

## Investigation of Dispersion Stability and IFT Reduction Using Surface Modified Nanoparticle: Enhanced Oil Recovery

Afaque Ahmed<sup>1</sup>, Ismail Mohd Saaid<sup>1</sup>, Abdul Haque Tunio<sup>1</sup>, Rashidah M. Pilus<sup>1</sup>,  
Mudassar Mumtaz<sup>2</sup>, Ishaq Ahmad<sup>1</sup>

<sup>1</sup>Department of Petroleum Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

<sup>2</sup>Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

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### ABSTRACT

Enhanced oil recovery (EOR) using nanoparticles has become a promising approach to produce the remaining oil from depleted fields. Advanced materials and additives are sought to make EOR economically feasible in reservoirs with challenging and harsh environments, i.e. high temperature, pressure and salinity. Nanoparticles have been widely studied for EOR, but nanoparticles coated with smart surfactants are an emerging class of materials for improving suspension stability and controlling the mobility of injected fluid. The goal of this work is to modify the silica nanoparticles using anionic surfactant (IOS<sub>19,23</sub>) in order to analyze the solubility and stability of colloidal solution, increase colloidal dispersibility, and interfacial tension (IFT) reduction for more facile transport through reservoir. These surface coated nanoparticles were characterized using Field Emission Scanning Electron Microscope (FESEM) technique. The optimum concentration of nanoparticles in aqueous phase was selected by in-depth analysis of transmission behaviour through the solution using Turbi Scan Classic. Moreover, to compare the potential of conventional nanofluid and surface coated nanofluid, the IFT measurements were performed by using Spinning Drop Tensiometer. It was found that IFT reduced when coated nanoparticles were introduced into the brine. Increasing concentration of nanoparticles reduced IFT and this mimic the EOR potential. Ultimately, the gained knowledge from this research could be used to interpret nanofluid's improvement mechanisms and forecasted as a benchmark for on-going and future EOR projects.

**KEYWORDS:** Nano Silica, Surfactant Coating, Dispersion Stability, IFT Reduction, Enhanced Oil Recovery.

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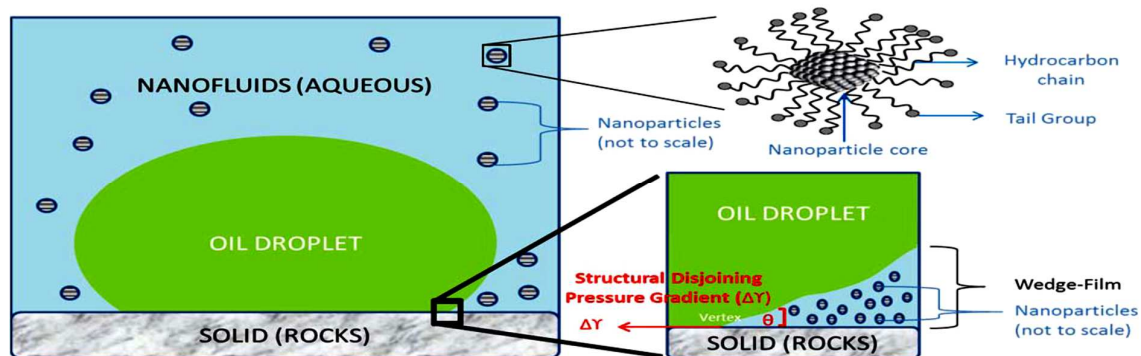
### INTRODUCTION

Enhanced oil recovery techniques have been acquiring more immersion worldwide as the proven oil reserves are getting reduced day by day. Nanoparticles having dimensions in 1-100 nm order have become the buzz word of the recent scientific works as the explicit manipulation of matter have revolutionized many industries including the oil and gas industry. Currently with the advent of nanotechnology, several means of improving the rheological properties of fluids at elevated and ambient temperatures have been provided; though, adverse effects originate above certain nanoparticle concentrations [1]. Nanoparticles possess rare characteristics due to their smaller size and greater surface area [2]. Various nano-fluids can be designed by introducing nanoparticles to different base fluids. The surface activity of the nanoparticles describe the stability or dispersion of nanoparticles in solutions. Due to this, nanoparticles' surfaces are usually functionalized or treated; thereby putting shields around them. These protections inhibit interaction between particles, therefore reduce aggregation probability of nanoparticles. During recent years, enormous interest has been gained by nanotechnology in petroleum industry that is reflected by presence of extensive literature availability. Nanoparticles for EOR purposes gradually seem developing into the leading-edge technology [3]. Nanoparticles are ideal in harsh environments such as reservoirs due to their mechanical and thermal stability. A lot of research supports their usage, as adding nanoparticles benefit EOR in wettability alteration of rocks, stabilization of foam or emulsions, sand consolidation strengthening, viscosity modification, interfacial tension reduction, improving capillary-trapped oil mobility and reduction of residual oil saturation, in order to improve oil recovery [4-5].

A nanoparticle consists of two entities: the core and a thin shell. The core and shell might be comprised of more than one entity and have underlying structures. The molecular shell consists of three separate regions; hydrocarbon chain, active head group and tail group, however in a specific case, one or more could not be present as illustrated in Figure 1. A hydrocarbon chain can be as long as a polymer chain or absolutely absent such as in an ion shielding nanoparticle [6]. This research aims to investigate the prospects of nanofluids as alternative or future IOR/EOR methods.

Experimental investigation of mechanism for oil recovery using nanoparticles suspension has been done and named disjoining pressure mechanism. It has been observed that the particles tend to form a wedge-like structure

that exist at three-phase contact region and force themselves between the discontinuous phase and the substrate as shown in Figure 1. The disjoining pressure force is imparted on the particles as bulk fluid exert pressure that force particles forward in the confined region. Later these drive mechanism energies were expressed as Brownian motion and electrostatic repulsion between the nanoparticles [7]. It was also found that when concentration of nanoparticles increase, this force also gets maximized. It was reported that the structural disjoining pressure gradient which is directed towards the wedge from the bulk solution is the driving force for the advancement of nanofluids. This gradient is higher near the vertex because of the nanoparticles structuring in the wedge confinement that help nanofluid to advance into wedge tip as the pressure surge towards the wedge vertex. It was also observed that spreading coefficient increases exponentially with a decline in the thickness of film or due to amount of particle layers reduction in the film inside. The structural disjoining pressure increases as the film thickness declines towards the vertex of wedge [8-10].



**Figure 1: Schematic of nanoparticle (not up to the scale) [8] and mechanism of nanoparticles structuring in the wedge-film [10]**

After reviewing the past investigations, it has been observed that silica-based nanoparticles (NPs) have been most commonly studied for future EOR processes [11-15]. It was reported that IFT reduction increases by 70 % in case of nanoparticles and anionic surfactants being used together than the surfactant used alone [16]. Certainly, due to the use of nanohybrid and surfactant together, IFT reduces to ultra-low. In petroleum upstreams, beside earlier applications of nanotechnology, enormous studies have been carried out on the title of employing nanoparticles for EOR [17]. Hence, in some researches, nanoparticle applications in oil industry have been categorized depending on preference. In chemical EOR techniques, the utilization of nanotechnology is highly recommended by the researchers [18]. Therefore, in most of the recent studies of EOR operations, the role of nanoparticles has been recorded [19-21].

## MATERIALS AND METHODS

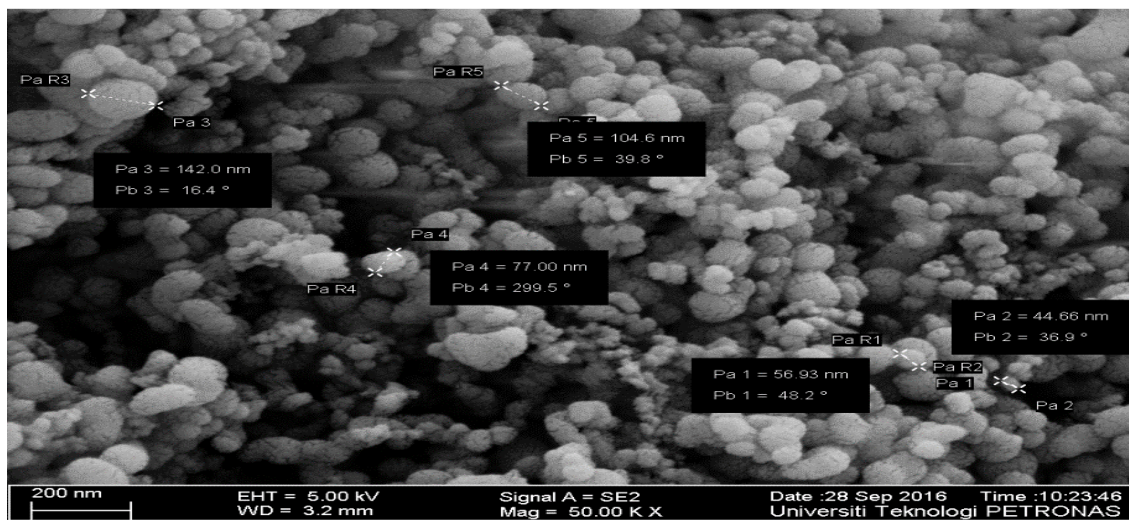
Nanoparticle used in the experiments was pure silica powder ( $\text{SiO}_2$ ) obtained from Evonik Industries. For surface modification of silica nanoparticle, anionic surfactant Internal Olefin Sulphonate (IOS19-23), ENORDETTM 0-342, was obtained from SHELL. The brine with salinity of 35000ppm was prepared for the experiments. This range of salinity was considered in accordance with the Malaysian sea water salinity. The degassed crude oil obtained from Melita resources (Canada) provided by Vision Petroleum Malaysia having API density 26.370 and viscosity 43.381cp at STP. The density and viscosity of fluids were measured using density meter (DM-40) and Electromagnetic Viscometer (EV-1000) respectively.

For the chemical modification experiments, 20gm of pure nanosilica was mixed with 200ml of 2 wt% surfactant solution for 48 hours at  $50^\circ\text{C}$ . The coated particles were separated from the mixture by centrifugation at 8000 rpm for 20 minutes. Thereafter, the samples were repeatedly washed and filtered to remove the uncoated surfactant. Finally, the particles were dried for 72 hours at  $500^\circ\text{C}$  in a laboratory oven to get the dry surfactant coated nanoparticles [22].

## RESULTS AND DISCUSSION

### Surface Activated Nanosilica Morphology

To examine the morphology of all the samples, ZEISS SUPRA™ 55 VP Field Emission Scanning Electron Microscope (FE-SEM) with scale of 200 nm was used. In the gold sputter unit, electrically non-conductive surfaces of samples were coated by gold. Two coatings were employed in order to get a better picture by improving the conductivity of the film surfaces.

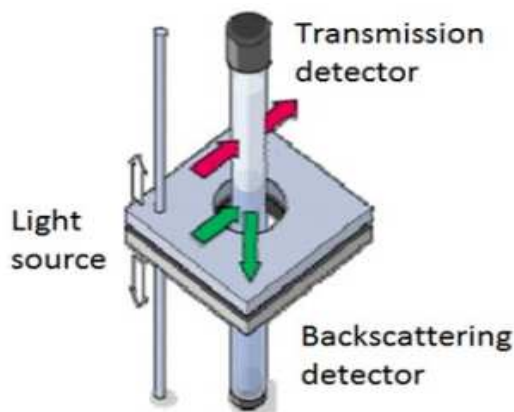


**Figure 2: Nanoparticles characterization under FE-SEM (magnification = 50k times)**

Figure 2 illustrates the FESEM surface images of nano silica particles after the surfactant (IOS) coating. From the FESEM image of the MNP, it is obvious that the silica particles are being coated with surfactant. It was also noted that silica particles were of nano size (averaging 85 nm). Besides that, the thin layer of surfactant on the nano silica reduces the attractive forces between the particles and provide significant dispersion stability in the aqueous phase. The coated nano particles attributes towards the IFT reduction and wettability modifier candidate compared to the pure nano silica.

**Effect of Concentration on Dispersion Stability**

The stability of nano silica dispersions were investigated using a Turbiscan Classic (Formulation, Figure 3). The Turbiscan head is made out of a vibrator near infrared light source ( $\lambda = 850 \text{ nm}$ ) and two synchronous indicators, a transmission detector that allows light to pass over the sample (at  $0^\circ$  from the incident beam) and a back scattering detector that receives the light scattered backward by the sample (at  $135^\circ$  from the incident beam). Samples were prepared from nanosilica of various concentrations 0.05, 0.1 and 0.3 wt. %, so as to analyze the effect of concentration on dispersion stability. The detection head examined throughout the length of sample gaining transmission data every  $40 \mu\text{m}$  and every 1 min over 1 hour. Transmission signal variations ( $\Delta T$ ) were figured at a given time.



**Figure 3: Principle of Turbiscan measurement [23]**

Figures 4(a) and 4(b) present transmission (T) intensities as a function of sample height over duration of analysis for different dispersion cases before and after coating. The variation of transmission was large in case of pure nano silica, indicating an aggregation of the particles and hence poor particles stability. At the point when coated nanosilica was used, this aggregation was not observed and particles stayed all around dispersed.

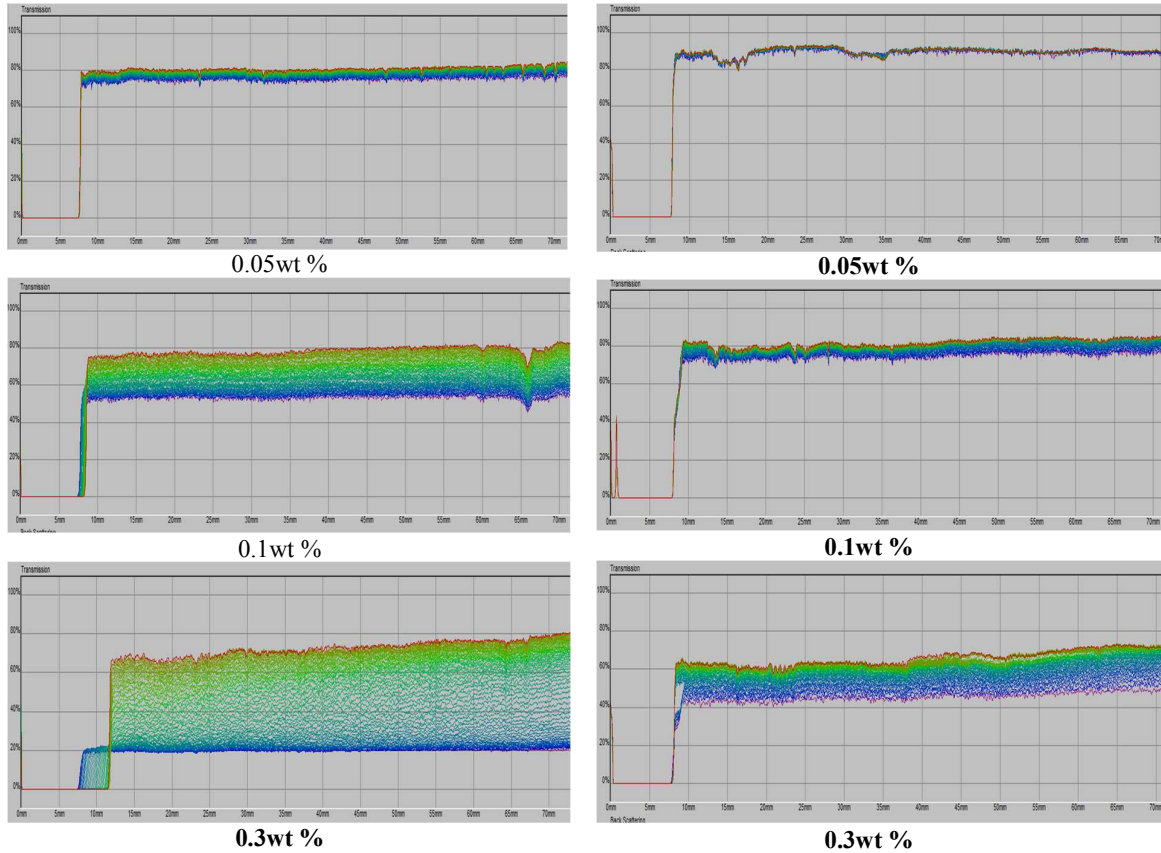


Figure 4(a): Transmission profiles of pure silica

Figure 4(b): Transmission profiles of coated silica

On the other hand, Figure 5(a) and 5(b) represent the mean transmission value for the middle part of the samples (20-40 mm). The particle aggregations dynamics have seen follow two different patterns, i.e. linear growth and rapid growth before reaching a stable end point.

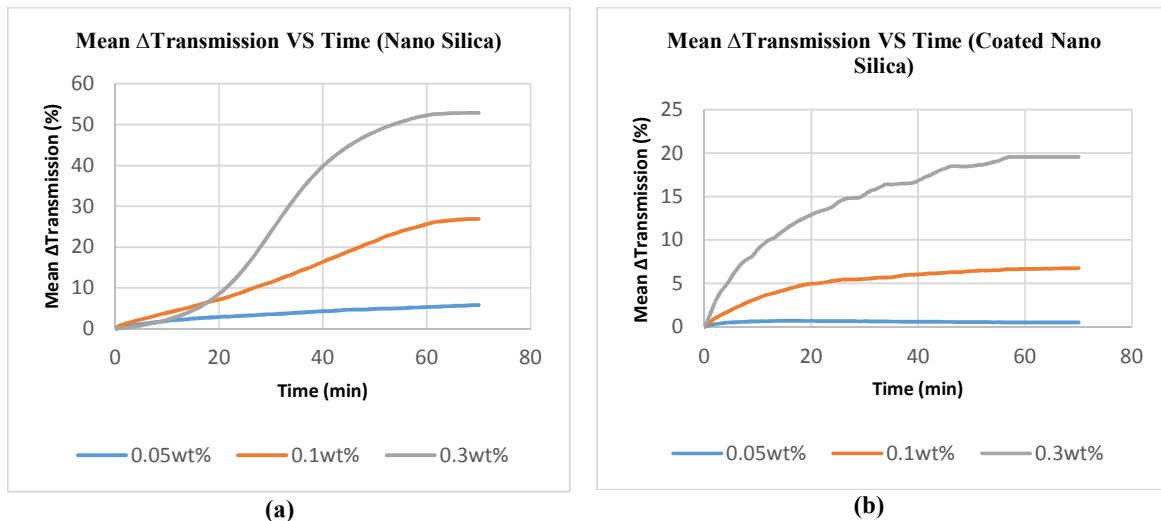


Figure 5: Effect of concentration on dispersion stability of nanosilica before (a) and after (b) modification

For all experiments except coated nanosilica, mean transmission increased linearly over a period of a few minutes, after which increased more rapidly. It was observed that the particles with concentration 0.05wt % nanosilica proved to be more stable as least value of change in mean transmission was found that shows maximum number of particles were retained in the solution for longer time and the separation is too slow as within 1 hour, changes appeared to be constant for transmitting light through the solution. Same observation was found in case

of coating however the stability was found to be more improved as the mean light transmission declined from 5% to less than 2% only after coating.

**Effect of Viscosity on Dispersion Stability**

Electromagnetic Viscometer (EV-1000) was used to measure the viscosity of all nano silica dispersion in aqueous brine. It was found that the viscosity increased as the concentration of nano particles in the dispersion increased (see Table 1). Also, most importantly reduction in viscosity of concentration after coating of nano silica was noted, as anionic surfactant affect the rheological properties of the nanosilica.

**Table 1: Viscosity of fluids**

Fluid	Viscosity, cp
Brine (35000ppm)	1.002
Nanosilica (0.05wt %)	1.016
Nanosilica (0.1wt %)	1.023
Nanosilica (0.3wt %)	1.074
Coated Nanosilica (0.05wt %)	1.005
Coated Nanosilica (0.1wt %)	1.018
Coated Nanosilica (0.3wt %)	1.070
Crude Oil	43.381

**Effect of Interfacial Tension on Dispersion Stability**

SVT20 Spinning Drop Video Tensiometer was used to measure the IFT between crude oil and brine/nanofluids as aqueous phase at ambient conditions with the rotation speed of around 2500-4000 rpm. Before measuring the IFT, refractive index was measured using Refractometer (RM40) for all aqueous phases as input data for spinning drop as summarized in Table 2 that shows the measurement of fluid properties of brine and different nanofluid concentrations at ambient temperature pressure conditions. Slight increase in refractive index was observed with increase in nanofluids’ concentration.

**Table 2: Density and refractive index of fluids**

Fluid	Density, g/cm <sup>3</sup>	Refractive Index
Brine (35000ppm)	1.0207	1.3382
Nanosilica (0.05wt %)	1.0211	1.3383
Nanosilica (0.1wt %)	1.0213	1.3384
Nanosilica (0.3wt %)	1.0222	1.3387
Coated Nanosilica (0.05wt %)	1.0209	1.3387
Coated Nanosilica (0.1wt %)	1.0208	1.3384
CoatedNanosilica (0.3wt %)	1.0159	1.3419
Crude Oil	0.8963	1.5041

In order to measure IFT, the formula used in accordance with [24] as follows:

$$\sigma = \frac{\Delta\rho.\Omega^2.(D_{app})^3}{8.n^3.J_0(\frac{L}{D})} \tag{1}$$

where  $\sigma$  is the IFT (dyne/cm),  $\Delta\rho$  is difference in density (g/cm<sup>3</sup>),  $\Omega$  is angular speed of cylinder (s<sup>-1</sup>),  $D_{app}$  is diameter of measured drop (cm),  $n$  is refractive index of the denser fluid,  $D$  is drop’s true diameter,  $J_0$  is correction factor and function of  $L/D$  while  $L/D$  is the ratio of the drop length to its diameter. Table 3 summarizes the measured IFT of each of the sample.

**Table 3: IFT measurements**

Sample	IFT (mN/m)
Brine/Crude	0.9010
Nanofluids	
Nanosilica 0.05wt %/Crude	0.8610
Nanosilica 0.1wt %/Crude	0.8170
Nanosilica 0.3wt %/Crude	0.7770
Coated Nanosilica 0.05wt %/Crude	0.8560
Coated Nanosilica 0.1wt %/Crude	0.7913
Coated Nanosilica 0.3wt %/Crude	0.7450

It has been observed that the IFT value decreased as the nanoparticles were injected into the brine as nano silica placed between oil and water interface caused reduction in IFT between water and oil. Declining IFT resulted a reduction in capillary pressure that revealed to better efficiency and oil recovery. Hence, remaining oil saturation



can be decreased and oil trapped by capillary pressure will be released due to reduction in IFT. Also, it was noted that the IFT reduces as the concentration of nanoparticles increases and this mimics the potential for EOR.

### CONCLUSION

The experiments indicated that newly developed surface coated nanosilica particles are suitable materials for HTHP oilfields. Surface modified nanoparticles possess the ability to increase the stability of dispersion in aqueous phase. Surfactant coated silica nanoparticles are generally more effective at dispersion stability compared to pure silica nanoparticles. Pure nano silica were aggregated and showed less dispersion stability as compared to coated nano silica for all concentrations. The coated nanosilica at same brine salinity reflected significant stability and less sensitive to the brine system used. Therefore, coating of nanoparticle resulted suitable and effective way for stabilizing the silica nano particle dispersion in the studied brine system. The surface coated Nano silica particles lowers the IFT and viscosity of the fluid. The coated nanoparticles arranged at the oil-water interface that lead to reduction in IFT between oil and water. The viscosity of brine is increased by introducing SiO<sub>2</sub> nanoparticles to the aqueous phase that forecast for better displacement efficiency during chemical assisted EOR. Further studies should be carried out in order to analyze the nanofluid behaviour at various wetting conditions with surfactants and core flood experiments should be performed to verify the results more appropriately.

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### REFERENCES

1. Evdokimov, I.N., N.Y. Eliseev, A.P. Losev and M.A. Novikov, 2006. Emerging Petroleum-Oriented Nanotechnologies for Reservoir Engineering. In the Proceedings of the 2006 SPE Russian Oil and Gas Technical Conference and Exhibition, pp: 1-24.
2. Singh, S. and R. Ahmed, 2010. Vital Role of Nanopolymers in Drilling and Stimulation Fluid Applications. In the Proceedings of the 2010 SPE Annual Technical Conference and Exhibition, pp: 1-7.
3. Engeset, B., 2012. The potential of hydrophilic silica nanoparticles for EOR purposes: A literature review and an experimental study. Master thesis, Norwegian University of Science and Technology, Trondheim, Norway.
4. Suleimanov, B.A., F.S. Ismailov and E.F. Veliyev, 2011. Nanofluid for Enhanced Oil Recovery. Journal of Petroleum Science and Engineering, 78 (2): 431-437.
5. Cheraghian, G., S.K. Nezhad, M. Kamari, M. Hemmati, M. Masihi and S. Bazgir, 2014. Adsorption Polymer on Reservoir Rock and Role of the Nanoparticles, Clay and SiO<sub>2</sub>. International Nano Letters, 4 (3): 1-8.
6. Sarit K. Das, Stephen U. Choi, W. Yu and T. Pradeep. 2007. Nanofluids science and technology. John Wiley and Sons.
7. Mc.Elfresh, P., D. Holcomb and D. Ector, 2012. Application of Nanofluid Technology to Improve Recovery in Oil and Gas Wells. In the Proceedings of the 2012 SPE International Oilfield Nanotechnology Conference and Exhibition, pp: 1-6.
8. Wasan, D.T. and A. Nikolov, 2003. Spreading of Nanofluids on Solids. Nature, 423 (6936): 156-159.
9. Chengara, A., A. Nikolov, D.T. Wasan, A. Trokhymchuck and D. Henderson, 2004. Spreading of Nanofluids Driven by the Structural Disjoining Pressure Gradient. Journal of Colloid and Interface Science, 280 (1): 192-201.
10. Wasan, D.T., A. Nikolov and K. Kondiparty, 2011. The Wetting and Spreading of Nanofluids on Solids: Role of the Structural Disjoining Pressure. Current Opinion in Colloid and Interface Science, 16 (4): 344-349.
11. Ju, B., T. Fan and M. Ma, 2006. Enhanced Oil Recovery by Flooding With Hydrophilic Nanoparticles. China Particuology, 4 (1): 41-46.
12. Miranda C.R., L.S. De Lara and B.C. Tonetto, 2012. Stability and Mobility of Functionalized Silica Nanoparticles for Enhanced Oil Recovery Application. In the Proceedings of the 2012 SPE International Oilfield Nanotechnology Conference and Exhibition, pp: 1-11.

13. Roustaei, A., S. Saffarzadeh and M. Mohammadi, 2013. An Evaluation of Modified Silica Nanoparticles' Efficiency in Enhancing Oil Recovery of Light and Intermediate Oil Reservoirs. *Egyptian Journal of Petroleum*, 22 (3): 427-433.
14. Cheraghian, G., 2015. Application of Nano Fumed Silica in Heavy Oil Recovery. *Petroleum Science and Technology*, 34 (1): 12-18.
15. Hendraningrat, L., S. Li and O. Torsæter, 2013. Enhancing Oil Recovery of Low-Permeability Berea Sandstone through Optimised Nanofluids Concentration. In the Proceedings of the 2013 SPE Enhanced Oil Recovery Conference, pp: 1-10.
16. Resasco, D., S. Drexler, J.H. Harwell, B.J. Shiau, M.J. Kadhum, J. Faria and M.P. Ruiz, 2013. Method and foam composition for recovering hydrocarbons from a subterranean reservoir. United States patent application US 14/344,241.
17. Hendraningrat, L., B. Engeset, S. Suwarno and O. Torsæter, 2012. Improved Oil Recovery by Nanofluids Flooding: An Experimental Study. In the Proceedings of the 2012 SPE Kuwait International Petroleum Conference and Exhibition, pp: 1-9.
18. Pourafshary, P., S.S. Azimipour, P. Motamedi, M. Samet, S.A. Taheri, H. Bargozin and S.S. Hendi, 2009. Priority Assessment of the Investment in Development of Nanotechnology in Upstream Petroleum Industry. In the Proceedings of the 2009 SPIE Saudi Arabia Section Technical Symposium, pp: 1-11.
19. Skauge, T., S. Hetland, K. Spildo and A. Skauge, 2010. Nano-Sized Particles for EOR. In the Proceedings of the 2009 SPE Improved Oil Recovery Symposium, pp: 1-10.
20. Cheraghian, G., 2015. An Experimental Study of a Surfactant Polymer for Enhanced Heavy-Oil Recovery Using a Glass Micromodel by Adding Nanoclay. *Petroleum Science and Technology*, 33 (13-14): 1410-1417.
21. Cheraghian, G., S.K. Nezhad, M. Kamari, M. Hemmati, M. Masihi and S. Bazgir, 2014. Effect of Nanoclay on Improved Rheology Properties of Polyacrylamide Solutions Used in Enhanced Oil Recovery. *Journal of Petroleum Exploration and Production Technology*, 5 (2): 189-196.
22. Van der Merwe, E., L.C. Prinsloo, R.A. Kruger and L.C. Mathebula, 2011. Characterization of Coal Fly Ash Modified by Sodium Lauryl Sulphate. In the Proceedings of the 2011 World of Coal Ash Conference, pp: 1-17.
23. Ahmed, A.A., I.M. Saaid and N.A.M. Akhir, 2016. Effect of Surfactant and Grafted Copolymer on Stability of Bentonite Particles Dispersion in Brine System. *ARPJ Journal of Engineering and Applied Sciences*, 11 (7): 4822-4827.
24. Than, P., L. Preziosi, D.D. Josephl and M. Arney, 1988. Measurement of Interfacial Tension between Immiscible Liquids with the Spinning Rod Tensiometer. *Journal of Colloid and Interface Science*, 124 (2): 552-559.