Experimental Investigation of the Base Fluid Miscibility Condition on the Oil Recovery Using Nanofluids Flooding

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Received: 2017.08.31                        Accepted: 2017.11.05                        Published: 2018.01.30

ABSTRACT

This research illustrates the effect of miscibility condition between nanofluid and oil on the process efficiency and to achieve this aim four types of fluid including distilled water, ethanol, n-hexane, and gas condensate were used to disperse silica nanoparticles. The prepared nanofluids were injected into a glass micromodel and the oil recovery factor and effective mechanisms were investigated. Results showed that in presence of nanoparticles, the oil recovery factor for miscible base fluids injection increases about 30%. But in immiscible base fluids, nanoparticles enhance the oil recovery factor up to 20% more than the base fluids. So nanoparticles are more efficient in miscible base fluids compared to immiscible ones.

Keywords: EOR, IFT, Immiscible, Miscible, Micromodel, Nanofluid, Oil Recovery Factor, Viscosity

INTRODUCTION

World’s demand for oil is growing due to applications of oil products in many industries. In the primary period of the reservoir production, oil recovery does not exceed 50% of the total oil in place by use of the reservoir natural energy.\cite{1} Therefore much enhanced oil recovery (EOR) methods have been applied to increase the oil production from reservoirs. But still lots of the oil is trapped in the reservoir and it would not be produced. So researchers are trying to find new technologies to improve the oil recovery factor.\cite{2} Nowadays researchers are attracted to use different additives such as surfactants, polymers, and nanoparticles to improve the injected fluids characteristics in order to enhance the oil recovery from reservoirs. Among these materials, nanoparticles due to their unique properties such as small size, good physical properties, application in deep reservoirs and etc. are suitable candidates and they have been applied in different EOR techniques.\cite{2-5} In other words, it has been found that nanotechnology can improve the oil recovery factor according to the high surface to volume ratio of nanoparticles.\cite{6,7} Owing to the small size of nanoparticles, they can even pass through the pore throat in tight reservoirs.\cite{8,9} Many nanoparticles such as SiO₂, TiO₂, CuO, and Al₂O₃ have been used in many studies to enhance the oil recovery, but still, the most efficient nanoparticle has not been found.\cite{10} Due to the results of silica nanoparticle in enhancing the oil recovery in all the previous researches, it seems that it is the best among different nanoparticles. Silica nanoparticle is one of the inexpensive nanoparticles and has properties similar to sandstone rock that makes it favorable in EOR processes.

Adding nanoparticles to base fluids (nanofluids) alter the fluid properties such as viscosity, thermal conductivity and surface tension.\cite{11,12} It seems that the most important mechanisms of nanofluids in enhancing the oil recovery factor are increasing the base fluid viscosity, altering
the porous medium wettability and reducing the interfacial tension (IFT) between the base fluid and oil.[13-15] Maghzi et al.[16] studied the effects of silica nanoparticles dispersed in water in a micromodel apparatus and concluded that addition of 0.1 wt.% SiO$_2$ nanoparticles caused an increment of 8.7% in production of the initial oil in place. It is worthy to note that a micromodel is an apparatus to visually analyze the flow behavior and dominant mechanisms in a porous medium in 2 dimensions. Visualization helps researchers to understand many different aspects of fluid flow in porous media such as miscible flow behavior, flow distribution in porous media, wettability alteration, pore throat plugging and others. Torsater et al.[17] dispersed silica nanoparticles in synthetic brine and by flooding the nanofluid into the oil saturated core, showed that the oil recovery factor compare to the brine injection improves about 8%. In addition, these researchers obtained that the dominant mechanism in improving the oil recovery was reduction of the interfacial tension between oil and the injected fluid.[13] Roustaie et al.[18] investigated the effect of polysilicon nanoparticles dispersed in brine on the oil recovery and their results illustrated that nanoparticles can alter the wettability of the porous medium and also decrease the interfacial tension. Suleimanov et al.[19] found that addition of nanoparticles to a surfactant solution results in 70-90% reduction in the interfacial tension. Henderaningrat et al.[20] studied the influence of metal-oxide nanoparticles dispersed in brine on the oil recovery and concluded that SiO$_2$ nanoparticles improved the oil recovery factor more than TiO$_2$ and Al$_2$O$_3$. It is due to the stability of water/SiO$_2$ nanofluid compare to other nanofluids. Researches also showed that use of nanofluids leads to a more water-wet media.[21-23].

As the literature illustrates, the most investigations were performed with water as the base fluid and effect of different base fluids on the oil recovery is not investigated yet. In other words, recent developments in nanotechnology illustrate that addition of nanoparticles can improve the efficiency of water as a base fluid in displacing oil and enhance the oil recovery factor. But there is not any precise report about other base fluids as mediums for dispersion of nanoparticles and it is not clear that which type of base fluids have a higher influence on the oil recovery factor in nanofluids flooding. Only Ogolo et al.[24] used different base fluids such as diesel and distilled water as the nanoparticles dispersing medium, but because of the miscibility condition between oil and diesel, they could not calculate the oil recovery factor for the diesel based nanofluids. Also tests were performed on a core, so it was not possible to observe the fluid flow through the porous medium and the area swept by diesel injection. As miscible fluid injection has a proper efficiency in oil production, it is a good idea to use nanoparticles

| Table 1. Nanoparticles properties |
|----------------------------------|------------------|-----------------|------------------|-------------------|
| Particle | Color | Average particle size (nm) | Density (gr/cm$^3$) | Specific surface area (m$^2$/gr) |
| SiO$_2$ | White | 11-14 | 2.4 | 600-785 |

![Fig. 1. (a) TEM and (b) SEM image of silica nanoparticles.](Image)
in this EOR process to increase the oil recovery of miscible fluid injection. Therefore, in this study the miscibility condition between injected fluid and in-situ heavy oil in a nanofluid injection process is investigated in a glass micromodel in order to visualize how it affects the oil recovery and how the injected nanofluid passes through the porous medium. It should be mentioned that miscible nanofluids flooding and calculating the oil recovery factor was done for the first time in this research and all the previous studies were performed using immiscible base fluids such as water and brine. In addition, in this study effects of different parameters affecting the process and their interactions have been analyzed and optimized using Design Expert software by General Factorial approach.

MATERIALS AND METHODS

There are different materials and facilities used in this work, and the properties and features are described below.

Materials

A recent study showed that nanoparticles are more efficient in improving heavy oil recovery compared to light oil.[25] So in this study the heavy oil sample from one of the Iranian oil fields with 17.5 API° and viscosity 340 cP (measured at ambient condition) was used to completely saturate the porous medium. In this study effect of irreducible water saturation on the oil recovery was neglected due to the lack of control on the place where water settles in the micromodel and the porous medium was completely saturated with oil.

Four types of base fluids including distilled water, ethanol, n-hexane, and gas condensate were used as the dispersing agent for nanoparticles. Water and ethanol were considered as immiscible fluids because they do not dissolve in heavy oil completely and n-hexane and gas condensate were supposed to be miscible with oil.

Ethanol and n-hexane were bought from Merck Company and the gas condensate was taken from one of the Iranian gas fields. The nanoparticles used in this research are silica nano-powders taken from US Research Nanomaterials, Inc., and their properties are given in Table 1. Also, SEM and TEM images of this nanoparticle have been shown in Fig. 1. In order to prepare nanofluids with 3 and 5 wt. % of nanoparticles, firstly powders were dispersed in the base fluids using the ultrasonic cleaner for 40 minutes in order to be sure that the injected nanofluids are stable. The stability tests have been performed for all nanofluids and they were kept up to 48 hours in order to check out their constancy over time. All the nanofluids were completely stable up to 48 hours. In addition, nanofluids viscosities were measured using a Brookfield viscometer (NDJ-4).

It should be mentioned that because SiO₂ nanoparticles are hydrophilic and have a tendency to be dispersed in water-based and polar fluids, surface treatment of particles was necessary for dispersion of silica nanoparticles in solvents and
organic fluids. In this study oleic acid was used to make SiO$_2$ a hydrophobic nanoparticle. Li et al.[26] showed that by means of this acid, some extent of -OH attached to SiO$_2$ nanoparticles, is replaced by –COOH, and reduction of OH groups connected to SiO$_2$ tends the nanoparticle surface to be more hydrophobic and as a result, the stabilized suspension of nanoparticles/solvent-base fluids generates. Oleic acid participates in a chemical reaction with SiO$_2$ nanoparticles as below:

$$\text{SiO}_2(\text{OH})_n + y\text{HOOCC}_{17}H_{33} \rightarrow \text{SiO}_2(\text{OH})_{n-y} \times (\text{OOC}_{17}H_{33})_y + y\text{H}_2\text{O}$$  \hspace{1cm} (1)

First, oleic acid and n-hexane are mixed with stirring at 1200 rpm, then an appropriate amount of SiO$_2$ nanoparticle is added to the mixture. The stirring process continues for 4 hours and after that, the solution is filtered and the precipitate is rinsed with a mixture of ethanol and deionized water completely. Then, the precipitate is kept in a vacuum desiccator for 24 hours, and the dried white powder remained is the hydrophobic silica nanoparticle.

In this work, a dolomite rock type pattern was selected as the micromodel pattern to perform the nanofluids injection tests. Properties of the micromodel pattern are given in Table 2. It is clear from the table that due to the thickness of generated micromodel, the fluid flows in the 2 dimensions. So to show the fingering effect and have obvious and large fingers of injected fluid passed through the oil, the injection pattern was selected as linear.

**Experimental Procedure**

In this research, a micromodel setup (Fig. 2) was used to visually analyze the flow behavior of the injected fluids. A syringe pump is used to saturate the glass micromodel and inject the fluids. A Canon 7D camera was placed on top of the porous medium to capture photos of the injection process. To evaporate the micromodel from air and washing fluids a vacuum pump was used.

12 injection tests were accomplished according to the general factorial approach and using Design Expert software to study the effects of parameters and their interactions on the oil recovery factor. Experimental design parameters and their levels are shown in Table 3. Before each injection, it was important to evacuate the glass micromodel in order to fully saturate it with the heavy oil. Then 1.2 PV (Pore Volume) of the fluids (nanofluids and the base fluids without nanoparticles) were injected through the saturated glass micromodel. This volume of injection was selected in order to have the ultimate recovery and making sure that there is no change in the oil recovery anymore.

To satisfy laminar flow regime, tests were performed at a very low injection rate 0.05 cc/hr using the syringe pump. As the injected fluid enters the porous medium, the camera mounted on top of the micromodel glass starts to capture photos of the injection process in 2 minute steps. Photos were saved on a laptop in order to be investigated. Analyses of photos were done using Photoshop software to calculate the oil recovery factor, and this

<table>
<thead>
<tr>
<th>Table 3. Experiment design parameters and their levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>Base Fluid type</td>
</tr>
<tr>
<td>Wt.% of nanoparticles</td>
</tr>
</tbody>
</table>

Fig. 3. IFT reduction versus wt.% of silica nanoparticle in water

Fig. 4. IFT reduction versus wt.% of silica nanoparticle in ethanol
was achieved by counting pixels of the injected and also total saturated fluid flow path using different tools of the software.

**Lateral Tests**

In order to investigate the mechanisms of nanoparticles on the EOR process, different lateral tests including viscosity and IFT measurements were performed. As viscosity is an important property of the injected fluids that affect the oil recovery, in this research nanofluids viscosity has been measured using Brookfield viscometer (NDJ-4). Therefore, one of the possible mechanisms of nanoparticles on the EOR process can be studied with more details.

In addition, to find out other effective mechanisms of nanoparticles used in this study IFT tests have been done using Sigma 700 tensiometer. This device measures the IFT by means of Du Noüy ring method. In this technique, oil and the injected fluid are poured into a container, and due to the difference in fluids density they can be separated from each other and an interface appears between them. Then a ring connected to a balance is immersed through the fluids, and as the ring is raised through the fluids, the force applied to the ring is calculated by the balance verses position of the ring. The force applied to the ring at the interface is related to the interfacial tension by the below expression.

\[
\text{IFT} = \frac{F_{\text{max}} - W}{4\pi r}
\]  

where \(F_{\text{max}}\) is the maximum force applied to the ring at the interface, \(W\) is the weight of the ring and \(r\) is the ring radius.

**RESULTS AND DISCUSSIONS**

IFT results showed that addition of silica nanoparticles to immiscible base fluids causes a decrease in the interfacial tension between the base fluid and oil. But at nanoparticles concentrations higher than 3 wt.% the slope of reduction decreases as shown in Fig. 3 and Fig. 4 for distilled water and ethanol as the base fluid, respectively.

Also, the addition of nanoparticles leads to an enhancement in the base fluid viscosity. So another mechanism that can increase the oil recovery factor using nanofluids may be improving the mobility ratio. Changes of nanofluids viscosity in the presence of nanoparticles is shown in Fig. 5.

Comparison of flooding tests in the presence and absence of nanoparticles illustrates that as the base fluid reaches the porous medium, it starts to build fingers and flow through the oil in place. So the breakthrough time happens quickly and a huge amount of oil is unswept. The low efficiency of the base fluids injections is due to their low viscosity and high interfacial tension with the heavy oil. As illustrated in Fig. 6 and Fig. 7 addition of silica nanoparticles into base fluids results in a piston-like flow behavior and better areal sweep efficiency due to the higher viscosity of nanofluids and a better mobility ratio between oil and the injected fluid. In miscible base nanofluids, the dominant mechanism improving the oil recovery is enhancing the base fluid viscosity in the presence of silica nanoparticles. In these floodings due to the mass transfer between the injected fluid and the oil in place, the base fluid starts to flow toward the end of the porous medium through the oil and a huge amount of oil is bypassed. Addition of silica nanoparticles causes the base fluid to flow widely and be in contact with a larger amount of the heavy oil. But in immiscible base fluids injections, the reduction in interfacial tension between the oil and nanofluids and an increase in the injected fluid viscosity are effective mechanisms that improve the oil recovery simultaneously.

As shown in Fig. 6 ethanol seems not to be a suitable base fluid for nanoparticles to enhance the oil recovery. The poor oil recovery factor in the nanofluids flooding using ethanol in comparison to distilled water as the base fluid for dispersion of nanoparticles is due to lower density of ethanol than distilled water. Nanoparticles are dispersed...
Fig. 6. Macroscopic photos of ultimate recovery for water (left) and Ethanol (Right) base fluid: A) 0 wt.%, B) 3 wt.% and C) 5 wt.% of silica nanoparticles

Fig. 7. Macroscopic photos of ultimate recovery for n-hexane (left) and gas condensate (Right) base fluid: A) 0 wt.%, B) 3 wt.% and C) 5 wt.% of silica nanoparticles
in base fluids at the same weight percent, so lower amount of nanoparticles exist in an equal volume of ethanol than water. This causes a lower efficiency in enhancing the oil recovery for ethanol as the base fluid. This issue was also observed in viscosity measurements of ethanol and water. From the macroscopic photos, it is obvious that nanoparticles efficiency is higher for miscible base fluids than immiscible base fluids. Quantitative results of the oil recovery factor up to 1.2 PV of the injected fluids are illustrated in Fig. 8 to Fig. 11. As shown in these figures the oil recovery factor increment above 3 wt.% of silica nanoparticles decreases and so the efficiency of nanofluids injections decreases. Therefore, it seems that using nanoparticles more than 3 wt.% for both miscible and immiscible base fluids may not be economical especially when particles are expensive. But still, the increment in the oil recovery is shown by the addition of nanoparticles above 3wt.%.

Besides macroscopic investigations of the process, microscopic ones are essential and can better present the influence of silica nanoparticles on the fluid flow behavior in the pore scale and also the microscopic sweep efficiency can be studied precisely. By analyzing the captured photos during the fluids injections it has been observed that existence of nanoparticles in the injected fluid can decrease the residual oil. As shown in Fig. 12 and Fig. 13, a thin film of the heavy oil remains on the matrix walls as the residual oil in the glass micromodel in distilled water and ethanol injections. In presence of silica nanoparticles, the injected fluids are more viscous and could remove the residual oil on the walls. Therefore, the oil recovery factor in the pore scale improves.

The ultimate oil Recovery data for all designed experiments (Table 4) were inserted in Design Expert software and a cubic model was used to analyze the obtained outcomes. According to
Fig. 12. Pore scale photos of different parts of micromodel glass: 
A) water injection and B) water-silica injection

Fig. 13. Pore scale photos of different parts of micromodel glass: 
A) Ethanol injection and B) Ethanol-silica injection

Table 4. List of Designed Injection Tests and the Results

<table>
<thead>
<tr>
<th>No.</th>
<th>Base Fluid</th>
<th>Weight Percent of Silica Nanoparticle (%)</th>
<th>Ultimate Oil Recovery Factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water</td>
<td>0</td>
<td>32.8</td>
</tr>
<tr>
<td>2</td>
<td>Water</td>
<td>3</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>Water</td>
<td>5</td>
<td>53.7</td>
</tr>
<tr>
<td>4</td>
<td>Ethanol</td>
<td>0</td>
<td>36</td>
</tr>
<tr>
<td>5</td>
<td>Ethanol</td>
<td>3</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>Ethanol</td>
<td>5</td>
<td>41.8</td>
</tr>
<tr>
<td>7</td>
<td>n-Hexane</td>
<td>0</td>
<td>37</td>
</tr>
<tr>
<td>8</td>
<td>n-Hexane</td>
<td>3</td>
<td>57.5</td>
</tr>
<tr>
<td>9</td>
<td>n-Hexane</td>
<td>5</td>
<td>68.5</td>
</tr>
<tr>
<td>10</td>
<td>Gas Condensate</td>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td>11</td>
<td>Gas Condensate</td>
<td>3</td>
<td>62</td>
</tr>
<tr>
<td>12</td>
<td>Gas Condensate</td>
<td>5</td>
<td>71</td>
</tr>
</tbody>
</table>

Table 5. ANOVA analysis

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>DOF</th>
<th>Mean Square</th>
<th>F- Value</th>
<th>P- Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>1883.42</td>
<td>8</td>
<td>235.43</td>
<td>352.00</td>
<td>0.0002</td>
</tr>
<tr>
<td>A-Base Fluid</td>
<td>682.52</td>
<td>3</td>
<td>227.51</td>
<td>340.15</td>
<td>0.0003</td>
</tr>
<tr>
<td>B-Wt.% of Nanoparticle</td>
<td>984.72</td>
<td>1</td>
<td>984.72</td>
<td>1472.29</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>AB</td>
<td>207.22</td>
<td>3</td>
<td>69.07</td>
<td>103.27</td>
<td>0.0016</td>
</tr>
<tr>
<td>B²</td>
<td>8.96</td>
<td>1</td>
<td>8.96</td>
<td>13.39</td>
<td>0.0353</td>
</tr>
<tr>
<td>Residual</td>
<td>2.01</td>
<td>3</td>
<td>0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>1885.43</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

this model, analysis of variance (ANOVA) was performed and results are shown in Table 5. Parameters with lower P-value have more effect on the ultimate recovery. Based on the table, it is clear that wt.% of nanoparticles due to its lower P-value has the most influence on the oil recovery factor.

The suggested model can predict the effect of parameters on the oil recovery factor and according to Fig. 14 the predicted results are in a good agreement with the experimental data and the deviation between them can be ignored. This observation besides the low P-value of the model presented in Table 5 verifies the model validity.

Effect of the base fluid type on oil recovery
factor at 5 wt. % of nanoparticles is shown in Fig. 15. It is clear that the oil recovery factors of immiscible nanofluids compare to miscible ones are lower and the slope of the line between 2 types of nanofluids (miscible and immiscible) indicate the great influence of miscibility condition of base fluids-oil on the oil recovery factor. In addition, results show that ethanol as one of the immiscible fluids due to its low density is not a good candidate to disperse nanoparticles. Also Fig. 16 represents the effect of nanoparticles weight percent on the oil recovery factor for gas condensate, according to the suggested model of the software. Based on the slope of the line in Fig. 16, weight percent of nanoparticles has a great influence on oil recovery factor. The noticeable point of Fig. 16 is the decrease in the slope above 3 wt.% of silica nanoparticles, and this indicates that nanoparticles have a lower
influence on oil recovery factor at higher than 3 wt. %. So it may not be economical to use nanoparticles more than 3 wt.% for each type of the base fluid in a nanofluid flooding.

CONCLUSION
- Addition of silica nanoparticles enhances the oil recovery factor in both miscible and immiscible base fluids.
- Miscibility condition of base fluids had a key role in enhancing oil recovery in presence of silica nanoparticle.
- The dominant mechanism of nanoparticles in miscible base fluids was increasing viscosity of the base fluid and in immiscible base fluids reduction in interfacial tension between oil and injected fluid was efficient too.
- The slope of oil recovery increment decreased above 3wt.% of nanoparticles.
- Silica nanoparticles reduce the residual oil saturation due to an increase of injected fluid viscosity in the microscopic scale.
- The most oil recovery in miscible base fluids was 71% achieved by gas condensate-silica 5wt.% nanofluid.
- The most oil recovery in immiscible base fluids was 53.7% achieved by water-silica 5wt.% nanofluid.

CONFLICT OF INTEREST
The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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