Simulation Study of Enhanced Condensate Recovery in a Gas-Condensate Reservoir

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Abstract

In gas-condensate reservoirs, by reservoir depletion, pressure decreases below the dew point pressure of the fluid and condensate forms in the reservoir. This heavy part of the gas has found many applications in industry and also in daily life. When condensate drops out in the reservoir not only is this valuable liquid lost, but also its accumulation results in forming a condensate bank near the wellbore region. The created bank makes a considerable reduction in gas well productivity. These facts demonstrate that finding an economical way to increase the condensate recovery from condensate reservoirs is essential.

In this study gas injection has been simulated in a gas condensate reservoir to increase the condensate recovery factor. In addition, capability of injection of different types of gas in condensate recovery has been compared through different injection schemes. The injection schemes that have been considered are: different injection rates, different reservoir pressures at which the injection is implemented and different injection durations.

A compositional simulator was applied to simulate a simplified gas condensate reservoir model. The injection pattern was a one-eighth of a five-spot pattern with finer grids near the producer and injector. The simulation results showed an increase in condensate recovery from 5% to 30% in all injection cases.

Many parameters can affect the decision of selecting the injection scheme, other than the gas and condensate recovery factor. Therefore, an economical evaluation and analysis is inevitable to take them all into account to determine the optimum scheme.

Keywords: Enhanced Condensate Recovery, Gas Condensate Reservoirs, Gas Recycling, Reservoir Simulation, Condensate Drop-Out

1- Introduction

In gas-condensate reservoirs gas injection is an operation applied to reduce the condensate drop-out in the reservoir. Condensate is formed from valuable heavy components of hydrocarbon mixtures. Accumulation of condensate in a reservoir can cause a reduction in gas permeability and result in decreasing gas well productivity [1]. However, according to the research, gas–condensate relative permeability varies with production rate at near wellbore condition[1].

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The flow in this region is controlled by the complex interaction of capillary, viscous and inertial forces [2]. At low condensate saturations the relative permeability values decrease when the flow rate increases, due to the dominance of the inertial effect. However, the positive coupling effect surpassed the inertial effect at higher condensate saturation, resulting in a net increase of relative permeability with rate [3,4].

Injection can be implemented at the initial reservoir pressure to maintain the pressure above the dew point (full pressure maintenance), or after the reservoir pressure falls below the dew point pressure (partial pressure maintenance) [5], in which injected gas re-vaporizes the condensate and reduces condensate accumulation in the reservoir. Gas cycling has been implemented in gas condensate reservoirs for many years, but due to more applications and the value of natural gas, engineers were forced to find an appropriate replacement for it in the injection process. N₂ and CO₂ were suggested as two alternatives which are now applied in some reservoirs [6, 7]. As N₂ is an available and a non-corrosive gas, it is a good alternative and can be properly applied for this purpose. Injection of these gases into the reservoir vaporizes condensate and increases the reservoir fluid dew-point pressure. The contact of the injected gas with the condensate leads to enrichment of the gas due to mass transfer [8].

This study compares the efficiency of injection of different gases of N₂, CO₂, and CH₄ and also gas cycling for condensate recovery from a gas condensate reservoir. For this work a compositional simulator has been applied and different injection schemes have been simulated. In these schemes the effect of changing the injection rate, injection pressure and injection duration on recovery have been investigated. The appropriate and optimum case can be selected considering the results of the simulation work and performing an economical analysis. In this case, all the affecting parameters such as the price of the gas and condensate, the price of the injection gases and the cost of the facilities needed in each scheme for each pressure level should be considered.

2- Model description

In order to simulate the model, a simplified gas-condensate reservoir model has been applied. The reservoir specifications and fluid properties have been tabulated in Tables 1-3.

<table>
<thead>
<tr>
<th>Layer</th>
<th>k_h (md)</th>
<th>k_v (md)</th>
<th>Thickness (ft)</th>
<th>Initial pressure (psia)</th>
<th>5248</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>130</td>
<td>13</td>
<td>30</td>
<td>Reservoir temperature (F)</td>
<td>219</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>4</td>
<td>30</td>
<td>Porosity</td>
<td>0.13</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>2</td>
<td>50</td>
<td>PV compressibility (psi⁻¹)</td>
<td>4.00E-06</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>15</td>
<td>50</td>
<td>water compressibility (psi⁻¹)</td>
<td>3.00E-06</td>
</tr>
</tbody>
</table>
A three dimensional model of one-eighth of a five-spot pattern has been considered to simulate the injection pattern. Due to the symmetrical form of the five-spot injection pattern one-eighth of it has been considered, which makes the simulation run time program remarkably shorter [9]. A schematic of this model has been shown in Fig. 1.

The constructed reservoir model (in CMG model builder module) is one-eighth of a 31×31×4 grid, with the dimensions of 2903.5 (ft) in I and J directions, and 110(ft) in K direction, which has been shown in Fig. 2. One injector and one producer are located in the corners of the grid. Smaller grids are made near the injector and producer in order to model the fluid flow more accurately. As the blocks located in the border of the simulation grid are smaller than that of the described model, their porosity and transmissibility have been reduced to half, quarter and one eighth of their initial size according to their location.

3- Results and discussion

Based on the aim of the study, different runs have been implemented on the simulated model. In this model the third and the forth layers are opened to production, and injection is performed through the first and the second layers. Production period is 15 years and the maximum rate of the production is 2.4 MMSCF/D, which has been set as the first constraint. The second constraint is the minimum bottom-hole pressure which is equal to 500 psia. Firstly, reservoir behavior by natural depletion was investigated. Reservoir pressure and average condensate saturation in the reservoir during this period have been shown in Fig. 3 and Fig. 4, respectively.
Figure 3. Average reservoir pressure during natural depletion period

Figure 4. Average condensate saturation during natural depletion period

3.1- Effect of injection gas type
In this section, the effects of three injection gases and gas cycling with different rates have been investigated. Composition of the recycled gas is given in Table 1. Injection was implemented at the initial reservoir pressure.

As can be observed from Fig. 5, when the injection rate is equal to the production rate, the performance of CO₂ and CH₄ in condensate recovery is almost the same. They make an increase of about 24% compared to the base case (no injection case).

Figure 5. Comparison of condensate recovery of different injection gases in different cases of injection rate at initial reservoir pressure
in which condensate recovery is about 50%, whereas N₂ can only make an increase of about 15% [10]. According to the previous studies, the addition of some nitrogen causes a considerable increase in mixture dew-point pressure. This dew-point eventually becomes much higher than the reservoir pressure. Depending on the level of mixing and dispersion, liquid drop out occurs, thus the efficiency of the process is reduced [11]. This fact can be observed from Fig. 6 in which the phase envelope of the fluids resulted from mixing N₂, CO₂, and CH₄ with the reservoir fluid has been compared. Gas cycling with a rate equal to the production rate was excluded.

High injection rate results in the early breakthrough of the injection gases and reduces the ultimate gas recovery to a very low value. Recovery of gas and condensate for all the injection cases has been given in Tables 2 through 5.

For the other injection rates, gas cycling is the most effective way to increase the condensate recovery. When the injection rate is 75% of the production rate (1.8 MMSCF/D), the recovery by gas cycling is about 80%, while by CO₂, CH₄ and N₂ injection, recoveries are 73%, 70%, and 65% respectively. Based on the experiments and studies done before, N₂ injection is not as effective as CH₄ and CO₂, as it causes higher liquid drop out, and has lower evaporating capacity than the other gases [12].

By lowering the injection rate, condensate recoveries for all the gases are similar to each other.

Table 2. Reservoir fluid composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>3.15</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.15</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.08</td>
</tr>
<tr>
<td>CH₄</td>
<td>83.32</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>5.37</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>1.89</td>
</tr>
<tr>
<td>iC₄H₁₀</td>
<td>0.43</td>
</tr>
<tr>
<td>nC₄H₁₀</td>
<td>0.69</td>
</tr>
<tr>
<td>iC₅H₁₂</td>
<td>0.31</td>
</tr>
<tr>
<td>nC₅H₁₂</td>
<td>0.26</td>
</tr>
<tr>
<td>Pseudo C₆</td>
<td>0.44</td>
</tr>
<tr>
<td>C₇+</td>
<td>1.03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid Molar Mass (g/mol)</td>
<td>21.85</td>
</tr>
<tr>
<td>C₇+ Molar Mass (g/mol)</td>
<td>141.02</td>
</tr>
<tr>
<td>C₇+ Density (g/cm³)</td>
<td>0.7888</td>
</tr>
</tbody>
</table>

It can be seen in Fig. 7 that during the injection period the capability of CO₂ in removing the condensate in the reservoir is less than the other gases, but after the injection, condensate saturation increases rapidly in all the cases except for the CO₂ injection.

Another difference between CO₂ injection and other gases is in condensate accumulation in the near wellbore region.
after the injection period finishes. By CO₂ injection the condensate accumulation in this region does not occur, contrary to the other cases in which condensate accumulation in the near wellbore region is even higher than that of natural depletion of the reservoir. Capability of CO₂ in removing the condensate plug from the near gas-condensate wells region and its long-term effect has also been shown in previous studies [12].

**Figure 7.** Effect of different injection gases on condensate saturation reduction during the production period (with the injection rate of 1.8 MMSCF/D at the initial reservoir pressure)

3.2- Effect of injection at different reservoir pressures

Injection can be started at the initial pressure of the reservoir (at the time of production), or after the reservoir pressure drops to a certain pressure. The second alternative demands a lower injection pressure so the required facilities will be less expensive.

Our model has been run at the reservoir pressures of 5248 psia (initial reservoir pressure), 4500 psia, 3500 psia and 2500 psia. The effect of injecting at different pressures has been investigated for four different rates. The results for the rate of 75% of the production rate, which are shown in Fig. 8, are discussed below.

**Figure 8.** Effect of different injection pressures on condensate recovery with the injection rate of 1.8 MMSCF/D
The results of CH$_4$ injection and gas cycling with the rate of the 1.8 MMSCF/D (75% of the production rate), show that when injection pressure is 4500 psi, recovery of the condensate reduces, but by further pressure reduction to 3500 psi, the recovery increases to a value equal to the injection at initial pressure or more (in the case of gas cycling).

The graph for N$_2$ injection shows that recovery does not change much by injecting at the lower pressures than the initial pressure. Finally, condensate recovery by CO$_2$ injection decreases by decreasing the injection pressure.

3.3- Effect of injection rate

Effect of four different rates (equal to 1, 0.75, 0.5, 0.25 times of the production rate) on the condensate recovery by all the injection gases can be observed in Fig. 9. Injection has been implemented in the initial reservoir pressure.

For the case of CO$_2$ injection, recovery of condensate for the two highest rates is almost the same, while the recovery of gas (given in Table 2) for the second rate is much higher than the first one. Condensate recovery by N$_2$ injection is not as sensitive to the rate and is equal for the first three levels of the rate. While the condensate recovery changes only about 5% from the higher rate to the lower one for N$_2$ injection, this change for CO$_2$ injection is 14%.

In the case of CH$_4$ injection and gas cycling, changing the rate makes a noticeable change in recovery, especially in gas cycling.

**Figure 9.** Effect of different injection rates on condensate recovery with the injection at initial reservoir pressure
3.4- Effect of injection duration
Effect of injection duration has been investigated by changing the injection duration from 10 years to 8 and 5 years for all the injection gases with an injection rate of 75% of the production rate, and the results are shown in Fig. 10.
In the cases of CO₂ and CH₄ injection and gas cycling, the recovery increases by increasing the injection duration from 5 to 8 years, while this increase is not considerable from 8 years of injection to 10 years.
In the case of N₂ injection, increasing the injection period from 5 years to 8 and 10 years makes no change in condensate recovery.

3.5- Consideration of gas and condensate recovery factor
The condensate and gas recovery factors of all of the runs of the simulated model have been given in Tables 4-7. In these tables, the effect of all parameters investigated in this study can be observed. The early breakthrough of all injection gases with high injection rates results in considerable reduction in the ultimate gas recovery, and discourages their use in condensate recovery enhancement.
It should be remembered that the result of an injection work in a reservoir greatly depends on the reservoir fluid. The effect of mixing the injection gases with the reservoir fluid can cause different responses in different reservoirs. This results from a thermodynamic analysis of gas injection in two gas-condensate reservoirs [13].

Figure 10. Effect of changing the injection duration on condensate recovery with an injection rate of 1.8 (MMSCF/D)
### Table 3. Composition of recycled gas

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S</td>
<td>0.0814</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2.1819</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.2028</td>
</tr>
<tr>
<td>C$_1$</td>
<td>84.5192</td>
</tr>
<tr>
<td>C$_2$</td>
<td>5.4475</td>
</tr>
<tr>
<td>C$_3$</td>
<td>1.9126</td>
</tr>
<tr>
<td>IC$_4$-NC$_4$</td>
<td>1.1253</td>
</tr>
<tr>
<td>IC$_5$-NC$_5$</td>
<td>0.5585</td>
</tr>
<tr>
<td>FC$_6$-C$_9$</td>
<td>0.9156</td>
</tr>
<tr>
<td>C$<em>{10}$-$C</em>{13}$</td>
<td>0.0554</td>
</tr>
<tr>
<td>C$_{14+}$</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

### Table 4. Recovery factors at the injection pressure of 5248 (psia), (initial reservoir pressure)

<table>
<thead>
<tr>
<th>Rate</th>
<th>Component</th>
<th>CO$_2$</th>
<th>N$_2$</th>
<th>CH$_4$</th>
<th>Cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4 (MMSCF/D)</td>
<td>Condensate</td>
<td>73.828</td>
<td>64.597</td>
<td>73.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>52.376</td>
<td>52.376</td>
<td>52.376</td>
<td></td>
</tr>
<tr>
<td>1.8 (MMCSF/D)</td>
<td>Condensate</td>
<td>72.828</td>
<td>64.938</td>
<td>69.836</td>
<td>80.139</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>78.349</td>
<td>78.524</td>
<td>78.571</td>
<td>78.571</td>
</tr>
<tr>
<td>1.2 (MMSCF/D)</td>
<td>Condensate</td>
<td>67.298</td>
<td>64.025</td>
<td>65.589</td>
<td>71.947</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>86.793</td>
<td>88.129</td>
<td>88.49</td>
<td>88.163</td>
</tr>
<tr>
<td>0.6 (MMSCF/D)</td>
<td>Condensate</td>
<td>59.989</td>
<td>59.796</td>
<td>60.604</td>
<td>63.003</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>89.009</td>
<td>89.856</td>
<td>89.855</td>
<td>89.646</td>
</tr>
</tbody>
</table>

### Table 5. Recovery factors at the injection pressure of 4500 (psia)

<table>
<thead>
<tr>
<th>Rate</th>
<th>Component</th>
<th>CO$_2$</th>
<th>N$_2$</th>
<th>CH$_4$</th>
<th>Cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4 (MMSCF/D)</td>
<td>Condensate</td>
<td>74.018</td>
<td>64.097</td>
<td>70.489</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>41.907</td>
<td>41.906</td>
<td>52.404</td>
<td></td>
</tr>
<tr>
<td>1.8 (MMCSF/D)</td>
<td>Condensate</td>
<td>71.197</td>
<td>64.739</td>
<td>67.323</td>
<td>76.365</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>77.839</td>
<td>70.719</td>
<td>78.593</td>
<td>78.593</td>
</tr>
<tr>
<td>1.2 (MMSCF/D)</td>
<td>Condensate</td>
<td>65.922</td>
<td>62.978</td>
<td>64.431</td>
<td>70.055</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>86.752</td>
<td>88.218</td>
<td>88.514</td>
<td>88.179</td>
</tr>
<tr>
<td>0.6 (MMSCF/D)</td>
<td>Condensate</td>
<td>59.547</td>
<td>58.767</td>
<td>59.921</td>
<td>61.702</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>88.832</td>
<td>89.793</td>
<td>89.855</td>
<td>89.596</td>
</tr>
</tbody>
</table>
Table 6. Recovery factors at the injection pressure of 3500 (psi)

<table>
<thead>
<tr>
<th>Rate</th>
<th>Component</th>
<th>CO₂</th>
<th>N₂</th>
<th>CH₄</th>
<th>Cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4 (MMSCF/D)</td>
<td>Condensate</td>
<td>72.057</td>
<td>63.167</td>
<td>72.808</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>52.376</td>
<td>27.077</td>
<td>27.077</td>
<td></td>
</tr>
<tr>
<td>1.8 (MMCSF/D)</td>
<td>Condensate</td>
<td>68.609</td>
<td>64.535</td>
<td>69.927</td>
<td>81.57</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>77.829</td>
<td>59.597</td>
<td>59.597</td>
<td>59.597</td>
</tr>
<tr>
<td>1.2 (MMSCF/D)</td>
<td>Condensate</td>
<td>64.247</td>
<td>61.587</td>
<td>63.227</td>
<td>67.668</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>86.628</td>
<td>88.422</td>
<td>88.571</td>
<td>88.211</td>
</tr>
<tr>
<td>0.6 (MMSCF/D)</td>
<td>Condensate</td>
<td>58.996</td>
<td>57.231</td>
<td>58.92</td>
<td>59.894</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>88.339</td>
<td>89.428</td>
<td>89.65</td>
<td>89.321</td>
</tr>
</tbody>
</table>

Table 7. Recovery factors at the injection pressure of 2500 (psi)

<table>
<thead>
<tr>
<th>Rate</th>
<th>Component</th>
<th>CO₂</th>
<th>N₂</th>
<th>CH₄</th>
<th>Cycling</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4 (MMSCF/D)</td>
<td>Condensate</td>
<td>67.33</td>
<td>61.678</td>
<td>64.641</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>52.405</td>
<td>52.405</td>
<td>52.405</td>
<td></td>
</tr>
<tr>
<td>1.8 (MMCSF/D)</td>
<td>Condensate</td>
<td>64.657</td>
<td>60.689</td>
<td>63.27</td>
<td>69.061</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>77.838</td>
<td>78.592</td>
<td>78.593</td>
<td>78.593</td>
</tr>
<tr>
<td>1.2 (MMSCF/D)</td>
<td>Condensate</td>
<td>62.122</td>
<td>58.811</td>
<td>61.202</td>
<td>63.702</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>83.553</td>
<td>85.811</td>
<td>86.894</td>
<td>86.125</td>
</tr>
<tr>
<td>0.6 (MMSCF/D)</td>
<td>Condensate</td>
<td>56.988</td>
<td>54.794</td>
<td>66.801</td>
<td>56.747</td>
</tr>
<tr>
<td></td>
<td>Gas</td>
<td>85.92</td>
<td>87.613</td>
<td>88.193</td>
<td>87.63</td>
</tr>
</tbody>
</table>
By doing an economical evaluation the optimum case for the injection can be determined. The factors that can affect the decision of selecting one of the cases studied are: the price of the gas and condensate, the price of the injection gas, expenses of the facilities needed in each injection condition and the separation of the injection gas from the reservoir gas.

4- Conclusions

- Gas cycling is the most effective way to increase the condensate recovery.
- By reducing the injection rate capability of CO₂, CH₄, N₂ and gas cycling in condensate recovery approaches together.
- CO₂ injection results in removing the condensate accumulated in the near wellbore region during the injection period and it can also prevent the accumulation of the condensate for a certain time after the injection is stopped.
- Condensate recovery by N₂ injection changes very slightly when the injection is implemented in different reservoir pressures.
- Injecting at pressures lower than the initial pressure of the reservoir results in greater or the same condensate recovery in some cases (compared to the case of injecting at initial reservoir pressure).
- Condensate recovery by N₂ injection changes slightly by changing the injection rate.
- Increasing the injection duration from 5 years to 8 and 10 years has no effect on the condensate recovery when N₂ is injected. In cases of CO₂ and CH₄ injection and gas cycling the recovery increases by increasing the injection duration, but this increase is not considerable from 8 years of injection to 10 years.

References


Extension of Trout Fish Shelf Life by Ozone Treatment

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1- Chemical Engineering Department, Islamic Azad University, Science and Research Branch, Tehran, Iran.
2- Food Engineering, Islamic Azad University, Science and Research Branch, Terhan, Iran.

Abstract
The shelf life of fish was extended using disinfection properties of ozone. For this purpose, Trout specimens were exposed to ozone in the aqueous media for two hours and their microbial growth and biochemical properties were measured over time. Microbial growth of ozone treated fish was significantly slower than the control sample, resulting in lower counts of bacteria (Acceptable point: less than $5 \times 10^4$/gr or cm$^2$). According to the biochemical tests, ozone treatment had no negative effects on fat, protein and the humidity of the fish. Peroxide and TVN (Total Volatile Nitrogen) measurements showed that treatment by ozone increased the trout shelf life from 4 days to 6 days. According to the sensory analysis, no changes were observed in the color or flavor of the ozone treated trout.

Keywords: Fish, Ozone, Shelf Life, Trout

1- Introduction
Fish is one of the most important resources of the human food. Fish is extremely perishable, which restricts its consumption in a reasonably fresh state to the immediate vicinity of where it is caught. Bacteria degrade fish constituents, particularly non-protein nitrogenous compounds, typically associated with fish spoilage [1]. As mentioned by Whittle [2] the nature of the fish species, handling and storage conditions are key parameters that affect fish spoilage. Different technologies have been applied in order to reduce the fish perishability and hence increase its short shelf life. It has been demonstrated elsewhere [3-6] that the use of slurry ice extends the shelf life of sardine and non-fat fish species, such as Farmed Sea Bream, European Hake and shrimp. Since the 1920’s scientists have tried to apply the powerful disinfection properties of ozone to slow down the spoilage and improve the safety of fishery products. Ozone (O$_3$) is generated from oxygen (O$_2$) by either ultraviolet (UV) radiation or a high voltage electrical discharge. Ozone kills micro-organisms by oxidizing and destroying their cell wall. It has the advantage of being able
to kill resistant microorganisms such as bacterial spores, cysts and viruses at relatively low concentrations, without requiring a long exposure time.

The United States Food and Drug Administration [7] granted "Generally Recognized As Safe" (GRAS) status for use of ozone in bottled water in 1982. Ozone was approved by the US Department of Agriculture [8] for reconditioning the recycled poultry chilling water in 1997. FDA has approved the use of ozone in gaseous and aqueous phases as an antimicrobial agent on food, including meat and poultry [9].

Various reports [10] explained the possibility of use of ozone to disinfect the food surfaces. In the present research, samples of caught trout were immersed in ozonated water for two hours time in order to achieve a better microbial control and improve the shelf life.

2- Materials and methods

Freshly caught trout specimens were obtained from local fish farms. The specimens were about 25 cm in size and their average weight was about 300gr. Ozone was generated by a compact ozone generator (Arda, Ozoneuf, Model COG 40A, France) which used atmospheric air as the source of oxygen. The produced combination of ozone and air was injected into the bottom of the water container by a suitable internal pump. Ozone concentration in the water reached 0.1mg/lit in 20 minutes of ozonation and was kept constant during the experiments. When ozone concentration reached 0.1 mg/lit, the experiments began by immersing the fish specimens in this ozone treated water. After two hours exposure to ozone the trout were removed and put in isolated containers (in a closed, sterile box) stored at 5 ºC in a refrigerator.

The microbial tests were performed on the trout sample exactly when the ozone treatment finished in accordance with "MICRO-ORGANISMS OF FOOD, published by the International Commission on Micro-biological Specification for Foods (ICMSF)". In microbiology, Colony-Forming Unit (CFU) is a measure of viable bacteria numbers. For convenience, the results are given as CFU/ml which measures viable cells (Colonies per milliliter). Generally, log (CFU/ml) or log (CFU/Cm²) are used for calculations.

Based on the test method, the microbial tests were performed at different concentrations (Dilutions). Brine 5% was used as the diluting agent. For the current research, three dilutions of the main sample were prepared (0.1, 0.01, and 0.001). Then the bacteria growths in these samples were measured. On days 1, 3, 5, 7 and 9 after treatment, the samples were taken from the ozone treated fish specimens for biochemical tests i.e., Humidity, Protein, Peroxide Number, TVN (Total Volatile Nitrogen) and Free Fat according to the international standards:

(1) Humidity: International Organization for Standardization R-1442,

(2) Free Fat: ISO 1444-1998 Meat and meat products, determination of fat content,


(4) TVN, (I.S.O.R. meat and meat products Determination of Reference method)

(5) Protein, the Association of Analytical
The aim of these measurements was to investigate the effect of ozone on biochemical properties of fish flesh. All tests were repeated three times, and the average results were reported.

3- Results

Results of microbial growth measurement on the skin of ozone treated trout (storage at 5°C) are depicted in Fig. 1. This figure shows that control fish allowed for a notable increase in the microbial population, whereas for the ozone treated fish, microbial growth was significantly slower, resulting in lower counts of bacteria.

![Figure 1. Microbial measurements for the ozone treated fish sample and control](image1)

Figs. 2 to 4 shows that ozone treatment has no destroying effect on the fish biochemical properties. Humidity and Free Fat of the control fish and the ozone treated samples are equal as depicted in Fig. 2. The results of the protein measurement are shown in Fig. 3. This diagram shows that the protein of the ozone treated fish is slightly higher than the control. Ozone removes the contaminants which can destroy the protein, resulting in detecting a better level of protein compared to control. Nonetheless, small observed changes can be because of experimental errors.

![Figure 2. Humidity and Free Fat changes in the ozone treated fish sample and control](image2)

TVN and peroxide tests (Fig. 4) show that ozone treatment increases the shelf life of trout from 4 days to 6 days as compared to the control fish.

![Figure 3. Changes in the protein of the ozone treated fish sample and control](image3)

![Figure 4. Variations in peroxide No. and TVN of ozone treated fish sample and control](image4)

4- Discussion

This research attempted to identify the effect of ozone treatment on the shelf life of fish. It was found that suitable treatment by ozone
before any storage improves the microbiological and biochemical qualities of fish specimens and consequently prolongs their shelf life. Combination of ozone treatment and cold storage (at 5°C) will increase the fish shelf life considerably. A summary of the results of measurements are as follows:

- Ozone treatment of fish slows down its bacterial growth significantly, resulting in lower counts of bacteria.
- Ozone removes the contaminants from the fish skin, causing a higher protein number.
- Ozone treatment increases the shelf life of fish and helps in longer preservation time.
- Ozone has no negative impact on the biochemical properties of fish such as humidity, protein and free fat.
- Ozone leaves no residue on the fish and creates no changes to its color and flavor.

References
[11] In 1997 ozone gained the FDA approval of GRAS (Generally Recognised As Safe) and later in 2001 was allowed as a direct food additive in contact with food including...
meat and poultry (Title 21 part 173 section 173.368).

    Vol 8 section 801.415 revised April, US

[13] Institute of Standards and Industrial
    Research of Iran number 2394-ICS:
    07.100.30
Surface Adsorption of Polyethylene Glycol and Polyvinyl Alcohol with Variable Molecular Weights on Zinc Oxide Nanoparticles

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Abstract
Polymer adsorption by nanoparticles improves the stability of these types of suspensions against aggregation. In this work, the surface adsorption of polyethylene glycol (PEG) and polyvinyl alcohol (PVA) with different molecular weights onto the Zinc oxide (ZnO) nanoparticles is studied. The effects of solution pH value and temperature on the adsorption process are also investigated. The ZnO nanoparticles are then analyzed using Fourier transform infrared (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA) techniques. The aggregation of nanoparticles before and after polymer adsorption is also investigated by scanning electron microscopy (SEM). The results show that by adsorbing the PEG and PVA, due to a relatively large electrostatic repulsive force between ZnO nano particles, the size of aggregated nanoparticles decreases. It has also been revealed that the low molecular weight polymers exhibit a higher adsorption rate on the particles’ surfaces in comparison to the polymers with high molecular weight.

Keywords: Zinc Oxide Nanoparticles, Adsorption, PEG, PVA, Molecular Weight

1- Introduction
Nanosized ZnO particles are extensively used in producing bioceramics [1], porous ceramic parts employed in drug delivery systems [2], biosensors [3], nanocomposite membranes [4], catalysts for liquid phase hydrogenation [5], UV shielding material [6] and chemical adsorbent [7].

Control of colloidal properties and stability of the dispersion of ZnO particles is significantly important in the manufacturing of high-quality products such as ceramics, paper coatings, cosmetics, paints, rubber and plastic [8]. Attempts have been made to develop new techniques for manufacturing and modifying the nanoparticle preparation methods, e.g. using polyelectrolyte [9] or polymeric dispersant [10]. Nevertheless, aggregation, which occurs during the formation of these particles is a common problem. Particle aggregation can form through various methods. Taking into

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account that one of the key parameters of the quality of ZnO nanoparticles is their tiny size, the production process should be designed in a way that the particles do not stick together, i.e. do not aggregate, since the aggregation results in an undesirable growth of ZnO nanoparticles [11]. Agglomeration of nanosized ZnO may occur because of the following reasons: 1) ZnO nanoparticles, having a tendency towards other nanoparticles, possess high surface energy, therefore agglomeration may occur when they are dispersed in an organic solvent and matrices. 2) Formation of the bonds of Zn-O-Zn among nanoparticles due to the existence of water molecules resulting in hard agglomerates, which impede the applications of ZnO nanoparticles [12]. Therefore, removal of water moiety in precursors is a key process for reducing hard agglomerates. Various methods were employed to remove the water in precursors, e.g. rinsing via organic solvent, and this has already been adopted by one research group [13]. Polymer coating is an effective way for modifying the particles’ surface and it also prevents the agglomeration of ZnO nanoparticles. A large number of studies have been conducted to investigate the effects of adsorption of polymers on the rheological and stability behavior of different metal oxide suspensions; such as aluminum oxide suspension [14], zirconium oxide suspension [15], and aluminosilicates (zeolites) suspension [16]. The adsorption of polymeric additives on the metal oxide surface is ascribed to a combination of chemical and electrostatic interactions, hydrogen bonding and van der Waals force. For nonionic polymers, hydrogen bonding is the primary adsorption mechanism [17]. In this study, polyethylene glycol (PEG) and polyvinyl alcohol (PVA) are used in order to prevent zinc oxide nanoparticles from aggregation. Effective factors of polymer adsorption such as molecular weight are discussed. The formed bonds between PEG and PVA macromolecules are due to the existence of hydrogen bonds and the ionic attractions between them. The repulsive electrostatic forces between the chains of these polymers prevent the nanoparticles from accumulating.

2- Experimental
2.1- Materials
Commercially available ZnO nanoparticles, purchased from Sepahan Ruy Company, Esfahan, Iran, are used for these experiments. It is claimed that the chemicals have been synthesized by sol-gel method. The specific surface area of the sample that is determined using BET method is 70 m$^2$/g. PEG with molecular weights of 1000, 2000, and 10000 and PVA with molecular weights of 49000, 70000-100000 are purchased from Merck. For all the experiments double distilled water is used.

2.2. Adsorption of various molecular weights of PEG and PVA on ZnO nanoparticles
1.5g of ZnO nanoparticles are mixed with 50cm$^3$ of distilled water. For monitoring the stability, the pH of suspension is monitored every 5 minutes and controlled by NaOH or HCl [18]. 10g of PEG with a molecular weight of 1000 are solved in 90cm$^3$ of distilled water. This solution is then added to the suspension of ZnO nanoparticles. In order for adsorption to take place, the mixture is stirred with a magnetic stirrer with
the medium speed at room temperature for 48 hours. The particles that are dissolved in water yet not adsorbed by ZnO are separated from those particles that have been absorbed by centrifuging. The powder is dried in an oven at 90°C for 8 hours. The aforesaid steps are repeated for PEG particles with molecular weights of 2000 and 10000, and for PVA particles with molecular weights of 49000, 70000-100000.

IR analysis is carried out on a FT-IR spectrometer (Model Galaxy series FT-IR 5000) to characterize the interface of ZnO/PEG and ZnO/PVA. The size and structure of the zinc oxide nanoparticles is analyzed by X-ray diffraction with monochromatic CuKα radiation (\( \lambda = 1.54 \AA \)). The amount of molar mass of the adsorbed polymer on the surface of ZnO nanoparticles is measured by thermogravimetry analysis (Perkin Elmer Diamond TG/DTA), using a heating rate of 10°C/min to 500°C and finally, the aggregation and accumulation of the nanoparticles is analyzed by Scanning electron microscope (Philips XL30).

3- Results and discussion

3.1- pH results

Table 1 shows the result of pH value for the suspension solution after adding PEG/PVA to the solution. Before polymer addition, pH is increased by adding water to the ZnO nanoparticles in the beaker because of the occurrence of two simultaneous reactions (Eqs. 1 and 2). Based on Figs. 1 and 2, both of these bond formations are desirable, therefore due to the presence of the hydrogen bonds, some bonds are formed between ZnO nanoparticles and the PEG and PVA macromolecules in the aqueous phase (Fig. 1) and the ionic attraction (Fig. 2). As Table 1 shows, the neutralization of the aqueous solution occurs after adding PEG/PVA to the ZnO suspension. This result agrees with the above theoretical description.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>&gt;25</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.19</td>
<td>7.20</td>
<td>7.28</td>
<td>7.33</td>
<td>7.34</td>
<td>7.36</td>
<td>7.36</td>
</tr>
</tbody>
</table>

The following reactions are suggested to take place.

\[
\begin{align*}
\text{ZnO} + \text{H}_2\text{O} & \leftrightarrow \text{Zn(OH)}_2 \\
\text{Zn(OH)}_2 & \leftrightarrow \text{Zn}^{2+} + 2\text{H}_2\text{O}
\end{align*}
\]

Based on the Kramer theory, this coating prevents nanoparticles from sticking together and aggregating, by the repulsive electrostatic forces formed between the polymeric chains (Fig. 3) [19].

![Figure 1. The formed bonds between ZnO nanoparticles and a) PEG, b) PVA macromolecules due to the presence of hydrogen bonds](archive_of_sid/figures/figure1.png)
Figure 2. The formed bonds between ZnO nanoparticles and a) PEG, b) PVA

3.2- IR spectra
IR spectroscopy gives qualitative information about the way in which the adsorbed PEG molecules are bonded to the surface of the ZnO nanoparticles. Fig. 4 compares the IR spectra of ZnO nanoparticles in the absence and presence of adsorbed PEG2000. According to Fig. 4(a), the peak seen at 3455 cm\(^{-1}\) indicates the presence of hydroxyl group.

Figure 3. The suggested model for the repulsive electrostatic forces formed between the coated polymers

Figure 4. FTIR analysis of a) ZnO Nanoparticles, b) ZnO Nanoparticles with PEG2000
The absorption peak in the 2850 cm\(^{-1}\) in the spectrum of Fig. 4(b) corresponds to the CH group stretching vibration of PEG 2000. It proves that the molecules of PEG 2000 are adsorbed by the ZnO nanoparticles. The peak appearing at 3410 cm\(^{-1}\) in Fig. 4(b) shows the presence of the hydroxyl group, which has shifted towards lower wave numbers in comparison with the hydroxyl group peak in the ZnO nanoparticles (3455 cm\(^{-1}\)). It proves that hydrogen bonds have been formed between the PEG particles and ZnO nanoparticles.

3.3- X-ray diffraction studies
To investigate the size and structure of zinc oxide nanoparticles, X-ray diffraction patterns of pure nano-ZnO particles and coated nano-ZnO particles are shown in Fig. 5. The XRD pattern of pure ZnO nanoparticles is shown in Fig. 5(a). No peaks from other phases of ZnO and impurities are observed; suggesting that high purity ZnO is obtained. The sharp peaks in this figure reveal a desirable crystalline structure.

![XRD patterns](image)

Figure 5. XRD patterns of a) ZnO nanoparticles, b) ZnO nanoparticles + PEG 1000, c) ZnO nanoparticles + PEG 2000, d) ZnO nanoparticles + PEG 10000, e) ZnO nanoparticles + PVA 49000, and f) ZnO nanoparticles + PVA 70000-100000.
The nanoparticles' diameter is calculated by Debye-Sherrer equation:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

(3)

where \( K \) is Sherrer constant, \( \lambda \) is the X-ray wavelength, \( \beta \) is the peak width of half-maximum, and \( \theta \) is the Bragg diffraction angle. The XRD peaks give the average diameter of about 44.2nm for pure ZnO nanoparticles. Comparing the XRD patterns of ZnO nanoparticles (Fig. 5-a) with those of ZnO nanoparticles coated with PEG 1000 (Fig. 5-b), PEG 2000 (Fig. 5-c), PEG 10000 (Fig. 5-d), PVA 49000 (Fig. 5-e), and PVA 70000-100000 (Fig. 5-f), indicates that the coated samples have the same patterns as the ZnO nanoparticles. This fact shows that adsorption of PEG and PVA with various molecular weights on ZnO particles does not change the crystalline structure of ZnO nanoparticles. Moreover, sharp peaks, which indicate a crystalline structure, are seen in all coated samples. Table 2 shows the size of the particles obtained by coating ZnO nanoparticles. It should be noted that the size of the ZnO nanoparticles without coating is about 44.2nm.

Table 2. Size of coated ZnO nanoparticles calculated by Debye-Sherrer equation

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Adsorbed Polymer on ZnO Nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.0</td>
<td>PEG 1000</td>
</tr>
<tr>
<td>44.2</td>
<td>PEG 2000</td>
</tr>
<tr>
<td>44.2</td>
<td>PEG 10000</td>
</tr>
<tr>
<td>35.4</td>
<td>PVA 49000</td>
</tr>
<tr>
<td>44.2</td>
<td>PVA 70000-100000</td>
</tr>
</tbody>
</table>

Considering the calculated sizes of the ZnO nanoparticles that adsorbed PEG with three different molecular weights and those that adsorbed PVA with two different molecular weights, reveals that the size of ZnO particles decreases as the molecular weight of the adsorbing material decreases. A possible explanation for this result is as follows: The low molecular weight prevents ZnO nanoparticles from aggregation and compression. Therefore, the size of these particles is smaller than the size of pure ZnO nanoparticles. As the molecular weight increases, the size of the coated particles does not significantly vary in comparison with the size of the ZnO nanoparticles. The reason is that the molecular weight of the polymer is very high and therefore, it causes nanoparticles to adsorb a lower amount of molecules with higher molecular weight, while it still prevents nanoparticles from aggregation.

3.4- TGA analysis of nanoparticles

The molar mass of the adsorbed polymer on the surface of ZnO nanoparticles is determined through the weight loss at 500°C in nitrogen using thermogravimetric analysis (TGA). The weight loss curve of coated ZnO nanoparticles is shown in Fig. 6. TG results show that there is a weight reduction in all tested samples when the temperature increases. Qualitative analysis shows that polymer molecules are adsorbed on ZnO nanoparticles.
Table 3. TGA results of polymer degradation adsorbed on ZnO nanoparticles

<table>
<thead>
<tr>
<th>Adsorbed Polymer on ZnO Nanoparticles</th>
<th>Initial weight (wt. %)</th>
<th>Final weight (wt. %)</th>
<th>Final temperature</th>
<th>Weight loss $\Delta W_{\text{mol}}$ (%)</th>
<th>Mole loss $\Delta W_{\text{mol}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG 1000</td>
<td>100</td>
<td>98.104</td>
<td>500</td>
<td>1.896</td>
<td>1.86× 10^{-3}</td>
</tr>
<tr>
<td>PEG 2000</td>
<td>100</td>
<td>96.936</td>
<td>500</td>
<td>3.064</td>
<td>1.53× 10^{-3}</td>
</tr>
<tr>
<td>PEG 10000</td>
<td>100</td>
<td>99.560</td>
<td>500</td>
<td>0.440</td>
<td>0.044× 10^{-3}</td>
</tr>
<tr>
<td>PVA 49000</td>
<td>100</td>
<td>98.543</td>
<td>500</td>
<td>1.457</td>
<td>2.973× 10^{-5}</td>
</tr>
<tr>
<td>PVA 70000-100000</td>
<td>100</td>
<td>98.435</td>
<td>500</td>
<td>1.565</td>
<td>1.565× 10^{-5}</td>
</tr>
</tbody>
</table>

Figure 6. TG graphs for: a) ZnO nanoparticles + PEG 1000, b) ZnO nanoparticles + PEG 2000, c) ZnO nanoparticles + PEG 10000, d) ZnO nanoparticles + PVA 49000, and e) ZnO nanoparticles + PVA 70000-100000
Values given in Table 3 show the molar percentage of adsorbed polymer on ZnO nanoparticles. As the molecular weight of both tested polymers increases, the amount of absorption decreases. The polymer chain length increases when the molecular weight of the polymer increases. When the polymer molecules form hydrogen bonds with ZnO nanoparticles, the polymeric chain starts to scatter around in a wave-like movement, thus preventing other polymeric chains from connecting to ZnO nanoparticles. The less the polymer molecular weight, the shorter the chains’ length will be. Therefore, the spatial prevention will decrease, resulting in an increase in the amount of adsorbed polymer (Fig. 7). In this work, ZnO nanoparticles are coated with polymers with lower molecular weights in order to increase the amount of adsorbed polymer, and the results of TG analysis are confirmed. Since the coated particles have a more extended distribution than the ZnO nanoparticles’ sample, their diameter is shorter than that of the main sample. This fact confirms the results of XRD analysis as well.

Fig. 8 shows the relation between molecular weight and molar weight percentage of adsorbed polymer on samples coated by PEG and PVA. These charts show that there is a linear relation between the molar weight percentage and the molecular weight of the samples.

![Figure 8. percentage change of molar weight verses molecular weight for samples adsorbed: a) PEG and b) PVA](image)

3.5- SEM images
The SEM images of the pure and coated ZnO particles are shown in Fig. 9. The images show that uncoated ZnO nanoparticles are aggregated and compressed (Fig. 9a), while coated nanoparticles have a better distribution and homogeneity. SEM images also show that the samples with less
molecular weight have a better distribution. This is because the particles are less aggregated in the lower molecular weight of the samples, and therefore the particles' sizes are smaller than the size of uncoated ZnO nanoparticles. This fact confirms the results of the XRD analysis.

**4- Conclusions**

IR spectroscopy shows that ZnO nanoparticles are prone to adsorption of polyethylene glycol and polyvinyl alcohol. PVA and PEG form hydrogen bonds with the surface of ZnO nanoparticles. Results obtained by XRD analysis show that the coating process does not change the crystalline structure of the ZnO nanoparticles. Therefore, the characteristics of the ZnO nanoparticles, which are dependent on its crystalline structure, will remain unchanged. The diameter of coated ZnO nanoparticles is shorter for lower molecular weights. The average diameter size of the particles coated with PEG 1000 is less than that of the particles coated with PVA 49000. Results obtained by TG analysis show that the amount of adsorbed polymer on ZnO nanoparticles increases as the molecular weight decreases. There is an approximate linear relation between the molecular weight and the molar weight percentage of the adsorbed polymer. SEM images show that in both methods of coating, the distribution of ZnO nanoparticles improves and particles aggregate less as the molecular weight decreases. The distribution of ZnO nanoparticles coated with PEG is more than even that of the particles coated with PVA. In addition, ZnO nanoparticles coated with PEG are more spherical and have a smaller size.

![Figure 9. SEM images (7500 x) of: a) ZnO nanoparticles, b) ZnO Nanoparticles + PEG 1000, c) ZnO Nanoparticles + PEG 2000, d) ZnO Nanoparticles + PEG 10000, e) ZnO Nanoparticles + PVA 49000, and f) ZnO Nanoparticles + PVA 70000-100000](image_url)
5- Acknowledgement
The authors would like to thank Ms. Niloufar Nabiyouni for her assistance in editing the English text.

References
[17] Zhang, Y. W., Tang, M. and Jin, X., "Polymeric adsorption behavior of


Abatement of Benzyl Alcohol and Methyl Ethyl Ketone (MEK) from Polluted Air Over Nanostructured Mn-Supported Alumina Catalyst

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Abstract
Total combustion of methyl ethyl ketone and benzyl alcohol as two models of volatile organic compounds (VOCs) using catalytic method was studied over γ-Al₂O₃ and Mn/γ-Al₂O₃ catalysts. Catalyst (Mn/γ-Al₂O₃) was prepared by wet impregnation and characterized using XRD, BET, ICP-AES and SEM methods and the nanostructure of the catalyst were approved. The activity of the catalysts was measured in a catalytic packed bed reactor under atmospheric pressure and different reaction temperatures at range 150 to 450°C. The studies confirmed that manganese supported on γ-Al₂O₃ can be suitable for the abatement of the mentioned pollutants from contaminated air and hopefully holds the promise for the elimination of VOC containing hazardous materials in industrial applications.

Keywords: Mn/γ-Al₂O₃, VOCs, Catalytic Oxidation, Benzyl Alcohol, Methyl Ethyl Ketone

1- Introduction
Abatement of pollutant volatile organic compounds (VOCs) has become one of the most important tasks for air pollution control. Among the VOCs, methyl ethyl ketone (MEK, 2-butanone) and benzyl alcohol are two of the main pollutants [1]. Methyl ethyl ketone is a ketone widely used as solvent in many industrial applications such as adhesives and paints. In addition, it is a natural component in food stuffs [2]. It is released into the environment from such sources as building materials, consumer products, and tobacco smoke [3]. It is hazardous and its emission into the atmosphere has to be controlled according to environmental regulations [4]. From the human health viewpoint, this odorant can be harmful even below its normal human perception level. The odor threshold values of this VOC have been prescribed by various authors and agencies such as 5400 ppb, by The United States Environmental Protection Agency (EPA) [5], and 440 ppb prescribed by Nagata and coworkers [6]. Benzyl alcohol, an aromatic primary alcohol, is used as a solvent in paint stripper and waterborne coating applications and as an intermediate

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for the synthesis of target molecules used in pharmaceuticals, cosmetics, preservatives, and flavoring and fragrance agents [7]. This alcohol is one of the pollutant VOCs and its abatement is necessary [8].

The oxidation of the VOCs is a way for removing these pollutants from the environment. The oxidation on catalysts takes place at temperatures which are lower than those required for thermal destruction [9]. This is important in order to improve the economy of the process. In the catalytic incineration, VOCs react with oxygen (usually, most of the VOCs emissions are diluted in air) in the presence of a catalyst, yielding H2O and CO2 without the formation of by-products and in such processes, partial oxidation reactions must be avoided. According to much stricter limits for the emissions of some oxidized compounds, the presence of even small amounts of species like aldehydes, can make the mixture resulting from catalytic combustion processes even more of a pollutant than the waste to be purified [10-16].

Nanostructure catalysts are of topical interest because of their intriguing properties different from those of their corresponding bulk catalysts. Due to their unique properties, they were employed in various catalytic applications. There are many reports in the literature on the synthesis of transition metal nanoparticles and their application as catalysts [17-20]. The metal oxide particles are the key compounds of the catalyst. They are responsible for the activity and selectivity of the catalyst. The activity of the catalyst will generally depend on the size of the metal oxide particles, where a catalyst with small particles will give high activity due to the large number of atoms available on the particles surfaces [21].

2- Material and methods

2.1- Materials
The commercial nanostructure γ-Al2O3 powder (BET=190 m²/g) was supplied by Merck industry and was used as a catalyst without further purification or treatment. The precursor metal salt, Mn(NO3)2 was also purchased from Merck Industry. All the other solvents and chemicals were obtained from commercial sources and were used without further purifications.

2.2- Preparation of Mn/γ-Al2O3 nano particles
Wet impregnation method was used for loading the metal on the support surface. The γ-Al2O3 particles was added to 0.1 M aqueous solution of Mn(NO3)2 and stirring was carried out for 12 h at room temperature. Afterward, the resulting emulsion was centrifuged and filtered using deionized water several times. Mn/γ-Al2O3 catalyst was obtained after drying at 105°C and consequently calcinating in air at 450°C for 4h. The prepared Mn/γ-Al2O3 contains 4.6 wt. % of manganese and its surface area was 145.5 m²/g.

2.3- Characterization of catalysts
The γ-Al2O3 and Mn/γ-Al2O3 were characterized by XRD, SEM, BET and ICP-AES methods. Powder X-ray diffraction (XRD) was used to identify the crystalline phase presence in the catalysts. A Siemens D500 diffractometer with Cu Kα (λ=0.154 nm) radiation was used. The morphology study of the catalysts was studied using scanning electron microscopy (SEM).
images of the samples were recorded on a EQ-C1-1 microscope. Brunauer-Emmett-Teller (BET) surface areas of the samples were determined by N₂ adsorption-desorption using a Micrometrics (Gimini2375) surface area analyzer. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) method was used for determining the amount of metal loaded on the support (based on the weight percent of metal in the final catalyst).

2.4- Determination of catalyst activity
The activity of the catalysts was measured in a 0.8 cm i.d continuous flow tubular glass reactor fixed in an experimental set up shown in Fig. 1. Catalyst (0.2 g) was placed over a plug of glass wool and placed inside of a U shaped reactor. The N₂ flow is used as the carrier gas for evaporation of VOC (MEK and benzyl alcohol) and purified air is used as the oxygen supplier flow. The feed gases were pre-mixed in the mixing chamber and sent to the reactor. The reaction was operated under steady state in atmospheric pressure. Gas phase products of the reaction were trapped and analyzed by gas chromatography using Shimadzu 2010 GC. The fractional conversion of VOC (Xᵥₒ₃) in this study is defined as equation (1).

\[
X_{\text{VOC}} = \frac{N_{\text{initial}} - N_{\text{final}}}{N_{\text{initial}}} \quad (1)
\]

Where \( N_{\text{initial}} \) is moles of VOC present initially and \( N_{\text{final}} \) is moles of VOC present after the reaction completes.

![Figure 1. Schematic of experimental setup](image-url)
3- Results and discussion

3.1- XRD characterization of catalysts

Fig. 2 shows the XRD patterns of γ-Al₂O₃ and Mn/γ-Al₂O₃ samples. Three intense characteristic peaks of γ-Al₂O₃ (2θ = 37°, 45° and 67°) were observed in both spectra, which was in agreement with the published literature [22, 23]. The crystal size of the γ-Al₂O₃ was determined using Scherer equation through the XRD pattern of γ-Al₂O₃, which was in nano scale (approximately 25-30 nm). From the Mn/γ-Al₂O₃ pattern, typical diffraction peaks of crystalline Mn oxides cannot be observed, except those of γ-Al₂O₃ support. In addition, decreasing the intensity of characteristic peaks corresponding to γ-Al₂O₃ can be observed. It seems to suggest that through the impregnation of γ-Al₂O₃ the adsorption of the salt solution has occurred and during the drying and calcination in air the Mn-oxide particles have been formed and physically supported on the γ-Al₂O₃ surface in high dispersion form. The above conclusion is reasonable if we accept that the Outer-Sphere complex has been formed when the adsorption of Mn²⁺ occurs [24].

3.2- Scanning electron microscopy

The scanning electron micrographs of both γ-Al₂O₃ and Mn/γ-Al₂O₃ catalysts are shown in Fig. 3. The particles of the γ-Al₂O₃ are small (< 100 nm) and they have an approximately similar size. SEM images approved the particle size of γ-Al₂O₃ predicted by Scherer equation. Mn/γ-Al₂O₃ particles are more agglomerate compared to γ-Al₂O₃.
3.3- Catalytic activity
To study the catalytic activity of catalysts for conversion of VOCs, conversions of methyl ethyl ketone and benzyl alcohol over $\gamma$-Al$_2$O$_3$ and Mn/$\gamma$-Al$_2$O$_3$ were investigated. At first, the conversion of these compounds in absence of catalyst at different temperatures (thermal oxidation) were studied. Afterwards, $\gamma$-Al$_2$O$_3$ and Mn/$\gamma$-Al$_2$O$_3$ catalysts were tested. Light-off curves of conversion of benzyl alcohol in the absence of catalyst (thermal oxidation), and over $\gamma$-Al$_2$O$_3$ and Mn/$\gamma$-Al$_2$O$_3$ catalysts are shown in Fig. 4. In the absence of catalyst, a maximum conversion of 27% resulted for benzyl alcohol at 450 °C and at lower temperatures the conversion is very low. Conversion of benzyl alcohol over $\gamma$-Al$_2$O$_3$ is more than the conversion of benzyl alcohol in the absence of catalysts. This shows that at the finite temperature, the efficiency of catalytic oxidation is more than thermal oxidation. In addition, the modification of $\gamma$-Al$_2$O$_3$ with transition metals oxide (here manganese oxide) causes the catalytic activity of catalysts to improve, revealing the catalytic roles of these oxides in the Mn/$\gamma$-Al$_2$O$_3$.

A similar trend was obtained for the conversion of methyl ethyl ketone (MEK) the and following order resulted for the conversion of MEK: thermal oxidation $< \gamma$-Al$_2$O$_3 < $ Mn/$\gamma$-Al$_2$O$_3$. The maximum conversion of MEK at thermal oxidation is 24 % at a temperature of 450 °C.

It is observed that the conversions of benzyl

![Figure 3. SEM patterns of (a) $\gamma$-Al$_2$O$_3$ (b) Mn/ $\gamma$-Al$_2$O$_3$](image)

![Figure 4. Light-off curves of conversion of benzyl alcohol](image)
alcohol and MEK differ in the definite temperature. This is because of the difference in the molecular structure of organic compounds and their reactivity on catalysts.

![Figure 5. Light-off curves of conversion of MEK](image)

4- Conclusions
Catalytic conversions of benzyl alcohol and MEK on nanostructure pure and Mn-supported \( \gamma \)-Al\(_2\)O\(_3\) were studied. The studies show the better efficiency of catalytic oxidation compared to thermal oxidation for the conversion of organic compounds. In addition, it is resulted that the introduction of manganese onto \( \gamma \)-Al\(_2\)O\(_3\) improves the activity of Mn/\( \gamma \)-Al\(_2\)O\(_3\), which confirms the catalytic role of manganese in Mn/\( \gamma \)-Al\(_2\)O\(_3\). It is concluded that Mn/\( \gamma \)-Al\(_2\)O\(_3\) catalysts can be used as suitable catalysts in the catalytic conversion of organic compounds.

5- Acknowledgement
The authors wish to thank the Iranian Nanotechnology Initiative Council for their financial support. Furthermore, the authors are grateful to Mr. Bahrami for the XRD analysis and Mr. Safi-Shalamzari for his assistance in GC analysis.

References
Abatement of Benzyl Alcohol and Methyl Ethyl Ketone (MEK) from Polluted Air Over Nanostructured Mn-Supported Alumina Catalyst


The Experimental Study of Effective Parameters on Mean Drop Size in a Mixer-Settler

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Abstract
In this investigation, in order to study the effect of hydrodynamic parameters such as impeller speed and hold-up, two series of experiments have been performed with a single stage horizontal mixer-settler equipped with 2 four-blade impellers. In the first series, 15 experiments were carried out with toluene/water system and in the second series, 60 experiments were carried out with toluene/acetone/water system. Results show that in both systems, when the hold-up is constant, the mean drop size decreases with increasing impeller speed and when the impeller speed is constant, the mean drop size increases with increasing hold-up, however, these manners for any system are different quantitatively. It shows that with the addition of solute (acetone) concentration in the system, the mean drop size decreases. The experimental results were compared with the Desnoyer and Quadros models, of which the Quadros model has a little deviation from Desnoyer model.

Keywords: Mean Drop Size, Hold-Up, Solute, Mixer-Settler, Impeller Speed

1- Introduction
Many industrial processes (solvent extraction, emulsification, polymerisation in emulsion) involve liquid–liquid dispersions in stirred vessels (mixers) and the knowledge of the resulting drop size distribution characteristics, or more exactly the evolution of this distribution with changes of external mechanical energy input, temperature or composition is of major importance. In solvent extraction processes for instance, the interfacial area of dispersion controls the mass transfer rate and is a key parameter for the design and scaling-up of gravity settlers that ensure the ultimate liquid phases separation. A large amount of work can be found in the literature concerning the prediction of drop size distributions in turbulent liquid–liquid dispersions in stirred vessels. The sizes of the drops depend on several factors such as impeller geometry, impeller speed, impeller location in the tank, feed phase ratio, and the physical properties of the description of the effect of all these factors on the drop sizes is required [1].

Among all the mean diameters, the Sauter mean diameter, D₃₂, is the most important since it is directly related to the interfacial

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area per unit volume, $a$, which determines the transfer rates of energy, mass and/or chemical reaction in dispersions. The relationship between the Sauter mean diameter, $D_{32}$, and the interfacial area per unit volume, is as follows:

$$a = \frac{6\phi}{D_{32}}$$  \hspace{1cm} (1)

Where, $\phi$ is the volume fraction of a dispersed phase (hold-up).

The Sauter mean diameter, $D_{32}$, is by definition the ratio of the third to the second moment of the probability density function [3]:

$$D_{32} = \frac{\int_{d_{\text{min}}}^{d_{\text{max}}} d^3 p(d) \, \text{d}d}{\int_{d_{\text{min}}}^{d_{\text{max}}} d^2 p(d) \, \text{d}d}$$  \hspace{1cm} (2)

or for any size distribution of discrete entities,

$$D_{32} = \frac{\sum_{i=1}^{k} n_i d_i^3}{\sum_{i=1}^{k} n_i d_i^2}$$  \hspace{1cm} (3)

Investigations were carried out for examination of the effect of parameters on the mean drop size in with and without solute. Some investigators studied the influence of the impeller speed and the dispersed phase hold-up fraction on the mean drop size for different systems (Chatzi et al. [4]; Skelland et al. [5]; Zerfa and Brooks [2]; Kumar et al. [6]; Boye et al. [7]; Ruiz et al. [8]; Ban et al. [9]; Desnoyer et al. [10]; Riberio et al. [11]).

2- Correlation for mean drop size

In order to accurately describe the phenomena occurring in an agitated liquid-liquid dispersion, appropriate models and correlations must be developed. A number of relationships have been proposed to describe the effects of column geometry, agitation condition, and physical properties of the liquid-liquid system on the drop size. Zhou and Kresta summarized the correlations proposed by many investigators.

It should be noted that most authors agree on the effect of Weber number on drop size, while the observed hold-up effects of the dispersed phase on the drop size are different, depending on the authors. This fact suggests that the drop coalescence behavior depends on the liquid-liquid systems investigated, and the physicochemical properties of liquid-liquid systems play an important role in controlling the drop size.

Some investigators focused their attention on the effect of interfacial tension and the direction of mass transfer on drop size. However, there have been few studies concerning the inherent physiochemical properties of solutes to influence the drop coalescence and breakage. Ban et al. succeed in quantitative prediction of the drop coalescence behavior in the toluene/acetone/water system from the viewpoint of mass transfer [9].

According to the Kolmogoroff theory of isotropic turbulence, drop size depends on $\text{We}^{-0.6}$, that is, $N^{-1.2}$.

$$\frac{D_{32}}{D} \propto (\text{We})^{-0.6} \text{ with } \text{We} = \frac{\rho_c N^2 D^3}{\sigma}$$  \hspace{1cm} (4)

Where $D$ is the impeller diameter, $\sigma$ and $\rho_c$ are interfacial tension and continuous phase...
density respectively [2].
The most frequently reported correlation is of the form:

$$\frac{D_{12}}{D} = C \tilde{f}(\phi)(We)^{0.6}$$ (5)

Here, C is constant.
The objective of this work is the study of the effect of hold-up and impeller speed on the mean drop size in with and without solute (acetone).

3- Apparatus description
The mixer-settler used in this work is single stage horizontal and contains 2 four-blade impellers. Impeller speed was controlled digitally and the flow rates of pumps were variable. The mixer-settler was made of glass and the flows were co-current. Fig. 1 shows a schematic diagram of the experimental set up. The mixer-settler geometry is tabulated in Table 1.

<table>
<thead>
<tr>
<th>Mixer-settler components</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing Chamber volume capacity</td>
<td>200 mL</td>
</tr>
<tr>
<td>Impeller type</td>
<td>2 four-blade</td>
</tr>
<tr>
<td>Impeller diameter</td>
<td>22.73 mm</td>
</tr>
<tr>
<td>Settling Chamber volume capacity</td>
<td>250 mL</td>
</tr>
<tr>
<td>Settling Chamber length</td>
<td>19.5 cm</td>
</tr>
</tbody>
</table>

4- Chemical systems used and experimental works
The plant was operated with and without solute. Acetone was chosen as the solute, water as a continuous phase and toluene as the dispersed phase. The physical properties of the liquid systems used are given in Table 2. Before the experiments, toluene and water were saturated. After the column was filled with the aqueous phase, the organic phase was dispersed in the aqueous phase. After agitation to attain steady state, drop size and hold-up were measured. In the experiments with solute, the acetone concentrations were 2, 3, 4, and 6wt% in the organic phase and the direction of mass transfer was from the dispersed to the continuous phase. A video technique has been used in order to measure the drop size in the mixer-settler with the help of a digital camera (8 M.P, DSC-F828). The AutoCAD software was used for the measurement of drop sizes and calculation of Sauter mean diameter.

Generally, for the study of effect of hold-up and impeller speed on mean drop size, the experiments were performed at 600, 650, 700, 750 and 800rpm and at hold-up fractions 0.27, 0.30 and 0.32, and for the
study of the effect of impeller location the experiments were performed at 750, 800 and 850 rpm and at hold-up 0.30.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Density (kg/m³)</th>
<th>Viscosity (mPa.s)</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>996</td>
<td>0.96</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Toluene</td>
<td>870</td>
<td>0.57</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Acetone</td>
<td>790</td>
<td>0.3</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

Table 2. Physical properties of liquid systems

5- Experimental results without solute

5.1- The effects of the impeller speed on mean drop size

Fig. 2 and 3 show the influence of the agitation intensity on the drop size for different dispersed phase hold-ups. The plots clearly show that an increase of the impeller speed leads to finer sized drops. Thus, agitation power increases the drop breakage frequency.

5.2- The effects of the hold-up on mean drop size

Fig. 4 shows the influence of the dispersed phase hold-up fraction on drop size. The plots clearly show that higher hold-ups lead to larger drops. Since the dispersed phase hold-up measure the volume fraction of the dispersed phase in the total dispersion volume, so the higher in this fraction lead to higher collision frequency between drops. This increased collision frequency promotes drop coalescence and, thus, increases drop sizes.

6- Experimental results with solute

6.1- The effects of solute (acetone) concentration on mean drop size

The resulting interfacial tension versus the acetone concentration curve is presented in
Fig. 5. Interfacial tension between water and toluene decreases with increasing of acetone concentration. The effect of acetone concentration on drop size is shown in Figs. 6, 7 and 8. The experiments were carried out in three hold-ups and five impeller speeds. As shown, when acetone concentration increases, interfacial tension between toluene and water decreases, therefore mean drop size reduces.

**Figure 5.** Interfacial tension between water and toluene versus acetone concentration

![Interfacial tension between water and toluene versus acetone concentration](image)

**Figure 6.** The effects of acetone concentration on $D_{32}$ at $\phi = 0.3253$

![The effects of acetone concentration on $D_{32}$ at $\phi = 0.3253$](image)

**Figure 7.** The effects of acetone concentration on $D_{32}$ at $\phi = 0.3030$

![The effects of acetone concentration on $D_{32}$ at $\phi = 0.3030$](image)

6.2- The effects of impeller speed on mean drop size

Fig. 9 shows the influence of the agitation intensity on the drop size for three different dispersed phase hold-ups. The results indicate that when $D_{32}$ is plotted versus the impeller speed for each acetone concentration (2, 3, 4 and 6 wt.%), the curves present the same trend. Therefore, the figures are plotted at 6 wt % of the acetone concentration. The plot clearly shows that increasing the impeller speed leads to finer drop size. Thus, agitation power increases drop breakage frequency. In comparison with the condition of without acetone, the slope of the linear relation between $\text{Ln}(N)$ and $\text{Ln}(D_{32})$ decreases and it reduces by increasing the acetone concentration.

**Figure 8.** The effects of acetone concentration on $D_{32}$ at $\phi = 0.2738$

![The effects of acetone concentration on $D_{32}$ at $\phi = 0.2738$](image)

**Figure 9.** Logarithmic variation of $D_{32}$ with impeller speed in the presence of 6wt% acetone

![Logarithmic variation of $D_{32}$ with impeller speed in the presence of 6wt% acetone](image)
6.3- The effects of hold-up on mean drop size

Fig. 10 shows the influence of hold-up fraction on drop size in different impeller speeds. The results indicate that when $D_{32}$ is plotted versus the hold-up for each acetone concentration (2, 3, 4 and 6 wt.%), the curves present the same trend. Therefore, the figures are plotted at 6 wt % of the acetone concentration. The plots clearly show that higher hold-ups lead to larger drops. Also, in comparison with the condition of without acetone, the effect of hold-up on drop size decreases and by increasing the acetone concentration, this reduction increases.

The experimental results were compared with Desnoy and Quadros models that are tabulated in Table 3. For the experiments with solute, there were no models or experimental data for comparison. Absolute average relative deviation was calculated by:

$$\% \text{AARD} = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{D_{32}^{(i)}_{\text{exp}} - D_{32}^{(i)}_{\text{model}}}{D_{32}^{(i)}_{\text{exp}}} \right) \times 100$$

Table 4 shows the results of the comparison.

As shown, the Desnoyer model has a good agreement with the experimental data. Generally operating conditions, the physical properties of system and apparatus geometry play an important role in controlling the drop sizes.

![Figure 10. The effects of hold-up on $D_{32}$ in the presence of 6wt% acetone](image)

Table 3. Drop size correlations for liquid-liquid dispersion in stirred vessels

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Correlation</th>
<th>Chemical system</th>
<th>Operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadros and Baptista (2003)</td>
<td>$D_{32} / D = 0.0286(1 + 13.24\phi)W_e^{0.6}$</td>
<td>di-isobutylene diluted with Benzen as the dispersed phase and sulfuric acid as the continuous phase mixture of TBP and Sobesso 150 as continuous phase and NiCl$_2$ as dispersed phase</td>
<td>0.061-0.166 straight blade paddles with four number of blades</td>
</tr>
<tr>
<td>Desnoyer et al. (2003)</td>
<td>$D_{32} / D = 0.28(1 + 0.92\phi)W_e^{0.6}$</td>
<td></td>
<td>0.1-0.6 four inclined blades(45)</td>
</tr>
</tbody>
</table>
7- Conclusions
After testing, observation and study, we can conclude that:

- Interfacial tension between water and toluene decreases when the acetone concentration increases and as a result, $D_{32}$ decreases. By increasing $6\text{wt}\%$ of acetone, $D_{32}$ decreases over $51\%$.
- By increasing the impeller speed in constant hold-up, $D_{32}$ decreases in with and without acetone. Also, the slope of the linear relation between $\ln(N)$ and $\ln(D_{32})$ for different phase hold-ups has a range between -1.22 and -1.3 in without acetone condition and a range between -0.98 and -1.21 in the presence of acetone. This slope increases by increasing hold-up and decreases by increasing acetone concentration.
- According to the Kolmogoroff theory of isotropic turbulence, the drop size depends on $\text{We}^{-0.6}$ that is $N^{-1.2}$. It is shown for the water/toluene system and for water/acetone/toluene with a lower concentration of acetone, that this dependence agrees with classical theory.
- By increasing hold-up, $D_{32}$ increases and these variations are linear in with and without acetone conditions approximately. Also, the slope of variation of $D_{32}$ versus hold-up, decreases by increasing acetone concentration.
- The experimental results in with and without acetone conditions were compared with Quadros and Baptista and Desnoyer models, which have a slight deviation from the Desnoyer model.

8- Nomenclature

\begin{itemize}
  \item $a$ The interfacial area per unit volume
  \item $C'$ Constants
  \item $d$ Drop diameter
  \item $D_{32}$ Sauter mean diameter, L
  \item $D$ Impeller diameter, L
  \item $N$ Impeller speed, T\(^{-1}\)
  \item $\text{We}$ Impeller Weber number ($= \rho_c N^2 D^3 / \sigma$)
  \item $d_{\text{max}}$ Maximum stable drop diameter, L
  \item $d_{\text{min}}$ Minimum stable drop diameter, L
\end{itemize}

Greek symbols

\begin{itemize}
  \item $\phi$ Volume fraction of dispersed phase
  \item $\rho_c$ Density of continuous phase, M/L\(^3\)
  \item $\sigma$ Interfacial tension, M/T\(^2\)
\end{itemize}
References


Prediction of Gas Hydrate Forming Pressures by Using PR Equation of State and Different Mixing Rules

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Abstract

In this work, the ability of different mixing rules for the prediction of hydrate formation pressure are compared. For this purpose, by using Van der Waals–Plautew model for solid hydrate phase and PR equation of state for calculation of fugasity of components in gas and liquid phases, the pressure of hydrate formation in different mixtures has been calculated by four different mixing rules: Van der Waals, Danesh, GNQ and Wong-Sandler, then by comparison of the calculated results with experimental data, the accuracy of the mixing rules were determined. Studied systems contain binary mixtures CH₄, C₂H₆, C₃H₈, i-C₄H₁₀, CO₂, and H₂S with water in hydrate forming conditions. The interaction parameters in each mixture have been optimized by using two phase equilibrium data (VLₜ⁰) and then the optimized parameters have been used for three phase equilibrium (VLₜ⁰ H) calculations. Comparison of the calculated pressure of hydrate forming with experimental pressure shows that for most mixtures in the studied temperature and pressure ranges, the GNQ mixing rule with an average percent of error 6% has more accuracy than the three other mixing rules: Van der Waals, Danesh and WS. According to the obtained results for methane equilibrium concentrations in liquid phase, it seems that Danesh mixing rule is more efficient for the prediction the mole concentrations of components. Since Danesh rule considers the polarity of the water molecule, it has greater precision in predicting the equilibrium fractions.

Keywords: Mixing Rules, Peng-Robinson, Equation of State, Gas Hydrate, Three Phase Equilibria

1- Introduction

Natural gas is one of the most important sources of energy in the world. One of the related problems to natural gas is gas hydrate formation. Gas hydrates are crystalline solids that form when gas or volatile liquid molecules suitable for hydrate formation are enclosed in a cage consisting of water molecules. Naturally occurring hydrates, containing mostly methane, exist in vast quantities and are being looked upon as a potential alternative energy source. Carbon dioxide hydrates are also important hydrates [1].
Although hydrate formation is referred to as an advantage, this circumstance in gas transportation lines causes some problems like plugging of the lines and sometimes the explosion of pipes. Thus awareness of equilibrium conditions of hydrate formation is necessary for preventing this event.

In this work, equilibrium conditions in hydrate formation for six mixtures that contain binary systems have been studied. (CH₄–H₂O), (C₂H₆–H₂O), (C₃H₈–H₂O), (i-C₄H₁₀–H₂O), (CO₂–H₂O) and (H₂S–H₂O). The forming pressure in each system was calculated.

2- Modeling

At phase equilibrium, the fugacities or chemical potentials of species in the various phases must be equal. For three-phase hydrate–liquid water–vapor, $VLW$ equilibrium, the basic equations for the equilibrium condition are:

$$f_i^V = f_i^L = f_i^H$$ (1)

Calculation of component fugacities in two phases, vapor and liquid, are based on the $(\phi - \phi)$ and $(\gamma - \phi)$ approach, and in this research the $(\phi - \phi)$ model is used. In this method the fugacity of a component must be calculated using a suitable equation of state and mixing rules. In this study, Peng – Robinson equation of state was selected. The PR equation is [2]:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}$$ (2)

$$b = 0.0778 \frac{RT_c}{P_c}$$

$$a = 0.45724 \frac{RT_c^2}{P_c} - \alpha(T_c)$$ (3)

$$\alpha(T_c) = \left[ 1 + m \left( 1 - \frac{T}{T_c} \right)^{0.5} \right]^2$$

$$m = 0.37464 + 1.5422 \omega - 0.26922 \omega^2$$

The coefficients $a$, $b$ of Eq (2) were obtained for mixtures using the Van der Waals, Danesh, GNQ (general non quadratic) and WS (Wong-Sandler) mixing rules. The Van der Waals mixing rule is:

$$a_{mix} = \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i x_j a_{ij} (1 - k_{ij})$$ (4)

$$b_{mix} = \sum_{i=1}^{NC} x_i b_i$$

Where $k_{ij}$ is the binary interaction parameter and:

$$a_{ij} = (a_i a_j)^{0.5}$$ (5)

In another applied mixing rule, the attraction parameter $a$ has been separated into two parts, the Van der Waals classical mixing rule part $a^C$ and the asymmetric contribution part $a^A$ are as follows [3]:

$$a = a^C + a^A$$ (6)

$$a^A = \sum_{P=1}^{NPOLAR} \sum_{i=1}^{NC} \sum_{j=1}^{NC} x^A_{ij} l_{ij}$$ (7)

$p$ stands for polar component and $l_{pi}$ is the binary interaction parameter between the polar component and the other components, which is a function of temperature,
calculated by the following expression [3]:

$$I_{p_2} = I_{p_1} - I_{p_1}(T - T_0) \quad (8)$$

Where $I_{p_1}$ and $I_{p_2}$ are binary interaction parameters and $T_0$ is the ice point in K.

Another mixing rule used in this research is GNQ (general non quadratic) mixing rule. The general form in this rule for $a_{mix}$ and $b_{mix}$ parameters is the same as Van der Waals mixing rule, but the combining rule for $a_{ij}$ has the following form [4]:

$$a_{ij} = \sqrt{a_i a_j (1 - k_{ij})}, \quad k_{ij} = \delta x_i + \delta_j x_j \quad (9)$$

In the WS mixing rule, the molar excess Gibbs free energy at infinite pressure, calculated from an EOS, is equated to the same property calculated from the NRTL excess free energy model. The WS mixing rules are [5]:

$$b_{mix} = \frac{Q}{1 - D} \quad (10)$$

$$\frac{a_{mix}}{RT} = Q \times \frac{D}{1 - D} = D \times b_{mix} \quad (11)$$

$$D = \sum x_i \frac{a_i}{b_i RT} + \frac{g^E}{C^* RT} \quad (12)$$

$$Q = \sum \sum x_i x_j (b - \frac{a_{RT}}{RT})_{ij} \quad (13)$$

$$(b - \frac{a_{RT}}{RT})_{ij} = \frac{1}{2} \left[ \left( b_i - \frac{a_i}{RT} \right) + \left( b_j - \frac{a_j}{RT} \right) \right] (1 - k_{ij}) \quad (14)$$

Where $xi$ is the mole fraction of component $i$ in that phase and $C^*$ is a constant depending on the EOS (where $C^* = -0.802$ for the PR EoS). The NRTL model was used for $g^E$.

$$\left( \frac{g^E}{RT} \right)_{NRTL} = \sum x_i \frac{\tau_{ii} g_{ij}}{\sum x_i g_{ii}} \quad (15)$$

$$\tau_{ij} = \frac{g_{ij} - g_{ii}}{RT} \quad (16)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (17)$$

The chemical potential of water in the hydrate phase is given by Van der Waals and Platteeuw [6]:

$$\frac{\Delta \mu_i}{RT} = \int_i \frac{\Delta h_i^{0/L}}{RT} dT + \int_i \frac{\Delta u_i^{0/L}}{RT} dP - \ln \left( \gamma_n x_n \right) \quad (18)$$

$$= \sum_{m=1}^{N_{cavity}} v_m \ln \left( 1 + \sum_{j=1}^{N} C_{jm} f_j \right)$$

Where, $v_m$ is the number of cavities of type $m$ per water molecule in the lattice, $C_{jm}$ is the Langmuir Constant, and $f_i$ is the fugacity of the gas component $i$.

The Langmuir constants account for the gas-H2O interaction in the cavity. Using the Lennard-Jones-Devonshire cell theory, Van der Waals and Platteeuw showed that the Langmuir constant is [7]:

$$C = \frac{4\pi^{3/2}}{kT} \exp \left( -\frac{\alpha(r)}{kT} \right) r^2 dr \quad (19)$$

Where $T$ is the absolute temperature, $k$ is Boltzmann's constant and $\omega(r)$ is the
spherically symmetric cell potential which is a function of the cell radius, the coordination number and the nature of the gas-H2O interaction. Usually the Kihara potential function with a spherical core for describing the interaction between the gas and water molecules in the cavity wall is used. Kihara parameters used in this work are given in Table (1) for the applied components.

Table 1. Kihara potential parameters [8]

<table>
<thead>
<tr>
<th>Component</th>
<th>a (Å)</th>
<th>σ (Å)</th>
<th>1/k</th>
<th>1/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.295</td>
<td>3.2512</td>
<td>153.69</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>0.488</td>
<td>3.4315</td>
<td>183.32</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>0.730</td>
<td>3.4900</td>
<td>189.27</td>
<td></td>
</tr>
<tr>
<td>i-C4</td>
<td>0.798</td>
<td>3.6000</td>
<td>209.58</td>
<td></td>
</tr>
<tr>
<td>n-C4</td>
<td>1.029</td>
<td>3.4000</td>
<td>195.36</td>
<td></td>
</tr>
<tr>
<td>CO2</td>
<td>0.753</td>
<td>2.9040</td>
<td>171.97</td>
<td></td>
</tr>
<tr>
<td>H2S</td>
<td>0.717</td>
<td>2.8770</td>
<td>210.50</td>
<td></td>
</tr>
</tbody>
</table>

3- Results and discussion

3.1- Results of optimization

For calculation pressure in equilibrium conditions using the \((\varphi - \varphi)\) model, first we must determine the interaction parameters in each mixing rule. These parameters are determined for each mixture by minimizing the following objective function:

\[
O.F = w_1 \sum_{i=1}^{NP} \left| \frac{p_i^{\text{cal}} - p_i^{\text{exp}}}{p_i^{\text{exp}}} \right| + w_2 \sum_{i=1}^{NP} \frac{x_i^{\text{cal}} - x_i^{\text{exp}}}{x_i^{\text{exp}}}
\]

(20)

Where \(w_1\) and \(w_2\) are the weight fraction in each term and \(w_1 = w_2 = 1\).

Binary interaction parameter in the Van der Waals mixing rule is \(k_{12}\), and this optimized value is given in Table (2). In the Danesh mixing rule, three parameters exist that contain \(k_{12}\), \(l_{21}^0\) and \(l_{21}^1\). The obtained parameters are presented in Table (3).

Tables (4) and (5) show the optimized values for GNQ and WS mixing rules respectively. In the GNQ mixing rule, \(\delta_1\) and \(\delta_2\), and in the WS mixing rule, \(g_{21} - g_{11}, g_{12} - g_{22}, \alpha_{12}, k_{12}\) are interaction parameters for binary mixtures.

Table 2. optimized parameters, \(k_{ij}\), for Van der Waals mixing rule in PR EOS

<table>
<thead>
<tr>
<th>Mixture</th>
<th>CH₄-H₂O</th>
<th>C₂H₆-H₂O</th>
<th>C₃H₈-H₂O</th>
<th>C₄H₁₀-H₂O</th>
<th>CO₂-H₂O</th>
<th>H₂S-H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_{12})</td>
<td>-0.35022</td>
<td>-0.22093</td>
<td>-0.25718</td>
<td>-0.31265</td>
<td>-0.14304</td>
<td>-0.02670</td>
</tr>
</tbody>
</table>

Table 3. optimized parameters, \(k_{ij}\) and \(l_{ij}\) for Danesh mixing rule in PR EOS

<table>
<thead>
<tr>
<th>Mixture</th>
<th>(k_{21})</th>
<th>(l_{21}^0)</th>
<th>(l_{21}^1 * 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄-H₂O</td>
<td>0.48960</td>
<td>1.74473</td>
<td>71.181</td>
</tr>
<tr>
<td>C₂H₆-H₂O</td>
<td>0.49209</td>
<td>1.45850</td>
<td>37.830</td>
</tr>
<tr>
<td>C₃H₈-H₂O</td>
<td>0.52681</td>
<td>1.56193</td>
<td>36.518</td>
</tr>
<tr>
<td>i-C₄H₁₀-H₂O</td>
<td>0.34199</td>
<td>1.31380</td>
<td>49.953</td>
</tr>
<tr>
<td>CO₂-H₂O</td>
<td>0.25023</td>
<td>0.83331</td>
<td>24.882</td>
</tr>
<tr>
<td>H₂S-H₂O</td>
<td>0.13137</td>
<td>0.36095</td>
<td>14.224</td>
</tr>
</tbody>
</table>
Table 4. optimized parameters, $\delta_i$ for GNQ mixing rule in PR EOS

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$\delta_1$</th>
<th>$\delta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$-H$_2$O</td>
<td>0.16875</td>
<td>0.07576</td>
</tr>
<tr>
<td>C$_2$H$_6$-H$_2$O</td>
<td>0.36333</td>
<td>0.06920</td>
</tr>
<tr>
<td>C$_3$H$_8$-H$_2$0</td>
<td>0.45046</td>
<td>0.092116</td>
</tr>
<tr>
<td>i-C$<em>4$H$</em>{10}$-H$_2$0</td>
<td>1.07940</td>
<td>0.11403</td>
</tr>
<tr>
<td>CO$_2$-H$_2$O</td>
<td>0.02552</td>
<td>0.05083</td>
</tr>
<tr>
<td>H$_2$S-H$_2$O</td>
<td>0.03256</td>
<td>0.01187</td>
</tr>
</tbody>
</table>

Table 5. optimized parameters for WS mixing rule in PR EOS

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$g_{21} - g_{11}$</th>
<th>$g_{12} - g_{22}$</th>
<th>$\alpha_{12}$</th>
<th>$k_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$-H$_2$O</td>
<td>60.1736</td>
<td>23938.7640</td>
<td>0.70966</td>
<td>3.27553</td>
</tr>
<tr>
<td>C$_2$H$_6$-H$_2$O</td>
<td>-1010.2922</td>
<td>137.0329</td>
<td>0.62357</td>
<td>3.77522</td>
</tr>
<tr>
<td>C$_3$H$_8$-H$_2$0</td>
<td>293.4141</td>
<td>15766.5426</td>
<td>0.27138</td>
<td>3.29269</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$-H$_2$0</td>
<td>285.3414</td>
<td>5888.9290</td>
<td>0.27696</td>
<td>3.29248</td>
</tr>
<tr>
<td>CO$_2$-H$_2$O</td>
<td>318.1248</td>
<td>14875.8500</td>
<td>0.39698</td>
<td>1.52926</td>
</tr>
<tr>
<td>H$_2$S-H$_2$O</td>
<td>137.1430</td>
<td>30296.7154</td>
<td>-0.17181</td>
<td>1.16000</td>
</tr>
</tbody>
</table>

3.2- Results of equilibrium calculation

Fig. 1 shows the equilibrium curve for the predicted methane hydrate formation pressure based on different mixing rules. Error of calculated pressure in the PR equation of state by using the Danesh mixing rule, Van der Waals, GNQ and WS respectively is 11.62%, 13.16%, 16.74% and 12.33%. So Danesh mixing has a minimum of error for methane hydrate in PR EOS. The reason for the high error in methane hydrate is high formation pressure. The error percent of the model increases at high pressures. As shown in Fig. 1, the obtained results of GNQ mixing rule has considerable deviation with the experimental data at high temperatures.

Model predictions of methane solubility in liquid water for temperatures between 262.4 and 320.1 K and for pressures between 17.9 and 3970 bar are presented in Fig. (2). Danesh mixing with 7.32% error has more accuracy than the three other mixing rules.

Results of three phase equilibrium calculation ($V_{LW} H$) for other systems are given in Figs. 3 to 7. These figures show the predicted values of ethane, propane, carbon dioxide and hydrogen sulfide hydrates formation temperatures, respectively.
Figure 1. Three phase equilibrium curve of methane hydrate based on four mixing rules by using PR equation of state.

Figure 2. Comparison of calculated methane solubility in liquid water by using PR EOS and four mixing rules, with experimental data.
**Figure 3.** Three phase equilibrium curve of ethane hydrate based on four mixing rules by using PR equation of state.

**Figure 4.** Three phase equilibrium curve of propane hydrate based on four mixing rules by using PR equation of state.
Prediction of Gas Hydrate Forming Pressures by Using PR Equation of State and Different Mixing Rules

Figure 5. three phase equilibrium curve of i-butane hydrate based on four mixing rules by using PR equation of state

Figure 6. three phase equilibrium curve of carbon dioxide hydrate based on four mixing rules by using PR equation of state
A summary of results and error percentage for the predicted pressure is given in Table 6 at all studied systems. As shown in this table, the GNQ mixing rule has the minimum error percent.

**Table 6.** Summary of three phase equilibrium calculation results \((VL_pH)\), by using PR EOS and four mixing rules, in six binary mixtures in the considered range of temperature and pressure

| Mixture   | T range (K) | P range (bar) | No. of Points | Error
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{4}-H\textsubscript{2}O</td>
<td>262.4-320.1</td>
<td>17.9-3970</td>
<td>38</td>
<td>8.05%</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{6}-H\textsubscript{2}O</td>
<td>273.7-286.5</td>
<td>5.1-27.30</td>
<td>16</td>
<td>6.13%</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{8}-H\textsubscript{2}O</td>
<td>273.2-278.4</td>
<td>1.65-5.62</td>
<td>16</td>
<td>6.70%</td>
</tr>
<tr>
<td>iC\textsubscript{4}H\textsubscript{10}-H\textsubscript{2}O</td>
<td>273.2-275</td>
<td>1.10-1.65</td>
<td>17</td>
<td>6.05%</td>
</tr>
<tr>
<td>CO\textsubscript{2}-H\textsubscript{2}O</td>
<td>271.6-283.3</td>
<td>10.40-44.68</td>
<td>34</td>
<td>5.57%</td>
</tr>
<tr>
<td>H\textsubscript{2}S-H\textsubscript{2}O</td>
<td>272.8-302.7</td>
<td>0.93-22.41</td>
<td>19</td>
<td>5.42%</td>
</tr>
</tbody>
</table>

\[
\text{Error} = \frac{1}{NP} \sum_{i=1}^{NP} \left| \frac{P_i^{\text{cal}} - P_i^{\text{exp}}}{P_i^{\text{exp}}} \right| \%
\]
4- Conclusions
In all of the studied mixtures (except CH₄ hydrate and CO₂ hydrate), among the mixing rules (with VPT equation), GNQ mixing rule for predicting equilibrium pressure with an average percent of error 6%, is more suitable. It is considerable that the calculated pressure from the GNQ rule is highly dependent on optimized interaction parameters.

Obtained equilibrium pressure from Van der Waals mixing rule is closest to the results of the WS mixing rule. Although the WS mixing is based on Gibbs free energy and has more difficulty than other mixing rules, the results are not suggested, so using it is not recommended.

Calculated results for methane fraction in liquid phase shows that, the Danesh mixing rule for predicting concentrations of liquid is more suitable, because this rule considers the polarity components (H₂O molecule).

References
Thermal and Morphological Properties of Thermoplastic Elastomer Nanocomposites Based on PA6/NBR

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2- Polymer Engineering Department, Amirkabir University of Technology, Tehran, Iran.
3- Iran Polymer & Petrochemical Institute (IPPI), Tehran, Iran

Abstract
Morphological and thermal properties of PA6/NBR nanocomposites prepared through a direct melt mixing process in an internal mixer were studied. The effects of the NBR content (10, 30, and 50%) and nanoclay loading (3, 5, and 7%) on the microstructure properties of nanocomposites have been reported and compared with PA6/NBR blends as well. The thermoplastic elastomer (TPE) nanocomposites were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), volume swelling in oil, differential scanning calorimeter (DSC) and dynamic mechanical thermal analysis (DMTA). XRD results show that Cloisite 30B is exfoliated into the PA6 and NBR. TEM image of the PA6/NBR/nanoclay composite confirms partial exfoliated structure of silicate layers dispersed into the both NBR and PA6 phases. The SEM photomicrograph of PA6/NBR nanocomposite shows an increasing of the rubber particles size in comparison with unfilled PA6/NBR TPE. By the presence of nanoclay, improved oil resistances of the prepared TPE nanocomposites were achieved. DSC studies show that loading of the nanoclay reduces the degree of crystallinity of the nanocomposite samples. The DMTA test shows that storage modulus of the PA6/NBR nanocomposite increases in comparison with the PA6/NBR blend. It also explains a reduction in damping by loading of the nanoclay.

Keywords: Nanocomposites, Thermoplastic Elastomers, Polyamide 6, NBR, Nanoclay

1- Introduction
Thermoplastics can simply be described as being able to deform plastically and flow on heating [1]. Polyamides, or nyons, thermoplastics have attracted interest in the past by virtue of their excellent strength properties, stiffness, chemical and wear resistances, low friction and high melting points [2]. Thermoplastic elastomers based on polyamides, prepared by melt mixing with suitable rubbers like NBR are expected to have excellent hot oil resistance and high strength properties at elevated temperatures [3]. Several articles presenting studies on different properties of the PA6/NBR blends are available in the literature. Radhesh Kumar et al. have studied the effect of blend ratio, dynamic vulcanization, compati-

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bibilization and temperature on the flow behavior of the nylon/NBR thermoplastic elastomers [4]. Chowdhury et al. have reported improved strength and set properties of a carboxylated NBR/PA6/66/610 ter-polymer composition [5]. Mehrabzadeh et al. have investigated the effect of different systems of curing and the amount of curing agent on thermal behavior and morphology of NBR/PA6 blends [6]. Although layered silicates such as clay are well-known filler materials, their interaction and exfoliation have attracted considerable attention as a route leading to the preparation of nanocomposites [7]. Moreover, many scientists are interested in polymer nanocomposites due to their unique properties comparative to pure polymers and typical composites. Naderi et al. have studied dynamically-vulcanized nanocomposite TPEs while investigating the effect of blend viscosity ratio and clay concentration on their microstructure and mechanical properties [8]. Kelnar et al. have focused on the compatibilizing ability of clay in dependence on elastomer structure and the dependence of mechanical properties on the resulting morphology [9]. Li et al. have identified the effect of clay addition on the morphology and thermal behavior of Polyamide 6 [10]. Furthermore, it has been suggested that stronger interactions between the clay particles and the Polyamide melt, result in better dispersion and exfoliation of clay platelets [11]. Our work presents experiments on the thermal and morphological properties of the PA6/NBR nanocomposites prepared through a direct melt mixing process. The effects of NBR and nanoclay contents on the microstructure and thermal properties of the PA6/NBR TPE nanocomposites have been reported.

2- Experimental

2.1- Materials
The characteristics of the materials used in this work are given in Table 1. Polyamide 6 (PA6) Akulon F130-B was supplied by DSM Co. (Netherlands). Acrylonitrile Butadiene Rubber (NBR) Kosyn-KNB 35L was purchased from Kumho Petrochemical Co. (Korea) and the nanoclay used was Cloisite 30B, obtained from Southern Clay Products (USA), which is a natural montmorillonite modified with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium.

Table 1. Characteristics of the materials used.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Characteristics</th>
</tr>
</thead>
</table>
| PA6       | Density (g/cc): 1.13  
Melting Point (°C): 220 |
| NBR       | Density (g/cc): 0.94  
Bound Acrylonitrile (%): 34  
Mooney Viscosity, ML(1+4) at 100°C: 41 |
| Nanoclay  | Density (g/cc): 1.98  
Modifier Concentration, meq/100g clay: 90  
X-Ray Diffraction d-Spacing (Å): 18.5 |

2.2- TPE nanocomposite preparation
PA6 and nanoclay were dried at 80°C for 24 hr in a vacuum oven. The TPE nanocomposites based on PA6/NBR/Cloisite 30B were prepared through a direct melt mixing process in a Haake Buchler Rheomix 750 internal mixer at 240°C and 80 rpm for 8 min. The samples formulations are given in Table 2. The compounds removed from the chamber were compression molded at 240°C
for 5 min to form 1-mm-thick sheets suitable for testing.

Table 2. The samples formulations (wt %).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>PA6 (wt %)</th>
<th>NBR (wt %)</th>
<th>Nanoclay (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN10</td>
<td>90</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>PN30</td>
<td>70</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>PN50</td>
<td>50</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>PN10C3</td>
<td>87</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>PN30C3</td>
<td>67</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>PN50C3</td>
<td>47</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>PN10C5</td>
<td>85</td>
<td>10</td>
<td>5</td>
</tr>
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<td>PN30C5</td>
<td>65</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>PN50C5</td>
<td>45</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>PN10C7</td>
<td>83</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>PN30C7</td>
<td>63</td>
<td>30</td>
<td>7</td>
</tr>
<tr>
<td>PN50C7</td>
<td>43</td>
<td>50</td>
<td>7</td>
</tr>
</tbody>
</table>

2.3- Characterization

X-ray diffraction patterns (XRD) were obtained by using a Philips X’Pert (The Netherlands) at room temperature in the low angle of 2θ under a 50 kV voltage generator and a current of 40 mA. Transmission electron microscope (TEM) images of the TPE nanocomposites were obtained using a Philips CM-200 with an accelerator voltage of 200 kV. Phase structure was observed using a Philips XL30 scanning electron microscope. The cryogenically fractured samples were etched with toluene to extract the NBR phase, and sputter coated by a thin layer of gold before taking SEM micrographs. Volume swelling in the oil of the samples was measured by immersing the samples in the oil with an aniline point of 77°C for 70 hr at 125°C according to ASTM D-471 and the changes in weight were recorded. Crystallization behavior was studied using a Maia-200F3 differential scanning calorimeter under nitrogen atmosphere. Samples were heated from 25 to 260°C at a rate of 10°C /min and then were cooled from 260 to 25°C after holding for 3 min and heated again from 25 to 260°C and held during 3 min at 25°C. Prior to DSC, the analysis samples were dried for 24 hr at 100°C. Dynamic mechanical thermal properties of the samples were carried out according to ASTM E1640-04 using a DMA, Tritec 2000, under the bending mode at a frequency of 1 Hz. The temperature range was from -100 to 100°C and the specimens were heated at a rate of 5°C /min.

3- Results and discussion

3.1- X-ray diffraction

The XRD results of TPE nanocomposites based on PA6/NBR with different nanoclay content and 10wt% of NBR are reported in Fig 1. Although the diffraction peak of Cloisite 30B appears at 2θ = 4.8° [12], it can be seen that XRD peaks of the silicate layers have disappeared, indicating the exfoliation of the nanoclay into polymer matrix. As shown in Fig. 2, similar trends were observed for the XRD patterns of the PA6/NBR nanocomposites containing 3wt% nanoclay and different contents of the rubber (10, 30 and 50wt% NBR). Moreover, the decrease in the intensity of the XRD peaks with increasing NBR content is due to the increase in the viscosity and high shear stress, which also leads to the exfoliation of Cloisite 30B into the polymer matrix [8].
3.2- Transmission electron microscopy
The TEM image of PA6/NBR nanocomposite containing 30wt% NBR and 7wt% nanoclay is illustrated in Fig. 3. The rubber phase is white in color while the PA6 phase is darker. The nanoclay layers, dark lines in the TEM image, are dispersed throughout both the NBR and PA6 phases. It can be seen that a fraction of the silicate layers are exfoliated in the PA6 matrix, while a slight amount of the nanoclay remained in a clustered state. Therefore, the partially exfoliated structure of the silicate layers dispersed through PA6 matrix can be observed in this image.

3.3- SEM photomicrograph
A SEM image of the PA6/NBR (70/30) sample is shown in Fig. 4. The NBR phase, which has been etched by toluene can be seen as the dark holes dispersed throughout the PA6 phase. The average particle diameter size of the dispersed rubber phase is calculated by measuring the diameter size of about 50 randomly selected domains, which is about 0.45±0.2 μm. A SEM image of the TPE nanocomposite based on PA6/NBR containing 30wt% NBR and 7wt% Cloisite 30B is shown in Fig. 5. As the average diameter particle size of rubber domains is measured (about 1.06±0.4 μm), it can be reported that the diameter size of rubber
particles has been increased by introduction of the nanoclay. The size of the dispersed rubber phase depends on the viscosity ratio and interfacial interactions between the NBR and the PA6 phases [8]. The presence of some nanoclay layers in the rubber phase increases the viscosity ratio between the two phases, leading to an increase in the NBR particles size. TEM image also confirms the existence of some Cloisite 30B in the NBR phase.

Figure 3. TEM micrograph of PN30C7

Figure 4. SEM photomicrograph of PA6/NBR (70/30)
3.4- Volume swelling in oil

Volume swelling for the samples was estimated as: 

\[ q - 1 = \left[ \frac{W_2}{W_1} - 1 \right] \frac{\rho_c}{\rho_s} \]

Where \( q \) is the ratio of the swollen volume to the original unswollen volume, \((q - 1 = \% \text{ of volume swell} / 100)\); \( W_1 \) and \( W_2 \) are specimen weights before and after swelling, respectively; \( \rho_c \) and \( \rho_s \) are the density of the composition and the oil, respectively [13].

Fig. 6 shows a reduction in volume swelling in oil for nanocomposites of PA6/NBR=10, 30, 50wt% by the addition of the nanoclay content as well. It has been mentioned that the extent of swelling of a blend depends on the structure of the polymer phases and can be related to the properties of the polymer chains such as molecular mobility and phase interaction. As the nanoclay reinforces the polymer phase, its introduction should reduce the volume swell of the blend, and reduce the overall volume swelling of the nanocomposite in oil [14]. On the other hand, with the increased percentage of NBR, higher volume swellings in oil were observed. This is due to the lower swelling resistance of the rubber phase than PA6.
3.5- DSC analysis

DSC thermograms of PA6/NBR (70/30) and PA6/NBR/nanoclay (63/30/7) samples are shown in Fig 7. The degree of crystallinity ($\chi_c$), calculated by the ratio of $\Delta H_m / \Delta H_m^\circ$, decreases by adding 7% nanoclay as it is reported in Table 3. $\Delta H_m^\circ$ is the heat of fusion of the purely crystalline forms of PA6, i.e. 240 J/g [15]. This decrease is due to the interaction between the nanoclay and the polymer matrix which reduces the crystallizable chain segments mobility [8, 15].

Table 3. Values of $\Delta H_m$ and $\chi_c$ of PN30 and PN30C7.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN30</td>
<td>52.06</td>
<td>21.7</td>
</tr>
<tr>
<td>PN30C7</td>
<td>45.9</td>
<td>19.12</td>
</tr>
</tbody>
</table>

3.6- DMTA analysis

Figs. 8 and 9 show the storage modulus (E’) and tan $\delta$ versus temperature for PA6/NBR (70/30) TPE and PA6/NBR nanocomposite containing 30wt% NBR and 7wt% nanoclay. As shown in Fig 8, the storage modulus of the PA6/NBR nanocomposite increases with nanoclay attendance, compared to PA6/NBR TPE. This increase in the storage modulus is because of strong interactions between the polymer matrix and the nanoclay interface [16]. The peak area under the tan $\delta$ curve at the glass transition is quantified by the energy dissipated during the dynamic experience and gives information about the viscous parts of the nanocomposites. As can be seen in Fig. 9, the tan $\delta$ peak area is reduced for the nanocomposite sample compared to the TPE based on PA6/NBR. This means that the damping is reduced by loading of the nanoclay [16].
4- Conclusions
We have prepared PA6/NBR nanocomposites containing 10, 30, 50wt% NBR and 3, 5, 7 wt% of the nanoclay by a direct melt mixing process. According to the XRD, TEM and SEM results, Cloisite 30B was partially exfoliated into both the NBR and PA6 phases. DSC and DMTA studies indicated the strong interactions between the polymer matrix and the nanoclay interface in
TPE nano-composites based on PA6/NBR. The storage modulus of the PA6/NBR nanocomposites increased with nanoclay loading in comparison with that of the PA6/NBR blend. The tan δ of the nanocomposite sample was reduced in comparison with the unfilled PA6/NBR TPE. By introduction of nanosilicate layers into the PA6/NBR blend, the volume swelling of the nanocomposite was decreased.

References


Notes for Authors

Aims and Scope
The Iranian Journal of Chemical Engineering (IJChE) is a research quarterly in Chemical Engineering and related fields. The Editorial Board of the Journal tries to establish a forum for exchange of scientific findings on the core areas of the profession, as well as to cover new emerging areas and an interdisciplinary outlook of the dynamic field of Chemical Engineering. This is a peer-reviewed journal in which original contributions in the following areas appear:

- Transport Phenomena
- Thermodynamics and Phase Equilibria
- Process Design and Economics
- Separations Technology
- Mathematical Modeling and Simulation
- Process Control and Automation
- Reactions Kinetics and Catalysis
- Process Safety and Loss Prevention
- Process Technology
- Process Systems Engineering
- Biochemical Engineering
- Polymer Technology
- Reservoir Engineering
- Sustainable Development
- Energy, Combustion and Fuels
- Process Technology
- Process Systems Engineering
- Biochemical Engineering
- Polymer Technology
- Reservoir Engineering
- Sustainable Development
- Energy, Combustion and Fuels
- Computer Applications and AI

State-of-the-Art and review articles, only as invited papers, will also appear in the Journal from time to time. Audience of the Journal includes industrial and academic researchers in Chemical and Process Engineering.

Preparation of Manuscripts
Contributed articles should contain new research findings which represent advances in chemical engineering research. Manuscripts are subject to peer-review by a board of referees. The average length of an article is 20 A4 pages double-spaced, including figures and tables. Contributed articles should be arranged in the following order:

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