Study of Hydrogen Production from Natural Gas by Autothermal Reforming

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Abstract: Hydrogen is the preferred feedstock for use in combining with oxygen in fuel cell. Processes for hydrogen production often use fuel oil as feedstock. In present, price of oil is highly increased so natural gas is given more attention. It consists mainly of methane (i.e. 80-95\% CH\textsubscript{4}), some higher hydrocarbons and carbon dioxide. It is a potential source for hydrogen production. In this work, a primary study of utilization of natural gas in Thai gulf reservoir as a feedstock for hydrogen production by autothermal process was attempted. Aspen plus 10.2 simulation program was used to simulate the autothermal process and study for the effect of its operating condition. The operating parameters, temperature, water to carbon feed ratio (W:C) and oxygen to carbon feed ratio (O\textsubscript{2}:C), were varied to evaluate their effects on changes in product composition. The temperature range of 400-800 \textdegree C, water to carbon feed ratio of 0.1-12.0 (mole ratio) and oxygen to carbon feed ratio of 0.01-2.5 (mole ratio), were investigated. The simulation results showed that the maximum H\textsubscript{2} yield can be obtained at higher values of water to carbon ratio and lower range of oxygen to carbon ratio. Equilibrium analysis results also showed that autothermal reaction is a suitable process to produce hydrogen from natural gas for fuel cell. For mobile application, autothermal reactor should be operated at the thermal neutral condition by using the optimum conditions of 500 \textdegree C, W:C ratio of 4 and O\textsubscript{2}:C ratio of 0.9.

Keywords: Natural Gas, Autothermal Reaction, Equilibrium, Hydrogen Production, Aspen Plus.

1. INTRODUCTION

Hydrogen is one of the important gaseous raw materials for petroleum and petrochemical industries. In the near future, it will be transformed to the electrical energy by "Fuel cell" for electrical vehicles and electrical power plants. Automotive fuel cells require hydrogen gas to operate. The most convenient way to obtain the gas would be the use an onboard fuel processor to convert or "reform" commonly [1]. Processes for hydrogen production often use fuel oil as feedstock. In present, cost of oil highly increases so that natural gas is considered to substitute.

There are three major thermochemical reforming techniques used to produce hydrogen, i.e., steam reforming, partial oxidation and autothermal reforming [2].

The steam reforming is an endothermic catalytic process of light hydrocarbon with steam by using catalyst [3]. The steam reforming reactions for natural gas (assuming pure methane) are:

\begin{align*}
\text{CH}_4 + H_2O \leftrightharpoons CO + 3H_2 & \quad \Delta H_{298} = 206 \text{kJ/mol} \quad (1) \\
\text{CH}_4 + 2H_2O \leftrightharpoons CO_2 + 4H_2 & \quad \Delta H_{298} = 165 \text{kJ/mol} \quad (2)
\end{align*}

The partial oxidation is an exothermic process at high temperature.

\begin{align*}
\text{CH}_4 + 0.5O_2 \leftrightharpoons CO + 2H_2 & \quad \Delta H_{298} = -36 \text{kJ/mol} \quad (3) \\
\text{CH}_4 + O_2 \leftrightharpoons CO_2 + 2H_2 & \quad \Delta H_{298} = -319 \text{kJ/mol} \quad (4)
\end{align*}

The autothermal reforming is a combination of steam reforming with partial oxidation reaction by feeding both water and oxygen into the reactor. These systems can be very productive, fast starting and compact, since the exothermic partial oxidation reaction can supply heat to steam reforming reaction directly [4].

\begin{align*}
2\text{CH}_4 + H_2O + 0.5O_2 \leftrightharpoons 2CO + 5H_2 & \quad (5) \\
2\text{CH}_4 + 2H_2O + O_2 \leftrightharpoons 2CO_2 + 6H_2 & \quad (6)
\end{align*}

In this investigation, a primary study of utilization of natural gas in Thai gulf reservoir as a feedstock for hydrogen production by autothermal process was attempted. AspenPlus10.2 simulation program was used to simulate the autothermal process and study for the effect of its operating condition to maximize hydrogen yield as well as to minimize carbon-monoxide.

2. SIMULATION

2.1 Thermodynamics approach

The thermodynamic equilibrium in a reforming reactor can be calculated by two different methods, the use of equilibrium constant with specified possible multiple reaction and the minimizing Gibbs free energy methods [5]. In fuel-reforming reactor analysis the method of minimizing the Gibbs free energy is normally preferred. In this work, for given operating condition (reactant composition and inlet condition, reaction temperature and pressure), the equilibrium compositions of product gas containing H\textsubscript{2}, CO, CO\textsubscript{2}, CH\textsubscript{4} and H\textsubscript{2}O have been calculated. This calculation can be made with any commercially available software. In this investigation, AspenPlus\textsuperscript{\textregistered} was used.

In the simulation, 1 kmol/hr of natural gas, oxygen to carbon feed ratio and water to carbon feed ratio were directly fed into the reactor. The composition of natural gas from Thai Gulf reservoir is shown in Table 1.

The objective of this work was to study the effect of operating parameters, temperature, water to carbon feed ratio (W:C) and oxygen to carbon feed ratio (O\textsubscript{2}:C) on product gas compositions. These parameters are defined as follows:

\begin{equation}
\text{Water to carbon feed ratio (W:C)} = \frac{\text{molar flowrate of water}}{\text{carbon molar flowrate in natural gas}}
\end{equation}

\begin{equation}
\text{Oxygen to carbon feed ratio (O\textsubscript{2}:C)} = \frac{\text{molar flowrate of oxygen}}{\text{carbon molar flowrate in natural gas}}
\end{equation}
Oxygen to carbon feed ratio \((O_2:C)\)
\[
= \frac{\text{molar flow rate of oxygen}}{\text{molar flow rate in natural gas}}
\]  

(8)

Table 1 Composition of natural gas from Thai Gulf reservoir

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>67.39</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>9.33</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>5.15</td>
</tr>
<tr>
<td>i-C₄H₁₀</td>
<td>1.16</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>1.06</td>
</tr>
<tr>
<td>i-C₅H₁₂</td>
<td>0.34</td>
</tr>
<tr>
<td>n-C₅H₁₂</td>
<td>0.19</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>0.18</td>
</tr>
<tr>
<td>CO₂</td>
<td>14.26</td>
</tr>
<tr>
<td>N₂</td>
<td>0.94</td>
</tr>
<tr>
<td>H₂S</td>
<td>&gt;10-20 ppm</td>
</tr>
<tr>
<td>H₂O</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2 Sensitivity analysis [6,7]

Sensitivity blocks of AspenPlus 10.2 was used to analyze the effect of operating variables of the process that generates a matrix of manipulated variables versus sampled variables. If there is more than one manipulated variable, the sensitivity analysis is performed for each combination of manipulated variables.

In sensitivity analysis tools, the studying parameters were varied as followed: the reaction temperature increased from 400 to 800 °C with a step change of 100 °C, oxygen to carbon feed ratio was in the range of 0.01-2.5 with a step change of 0.1 and water to carbon feed ratio increased from 0.1 to 12.0 with a step change of 0.5 while keeping the reaction pressure at 1 bar. The conversion of natural gas is defined as follows:

\[
\text{Conversion} \ CH_4 = \frac{(CH_4)_i - (CH_4)_o}{(CH_4)_i} \]  

(9)

Gas products, H₂, CO, CO₂, CH₄ and H₂O, can be considered in terms of product yields defined as mole of component \(x\) per mole of carbon component in feed as follows:

\[
X \text{ yield} = \frac{\text{mole flow rate of component } x \text{ in product}}{\text{mole flow rate of carbon in feed}}
\]  

(10)

3. SIMULATION RESULTS AND DISCUSSION

3.1 Methane conversion in autothermal reactor

Fig. 1-5 show three-dimensional plots of methane conversion as a function of water to carbon feed ratio and oxygen to carbon feed ratio at five different temperatures of 400, 500, 600, 700, and 800 °C, respectively.
reaction is dominant. At higher W:C ratio, the H₂ yield is lower than 0.9 as O₂:C is higher than 0.6. The high H₂ conversion region is large when the temperature rises especially at temperature higher than 600 °C. By comparing between these two operating parameters, O₂:C ratio has more influence on CH₄ conversion than W:C ratio except in low reaction temperature range (< 600 °C). At higher temperature (800 °C), CH₄ is converted almost 100% not depending on W:C ratio when O₂: C ratio is higher than 0.5.

3.2 Effect of operating parameters on gas product compositions

Equilibrium compositions of autothermal reforming gas obtained from the simulation have been shown that only light products at equilibrium, H₂, CO, CO₂, CH₄ and H₂O, were produced whereas higher molecular weight hydrocarbons, i.e. C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂ and C₆H₁₄ were completely converted to lower molecular weight gases. The effect of operating parameters (temperature, W:C ratio and O₂:C feed ratio) on equilibrium gas products can be considered from equation (10).

Fig. 6 shows the autothermal equilibrium percent yield of hydrogen (H₂ yield) at operating temperature of 600 °C. The maximum H₂ yield is observed at lower value of O₂:C ratio and higher value of W:C ratio. At this condition, the reforming reaction is dominant. At higher W:C ratio, the H₂ yield is decreased as O₂:C ratio increases since the H₂ gas product is further reacted with excess O₂ to form water (see Fig.7) according to the combustion reaction as follows:

\[ H₂ + 0.5O₂ \rightleftharpoons H₂O \] (exothermic) (11)

However, at lower W:C ratio, the O₂:C ratio has the optimum value in which the maximum H₂ yield is obtained. Starting from the lower O₂:C ratio, partial oxidation reaction of hydrocarbon is enhanced as O₂:C ratio increases resulting in the increase of H₂ yield. Further increase of O₂:C ratio promotes total oxidation of H₂ and diminishes H₂ yield as in the above equation.

Among the hydrocarbon in natural gas, methane is the only hydrocarbon component that exists in the equilibrium as illustrated in Fig. 8. The methane yield (CH₄ yield) decreases when both W: C ratio and O₂: C ratio increase. It can be seen that the CH₄ yield falls abruptly at W: C ratio and O₂: C ratio higher than 0.5 and 0.3, respectively.

In addition to CH₄ and H₂, the oxygenated components, CO and CO₂, are also the main components in reforming gas as displayed in Fig. 9 and 10, respectively. The carbon-dioxide production evolves inversely to the carbon-monoxide one. As O₂:C ratio increases, the CO₂ yield increases with the corresponding decrease of CO yield. This is because of the oxidation reaction of CO as follows:

\[ CO + 0.5O₂ \rightleftharpoons CO₂ \] (12)

Fig.10 also indicates that CO yield is reduced as the W:C ratio increases. This can be explained by the water-gas shift reaction.

\[ CO + H₂O \rightleftharpoons CO₂ + H₂ \] (endothermic) (13)

As the amount of H₂O increases, the equilibrium is shifted to the right hand side of eq(13). Hence, the H₂ production is promoted as confirmed in Fig.8.
Fig. 9 Effect of oxygen to carbon ratio and water to carbon ratio on carbon-monoxide yield at temperature 600 °C.

Fig. 10 Effect of oxygen to carbon ratio and water to carbon ratio on carbon-dioxide yield at temperature 600 °C.

Unlike steam reforming reaction, autothermal reaction does not require external heat supply since both water and oxygen are fed with fuel to the reactor. All of the heat for steam reforming reaction is provided by partial oxidation (POX) of fuel. So no complex heat management engineering is required which makes autothermal process very attractive for mobile application.

In the simulation method, the reactor in the model was run with isothermal mode in order to study the effect of reaction temperature. To find the conditions of thermal neutral point, heat duty of the reactor for each case must be plotted, as shown the example of 600 °C case in Fig. 11.

Fig. 11 Effect of oxygen to carbon ratio and water to carbon ratio on heat duty at temperature 600 °C.

From Fig. 11, as water to carbon feed ratio is increased, heat duty of the reactor has more positive number indicating that more steam reforming (SR) is occurred (see Fig.11). On the other hand, the heat duty approaches the negative values as oxygen to carbon feed ratio increases since the partial oxidation reaction is an exothermic reaction.

The balance of heat consuming by steam reforming reaction and heat generating by partial oxidation reaction occurs at the thermal neutral point which is located at the intersection between heat duty curve and the abscissa. Therefore for each O₂:C feed ratio condition, the W:C feed ratio at the neutral point can be specified from Fig. 11. The corresponding H₂ and CO yield at the neutral point can be determined from Fig.12 and Fig.13, respectively. This method was used in the same manner at all temperature values studied. The results are concluded in Table 2.
For the fuel cell application, hydrogen is the most preferable product among all reformed gas. Since the anode of the proton exchange membrane fuel cell (PEMFC) can not tolerate carbon-monoxide which is a component in the reformed gas. Therefore, another objective is to determine an optimum operating regime (optimal W:C and O₂:C ratio) that can maximize the hydrogen yield with the lowest possible carbon-monoxide production under the desirable equilibrium temperature. Table 2 illustrates that for all W:C ratio under the neutral condition, there exists a range for maximum H₂ yield between O₂:C ratio of 0.7 to 1.1 at 600 °C and 0.9 at 500 °C. The optimum condition that satisfies both maximum H₂ yield and lowest CO yield is at W:C of 4.0, O₂:C of 0.9 and at 500°C.

4. CONCLUSION

A thermodynamic analysis of autothermal process has been conducted to investigate the possibility to use Thai Gulf natural gas to produce hydrogen gas for fuel cell application. This simulation results provide the information about the effect of operating conditions, i.e. temperature, water to carbon feed ratio and oxygen to carbon feed ratio on the reformed product gas compositions and hydrocarbon conversion. For the process of autothermal reforming, the key findings are as follows: From a thermodynamic point of view, natural gas can be used as a raw material for hydrogen production. At higher temperature, 100% of CH₄ conversion can be easily obtained, whereas at lower temperature higher W:C and O₂:C ratios are required for complete conversion. An increase in amount of water in feed gives higher H₂ yield and lower amount of undesirable products, CO and CH₄. At O₂:C ratio higher than 0.5-1.0 depending on temperature and W:C ratio, H₂ yield tends to decrease and the amount of water in product tend to increase. Favorable operating parameters under thermal neutral condition have been determined, which simultaneously satisfy the requirements for maximum H₂ yield and lowest CO yield, a reactor temperature of 500º C, the O₂:C ratio of 0.9 and W:C ratio of 4.0.

Table 2 Thermal neutral points of autothermal reactor

<table>
<thead>
<tr>
<th>O₂:C</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>H₂ yield</td>
<td>CO yield</td>
<td>H₂ yield</td>
<td>CO yield</td>
<td>H₂ yield</td>
</tr>
<tr>
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*NNP = no neutral point

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REFERENCES