The Condition Optimization of Synthesis Gas Production via Steam Methane Reforming Process of Natural Gas

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Abstract: The optimum conditions of synthesis gas production via steam methane reforming (SMR) process of natural gas were investigated. For that purpose we varied the feed gas (90%vol CH4 with the remains being C2+ hydrocarbons, pure methane of 99.99%vol CH4 and mixed methane with carbon dioxide 9:1 volume ratio), the temperature (700°C, 750°C and 800°C) and the feed steam to carbon ratio (2, 2.5 and 3). We found an increased methane conversion and CO yield with decreased CO2 side products at reaction conditions of 800°C with a steam to carbon ratio of 3:1. In addition, we could not detect any significant difference in the reaction product compositions after a change of the feed gas from associated gas to pure methane. Thus, we assume that an installment of a pre-reformer unit to convert C2+ hydrocarbon to methane is not necessary. However, we could detect a significant influence of the feed gas containing CO2 on the reforming process affecting the methane conversion.

Keywords: Steam reforming, Natural gas, synthesis gas

1. INTRODUCTION

The gas-to-liquid (GTL) process is a very appealing method for the conversion of natural gas (NG) to high quality liquid synfuels. This is usually achieved in several stages via the production of long-chain hydrocarbons by the Fischer–Tropsch synthesis (FTS) and hydrocracking of the heaviest fractions for naphtha, diesel and lubricants production [1]. The steam reforming of natural gas is probably the most important process for the production of hydrogen and synthesis gas, which acts as a base for chemicals used in numerous industrial processes. The first reported catalysts for steam reforming of hydrocarbons were based on nickel as early as 1889 by Mond [2]. The process was exploited on industrial scale for the first time by Standard Oil of New Jersey in 1931 [3].

Synthesis gas will be produced by the SMR process in which methane reacts with steam to generate hydrogen, carbon monoxide and carbon dioxide, as shown in reaction (1). This reaction is highly endothermic and requires high temperature (> 850°C) and a fast transport of large amount of heat into the reaction zone in order to sustain the reaction at the desired reaction rate [4]. In general, the steam reforming reaction (1) is followed by the water gas shift reaction (WGSR), which is slightly exothermic, as shown in reaction (2) [5-6].

Steam reforming of methane

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (\Delta H_{298}^o = +206 \text{ kJ/mol}) \]  (1)

Water gas shift reaction

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (\Delta H_{298}^o = -41 \text{ kJ/mol}) \]  (2)

Since natural gas usually contains ca. 10% of higher hydrocarbons, a third reaction occurs. These higher hydrocarbons react with steam as shown in reaction (3).

\[ \text{C}_n\text{H}_m + n\text{H}_2\text{O} \rightarrow n\text{CO} + ½(n+m)\text{H}_2 \]  (3)

SMR is currently the most cost effective and highly developed method for the production of hydrogen gas, because natural gas used in this process is abundant and available at relatively low cost and high H2/CO ratios are desired for hydrogen production. Commonly used catalysts for SMR are Al2O3- supported Ni-based catalysts. However, these catalysts were found before to deactivate easily because of coking and sintering of the Ni Metal [7-9]. Industrial reaction conditions of this process vary in the ranges of 600–900°C and 5–40 bar. A high temperature culminating in a reactor exit temperature of 800–900°C is necessary to overcome the adverse effect of lower temperatures on equilibrium
yields. The pressure on the other hand seems to be of lower influence. In general, equilibrium yields are improved at lower pressures, but operating pressures are often determined by the process requirements of the downstream plant.

In this work, our study focused on parameters that affect the activity and productivity of the SMR process from associated gas. The optimum temperature for the reaction and the molar ratios of steam to carbon in the feed gas for producing synthesis gas were investigated based on the commercial Ni catalyst. In addition, the feed gas composition was changed from associated gas (90%vol CH₄ and the rest were C₂+ hydrocarbon) to pure methane (99.99%vol CH₄) and mixed methane with carbon dioxide (90%vol CH₄ and 10%vol CO₂).

2. EXPERIMENTAL

In our experiments we used a commercial Ni-based catalysts for the condition optimization of synthesis gas production via steam reforming from associated gas. The reaction was performed in a down-flow fixed-bed reactor (i.d = 0.5 inch), which is controlled by a computer as shown in Fig. 1. The experiments were performed at a constant pressure of 3 MPa and the reaction temperature was varied from 700°C to 800°C. We furthermore changed the feed steam to carbon ratio from 2, 2.5 and 3. The effect of feed gas composition was investigated by using pure methane and mixed methane with 10%vol carbon dioxide as the reactant gas. The associated gas compositions are shown in Table 1.

![Fig. 1 Flow diagram of steam reforming micro-reactor rig.](image)

**Table 1 Compositions of associated gas**

<table>
<thead>
<tr>
<th>Gas Composition</th>
<th>Feed Gas Concentration (mole%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>90.95</td>
</tr>
<tr>
<td>Ethane</td>
<td>3.20</td>
</tr>
<tr>
<td>Propane</td>
<td>1.90</td>
</tr>
<tr>
<td>iso-Butane</td>
<td>1.40</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.80</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>0.05</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.05</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.05</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.00</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.60</td>
</tr>
</tbody>
</table>
If not otherwise mentioned we loaded the reactor with 22.4 g of commercial Ni-based catalyst diluted by SiC. Prior to the steam reforming process, the catalyst was reduced at a temperature of 390°C at a H₂ flow rate of 150 ml/min for 16 h. After the catalyst reduction, N₂ gas was purged with a flow rate of 250 ml/min for 30 min. Then the pressure was increased to 3 MPa and the temperature was increased from the reduction temperature to the reforming temperature of 700°C, 750°C and 800°C (heating rate 2.5°C/min), respectively and held at each temperature for 48 h. The optimal condition testing of the steam reforming of associated gas was carried out by feeding 200 ml/min of a gas mixture with steam to carbon ratio of 2:1, 2.5:1 and 3:1, respectively. The effluent gas compositions after the reaction were analyzed online at 1 h intervals, by gas chromatographs RGA 1115 (Perkin-Elmer). CH₄ conversion, which is defined as eq. (4) and the product selectivity were calculated from the GC results.

\[
\% \text{CH}_4 \text{ conversion} = \left[ \frac{\text{Flow CH}_4 \text{ output} - \text{Flow CH}_4 \text{ input}}{\text{Flow CH}_4 \text{ input}} \right] \times 100
\]  

(4)

The optimum steam to carbon ratio and the optimum temperature of the associated gas in the steam reforming reaction was used for further study on the effect of the feed gas composition at a constant pressure of 3 MPa.

3. RESULTS AND DISCUSSION

3.1 Effect of temperature and steam to carbon ratio

Table 2 show %product selectivity, %CH₄ conversions and H₂/CO ratio (by mole) from the steam reforming reaction of the associated gas on the commercial Ni-based catalysts at a constant pressure of 3 MPa at a temperature from 700°C to 800°C and a steam to carbon ratio of 2-3. We found that at the higher temperature of 800°C, the %CH₄ conversion and %CO selectivity increased significantly, whereas the %CO₂ selectivity decreased. Moreover, we could show this high temperature had little effect on the %H₂ selectivity which resulted in a decrease of the H₂/CO ratio.

The change of the steam to carbon ratios in the inlet feed stream from 2:1 to 3:1 resulted in a higher %CH₄ conversion and %CO₂ selectivity but decreased %CO selectivity. It is interesting to note that we could not find a high impact of an increased steam to carbon ratio on the %H₂ selectivity. This finally lead to the increased H₂/CO ratio of the product.

From the results above, we can conclude that the optimum conditions of the steam reforming process of associated gas is a reaction temperature of 800°C with a steam to carbon ratio of 3:1. These conditions gave the highest CH₄ conversion and suitable H₂/CO ratio and are therefore suitable for further employment in the Fischer-Tropsch process. We would like to note that a steam to carbon ratio of 3:1 also reduced the risk of coke formation on catalyst. This observation is consistent with the earlier finding of D.L. Hoang et al. [10]

Table 2 %Product selectivity, %CH₄ conversion and H₂/CO ratio of the steam reforming of associated gas at 3 MPa, a temperature from 700–800°C and a steam to carbon ratio of 2:3.

<table>
<thead>
<tr>
<th>S:C</th>
<th>Temperature (°C)</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
<th>% CH₄ conversion</th>
<th>H₂/CO ratio (by mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>700</td>
<td>64.79</td>
<td>9.1</td>
<td>26.08</td>
<td>22.17</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>65.77</td>
<td>13</td>
<td>21.38</td>
<td>34.35</td>
<td>5.12</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>65.68</td>
<td>16</td>
<td>17.83</td>
<td>45.72</td>
<td>3.98</td>
</tr>
<tr>
<td>2.5:1</td>
<td>700</td>
<td>65.33</td>
<td>8.2</td>
<td>26.5</td>
<td>29.27</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>65.67</td>
<td>12</td>
<td>22.66</td>
<td>39.95</td>
<td>5.63</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>66.09</td>
<td>15</td>
<td>18.54</td>
<td>53.9</td>
<td>4.3</td>
</tr>
<tr>
<td>3:1</td>
<td>700</td>
<td>65.31</td>
<td>7.5</td>
<td>27.2</td>
<td>35.88</td>
<td>8.73</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>65.73</td>
<td>11</td>
<td>23.63</td>
<td>50.08</td>
<td>6.17</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>65.94</td>
<td>14</td>
<td>20.16</td>
<td>64.09</td>
<td>4.74</td>
</tr>
</tbody>
</table>
3.2 Effect of feed gas compositions and CO2

Fig. 2. The comparison of feed gas compositions: associated gas (90%vol CH4 with the rest being C2+ hydrocarbon) and pure methane (99.99%vol CH4) in the steam reforming reaction. Reaction conditions: T = 800°C, P = 3 MPa, steam to carbon ratio = 3:1

Fig. 2 shows the results for different feed gas compositions. One being associated gas (90%vol CH4 with other being C2+ hydrocarbon), which enters the steam reforming unit directly without any pre-reformer unit. The second one being pure methane (99.99%vol CH4), which passes through a pre-reformer unit before entering the steam reforming unit. The catalyst and reaction conditions for both feed gas compositions were same (commercial Ni-based catalysts at 800°C, 3 MPa, and steam to carbon ratio of 3:1). We found no significant difference on %CH4 conversion, %product selectivity (%H2 selectivity, %CO selectivity and %CO2 selectivity) or H2/CO molar ratio between associated gas feed and methane gas feed. Thus, we conclude that such a pre-reformer unit to change C2+ hydrocarbon to methane is not necessary reducing investment costs.

Fig. 3. The effect of CO2 in the feed gas in the steam reforming. Reaction conditions: T = 800°C, P = 3 MPa, steam to carbon ratio = 3:1

Fig. 3 shows the effect of CO2 containing feed gas on the steam reforming reaction at 800°C, 3 MPa, and steam to carbon ratio of 3:1. We found that at a CO2 concentration of approximately 10%vol in the feed gas the %CH4 conversion and %CO2 selectivity were increased while %H2 selectivity and H2/CO ratio were decreased. Furthermore, we did not observe any significant change of %CO selectivity between pure methane and mixed methane with 10%vol carbon dioxide. We explain this with two simultaneous reactions of dry and steam reforming induced by the CO2 in the feed gas, which increased the methane conversion.

4. CONCLUSION

We performed an experimental study on the condition optimization of synthesis gas production via steam reforming from associated gas (90%vol CH4 with residual C2+ hydrocarbon) using commercial Ni-based catalysts in a micro-reactor system. For that purpose we varied the temperature and the steam to carbon ratio and found best conditions for 800°C with steam to carbon ratio of 3:1 and a pressure of 3 MPa giving the highest CH4 conversion (63–64%) and suitable H2/CO ratio for further Fischer-Tropsch process with reduced risk of deactivation of the catalyst by coke
formation. We furthermore investigated the effect of feed gas and found no significant change in reaction product compositions when changing the feed gas from associated gas to pure methane. This is remarkable, because it suggests that the installment of a pre-reformer unit to convert C₂⁺ hydrocarbon to methane is unnecessary reducing operation costs. In the presence of CO₂ in the feed gas, we noticed a difference of %CH₄ conversion and %product selectivity, which seems to affect the reforming process inducing a second reaction pathway via dry reforming.

5. ACKNOWLEDGMENTS

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6. REFERENCES