, ZnO and aluminium oxide, Al_2O_3 are to be compared in these series of experiment for their effect of particles size in the occurrence of spontaneous emulsification.

Interfacial Tension (IFT) measurement. Interfacial tension measurements were conducted using SVT 20 Multiphysics Spinning Drop Tensiometer at temperature 60°C and at ambient pressure by injecting an oil drop, known as Phase 2 into the excess injection fluid, known as Phase 1 at 800 rpm. The speed of rotation was gradually increased until the diameter of the oil drop elongated to at least 3 times of its initial diameter. Interfacial tension between oil and aqueous phase, γ in mN/m is calculated according to following equation:

$$\gamma = 2.74156 \exp(-3)\frac{(\rho_h - \rho_d)\omega^2}{C} \qquad (1)$$

where ρ_h is the density of Phase 1 (g/cm^3), ρ_d is the density of Phase 2 (g/cm^3), ω is the rotational velocity (rpm), D is the measured drop width (mm) and C is a coefficient determined by the ratio of the length to the width of the oil drop.

Core flooding test. An unconsolidated core sample made of glass beads having an average size of 150-300 μm was packed homogeneously and saturated with brine of 30,000 ppm. Pressure measurement was made at a point just upstream of the inlet to the porous medium. Its significant properties e.g. permeability, porosity and pore volume were determined at this stage. Subsequently, Arab Heavy crude oil was injected into the porous medium horizontally until irreducible water saturation, S_{wi} was achieved. To replicate the waterflooding process, brine was injected at a constant rate and continued until 30% watercut level was reached. EOR stage took place by the injection of the nanofluids. All fluids were injected at a constant flow rate of 2.5 mL/min.

Results and Discussion.

   Characterization of nanoparticles. Figure 1 shows FESEM images for all nanoparticles which have shown severe agglomeration of nanoparticles without proper coating or surfactant. A rod-like morphology can be observed in both ZnO samples, with better defined shape and less agglomeration in the ZnO-RM sample. Morphology images of both Al_2O_3 samples depicted irregular shape and non-uniform distribution. Elemental composition from EDX analysis is presented in Table 1, which validate the chemical purity of all samples expressed in terms of weight and atomic percentage in comparison to the theoretical values.
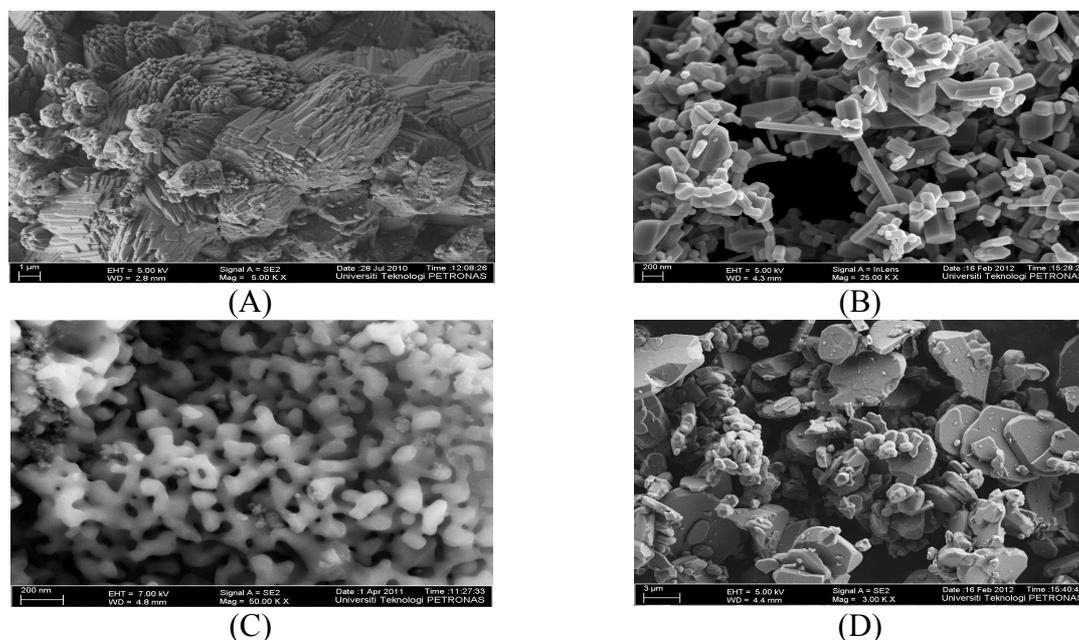

(A)	(B)

(C)	(D)

Figure 1. Morphology of nanoparticles (A) ZnO-SG-300, (B) ZnO-RM, (C) Al_2O_3 -SG-1100 and (D) Al_2O_3 -RM from FESEM analysis.

Table 1. Elemental composition analysis of ZnO and Al_2O_3 nanoparticles

Sample	Element	Atomic Weight (amu)	Expt Weight (%)	Theoretical atomic (%)	Expt Atomic (%)
ZnO-SG-300	O	15.9994	20.36	0.5	51.09
	Zn	65.38	79.64	0.5	48.91
ZnO-RM	O	15.9994	25.24	0.5	57.97
	Zn	65.38	74.76	0.5	42.03
Al_2O_3-SG-1100	O	3 x 15.9994	54.01	0.6	66.45
	Al	2 x 26.9815	45.99	0.4	33.55
Al_2O_3-RM	O	3 x 15.9994	51.38	0.6	64.06
	Al	2 x 26.9815	48.62	0.4	35.94

Average particle size, D_{hkl} was calculated from the X-Ray line broadening method using the Scherrer equation:

$$D_{hkl} = \frac{k\lambda}{\beta_{hkl}\cos\theta} \qquad (2)$$

where λ is the wavelength of radiation (1.5406 Å for Cu K_α radiation), k is the Scherrer constant, β_{hkl} is the peak width at half maximum intensity and θ is the peak position [8]. From the diffraction pattern, the major peaks (1 0 1) of ZnO and (1 1 3) for aluminum oxide were chosen for particle size calculation and presented in Table 2.

Table 2. Comparative values of d-spacing, lattice parameter, structure and crystallite size of ZnO nanoparticles annealed at various temperatures of major crystal planes

X-Ray Diffraction				
Samples/Annealing Temperature	Crystal planes [(h k l)]	d-spacing [Å]	Average particle size, D_{hkl} [nm]	Crystal structure
ZnO-SG- 300	(1 0 1)	2.473	45.93	Hexagonal
ZnO-RM	(1 0 1)	2.477	108.70	Hexagonal
Al_2O_3-SG-1100	(1 1 3)	2.084	38.25	Hexagonal (Rh)
Al_2O_3 - RM	(1 1 3)	2.552	72.94	Hexagonal (Rh)

Interfacial Tension (IFT) measurement. Dynamic IFT between oil and aqueous phase of different nanofluids were measured and are presented in Figure 2. Initially, when IFT between crude oil and SDS solution is measured, a tremendous reduction in IFT value was observed, in comparison with the brine-crude oil IFT. However, when the same concentration of SDS solution is used with additional 0.05 wt% ZnO nanofluid, the IFT value had increased slightly higher than before. A similar trend was observed with other nanofluids in agreement with the work done by Liu Yang et al. where it was observed that there was an increase in the surface tension of the fluids with nanoparticles addition when the concentration of surfactant is lower than the critical micelle concentration (CMC) of the system. Those increases may be explained by the decrease in the free surfactant molecules present in the solution due to the surfactant adsorption on the surface of nanoparticles [9].
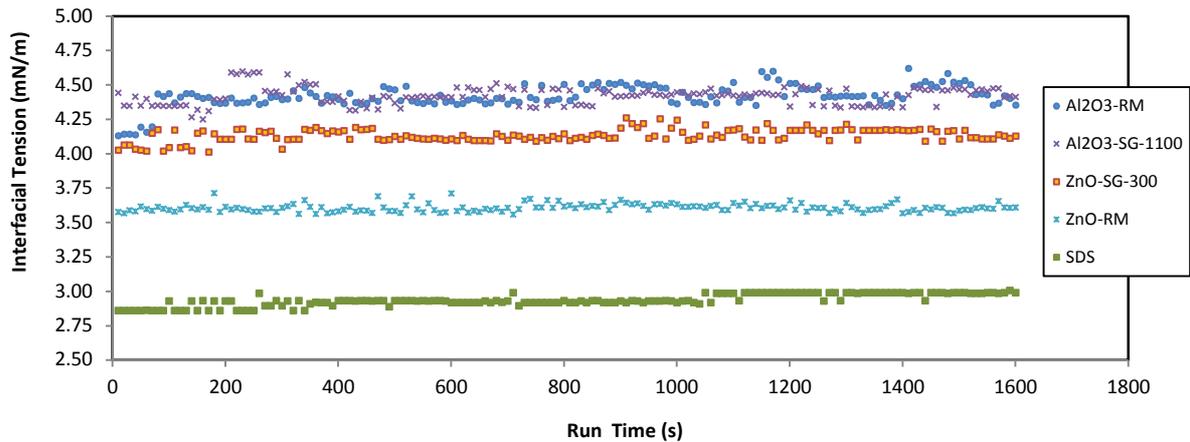

Figure 2. Dynamic IFT between oil phase and aqueous phases measured in 1600 s

Another reason for the variation in IFT values of different nanofluids could be attributed to the surface energy of the nanoparticles, which directly related to the average particle size, as predicted in Eq. 2, where the energy required to detach a particle from a fluid-fluid interface, E is given as:

$$E = \pi r^2 \gamma_{\alpha\beta} (1 \pm \cos \theta). \tag{3}$$

where r is the particle radius, $\gamma_{\alpha\beta}$ is the interfacial tension between two fluids and θ is the contact angle which the particle makes with the interface. Larger particles will have a higher detachment energy since it is proportional to the square of particle radius, thus particles once at the interface will be irreversibly adsorbed unlike surfactant molecules which are smaller and reversibly adsorbed and desorbed on a relatively fast timescale [10]. For that reason, the IFT values for all samples with nanoparticles addition are larger than that of SDS aqueous solution alone.

Core flooding test. A series of core flooding tests were conducted using various injection fluids to improve oil production after the water flooding stage. The Recovery factor, RF for all injection fluids was determined by calculating the percentage of volume of oil recovered after nanofluid

injection in comparison with the volume of oil remaining after being water flooded. Table 3 summarizes the recovery factor for all injection fluid, which shown a higher percentage of oil recovered with the addition of nanoparticles into the SDS solution, even though it was anticipated earlier that the SDS solution, which has the lowest IFT value among all injection fluids, will yield the higher recovery.

Table 3. Cumulative oil recovery of various injection fluids

Injection Fluid	RF [%ROIP]	Min. IFT Value [mN/m]
SDS aqueous (base fluid)	23.28	2.824
SDS + ZnO-SG-300	29.42	4.031
SDS + ZnO-RM	72.26	3.558
SDS + Al_2O_3 -SG-1100	32.88	4.131
SDS + Al_2O_3 - RM	53.53	4.249

After 2 PV of injection, all samples exhibited a similar pattern as shown in Figure 2, except for Al_2O_3-RM which has exhibited a slower increase in the oil recovery but has sustained for a longer duration. At the first 0.1 PV of fluids injected, they were left to soak in the porous medium for 5 minutes before the next injection resumes providing ample time for reaction and mixing up to occur. In the absence of nanoparticles, oil production began to deplete after 0.4 PV injected and completely stopped after 1 PV. Similarly for ZnO-SG-300 injection, early depletion was observed but stopped at a higher recovery factor. Much improvement was observed with the ZnO-RM where the oil production was at a higher rate until completely stopped after 1.7 PV. A 145% increase in the production of oil by ZnO-RM nanofluid injection may be justified by its lower IFT value, in comparison with ZnO-300-SG. The explanation can be found in the IFT measurement section. However, a dissimilar trend was observed in aluminum oxide nanofluid flooding; 63% more oil was recovered although Al_2O_3-SG-1100 has a lower IFT value as compared to Al_2O_3-RM.
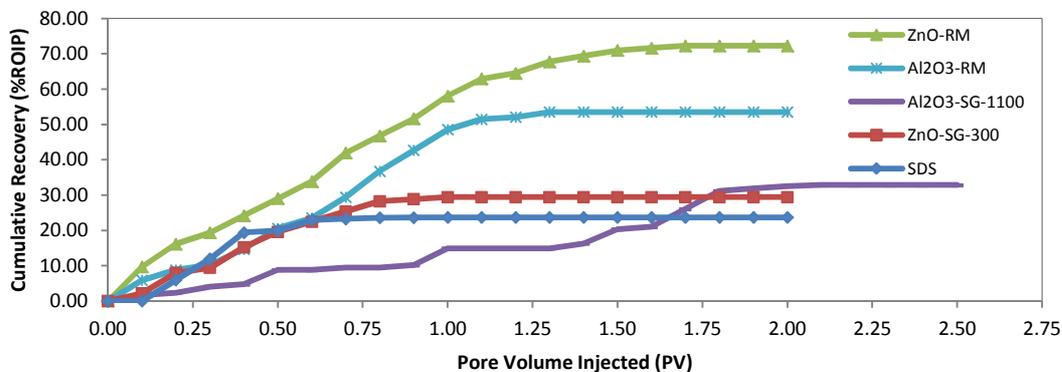

Figure 3. Cumulative oil recovery of various injection fluids for 2 PV injections

During the nanofluid flooding, the appearance of a cloudy layer at the oil-water interface was observed. In the first 0.2 PV injection, the displacement of oil began most probably due to the displacement of the disconnected oil ganglia that were left behind after water flooding since the nanofluid has a higher viscosity as compared to brine [11]. Beyond 0.2 PV, a brownish emulsion starts to emerge at the outlet and continues for the next 0.5 to 0.7 PV, until a clear solution starts to emerge at the end of emulsification process and oil production. Spontaneous emulsification may be responsible for the oil mobilization, which was demonstrated in the dynamic IFT whereby no time dependent minimum was observed when fresh nanofluid is in contact with an oil drop [12]. Fluid injections were stopped after 2 PV when no more oil drop displaced from the column, except for Al_2O_3-SG-1100 which was prolonged to 2.5 PV due to slower recovery rate.

Summary

The size of nanoparticles dispersed in the aqueous surfactant solution affected the oil recovery process by inducing the emulsification process *in-situ*. From the study, the ZnO-RM nanofluid which consists of larger particles size gives a 145% increase in the oil recovery as compared with the smaller ZnO nanoparticles. In contrast, 63% more oil was recovered although the Al_2O_3-SG-1100 nanofluid has smaller particles size as compared to Al_2O_3-RM. Appearance of a cloudy layer at the oil-water interface was observed during the test which indicated the occurrence of *in-situ* emulsification process. A low IFT is not necessarily a valid indicator of the ability of oil-water system to emulsify spontaneously. A sufficiently high recovery factor can be achieved even with higher IFT value. Other factors could be considered in future work *e.g.* sweep efficiency improvement by the higher viscosity nanofluids as compared to brine as well as the rate of emulsification among various nanofluids, since such factors are not investigated in this study.

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