Development and evaluation of fly ash particle for foam stability for possible application to foam flooding

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Abstract: In Chemical EOR (enhanced oil recovery), nanoparticles gained the potential to improve the foam stability, therefore, a low concentration of surfactant or polymer is needed to control gas mobility in the reservoir. The aim is to improve the foam forming ability and foam stability both in the absence and presence of oil. In this paper, the potential of fly ash to produce stable foam by the injection of nitrogen (N_2) gas was studied. Fly ash nanoparticles were developed by the chemical treatment of alkali. Various characterization techniques were applied to investigate the nature and particle size of the fly ash. The fly ash at various concentrations (ppm) was mixed with best performing anionic foaming surfactants. The anionic surfactants used were AOS[14-16] and IOS[15-18]. Static foam tests were performed at ambient by sparging of N_2 gas through the solution. It was analyzed that contents of silica and smaller size of nanoparticles of fly ash have more potential towards foam ability and foam stability. Therefore, by using the developed alkali treated nano fly ash results in a considerably increased EOR.

Key words: Fly Ash (FA); Anionic surfactant; Foam; EOR

1. Introduction

During the past few years, nanotechnology has being widely applied to various fields such as material design, biomedicine, and electronics etc. Nanoparticles have potential in several branches of petroleum engineering. This emergence is becoming very relevant as the need to cater for the increasing demand in the energy sector is expecting to be met by the oil and gas industry (Jikich, 2012). The use of nanotechnology has become a noticeable aspect in the petroleum engineering sector (Chevalier & Bolzinger, 2013). The increasing demand of fuel tends to increase the recovery of oil. In primary recovery method, the oil comes up by a natural drive, included rock and fluid expansion, gas cap, water influx and gravity drainage etc. In a secondary method of oil recovery, the oil is produced by the injection of external fluids, such as gas and water. However, in tertiary oil recovery method the trapped oil is recovered by the injection of special fluids, chemicals, miscible gas and the thermal injection (Johns & Dindoruk, 2013). Tertiary oil recovery may also refer to as enhanced oil recovery (EOR). Chemical Enhanced oil recovery (CEOR) is the leading method to sweep trapped oil left after primary and secondary oil recovery methods. The promising chemicals used in CEOR are the alkali, surfactants and polymer (Hirasaki, Miller, & Puerto). The selection of the method depends on the nature and characteristics of the reservoir. The low viscosity and density of CO_2 lead to its severe

channeling and gravity segregation, making it highly mobile through high-permeability zones thus resulting in poor sweep efficiency (Lee & Kam, 2013).

Foam assisted EOR has huge momentum for controlling the CO_2 mobility, resulting in improved sweep efficiency (Farzaneh & Sohrabi, 2013). The foam is thermally unstable, and thus additives (surfactant/polymer/ nanoparticle) are required to generate the stable foams. Surfactants are the commonly used agents to produce stabilized foams (Farajzadeh et al., 2012). However, the surfactant-based foams require continuous regeneration because the surfactant is adsorbed on the rock, leading to increased material costs. However, polymers are not compatible with reservoir temperature, pressure and salinity conditions. The usage of nanoparticles is the alternate to answer several problems in the surfactant, and polymer EOR owing its ability to change certain factors in oil properties (Horozov, 2008; Suleimanov et al., 2011).

The self-production of foam was observed when nanoparticles injected at high shear fracture zones, which is beneficial for the foam assisted EOR applications. It was reported that small solid particles contribute to the stabilization of a froth or foam. Solids of very fine degree of dispersion enhanced the foam stability (Horozov, 2008; Platikanov & Exerowa, 2008). The aqueous foams are stabilized by the addition of small amount of powdered silica or ferric oxide (Ju et al., 2006). The foam stability is increased by increasing the amount

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of silica and found that fine silica particles provide greater stability effect (Binks & Whitby, 2005). The nanoparticles used for EOR are able to promote wettability alteration, viscosity reduction of oil, stabilization of foam or emulsions, and improves interfacial properties between water and oil. The small-sized nanoparticles are able to go through narrow pores and clear out dead end pores, adding to the sweep efficiency (Maghzi et al., 2012; Sun et al., 2015)

In particular, fly ash particles used in this study for static foam generation by utilizing inexpensive nanoparticles. Coal fly ash (FA) is the potential source, which is produced as waste from coal-fired power plants and has essentially no economic value (Lee et al., 2015). The coal fly ash has a variety of components that contains complex anthropogenic materials and difficult to characterized. The annual production of FA is about 750 million tonnes, whereas its consumption is only 25%. The remaining coal ash subsequently disposed of and causing environmental problems without any benefit. The major, minor and trace components of FA may contain sodium oxide (Na_2O), potassium oxide (K_2O), magnesium oxide (MgO), silica (SiO_2), alumina (Al_2O_3), ferrous oxide (Fe_2O_3), and calcium oxide (CaO) etc. (Noor-ul-Amin, 2014)

However, the particles of fly ash are irregular, porous, coke-like shape and contain unburned carbon material, which led different surface characteristics from the mineral fly ash components. The particle size and the surface properties of the fly ash must be tuned to utilize them as foam stabilizer.

Fly ash is reported as the CO_2 foam stabilizing agent. The fly ash was separated into carbon-rich and carbon-lean materials and o/w emulsions and CO2-in-water foams/emulsions were developed and tested in terms of their stability (Lee et al., 2015).

The objectives of this study were to efficiently produce nanoparticles by grinding method to make very fine powder and the development of alkali treated nanoparticle. The multi-stage grinding was employed to produce fly ash nanoparticles. In this study inexpensive nano fly ash is utilized for the stable foam generation.

2. Material and Methods

2.1. Material

The fly ash was collected from coal power plant inside Malaysia. Anionic foaming surfactants, Alpha Olefin Sulphonate (AOS_{14-16}) and Internal Olefin Sulfonate (IOS_{15-18}) were used in this research. AOS_{14-16} (Bio-Terge AS-40) was obtained from Stepan Company, USA, and IOS_{15-18}, (ENORDET-332) was requested from Shell, USA. Sodium hydroxide (NaOH) was purchased from J. T. Baker, Sweden. The oil used was Tapis crude oil. The API gravity of Tapis crude is 43. The chemical composition of fly ash, determined by X-rays fluorescence spectroscopy, is shown in Fig. 1.
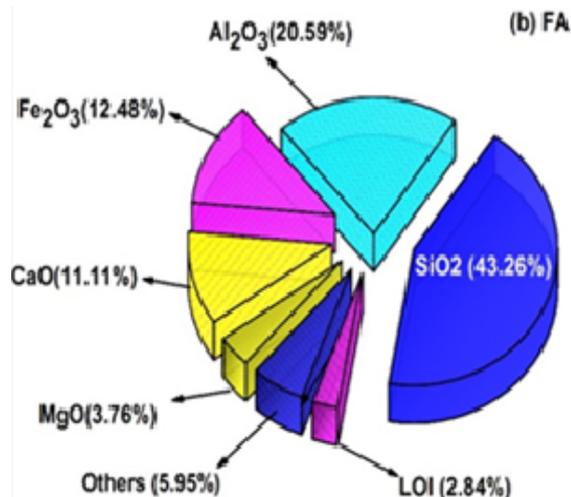

Fig. 1: Percentage of various components of fly ash using XRF

SiO_2 is the major component along with considerable amounts of the oxides of aluminum, iron and calcium.

2.2. Methods

2.2.1. Treatment of fly ash

The alkali treatment of fly ash was performed by the mixing of fly ash and 2M sodium hydroxide (NaOH) solution. 12.5 g of fly ash was dissolved in 100 ml of 2M NaOH. The mixing of alkali with fly ash was done at 80° C for 6 hours. After the treatment, fly ash particles were separated from the solution by centrifugation at 4000RPM for 30mins. The separated particles were then dried at 150^0 C in the drying oven for 24hours. The dried fly ash particles were then grinded in the ball mill for 8hours and then sieved through the mesh of 10micron.

The fine powder of fly ash was then characterized by Field Emission Scanning Electron Microscopic (VPFESEM, Zeiss Supra, Switzerland). In this method, fine powdered sample was mounted on aluminum stub using carbon tape. The instrument was run at lower pressure and different magnifications. As FESEM shows a single size of particles after the particle sizer was used to cheek the area size before and after treatment. Malvern mastersizer (AS2000, US) was used for the particle size analysis. Finally, the fine powder of fly ash was then tested to evaluate the effect of solid particles to improve the foam stability performance.

2.2.2. Static foam tests

The static foam ability and foam stability tests were performed based on foam height and foam drainage in the 1000ml measuring cylinder. The N_2 gas was sparged in solution for foam generation at a constant flow rate of 2ml/sec for 30 seconds. The total volume of each solution used for foam generation was 150ml. The percent composition of surfactants (AOS & IOS) with nano fly ash was shown in Table 1.

Table 1: Percentage compositions of surfactant and nano FA solution

| Sample ID	AOS	IOS	Fly ash (FA)	Alkali FA
A	100	—	—	—
B	—	100	—	—
C	70	—	30	—
D	70	—	—	30
E	—	70	30	—
F	—	70	—	30

The static foam stability measurements were conducted at ambient conditions of temperature and pressure. The stability of foam was analyzed by noting the drainage time of the foam generated in the cylinder. The foaming was observed both in the presence and absence of crude oils. For foam oil study 10 wt % of the oil was added in the mixture of 150ml of 1wt% of surfactant and fly ash solution. The major variables for foam height and drainage tests were the type of surfactant and fly ash used.

3. Results and discussions

Particles size analysis: The particle size analysis of fly and alkali treated fly ash (AFA) is given in Table 2. The D (0.5) of FA was 16.3 um which reduced to 10.5 um upon alkali treatment. A considerable decrease in particle size was also observed in D (0.1) and D (0.9), as well. The effect was more profound on the overall size. Initially, some of the Fly ash was having sizes as big as 115.4 μm which was decreased to 51.4 μm. which is mention in the Fig. 2.

Particles size of Alkali FA: The use of alkali for fly ash treatment, the rates of breakage of smaller particles are higher. It shows the effect of the alkali treatment on fly ash samples. However, the results showed that D (0.1) 2.309μm and D (0.5) 10.519μm and D (0.9) is 51.447 because some of the elements have gone and by treatment the alkali effects on the size of the FA. Fig. 2 and Fig. 3 illustrate the particle size result and shows that the possible reduction of surface area for alkali treated fly ash is different then fly ash (FA).
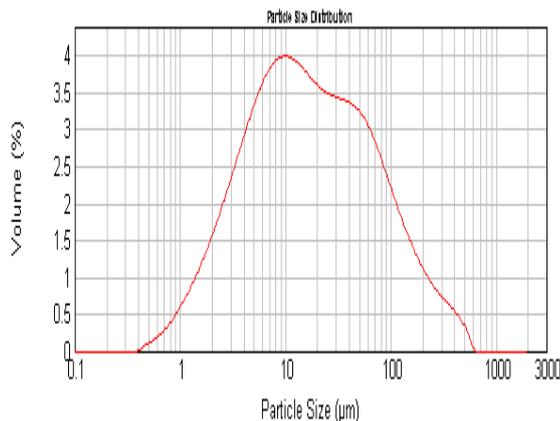
Fig. 2: Particle size of fly ash
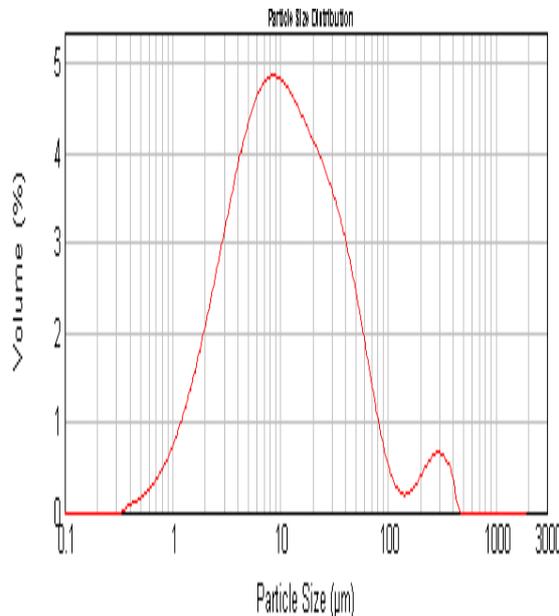
Fig.3: Particle size of alkali treated fly ash

As described in Table 2, Fly ash consists of silica (SiO_2), alumina ($Al2O_3$), ferrous oxide (Fe_2O_3), and calcium oxide (CaO), therefore, the particle size analysis shows different size of fly ash. The morphology and size of fly ash particle is a function of the process condition, chemical composition, degree of crystallinity, and carbon content. The fly is generated at temperature as high as 1500^0C, therefore they different types of particles.

Table 2: PSD analysis of FA and AFA using particle size analyzer

Sample	D (0.1)	D (0.5)	D (0.9)
FA	2.8um	16.3 um	115.4 um
AFA	2.3 um	10.5 um	51.4 um

The alkali treatment of fly ash resulted in the decrement of particle size. This decrease in particle size is related to the dissolution of fly ash in sodium hydroxide. The amorphous oxides of silicon are leached out with sodium hydroxide as given below;

$$2NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O$$

Interestingly, the bigger fly ash has shown more size reduction and it showed that larger particles were more porous and absorbed a high quantity of caustic soda. The increase in surface area from the 0.856 m^2/g to the 1.09 m^2/g evidenced the decrease in particle size.

To know what type of morphological changes have taken place, FESEM analysis was used and is discussed in next section.

3.1. Microscopic investigation

The surfactants having the suitable range of salinity tend to stabilize the foam. The surface of fly ash was thereby modified with alkali in order to analyze the effect of foam stability. Fig. 4 and Fig. 5 indicate the FESEM surface images of fly ash particles before and after the treatment of alkali.
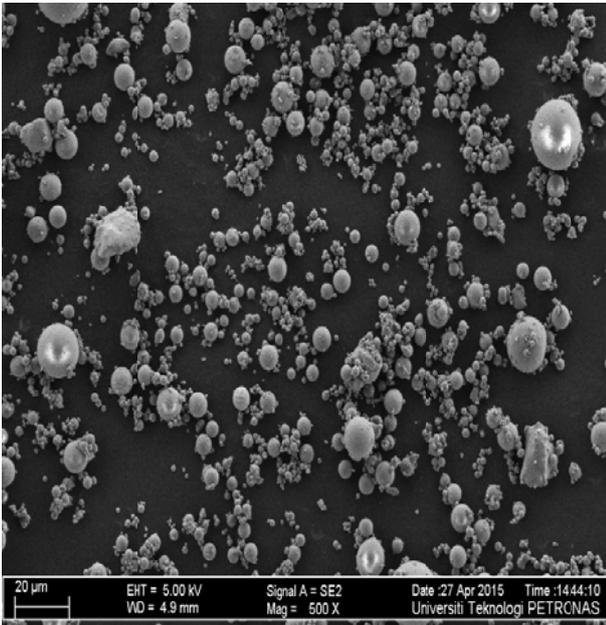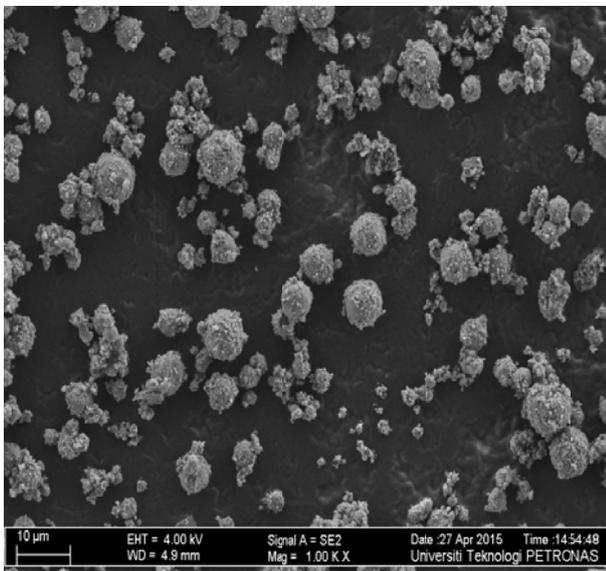
Fig. 4: FESEM images of fly ash (FA)

Fig. 5: FESEM images of alkali treated FA

The untreated FA particles seem rough while the alkali treated becomes more irregular in shape. Different morphologies were observed in FESEM analysis of FA. The majority of fly ash consisted of spherical particles. The smooth surface of these particles is closely related to the high temperature production process. The fewer irregular shapes represent the existence of unburnt carbon residue which is consistent with LOI. The surface activated FA with alkali made it more hydrophilic, therefore, found strong foam generation properties.

3.2. Effect of nano fly ash on foaming

Surfactants itself have the low potential for stable foam generation. Fig. 6 describes the foaming of AOS, IOS with and without nano fly ash. The addition of fly ash increases the stability of foam lamella. In case of alkali treated nano fly ash when mixed with surfactant the improvement of foam stability was noted.

Fig. 6: Foam by N_2 sparging through solution

In order to study the fly ash behavior on foaming the 6 sample were designed A, B, C, D, E and F to indicate the single and binary combinations of surfactants and fly ash.

In Fig. 7, the foam ability for sample A, B, D and E were almost the same. However, the foam ability of surfactant mixed with pure fly ash was very low. The surfactant itself, AOS (sample A) and IOS (sample B), was found more stable as compared with the combinations of surfactant with FA particles As shown in Fig. 7. The mixture of surfactants with pure fly ash, sample C, and E seems unstable and the foam drainage was comparatively fast. The maximum foam stability was observed for the combinations of AOS and IOS mixed with the alkali treated fly ash particles. The foam stability was found to be 180 minutes of sample D, AOS with AFA (70:30 of AOS: AFA) for 75% drainage. However, IOS mixture of AFA had less foam stability and the drainage time was recorded 160 minutes. The performance of AOS to generate the stable foam was found superior as compared to the IOS, both with and without nanoparticles.

Therefore, utilization of nanoparticles led to successful amplification of foam stability and helps to reduce the amount and cost of surfactant for the foam EOR process.
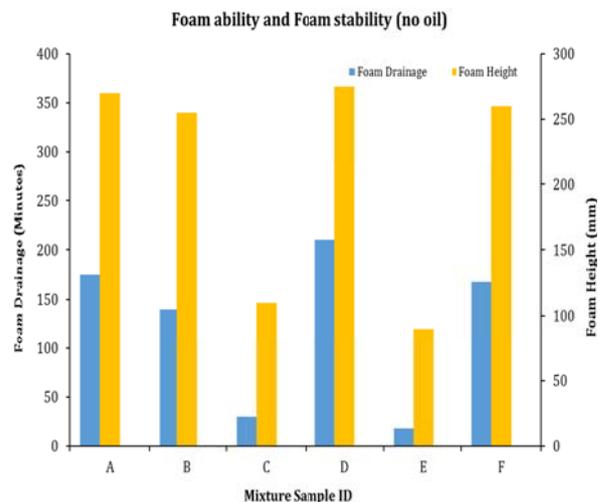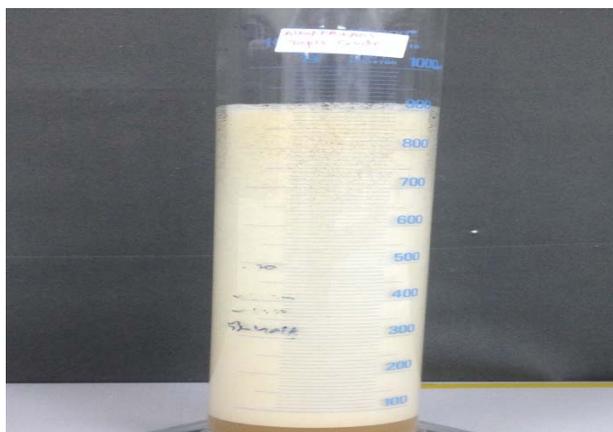

Fig. 7: Foam ability and foam stability

3.3. Effect of crude oil on foaming

The effect of Tapis crude on foaming was studied to identify the tolerance for oil. The foaming of formulated samples with Tapis crude is shown in Fig. 8.

Fig. 8: Foam by N_2 sparging through solution and Tapis crude

The foam stability was decreased when the foaming performed in the presence of oil. The addition of oil in the solution led to increase the foam drainage rate. The formulations presented in Table 1 were mixed each with 10 wt. % of Tapis crude oil. The foam ability and foam stability in terms of height and drainage was shown in Fig. 8. The foam column height or foam ability of recipe A, B, D, & F was almost the same with oil but the samples C, and E showed less foam stability with pure fly ash.

The stability of each mixture was examined by noting the drainage time. In case of surfactants, the samples A and B performed better in the presence of crude oil. But the performance of sample C and E, AOS and IOS mixture with pure fly ash is found lesser. However, the performance of sample D, AOS with AFA (70:30 of AOS: AFA) for 75% drainage was superior both in the presence and absence of oil. From the static foam test, it was found that the performance of AOS was better than IOS in each case when contact with oil (Fig. 9).
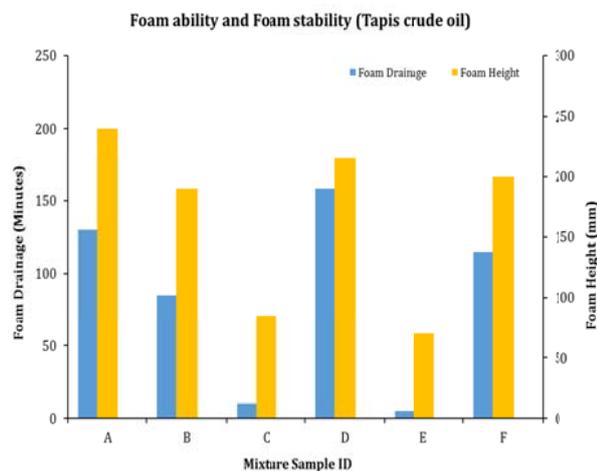
Fig. 9: Foam ability and foam stability with Tapis crude

4. Conclusion

The mixture of surfactant and nano fly ash produced strong foam as compared to surfactant alone. However fly ash alone has the worst foam drainage resistance. The sample D of AOS and fly ash (70:30) gave the best stable foam and in the presence of oil. The reduction of surfactant injection volume tends to lower the cost of surfactant EOR process. As discussed in this paper, the surfactants performance for foam generation can be tuned in order to produce the formulation with nano fly ash essential for a successful EOR. Therefore, the experiment demonstrated that alkali treated fly ash nanoparticles stabilized foam for longer time duration than the other remaining solutions. Moreover, considerable foam stability was also observed by using fly ash nanoparticles both in the presence and absence of crude oil. In the future study, development would be required for precise foam stability analysis with different sample of fly ash nanoparticles.

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