Improvement of Chemical Demulsifier Performance Using Silica Nanoparticles

G. E. Gandomkar, E. Bekhradinassab, S. Sabbaghi, M. M. Zerafat

Abstract—The reduction of water content in crude oil emulsions reduces pipeline corrosion potential and increases the productivity. Chemical emulsification of crude oil emulsions is one of the methods available to reduce the water content. Presence of demulsifier causes the film layer between the crude oil emulsion and water droplets to become unstable leading to the acceleration of water coalescence. This research has been performed to study the improvement performance of a chemical demulsifier by silica nanoparticles. The silica nano-particles have been synthesized by sol-gel technique and precipitation using poly vinyl alcohol (PVA) and poly ethylene glycol (PEG) as surfactants and then nano-particles are added to the demulsifier. The silica nanoparticles were characterized by Particle Size Analyzer (PSA) and SEM. Upon the addition of nanoparticles, bottle tests have been carried out to separate and measure the water content. The results show that silica nano-particles increase the demulsifier efficiency by about 40%.

Keywords—Demulsifier, dehydration, silicon dioxide, nanoparticle.

I. INTRODUCTION

EMULSIONS are generally defined as heterogeneous systems of one liquid dispersed in another. Based on the size of dispersed phase, emulsions are classified as macro-emulsions (with a droplet size range of 0.2–50 mm) or micro-emulsions (with a particle size range of 0.01–0.02 m) [1]. Emulsions may consist of oil droplets dispersed in a water phase (oil-in-water) or water dispersed in oil phase (water-in-oil) [2]. Emulsion stability is related to the amount of surfactant that is adsorbed at the interface. When more surfactant adsorbs at the interface, the interfacial tension is decreased and surfactant molecules play as a barrier delaying the coalescence of droplets by electrostatic or steric repulsion [2]. As a current preliminary step of refinery treatment, crude oil is normally desalted to decrease species such as chloride ions which deactivate catalysts and cause further corrosion in distillation columns [3]. Demulsification is a process of oil and water separation from emulsions [4]. There are several techniques available, for enhancing the separation of water-in-oil emulsions such as the addition of chemical demulsifiers [5], pH adjustment [5], gravity or centrifugal settling [6], filtration [7], heat treatment and electrostatic demulsification [8], [9], each with its own benefits and disadvantages. Centrifugation has a high operating cost. Heat treatment can reduce the viscosity of

the oil, thus allowing water droplets to fall more rapidly through the oil phase and to help the separation of entrained gas in the crude oil. However, heat treatment and chemical treatment are rather expensive. Chemical demulsification is the most widely applied method of emulsion treatment involving the application of chemical additives to accelerate the emulsion breaking process. In chemical demulsification, chemicals known as demulsifiers are added to the water-in-crude oil emulsion. Demulsifiers are surface active agents (surfactants) developing high surface tension at crude-oil-water interface [10], [11]. Not all crude oil emulsions can be broken by demulsifiers because the demulsification mechanism is quite complicated and also chemical demulsifiers are not safe for the environment. Nowadays, nanotechnology has been applied successfully in various fields. This research has been performed to study the performance improvement of chemical demulsifiers by silica nanoparticles. The silica nanoparticles have been synthesized by sol-gel and precipitation with PVA and PEG as surfactants and then nanoparticles are added to the demulsifier. This study is performed to show the impact of nanotechnology on dewatering and desalting processes.

II. EXPERIMENTS

A. Materials

Tetraethyl orthosilicate (TEOS), Acetic acid ($C_2H_4O_2$, 100%) and Polyvinyl Alcohol (PVA) were procured from Merck Co. All chemicals used in this study are of analytical grade utilized without further purification. Deionized water is also used for the solution preparation.
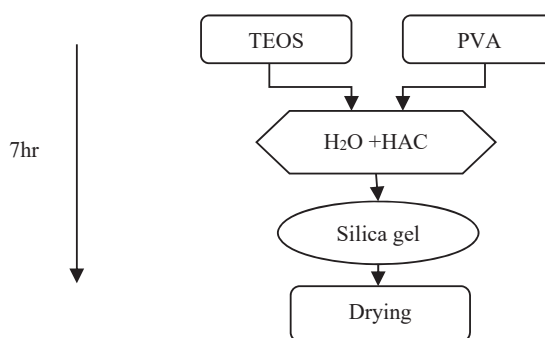

Fig. 1 Synthesis diagram

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A. Preparing of W/O Oil Emulsion

The water/oil emulsions were prepared by adding 5% water to crude oil at 65ºC upon mixing. The emulsion was stable for weeks without phase separation.

B. Synthesis of Silica Nanoparticles

Silica nano-particle is synthesized using the Stober method. In this method, appropriate quantities of ethanol, tetra ethoxy orthosilicate and distilled water are taken and stirred continuously for 30 min. After that, ammonia is added to the mixture and allowed for continuous stirring for 2 h. After 2 h, TEOS is added upon stirring. After 30 min, ammonia is added and the reaction mixture is allowed to be stirred constantly for 24 h. A white color solution is obtained which is centrifuged at 6000 rpm for 15 min. After centrifugation, drying is carried out and a pure white silica powder is obtained.

C. Synthesis of Silica Nanoparticles with PVA

PVA was applied in the nano-layered SiO_2 structures with sol-gel technique. In this method, Silica nano-layers were synthesized by modifying the Stober method. As can be seen in Fig. 1, the sample was prepared by mixing suitable volumes of TEOS and PVA solution added drop-wisely to 3 ml solution of deionized water and acetic acid at a 0.1 ml/min rate while being stirred vigorously. Stirring was continued for a further 6 hr, to complete the reaction and aging which results in the increase of gel time. The product is centrifuged at 4000 rpm for 20 min and washed several times and finally dried at 40^0C in vacuum oven. Nanostructures have different sizes due the modified procedure (Figs. 2 and 3).

D. Demulsification Performance Test

The demulsification performance test was conducted by pouring 100 ml of the w/o emulsion into a capped 100 ml graduated cylinder and a normal amount of demulsifier and nanoparticles are added and shaken for complete mixing and then placed into an electrical oven and heated to 65ºC. The demulsifier was added using a micropipette. The volume of water separated from the emulsion was monitored after 24 h. The performance of demulsifiers was measured in terms of vol. % of water separated [12].

E. Salt Content

A certain amount of crude oil was heated to 60^0C and 40ml toluene was added slowly with constant stirring (IP77). Then it was transferred to the flask of the extraction apparatus through the thistle tube and was washed two times with toluene after cooling and adding hot alcohol and acetone. When boiling is ceased, distilled water was added, then the mixture was boiled for a further 15 min. IP77 is followed. After several steps, water is separated from crude oil and titrated. Titration procedure was done using 3-methylbutanol, thiocyanate and silver nitrate ferric alum. When color changes, NaCl amount is calculated by (1):

$$9.35 \times 10^4 \; G \; [(V_1 - V_2)\,M - (V_3 - V_4)\,m]/w \qquad (1)$$

where V1= Volume of silver nitrate solution used to titrate sample; V2= Volume of silver nitrate solution used to titrate blank; V3=Volume of silver thiocyanate used to titrate sample; V4=Volume of silver thiocyanate used to titrate blank; M= molarity of the silver nitrate solution; m= molarity of the thiocyanate solution; W= weight of sample in gram; G= density of the sample at 15C.

F. Characterization of Silica Nanoparticles

Upon synthesis, pure silica nano-particles and silica nanoparticle with PVA were characterized by PSA and SEM.

III. RESULTS AND DISCUSSION

A. Particle Size Analyser (PSA) and SEM

Particle Size Analysis of pure silica and PVA- assisted and commercial Silica nano-particles are shown in Figs. 2 (a)-(c). The results show that the synthesized pure Silica nanoparticles have a uniform size distribution of 70-80nm.
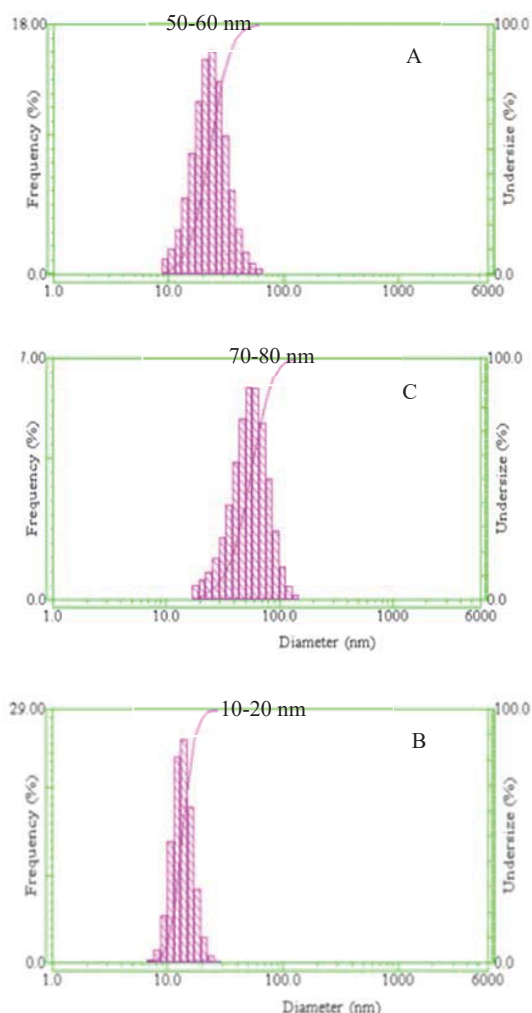

Fig. 2 PSA of nanoparticles: (a) Synthesized silica nanoparticles with PVA, (b) Commercial silica nanoparticles, (c) synthesized pure silica nanoparticles

The smallest nanoparticles used in this study were commercial Silica nano-particles with an average 10-20 nm size. Synthesized Silica nanoparticles with PVA had an average size of 50-60 nm.
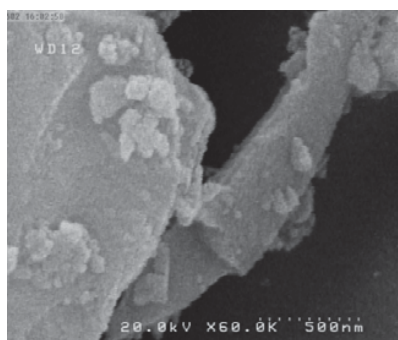

Fig. 3 SEM micrograph of the nanostructure synthesized by PVA

As shown in Fig. 3, the morphology of the nanostructure synthesized by PVA in SEM indicate they nano-layer form.

B. Demulsification Performance

The demulsification performance using different types of nano-SiO_2 is shown in Fig. 4. The results clearly illustrate that the combined demulsification performance of the nano-SiO_2 enhanced demulsifier is higher. Nano-SiO_2 with PVA results in the highest demulsification performance increasing the dewatering by 40%. Dewatering percentage of the blank sample was 50%. PVA is used as a surfactant through the synthesis also improving the hydrophobicity of nanoparticles and helping them have better performance. The small size of nanoparticles makes them more active to adsorb water and pass through the oil-water interfacial films and increase the density of water phase and help their faster coalescence. Commercial nanoparticles were at the second rank in dewatering. Because of size, this nanoparticle increased dewatering by 20%. Finally, pure nanoparticles modify dewatering by 10%. These nanoparticles were smaller than PVA-enhanced nanoparticles, although lacking the hydrophobic factor. Their larger size compared to the commercial nanoparticles prevents them to improve dewatering more than commercial nanoparticles.
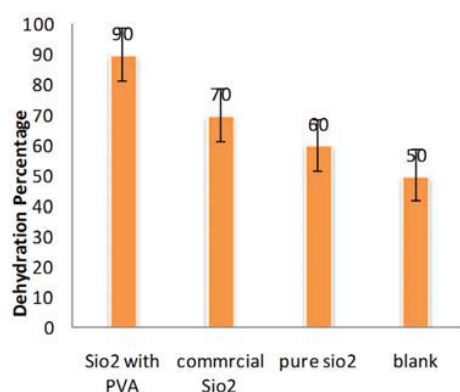

Fig. 4 Separation of different types of nanoparticles and control sample

Experiments showed that the demulsification performance of the new demulsifier with nano-SiO_2 was improved greatly. The demulsification mechanism can be considered as follows: Nanoparticles have a higher activity and hydrophobicity compared to the chemical demulsifier, so the nanoparticles had more chance to pass through the oil-water interfacial films and reach the water phase and increase the density of water phase, propitious to quicken the interfacial film rupture and oil-water separation. According to this analysis, the chemical bonds can form between nano-SiO_2 and the chemical demulsifier. The hydrophilic head of new demulsifiers was easier to reach the oil-water interfacial film substituting the natural emulsifier and decreasing the oil-water interfacial tension destroying the structure of original interfacial film, which made the interfacial film become thinner.

C. Salt Content

The desalting performance of the demulsifier with different types of nano-SiO_2 is shown in Fig. 5. The results clearly illustrate that the desalting performance of the nano-SiO_2 enhanced demulsifier was better than the demulsifier itself. When nano-SiO_2 with PVA was used, the desalting performance was the highest decresing the salt content to 270 gr/m^3. Desalting of the blank sample was 970 gr/m3. Synthizied nano-SiO_2 with PVA modified the chemical demulsifier and improved the desalting performance. PVA used as a surfactant in the synthesis. Commercial nanoparticles had the second rank in dewatering. Pure synthesized nano-particles can also improve desalting about 170 gr/m3.
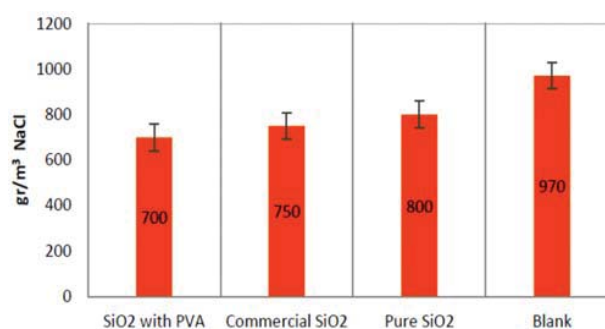

Fig. 5 Content of NaCl in blank sample with other samples with different type of nanoparticles

IV. CONCLUSIONS

Dispersing nano-SiO_2 in chemical demulsifier could increase its demulsification and desalting performance. Nano-SiO_2 with PVA results in the highest demulsification and desalting performance increasing the dewatering rate by 40% and decreasing the salt content to 270 gr/m^3.

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