Investigation of a Dual-Bed Autothermal Reforming of Methane for Hydrogen Production

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This paper presents a performance analysis of a dual-bed autothermal reformer of methane for hydrogen production. The first section of Pt/Al_2O_3 catalyst is designed for oxidation reaction, whereas the second one involves steam reforming reaction based on $Ni/MgAl_2O_4$ catalyst. A one dimensional, non-isothermal reactor model was employed to examine the reformer performance regarding important operating conditions such as H_2O/CH_4 feed ratio; O_2/CH_4 feed ratio, temperature and location of steam feed. The simulation results indicate that when the dual-bed reformer was operated at the H_2O/CH_4 feed ratio of 1.0–2.0 and O_2/CH_4 feed ratio of 0.45–0.60, the methane conversion of 93% and the H_2/CO product ratio of higher than 2.9 were obtained. In addition, it was found that adding steam at lower temperatures to the steam reforming section of the dual-bed reformer can produce the synthesis gas with a higher H_2/CO ratio.

1. Introduction

Hydrogen is considered a clean and sustainable energy that can be efficiently converted into many useful energy forms. In addition, it is a significant energy source along with the development of a fuel cell technology. Presently, most hydrogen is derived from methane using various reforming methods, i.e., steam reforming, partial oxidation and autothermal reforming. Although a steam reforming provides the highest hydrogen yield compared with the other reforming processes, it involves a highly endothermic reaction, which requires high external heat source. In a partial oxidation process, methane is combusted under a condition of limited oxygen. Although a large energy input is not needed for this process, hydrogen yield is a major concern. Recently, various studies have been conducted to develop an autothermal reforming process by coupling an endothermic steam reforming with an exothermic partial oxidation (Hoang and Chan, 2007; Wang, 2008; De Castro et al., 2010). The heat balance of both the reactions leads to a thermally neutral process and thus a more compact system (Authayanun et al., 2010).

In the autothermal reforming process, a consecutive reaction pathway that a total oxidation of part of fuel is carried out to produce CO_2 and H_2O, followed by a steam reforming of the remaining fuel with steam, is occurred. Since the oxidation reaction is faster than the reforming reaction, a large temperature gradient in the autothermal reformer is generally observed. The presence of a hot spot in the autothermal reformer

may affect stability and safety of the process and severe catalyst deactivation by sintering and carbon formation (Li et al., 2006). In order to control the reaction temperature, the autothermal reformer should be operated under suitable conditions. Previous investigations showed that the addition of more steam to the autothermal reformer decreases the reformer temperature and increases hydrogen yield because the methane oxidation is less pronounced (Simeone et al., 2008). Considering an operation of the autothermal reactor, Ni-based catalyst is normally employed to catalyze both steam reforming and oxidation reactions. However, the use of different catalysts for each reaction in the autothermal reactor is more effective (Zhu et al., 2004; Li et al., 2006; Meng et al., 2010).

In this work, a performance of the dual-bed autothermal reforming of methane for hydrogen production is analyzed. A non-isothermal, one-dimensional reactor model is used to investigate the reformer performance in terms of methane conversion and H_2/CO product ratio. The effects of H_2O/CH_4 feed ratio, O_2/CH_4 feed ratio and temperature and location of steam feed are examined to determine an optimal condition of the dual-bed autothermal reformer.

2. Mathematical model of a dual-bed autothermal reformer

A dual-bed autothermal reformer is generally an adiabatic fixed-bed reactor in which the catalyst bed is divided into two sections, as schematically represented in Figure 1. The first section involves the oxidation reaction based on Pt/Al_2O_3 catalyst, whereas the second one involves the steam reforming reaction based on $Ni/MgAl_2O_4$ catalyst. The reformer feeds consist of methane, steam and air. Methane is reacted with oxygen to produce carbon dioxide and steam - Eq. (1). Then, the remaining methane and the other gaseous components enter the second catalytic zone, where hydrogen-rich gas is produced via steam reforming and water gas-shift reactions (Eqs. (2)-(4)). In this study, it was assumed that the oxidation section occupies the reactor volume of 10%.
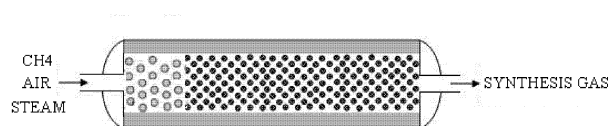
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H^\circ = -802.3 \ kJ/mol \qquad (1)$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^0 = 206.2 \ kJ/mol \qquad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^\circ = -41.2 \ kJ/mol \qquad (3)$$

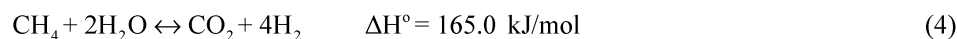$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad \Delta H^\circ = 165.0 \ kJ/mol \qquad (4)$$
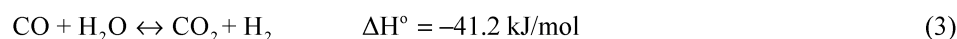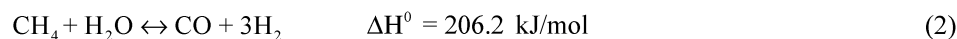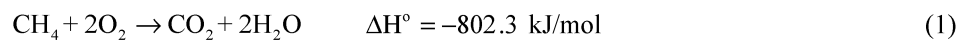

Figure 1: Schematic of a dual-bed autothermal reformer.

A one-dimensional model was employed to investigate the performance of the autothermal reforming of methane in a dual-bed reformer:

Mole balance equations for component i:

$$\frac{dn_i}{dz} = (1-\varepsilon)A\rho_{cat}\sum_{j=1}^{4} \upsilon_i \eta_j r_{i,j} \tag{5}$$

Energy balance equations:

$$\sum_i n_i C_{p,i} \frac{dT}{dz} = (1-\varepsilon)A\rho_{cat}\sum_{j=1}^{4} \eta_j r_j \left(-\Delta H\right)_j \tag{6}$$

The value of the effectiveness factor (η_j) of the reactions - Eqs. (1-4) - used to account for a intraparticle transport limitation are 0.05, 0.07, 0.70 and 0.06, respectively (Chan et al., 2005). The kinetic rate expression for the total oxidation, steam reforming and water gas-shift reactions are extracted from Halabi et al. (2008) as shown below:

$$r_1 = \frac{k_{1a}p_{CH_4}p_{O_2}}{(1+K_{CH_4}^{ox}p_{CH_4}+K_{O_2}^{ox}p_{O_2})^2} + \frac{k_{1b}p_{CH_4}p_{O_2}}{(1+K_{CH_4}^{ox}p_{CH_4}+K_{O_2}^{ox}p_{O_2})} \tag{7}$$

$$r_2 = \frac{k_2/p_{H_2}^{2.5}(p_{CH_4}p_{H_2O}-p_{H_2}^3 p_{CO}/K_{eq,2})}{(1+K_{CO}p_{CO}+K_{H_2}p_{H_2}+K_{CH_4}p_{CH_4}+K_{H_2O}p_{H_2O}/p_{H_2})^2} \tag{8}$$

$$r_3 = \frac{k_3/p_{H_2}(p_{CO}p_{H_2O}-p_{H_2}p_{CO_2}/K_{eq,3})}{(1+K_{CO}p_{CO}+K_{H_2}p_{H_2}+K_{CH_4}p_{CH_4}+K_{H_2O}p_{H_2O}/p_{H_2})^2} \tag{9}$$

$$r_4 = \frac{k_4/p_{H_2}^{3.5}(p_{CH_4}p_{H_2O}^2-p_{H_2}^4 p_{CO_2}/K_{eq,4})}{(1+K_{CO}p_{CO}+K_{H_2}p_{H_2}+K_{CH_4}p_{CH_4}+K_{H_2O}p_{H_2O}/p_{H_2})^2} \tag{10}$$

Tables 1 and 2 show the Arrhenius kinetic parameters of reaction rate constants and the Van't Hoff parameters for species adsorption used for calculation of reaction rate and equilibrium constants, respectively.

Table 1: Reaction equilibrium constants and Arrhenius kinetic parameters

Reaction		k_{0j} (mol/(kg$_{cat}$ s))	Ea_j (kJ/mol)	K_{0j}	H_j
1	$k_{1,a}$	8.11×10^5 bar^2	86.00		
	$k_{1,b}$	6.82×10^5 bar^2	86.00		
2	k_2	1.17×10^{15} bar$^{0.5}$	240.10	5.75×10^{12}	11476
3	k_3	2.83×10^{14} bar$^{0.5}$	243.90	7.24×10^{10}	-4639
4	k_4	5.43×10^5 bar^{-1}	67.13	1.26×10^{-2}	21646

Table 2: Van't Hoff parameter for species adsorption

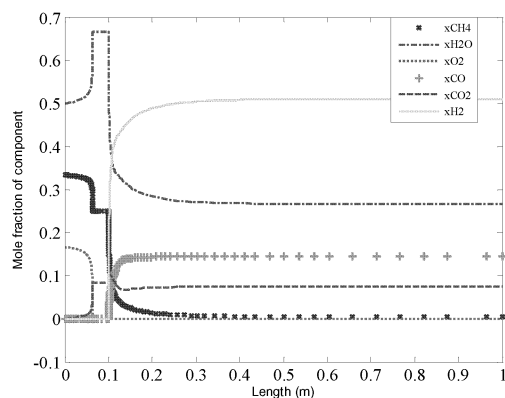|	K_{oi}	$\Delta H_{ads,i}$ (J/mol)		K_{oi}	$\Delta H_{ads,i}$ (J/mol)
K^0_{CH4}	1.26×10^{-1} bar^{-1}	-27.23	K_{CO}	8.23×10^{-5} bar^{-1}	-70.65
K^0_{O2}	7.87×10^{-7} bar^{-1}	-92.80	K_{H2}	6.12×10^{-9} bar^{-1}	-82.90
K_{CH4}	6.65×10^{-4} bar^{-1}	-38.28	K_{H2O}	1.77×10^5	88.68

Figure 2: Composition profiles in a dual-bed autothermal reactor at standard conditions.

3. Results and discussion

The fixed-bed reformer considered in this work is of cylindrical shape with 0.04 m in diameter and 1 m in length. Under the standard conditions, steam and oxygen are mixed with methane and introduced to the reformer at the temperature of 800 K and the ratios of 1.5 and 0.5, respectively. Figure 2 shows the composition profile of each component in the dual-bed autothermal reformer. In the oxidation section, O_2 is completely reacted with CH_4 and H_2O and CO_2 are produced. When the product gas passes through the reforming section, CH_4 and H_2O are rapidly consumed to generate H_2, CO and CO_2. It is observed that H_2 is more produced due to the water gas-shift reaction. Considering a reformer temperature of the dual-bed reformer, it is found that the temperature increases sharply and reaches to its maximum value of 1692 K in the oxidation section and then drops to 1063 K due to an increase in the methane reforming rate. In comparison with a conventional autothermal reformer, the dual-bed reformer provides a higher maximum temperature, whereas the outlet temperature is identical.

3.1 Effect of H_2O/CH_4 feed ratio

A H_2O/CH_4 feed ratio is varied in the range of 1.0-4.0 while an O_2/CH_4 feed ratio is kept constant at 0.5. The results show that the methane conversion decreases but the H_2/CO product ratio increases with increasing the H_2O/CH_4 feed ratio. When more steam is added to the reformer, the reactor temperature is reduced which in turn leads to lower reforming and oxidation rates. In addition, the equilibrium of the water gas shift reaction moves towards the product side, resulting in a higher H_2/CO product ratio. This implies that the addition of steam has a key effect on the reforming rates and the temperature of autothermal reactor. However, it can be observed that an increase in the H_2O/CH_4 feed ratio from 1.0 to 2.5 has no impact on the methane conversion. This is because O_2 is more active than steam; thereby, the oxidation reaction is more significant than the reforming reaction. Comparing with a conventional reformer, when operating at the H_2O/CH_4 feed ratio of 1.0-2.5, the dual-bed reformer shows slightly higher

methane conversion and gives the hydrogen-rich gas with a lower H_2/CO ratio due to the increased reformer temperature. For an operation at the H_2O/CH_4 feed ratio of more than 2.5, the methane conversion and the temperature outlet of the conventional and dual bed reformer decrease with increasing the H_2O/CH_4 ratio because a high amount of steam in feed lowers the oxidation and reforming rates.

3.2 Effect of O_2/CH_4 feed ratio

In this section, the effect of O_2/CH_4 feed ratio on the reformer performance is studied. The H_2O/CH_4 feed ratio is kept constant at 1.4. The results indicate that when the content of O_2 in the feed stream is higher, the methane conversion increases but the H_2/CO product ratio decreases. An increase in the O_2/CH_4 feed ratio raises the rate of methane oxidation which in turn increases the reformer temperature and thus, the steam reforming reaction is more pronounced. However, water gas-shift reaction disfavors a high temperature operation, more CO in the product stream remains. Similar result is observed for a convention autothermal reformer.

3.3 Effect of steam feed position

Since the addition of steam has a significant effect on the dual-bed autothermal reactor, especially in the steam reforming section. The position of steam feed is investigated here and it is found that adding steam in the oxidation section of the reformer does not affect the methane conversion and the H_2/CO product ratio. This is because the oxidation reaction dominates the reformer performance in this section. However, the addition of steam in the steam reforming section ($z = 0.1$-0.125 m) leads to a reduced methane conversion while the H_2/CO product ratio can be improved due to an increased rate of the water gas shift reaction. At $z > 0.125$ m, the steam reforming process is completely carried out and thus, the variations in the methane conversion and H_2/CO product ratio are not observed.

3.4 Effect of steam feed temperature

An impact of the steam temperature on the methane conversion and H_2/CO product ratio is studied. Steam with different temperatures varying between 400 and 800 K is introduced to the reformer at $z = 0.10$ m. The simulation results show that an increase in the feed temperature of steam rises the reformer temperature. As a result, the oxidation and reforming reaction rates is increased and a higher methane conversion can be observed. By contrast, feeding steam with a higher temperature decreases the H_2/CO product ratio due to a decreased water gas-shift reaction.

4. Conclusions

In this work, a dual-bed autothermal reformer in which two pack beds of Pt/Al_2O_3 and $Ni/MgAl_2O_4$ is connected in series, to produce hydrogen from methane was investigated by using a one-dimensional model under steady-state and non-isothermal conditions. The simulation results show that the dual-bed autothermal reactor provides higher reactor temperature and methane conversion compared with a conventional fixed-bed reformer. When the dual-bed reactor was operated with the H_2O/CH_4 ratio of 1.0–2.5 and O_2/CH_4 ratio of 0.45–0.60, the methane conversion and H_2/CO product ratio are more than 93% and 2.9. Adding more steam at the same temperature of feed stream into

the steam reforming section can improve both methane conversion and H_2/CO product ratio. When steam is added at lower temperatures, it was found that the H_2/CO product ratio is enhanced even the methane conversion is lower.

5. Acknowledgement

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