Bi-reforming of methane: thermodynamic equilibrium analysis and selection of preferable reaction conditions

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Abstract. To determine the optimal reaction conditions of bi-reforming of methane thermodynamic analysis of reaction was performed. The effects of process variables, such as temperature (T = 500–1000°C), pressure (P = 1–30 atm), and feed composition CH₄/CO₂/H₂O on the product distribution were studied. It was shown that to maximize the conversion of reagents and yield of target products the high reaction temperatures (T ≥ 800°C) and atmospheric pressure should be applied. The reaction pathway of the bi-reforming of methane is affected by the feed composition. At 800°C the molar ratio of O/C ≥ 1.1 are preferable to work at region free of carbon formation. The CO₂ conversion and H₂/CO ratio are controlled by the value of CO₂/H₂O ratio. Depending on the field of application of synthesis gas, this ratio can be tuned from 1.2 to 2.8 through variation of CO₂/H₂O ratio from 3 to 0.1. The selected reaction conditions (T = 800°C, P = 1 atm, CH₄/CO₂/H₂O = 1/0.8/0.4) were applied for bi-reforming reaction over Ni catalyst which provided the process parameters close to thermodynamic equilibrium results.

1. Introduction
Carbon dioxide is one of the main "greenhouse gases". Over the past 200 years, the concentration of CO₂ in the atmosphere has increased from 270 to 385 ppm, mainly due to the continuous growth of consumption of carbon-rich fossil fuels (coal, oil, or natural gas) as energy resources [1]. At present, the technogenic emission of carbon dioxide into the atmosphere remains at a high level and averages 30 billion tons per year. To prevent changes in natural conditions on Earth, a decrease in CO₂ emissions is required. There are three main strategies for reducing atmospheric carbon dioxide – reducing the amount of CO₂ produced; CO₂ capture and storage; use of CO₂ as a reagent in the industry [2]. Sorption methods for capturing and concentrating carbon dioxide are very attractive due to their low cost and simple technical design. Various types of CO₂ adsorbents have been proposed, differing in their chemical composition, texture, morphology, and, accordingly, in the capacity and selectivity [3–5]. Once captured and concentrated, CO₂ can serve as a raw material for the production of many chemical products.
Combined steam and carbon dioxide reforming of methane (bi-reforming) can be considered as an environmentally friendly process since greenhouse gases – carbon dioxide and methane – are used as the main feedstock for the production of synthesis gas.

\[ 2\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow 3\text{CO} + 5\text{H}_2 \quad \Delta H^\circ_{298} = 453.0 \text{ kJ/mol} \]

The theoretical \( \text{H}_2/\text{CO} \) molar ratio is 1–2, which is suitable for further synthesis of hydrocarbon feedstock with added value by the Fischer-Tropsch or methanol synthesis reaction [6–8]. In the case of bi-reforming, in comparison with carbon dioxide reforming, it becomes possible to flexibly regulate the \( \text{H}_2/\text{CO} \) value, as well as to reduce the rate of catalyst coking. The bi-reforming of methane is a complex reaction. It involves the reactions of steam (1, 2) and carbon dioxide (3) reforming of methane, leading to the receipt of the target product – synthesis gas, a number of additional reactions that increase the yield of hydrogen (4, 5), as well as side reactions of the formation of carbon deposits (5–8) (Table 1).

| No. | Reaction                              | Reaction Equation       | \( \Delta H^\circ_{298} \), kJ/mol |
|-----|---------------------------------------|-------------------------|------------------------------------|
| 1   | Steam reforming of methane            | \( \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \) | 206.0                             |
| 2   | Carbon dioxide reforming of methane   | \( \text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow 2\text{CO} + 4\text{H}_2 \) | 164.7                             |
| 3   | Water-gas shift reaction              | \( \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \) | 41.1                              |
| 4   | Decomposition of methane              | \( \text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2 \) | 74.6                              |
| 5   | Disproportionation reaction           | \( 2\text{CO} \leftrightarrow \text{CO}_2 + \text{C} \) | –172.5                            |
| 6   | CO reduction                          | \( \text{CO} + \text{H}_2 \leftrightarrow \text{C} + \text{H}_2\text{O} \) | –131.3                            |
| 7   | CO\(_2\) reduction                   | \( \text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{C} + 2\text{H}_2\text{O} \) | –90.1                             |

The reaction pathway of the bi-reforming of methane is affected by the feed composition, temperature, and pressure. The thermodynamic analysis is an effective approach to predict the optimal reaction conditions to maximize reagent conversions and the yield of target products and avoid the formation of carbon deposits [9–11]. In the present work, thermodynamic analysis of the bi-reforming of methane was performed to elucidate the effects of process variables, such as temperature (500–1000°C), pressure (1–30 atm), and inlet mole ratios \( \text{CH}_4/\text{CO}_2/\text{H}_2\text{O} \) on the product distribution. The optimal conditions were selected and applied to bi-reforming of methane over Ni catalysts. The experimental data were compared with the thermodynamic equilibrium results.

2. Experimental

The thermodynamic equilibrium analysis was carried out by using the Gibbs free energy minimization method. The program IVTANTHERMO was used. The major components of bi-reforming of methane are gas-phase species such as \( \text{CH}_4, \text{CO}_2, \text{H}_2\text{O}, \text{CO}, \text{H}_2 \). The solid species C was also considered due to the coke formation during the reaction.

The bi-reforming of \( \text{CH}_4 \) reaction over Ni catalyst was studied in a quartz flow reactor (i.d. 14 mm) at atmospheric pressure, a temperature of 800°C, a gas flow rate of 200 mlN/min, and a molar ratio between reagents \( \text{CH}_4 : \text{CO}_2 : \text{H}_2\text{O} : \text{Ar} = 1:0.8:0.4:2.8 \). The catalyst was prepared by a polymerizable complex method with the following procedure of calcination and activation [12-14]. Prior to each catalytic activity test, the catalyst was reduced in 30%H\(_2/\text{Ar} \) flow (100 mlN/min) at 800°C for 1 h. The analysis of reaction mixtures was performed using the online automatic gas chromatography (GC) system Kristall 2000 m (Russia) with a flame ionization detector (FID) and thermal conductivity detector (TCD).

The values of conversion and yield were calculated using the following formulas:
\[ X_{\text{CH}_4} = 100 \times \frac{n_{\text{CH}_4}^{\text{in}} - n_{\text{CH}_4}^{\text{out}}}{n_{\text{CH}_4}^{\text{in}}} \]

CH\(_4\) conversion:

\[ X_{\text{CO}_2} = 100 \times \frac{n_{\text{CO}_2}^{\text{in}} - n_{\text{CO}_2}^{\text{out}}}{n_{\text{CO}_2}^{\text{in}}} \]

CO\(_2\) conversion:

\[ Y_{\text{H}_2} = 100 \times \frac{n_{\text{H}_2}^{\text{out}}}{2n_{\text{CH}_4}^{\text{in}} + n_{\text{H}_2}^{\text{in}}} \]

H\(_2\) yield:

\[ Y_{\text{CO}} = 100 \times \frac{n_{\text{CO}}^{\text{out}}}{n_{\text{CH}_4}^{\text{in}} + n_{\text{CO}_2}^{\text{in}}} \]

CO yield:

\[ Y_{\text{C}} = 100 \times \frac{n_{\text{C}}^{\text{out}}}{n_{\text{CH}_4}^{\text{in}} + n_{\text{CO}_2}^{\text{in}}} \]

Coke yield:

where \( n \) is moles of reagent before (in) and after (out) reaction.

3. Results and discussions

Figure 1 illustrates the effect of temperature and pressure on the values of conversion and product yield. An increase in the reaction temperature leads to an increase in the conversion of both methane and CO\(_2\) that is determined by the endothermic behavior of reaction. An increase in the yields of CO and H\(_2\) is also observed. The significant changes in the parameters are observed with growth of temperature up to 800°C, and then the values of the conversion of reagents and the yield of reaction products reach a plateau. An increase in pressure has a negative effect on the conversion of the initial reagents and yields of target products.

It should be noted that the high content of carbonaceous deposits formed at the temperatures \( T \leq 700^\circ \text{C} \) (Figure 1a). In this region the high methane conversion and low CO yield were obtained which indicates the contribution of side reactions in product distribution. With increasing pressure, an intensification of the coking is observed (Figure 1b).
Figure 1. Effect of temperature (a) and pressure (b) on values of conversion and product yield at fixed feed composition CH$_4$/CO$_2$/H$_2$O = 1/0.8/0.4: (a) pressure = 1 atm; (b) temperature = 800°C

Figure 2 demonstrates the effect of the feed composition on values of conversion and product yield. The methane conversion is weakly dependent on the feed composition. Its values are more than 90% in the entire investigated range of feed composition. Methane conversion tends to decrease when the amount of oxidizing agent is insufficient. With an increase of CH$_4$/(CO$_2$+H$_2$O) ratio to 0.75, X$_{CO2}$, Y$_{H2}$, and Y$_{CO}$ increase (Figure 2a). Then the values reach a plateau, with the exception of Y$_{CO}$. In case of CO yield, it decreases with an increase of CH$_4$/(CO$_2$+H$_2$O) ratio from 0.75 to 3. The lack of an oxidizing agent (C/O > 0.9) results in the formation of significant amounts of coke. Similar tendency is observed at variation of CO$_2$/CH$_4$ and H$_2$O/CH$_4$ ratios (Figures 2c and 2a). At low values of ratios, the coke formation is observed. An increase in the ratios leads to a transition to a region free of carbon. However, with an excessive content of the oxidant, the conversion of CO$_2$ and the yield of the target reaction products decrease.

Figure 2. Effect of the feed composition on the values of conversion and product yield at fixed temperature of 800°C and pressure of 1 atm: molar ratio of CO$_2$/H$_2$O = 2 (a); (b) CH$_4$/(CO$_2$+H$_2$O) = 0.8; (c) H$_2$O/CH$_4$ = 0.4; (d) CO$_2$/CH$_4$ = 0.8
It was shown that variation of CO$_2$/H$_2$O ratio has no significant effect on the X$_{CH4}$, Y$_{H2}$ and Y$_{CO}$, but significantly affects the X$_{CO2}$ (Figure 2b). With an increase in the CO$_2$/H$_2$O ratio from 0 to 1.5, the conversion of carbon dioxide increases and then reaches a plateau. The H$_2$/CO ratio is also controlled by value of CO$_2$/H$_2$O ratio. Depending on the field of application of synthesis gas, this ratio can be tuned from 1.2 to 2.8 through variation of CO$_2$/H$_2$O ratio from 3 to 0.1.

The study of the bi-reforming of methane without catalyst showed that the contribution of thermal conversion of the reagents is insignificant at 800°C (Figure 3). In the presence of a Ni catalyst, the process parameters are close to thermodynamic equilibrium results. The catalyst provides X$_{CH4}$=90%, X$_{CO2}$=86%, Y$_{H2}$= 90 % and Y$_{CO}$ = 87%, that is comparable to or higher than the process parameters described in the literature [15,16].

**Figure 3.** Bi-reforming of methane: experimental data vs. thermodynamic equilibrium results.
Reaction conditions: pressure = 1 atm, temperature 800°C, CH$_4$ : CO$_2$ : H$_2$O : Ar = 1:0.8:0.4:2.8

4. Conclusion
The thermodunamic analysis of bi-reforming reaction was performed using the Gibbs free energy minimization method. The dependence of the conversion of reagents and the yield of products on the reaction conditions (T = 500–1000°C, P = 1–30 atm, CH$_4$/CO$_2$/H$_2$O molar ratio) was studied. The product distribution during bi-reforming of methane was elucidated and conditions provided carbon free pathway was chosen. The atmospheric pressure, the temperature of at least 800°C, O/C ratio greater than 1.1 and CO$_2$/H$_2$O 1.5–2 are preferable reaction conditions. The bi-reforming reaction over Ni catalyst was evaluated under next selected reaction conditions T = 800°C, P = 1 atm, CH$_4$/CO$_2$/H$_2$O = 1/0.8/0.4. The Ni catalyst provides high process parameters X$_{CH4}$=90%, X$_{CO2}$=86%, Y$_{H2}$= 90 % and Y$_{CO}$ = 87% that close to thermodynamic equilibrium results.

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