

## Methane steam reforming for synthetic diesel fuel production from steam-hydrogasifier product gases

Seok Ku Jeon<sup>\*\*\*\*\*,†</sup>, Chan Seung Park<sup>\*</sup>, Sang Done Kim<sup>\*\*</sup>, Byung Ho Song<sup>\*\*\*</sup>, and Joseph M. Norbeck<sup>\*</sup>

<sup>\*</sup>Bourns College of Engineering - Center for Environmental Research and Technology (CE-CERT),  
Department of Chemical and Environmental Engineering, University of California, Riverside, California 92521-0425, USA

<sup>\*\*</sup>Department of Chemical and biomolecular Engineering, Korea Advanced Institute of Science and Technology,  
Daejeon 305-701, Korea

<sup>\*\*\*</sup>Department of Chemical Engineering, Kunsan National University, Gunsan, Jeonbuk 573-701, Korea

<sup>\*\*\*\*</sup>Process Plant Group, Hyundai Engineering Co. Ltd., Seoul 158-723, Korea

(Received 16 January 2008 • accepted 23 April 2008)

**Abstract**—Steam-methane reforming (SMR) reaction was studied using a tubular reactor packed with NiO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst to obtain synthesis gases with H<sub>2</sub>/CO ratios optimal for the production of synthetic diesel fuel from steam-hydrogasification of carbonaceous materials. Pure CH<sub>4</sub> and CH<sub>4</sub>-CO<sub>2</sub> mixtures were used as reactants in the presence of steam. SMR runs were conducted at various operation parameters. Increasing temperature from 873 to 1,023 K decreased H<sub>2</sub>/CO ratio from 20 to 12. H<sub>2</sub>/CO ratio decreased from 16 to 12 with pressure decreasing from 12.8 to 1.7 bars. H<sub>2</sub>/CO ratio also decreased from about 11 to 7 with steam/CH<sub>4</sub> ratio of feed decreasing from 5 to 2, the lowest limit to avoid severe coking. With pure CH<sub>4</sub> as the feed, H<sub>2</sub>/CO ratio of synthesis gas could not be lowered to the optimal range of 4-5 by adjusting the operation parameters; however, the limitation in optimizing the H<sub>2</sub>/CO ratio for synthetic diesel fuel production could be removed by introducing CO<sub>2</sub> to CH<sub>4</sub> feed to make CH<sub>4</sub>-CO<sub>2</sub> mixtures. This effect can be primarily attributed to the contributions by CO<sub>2</sub> reforming of CH<sub>4</sub> as well as reverse water-gas shift reaction, which led to lower H<sub>2</sub>/CO ratio for the synthesis gas. A simulation technique, ASPEN Plus, was applied to verify the consistency between experimental data and simulation results. The model satisfactorily simulated changes of H<sub>2</sub>/CO ratio versus the operation parameters as well as the effect of CO<sub>2</sub> addition to CH<sub>4</sub> feed.

Key words: Steam-methane Reforming, Operation Parameters, CO<sub>2</sub> Addition to CH<sub>4</sub> Feed, ASPEN Simulator, Optimal H<sub>2</sub>/CO Ratio

### INTRODUCTION

Steam-methane reforming (SMR) has been extensively used as the major route to produce synthesis gas for synthetic diesel fuel production and fuel cell application [1,2]. SMR is composed of three main reactions:



Eqs. (1) and (2) are steam-methane reforming (SMR) reactions and are highly endothermic. Eq. (3) is a water-gas shift (WGS) reaction that is slightly exothermic [3]. Therefore, the SMR reaction favors a high temperature and low pressurized condition, while the WGS reaction favors a low temperature condition [4]. For the fuel cell application, a synthesis gas with high yield of H<sub>2</sub> and minimal CO is desirable since fuel cells require H<sub>2</sub> preferentially and CO is a poison to the catalyst used for the electrode of a fuel cell [5-9]. On the contrary, synthetic diesel fuel production such as Fischer-Tropsch synthesis requires synthesis gases with less H<sub>2</sub> and more CO because a hydrogen to carbon monoxide ratio of 2.1 : 1 is typically recommended for the synthesis [10-12].

The CE-CERT process, which we developed for the purpose of producing synthetic diesel fuel from carbonaceous materials, consists of three consecutive steps: steam-hydrogasification, steam-methane reforming and Fischer-Tropsch synthesis [13,14]. The process is unique in that a relatively large amount of water is used for the multiple purposes: (1) as a medium to transport the feedstock in a slurry form to a hydrogasifier, (2) as the pyrolysis-enhancing agent in vapor for steam-hydrogasification, and (3) as the reactant in vapor for steam-methane reforming. Due to the water-bearing feature of the CE-CERT process, the steam-hydrogasification product gas has a steam content high enough to favor the WGS reaction in a steam-methane reformer, which may cause the H<sub>2</sub>/CO ratio of synthesis gas to increase. Meanwhile, from the SMR reaction of the CE-CERT process, it is required to obtain a synthesis gas with H<sub>2</sub>/CO ratio of 4-5, because for each mol of CO produced, 2 or 3 mol of H<sub>2</sub> has to be allocated to Fischer-Tropsch reaction and an additional 2 mol of H<sub>2</sub> has to be recycled to steam-hydrogasification. Given the unique feature and hydrogen-recycling requirement of the CE-CERT process, the SMR reaction of the CE-CERT process should be operated with the parameters such as temperature, pressure and steam/CH<sub>4</sub> ratio optimized to obtain synthesis gas with H<sub>2</sub>/CO ratio of 4-5.

Ni catalysts used for the SMR reaction of the CE-CERT process have been commonly used because of metal availability and economic considerations. However, with Ni catalysts, the reaction is quite often accompanied by coke formation and sintering of Ni par-

<sup>†</sup>To whom correspondence should be addressed.

E-mail: dolgujsk@naver.com

ticles, leading to the catalyst deactivation [15]. Therefore, most SMR operations require large excess of steam to alleviate coking problem, which tends to result in high  $H_2/CO$  ratio for the synthesis gas. In order to resolve this restriction, some researchers have considered adding  $CO_2$  to the reactant mixture to reduce the  $H_2/CO$  ratio and prevent coking. Effendi et al. and Hufton et al. found that adding  $CO_2$  to SMR feed could decrease the  $H_2/CO$  ratio since the presence of  $CO_2$  not only initiates side reactions, but also affects the chemical equilibrium of the SMR reaction [16,17]. Zhang et al. also showed that  $CO_2$  plays a role in decreasing  $H_2/CO$  ratio, by producing additional CO from  $CO_2-CH_4$  reaction noted hereafter as dry reforming reaction [18].



Meanwhile, Snoeck et al. demonstrated by using a simulation model that  $CO_2$  added to SMR feed is consumed by reverse WGS reaction leading to CO production and  $H_2$  consumption, which explains the decrease of  $H_2/CO$  ratio for the synthesis gas [19]. As for the CE-CERT process, due to the relatively high  $CO_2$  content of the steam-hydrogasification product gas, a dry reforming reaction as well as reverse WGS reaction is favored to occur [13]. In fact, the occurrences of these reactions may be beneficial to the CE-CERT process, because they can contribute to lower  $H_2/CO$  ratio for the synthesis gas. The use of  $CO_2$  in the SMR reaction can find significance because it serves to provide a route to decrease the concentration of a greenhouse gas in the atmosphere [20].

In this study, motivated by the needs described above, the effects of temperature, pressure, steam/ $CH_4$  ratio and  $CO_2$  addition to  $CH_4$  feed were studied to determine the operating condition of the SMR reaction for obtaining the optimal  $H_2/CO$  ratios of synthesis gas for the CE-CERT process. In other words, we attempted to determine the specific operation parameters of the SMR reaction for the CE-CERT process, which has such uniqueness and requirement that the SMR feed has unusually high steam/ $CH_4$  ratio and  $H_2$  has to be recycled from steam-methane reformer to steam-hydrogasifier. Comparison of the experimental data with the results obtained by using the ASPEN PLUS simulator was discussed to verify the consistency between each other.

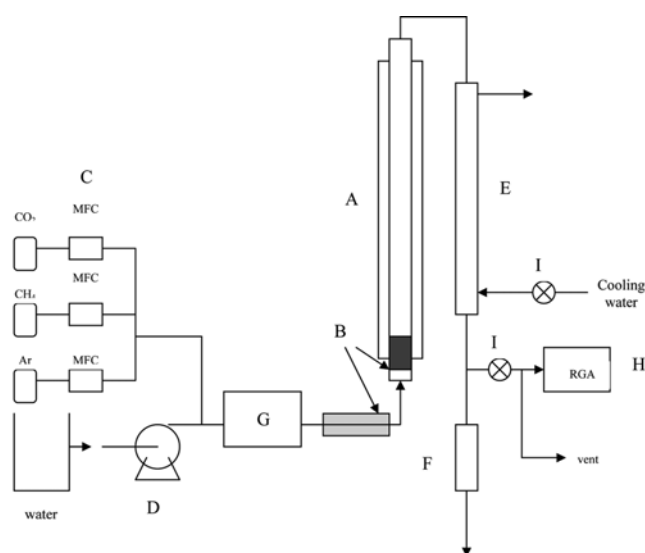
## EXPERIMENTAL PROCEDURE AND COMPUTER SIMULATION

### 1. Material

The SMR catalyst used in this study was G-90B catalyst obtained from Sud-Chemie Incorporated. Active phase of the catalyst was nickel supported on alumina in cylindrical pellet with center hole. The properties of the catalyst are listed in Table 1. Typically, 240 g (64  $cm^3$  volume) of the catalyst was loaded into the reactor. The catalyst was reduced initially by following the instruction provided

**Table 1. Catalyst properties**

NiO content (wt%)	15-20
Bulk density ( $g/cm^3$ )	0.929
Surface area ( $m^2/g$ )	3-15
Size (mm)	16 (O.D) * 10 (I.D) * 8 (H)
Side crush strength (N)	800



**Fig. 1. Schematic diagram of steam-methane reforming reaction system.**

- A. Main reactor
- B. Filter and preheating system
- C. Gas mixing system
- D. Water pump
- E. Condenser
- F. Condensed water collector
- G. Steam generator
- H. Mass spectrometer
- I. Flowmeter

by the manufacturer. The gases used in this study were of chemically pure grade (>99.99%) purchased from Prax-Air and were used without further purification.

### 2. Apparatus

The schematic diagram of the experimental system is shown in Fig. 1. The gas flow system provides various blends of different gases ( $CH_4$ ,  $CO_2$  and  $H_2$ ) and argon (Ar) by a combination of mass flow controllers (Brooks 5850 E and costal instrument 5870). Steam is generated with a high-pressure piston pump (Beckman model 110A) and a stainless steel heating block with a resistive heating element. The reactor is made from a stainless steel tube with 25.4 mm O.D. and 1,630 mm length. The reactor tube is heated by a series of electric heaters coiled in gypsum block (total electric capacity 1.9 kW). The heater is insulated by Kaowool ceramic wool. Four thermocouples are placed on the surface of the reactor. The thermocouples (K and J types) are connected to a temperature indicator, computer monitoring system and temperature controllers. Two PID controllers are used to control the temperature of each reaction zone in the reactor. A backpressure regulator is used to control the pressure of the reactor.

### 3. Test Procedure

Before the experiment was started, the SMR reactor and steam generator were heated to 673 K under argon flow. When the temperature reached 673 K, steam generation was initiated to protect the catalyst from inadvertent damage. When the reactor temperature reached the normal operating temperature, the gas stream was switched to the reactant gas. Pure  $CH_4$  or  $CH_4-CO_2$  mixture was used as reactant, which was mixed with steam in the steam generator and then preheated before entering the reactor. With pure  $CH_4$  feed, the SMR runs were performed at various conditions with temperature changing from 873 to 1,023 K, pressure changing from

1.7 to 12.8 bar, and steam/CH<sub>4</sub> ratio changing 2-5. Space velocity was fixed as 240 (ml/g cat hr). The SMR product gas and unreacted steam exiting the reactor were sent to a condenser where steam was condensed. The SMR product gas was then sent to a computer-interfaced RGA system for analysis. The RGA (QMS 300 series, Stanford research systems) analyzed the gas components in real time.

#### 4. Computer Simulation of SMR Reaction

The equilibrium calculation of SMR reaction was conducted with the ASPEN PLUS process simulator. The calculation was performed by the ASPEN built-in Gibbs reactor module that predicts the final product composition based on minimization of the total Gibbs free energy of the product gas. The components considered in this simulation include C(s), CH<sub>4</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>. To study the effects of temperature, pressure, steam/CH<sub>4</sub> ratio and CO<sub>2</sub> addition to CH<sub>4</sub> feed upon the product gas composition, a series of sensitivity analyses were also performed.

### RESULTS AND DISCUSSION

#### 1. SMR Reaction at the Reference Condition

Fig. 2 and Table 2 (run C) show the typical composition of the SMR product gas obtained from pure methane feed at the reference condition: temperature=973 K, steam/methane=3, pressure=

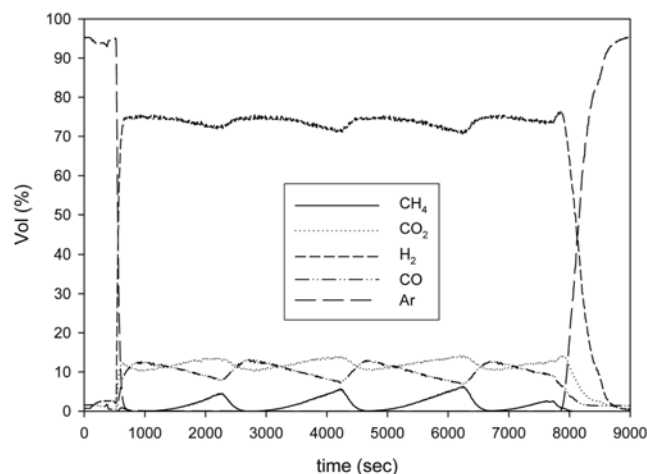


Fig. 2. Real-time composition profile of SMR product gas on a dry basis obtained from pure CH<sub>4</sub> feed at the reference condition.

Table 2. Typical composition of SMR product gases

SMR run	A	B	C	D	E
Temperature (K)	873	923	973	1,023	973
Pressure (bar)	1.7	1.7	1.7	1.7	12.8
Steam/CH <sub>4</sub> ratio	5.0	3.0	3.0	3.0	5.0
S.V (ml/g cat·hr)	240	240	240	240	240
H <sub>2</sub>	75.0	72.9	75.3	78.2	73.6
CO	3.6	7.6	10.6	12.8	4.5
CO <sub>2</sub>	16.6	13.5	12.2	9.7	14.8
H <sub>2</sub> /CO	20.7	9.55	7.09	6.12	16.5
CO/CO <sub>2</sub>	0.22	0.56	0.87	1.32	0.30

1.7 bar, space velocity=240 (ml/g cat·hr). At the reference condition, the SMR product gas exhibited H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratios of 7.09 and 0.87, respectively. This composition is to be used as the reference data for evaluating the effects of various operation parameters described in the subsequent section.

#### 2. Effect of Temperature

Temperature is known to be the most important variable to affect kinetic rate and composition of the product gas. Fig. 3 shows the increase of CH<sub>4</sub> conversion as temperature increases. In the case of pure CH<sub>4</sub> feed with steam/CH<sub>4</sub> ratio of 3, CH<sub>4</sub> conversion increased from 70% to 98% as temperature increased from 873 to 1,023 K, the trend of which is consistent with the literature [21]. Fig. 4 shows changes of H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratios of the product gas versus temperature. With pure CH<sub>4</sub> feed of steam/CH<sub>4</sub>=3 at 1.7 bar pressure, H<sub>2</sub>/CO ratio decreased from 16 to 7 and CO/CO<sub>2</sub> ratio increased from 0.3 to 1.3, as temperature increased from 873 to 1,023 K. Production of CO was favored as temperature increased, which is attributed to suppression of WGS reaction at higher temperature, as reported earlier [3,18]. The reverse WGS reaction to form CO from

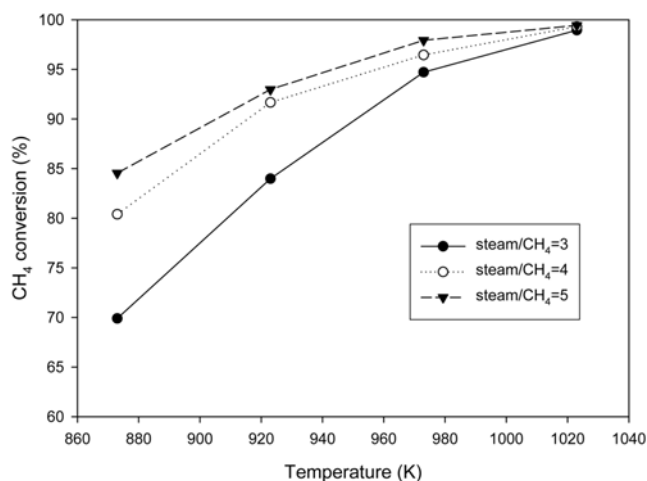


Fig. 3. CH<sub>4</sub> conversion from SMR reaction with the change in temperature (pressure=1.7 bar).

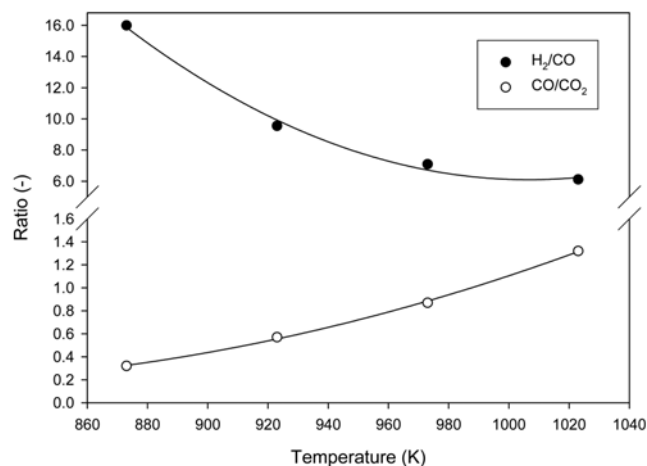


Fig. 4. H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratios of SMR product gas with the change in temperature (pressure=1.7 bar, steam/CH<sub>4</sub>=3).

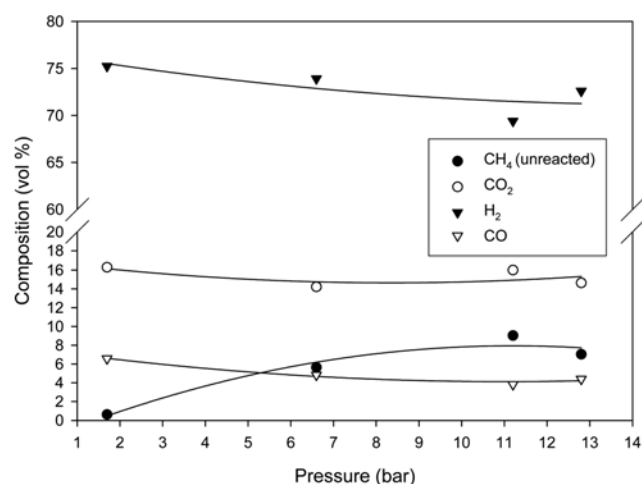


Fig. 5. Product gas composition on a dry basis with the change in pressure (temperature=1,023 K, steam/CH<sub>4</sub>=3).

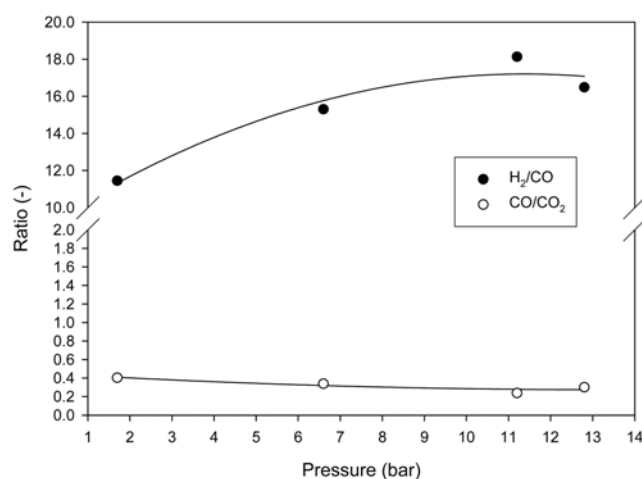


Fig. 6. H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratio of SMR product gas with the change in pressure (temperature=1,023 K, steam/CH<sub>4</sub>=3).

CO<sub>2</sub> can also be dominant as temperature increases. From these results, we can conclude that SMR reaction should be operated at high temperature to get a lower H<sub>2</sub>/CO ratio.

### 3. Effect of Pressure

Fig. 5 shows the effect of reactor pressure on the composition of the product gas. Changes of H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratios versus pressure are shown in Fig. 6. The production of H<sub>2</sub> and CO decreased as pressure increased from 1.7 to 12.8 bar, accompanied by the increase of CH<sub>4</sub> slippage. Higher sensitivity of CO versus pressure, relative to other species, gave rise to the increase of H<sub>2</sub>/CO ratio and decrease of CO/CO<sub>2</sub> ratio as pressure increased. With pure CH<sub>4</sub> feed of steam/CH<sub>4</sub>=5 at 1,023 K, H<sub>2</sub>/CO ratio increased from 11.6 to 16.0 and CO/CO<sub>2</sub> ratio decreased from 0.4 to 0.3, as pressure increased from 1.7 to 12.8 bar. From these results, it can be noted that low pressure may be favored for our SMR reactor in order to obtain lower H<sub>2</sub>/CO ratio, while in reality, most SMR reactors are operated under high pressure, e.g., 15–30 bar, in order to avoid coking [22]. Therefore, it is necessary to operate our SMR reactor under a pressure close to 15 bar in order to obtain lower H<sub>2</sub>/CO ratio and

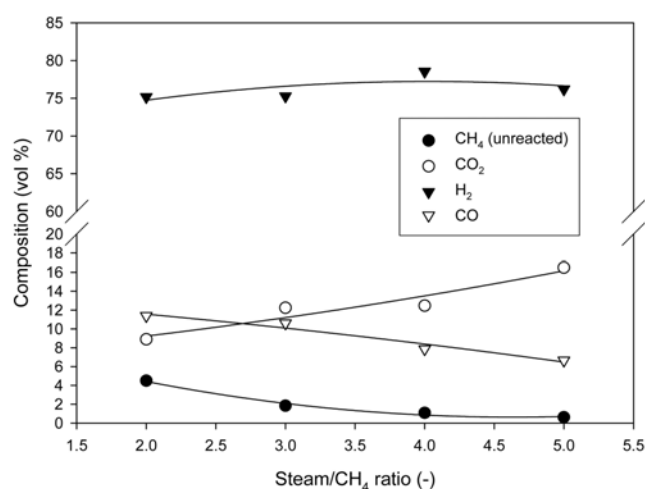


Fig. 7. Product gas composition on a dry basis with the change in steam/CH<sub>4</sub> ratio (temperature=973 K, pressure=1.7 bar).

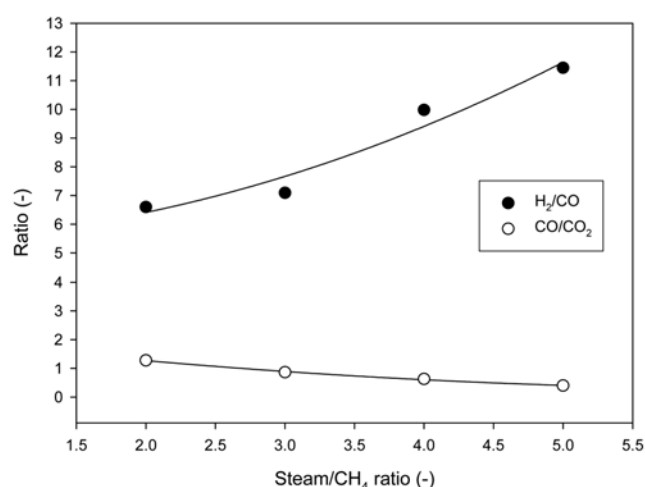


Fig. 8. H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratios of SMR product gas with the change in steam/CH<sub>4</sub> ratio (temperature=973 K, pressure=1.7 bar).

avoid catalyst fouling by carbon deposit formation.

### 4. Effect of Steam/Methane Ratio

Figs. 7 and 8 show the composition of the product gas, and H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratios for pure CH<sub>4</sub> feeds of various steam/CH<sub>4</sub> ratios. H<sub>2</sub> concentration increased and CO concentration decreased as steam/CH<sub>4</sub> ratio increased from 2 to 5. As the concentration of steam increased, the equilibrium of the SMR reaction shifted to the right to bring about more H<sub>2</sub> and CO formation; however, the produced CO reacted subsequently with steam to produce CO<sub>2</sub> and H<sub>2</sub> because the equilibrium of WGS reaction also shifted to the right. Therefore, as shown in Fig. 8, the H<sub>2</sub>/CO ratio increased from 6.6 to 11.45 and the CO/CO<sub>2</sub> ratio decreased from 1.28 to 0.4 as steam/CH<sub>4</sub> ratio increased from 2 to 5. From this, it is necessary to operate our SMR reactor at lower steam/CH<sub>4</sub> ratio in order to obtain H<sub>2</sub>/CO ratio optimal for SDF production, although a steam/CH<sub>4</sub> ratio lower than 2 should be avoided to prevent catalyst coking.

### 5. Effect of CO<sub>2</sub> Addition

The results described above indicate that variation of the opera-



tion parameters such as temperature, pressure and steam/CH<sub>4</sub> ratio of pure CH<sub>4</sub> feed can adjust the H<sub>2</sub>/CO ratio of our SMR product gas to some extent; however, it is difficult to obtain an H<sub>2</sub>/CO ratio optimal for Fischer-Tropsch synthesis of the CE-CERT process, i.e., H<sub>2</sub>/CO=4-5. Therefore, CO<sub>2</sub> was added to the pure CH<sub>4</sub> feed and its effect upon H<sub>2</sub>/CO ratio studied. Since the SMR and WGS reactions occur simultaneously, we have to consider the equilibrium constants for these reactions,  $K_{SMR}$  and  $K_{WGS}$ . Hufton et al. rearranged the equations for these constants and obtained H<sub>2</sub> and CO mole fractions from them [17].

$$y_{H_2} = \frac{[K_{SMR}K_{WGS}]^{0.25} \cdot [y_{CH_4}]^{0.25} [y_{H_2O}]^{0.5}}{[P]^{0.5} \cdot [y_{CO_2}]^{0.25}} \quad (5)$$

$$y_{CO} = \frac{[K_{SMR}]^{0.25} \cdot [y_{CH_4}]^{0.25} [y_{CO_2}]^{0.75}}{[K_{WGS}]^{0.75} [P]^{0.5} \cdot [y_{H_2}]^{0.25}} \quad (6)$$

where P denotes the total pressure.

Rearranging the above equations gives an equation for H<sub>2</sub>/CO ratio as follows:

$$y_{H_2}/y_{CO} = [K_{WGS}] \cdot \frac{[y_{H_2}]^{0.25} [y_{H_2O}]^{0.5}}{[y_{CO_2}]} \quad (7)$$

From Eq. (5), we can see that H<sub>2</sub> mole fraction decreases as CO<sub>2</sub> mole fraction increases. We can also see from Eq. (6) that CO mole fraction increases as CO<sub>2</sub> mole fraction increases. Therefore, the H<sub>2</sub>/CO ratio decreases as the CO<sub>2</sub> mole fraction increases, as explained by Eq. (7). Fig. 9 demonstrates the effect of CO<sub>2</sub> addition to CH<sub>4</sub> feed upon H<sub>2</sub>/CO ratio of SMR product gas. Our study shows that the H<sub>2</sub>/CO ratio of SMR product gas with CO<sub>2</sub> added to CH<sub>4</sub> (CO<sub>2</sub>/CH<sub>4</sub>=0.56) is 2.5 times lower than that with pure CH<sub>4</sub>, indicating that CO<sub>2</sub> can play a significant role in lowering H<sub>2</sub>/CO ratio, owing to the reactions (3) and (4) described above. This result is consistent with the literature: Effendi et al. showed that CO<sub>2</sub> addition to CH<sub>4</sub> (CO<sub>2</sub>/CH<sub>4</sub>=0.67) resulted in lower H<sub>2</sub>/CO ratio of SMR product gas as compared with Hardiman et al.'s work conducted in the absence of CO<sub>2</sub> [16,23]. Compared with these previous works, our study dealt with the effect of CO<sub>2</sub> addition to CH<sub>4</sub> feeds of broader

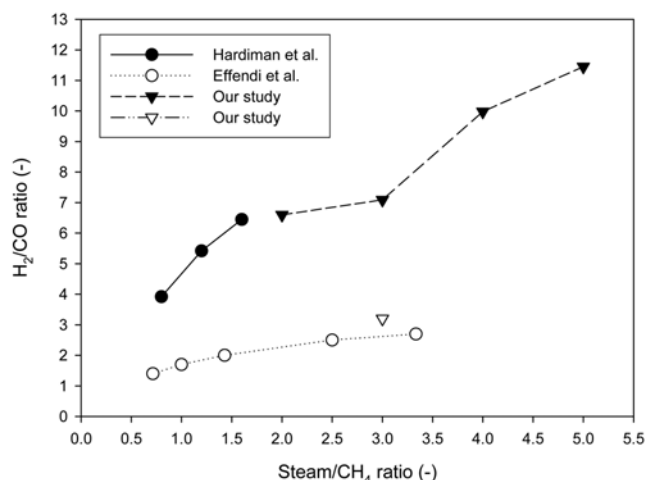


Fig. 9. Comparison of our work with the literature for pure CH<sub>4</sub> and CH<sub>4</sub>-CO<sub>2</sub> mixture feeds (●: CO<sub>2</sub>/CH<sub>4</sub>=0, ○: CO<sub>2</sub>/CH<sub>4</sub>=0.67, ▼: CO<sub>2</sub>/CH<sub>4</sub>=0, ▽: CO<sub>2</sub>/CH<sub>4</sub>=0.5).

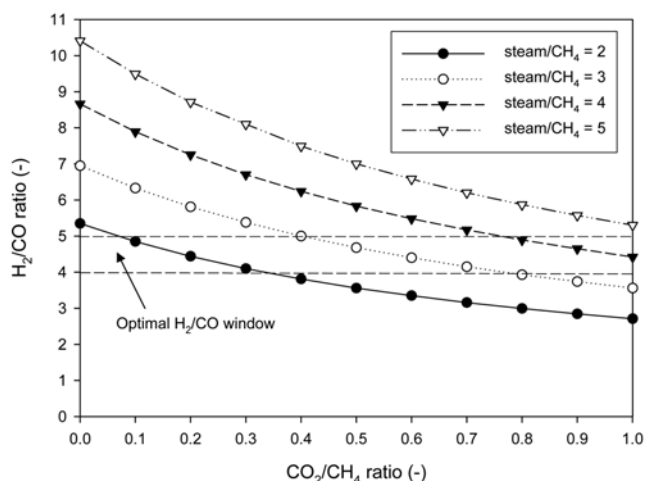


Fig. 10. H<sub>2</sub>/CO ratio of SMR product gas with the change in CO<sub>2</sub>/CH<sub>4</sub> ratio (temperature=973 K, pressure=1.7 bar, steam/CH<sub>4</sub>=2-5).

steam/CH<sub>4</sub> ratios. It should be considered that besides the reverse WGS reaction and the dry reforming reaction, CO<sub>2</sub> can also play a role in reducing H<sub>2</sub>/CO ratio by Boudouard reaction (C+CO<sub>2</sub>→2CO) [24,25]. Fig. 10 shows the H<sub>2</sub>/CO ratio of the SMR product gas versus CO<sub>2</sub>/CH<sub>4</sub> ratio as simulated by ASPEN PLUS process simulator. This plot supports the experimental findings: increasing the CO<sub>2</sub>/CH<sub>4</sub> ratio of the SMR feed gives birth to lower H<sub>2</sub>/CO ratios of the SMR product gas. From these results, we can optimize the CO<sub>2</sub>/CH<sub>4</sub> ratio of SMR feed for SDF production.

## 6. Comparison between Experiments and Simulation

Figs. 11 and 12 illustrate a comparison of the H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratios between the experiment and calculation obtained by ASPEN

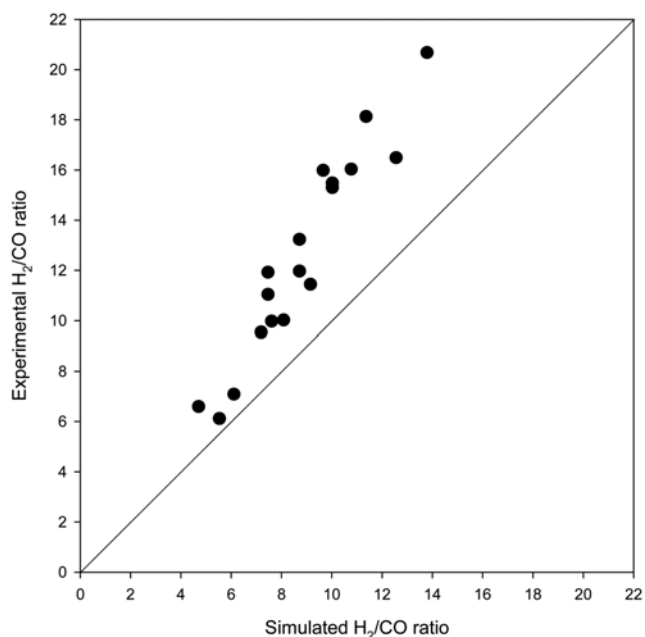


Fig. 11. Comparison of H<sub>2</sub>/CO ratio between experiment and simulation for pure CH<sub>4</sub> feeds (temperature: 873-1,023 K, pressure: 1.7-12.8 bar, steam/CH<sub>4</sub>: 2-5).

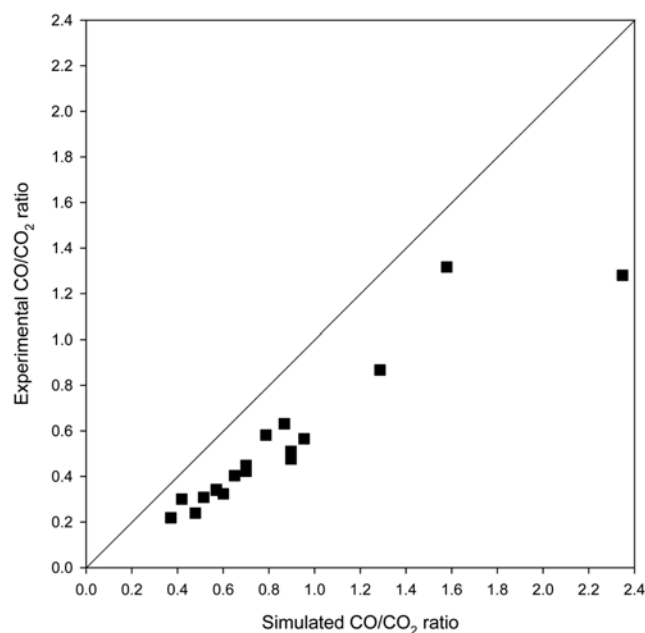


Fig. 12. Comparison of CO/CO<sub>2</sub> ratio between experiment and simulation for pure CH<sub>4</sub> feeds (temperature: 873-1,023 K, pressure: 1.7-12.8 bar, steam/CH<sub>4</sub>: 2-5).

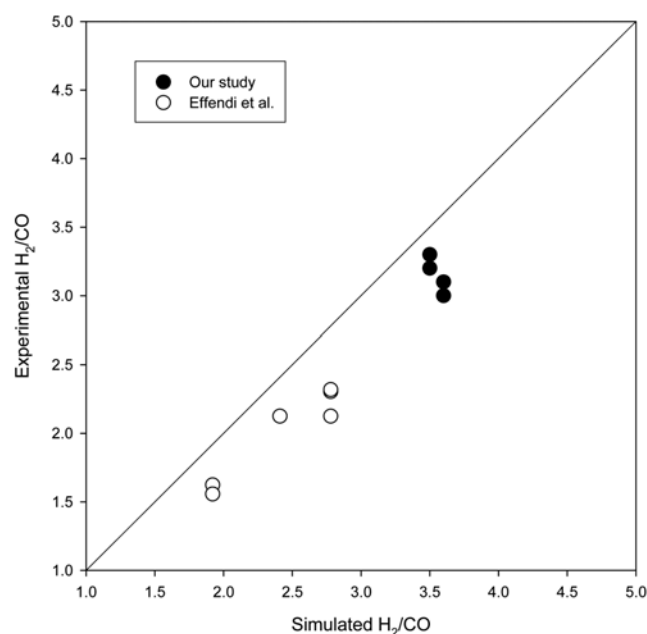


Fig. 13. Comparison of H<sub>2</sub>/CO ratio between experiment and simulation for CH<sub>4</sub>-CO<sub>2</sub> mixture feeds (temperature: 1,086-1,106 K, pressure: 20.4 bar, steam/CH<sub>4</sub>: 2.3-3.1, CO<sub>2</sub>/CH<sub>4</sub>: 0.36-0.67).

PLUS process simulator for pure CH<sub>4</sub> feed. Fig. 13 shows the comparison for CH<sub>4</sub>-CO<sub>2</sub> mixture feed. These figures demonstrate that whereas the experimental H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratios are not in good agreement with the simulated ratios for pure CH<sub>4</sub> feed, the addition of CO<sub>2</sub> to CH<sub>4</sub> feed results in improvement of the agreement between the experimental and simulated ratios. This strongly supports our discussion of the experimental results indicating that CO<sub>2</sub>

added to CH<sub>4</sub> feed can play a significant role in lowering the overall H<sub>2</sub>/CO ratio of SMR product gas.

## CONCLUSION

The steam-methane reforming reaction was studied in pure CH<sub>4</sub> and CH<sub>4</sub>-CO<sub>2</sub> mixture environments. Experimental results were compared with simulated data obtained by ASPEN PLUS process simulator. The effects of temperature, pressure, steam/methane ratio and CO<sub>2</sub> addition were discussed to obtain the optimal H<sub>2</sub>/CO ratio of synthesis gas for SDF production. As the reaction temperature increased from 873 to 1,073 K, the H<sub>2</sub>/CO ratio decreased and conversion of CH<sub>4</sub> increased. Meanwhile, as the pressure increased from 1.7 to 12.8 bars, the H<sub>2</sub>/CO ratio increased and CO/CO<sub>2</sub> ratio decreased; the same trends were observed when the steam/CH<sub>4</sub> ratio increased. The H<sub>2</sub>/CO ratio decreased as CO<sub>2</sub> was added to the SMR feed gas. Experimental and simulated H<sub>2</sub>/CO and CO/CO<sub>2</sub> ratios were consistent with each other satisfactorily. With pure CH<sub>4</sub> as the feed, H<sub>2</sub>/CO ratio of synthesis gas could not be lowered to the range of 4-5 by adjusting the operation parameters such as temperature, pressure and steam/CH<sub>4</sub> ratio. This limitation in optimizing the H<sub>2</sub>/CO ratio for synthetic diesel fuel production could be removed by introducing CO<sub>2</sub> to CH<sub>4</sub> feed to make a CH<sub>4</sub>-CO<sub>2</sub> mixture. In other words, adding CO<sub>2</sub>, we can obtain 4-5 of H<sub>2</sub>/CO ratio of synthesis gas using the same operating condition and we can also avoid the coking problem. A simulation technique, ASPEN Plus, was applied to experimental results in order to verify the consistency between experimental data and simulation results. The model satisfactorily simulated the changes of H<sub>2</sub>/CO ratio versus the operating parameters (temperature, pressure and steam/CH<sub>4</sub> ratio) and also verified the effect of CO<sub>2</sub> to CH<sub>4</sub> feed.

## REFERENCES

1. S. M. Leiby, *PEP Report No. 212*, SRI International, Menlo park (1994).
2. J. Xu and G. F. Froment, *AIChE J.*, **35**, 88 (1989).
3. D. Lee, I. Baek and W. Yoon, *Chemical Engineering Science*, **59**, 931 (2004).
4. P. L. Spath and D. C. Dayton, *Technical Report*, NREL/TP-510-34929 (2003).
5. P. Waszczuk, A. Wieckowski, P. Zelenay, S. Gottesfeld, C. Coutanceau, J.-M. Léger and C. Lamy, *Journal of Electroanalytical Chemistry*, **511**, 55 (2001).
6. G. L. Semin, V. D. Belyaev, A. K. Demin and V. A. Sobyenin, *Applied Catalysis A: General*, **181**, 131 (1999).
7. M. A. Peña, J. P. Gómez and J. L. G. Fierro, *Applied Catalysis A: General*, **144**, 7 (1996).
8. S. J. Lee, S. Mukerjee, E. A. Ticianelli and J. McBreen, *Electrochim. Acta*, **44**, 3283 (1999).
9. M. Murthy, M. Esayan, A. Hobson, S. Mackenzie, W. Lee and J. W. Van Zee, *J. Electrochem. Soc.*, **148**, A1141 (2001).
10. R. B. Anderson, *The Fischer-Tropsch synthesis*, Academic Press, New York (1984).
11. M. E. Dry, in: J. R. Anderson, M. Boudart, *Catalysis Science and Technology*, **1**, 159 (1981).
12. K. Terblanche, *Hydrocarbon Engineering*, **March/April**, 2 (1997).

13. S. K. Jeon, C. E. Hackett and J. M. Norbeck, *Journal of Scientific and Industrial Research*, **62**, 81 (2003).
14. S. K. Jeon, C. Park, C. Hackett and E. Norbeck, *Fuel*, **86**, 2817 (2007).
15. M. C. J. Bradford and M. A. Vannice, *Catal. Rev. Sci. Eng.*, **41**, 1 (1999).
16. A. Effendi, Z.-G. Zhang, K. Hellgardt, K. Honda and T. Yoshida, *Catalysis Today*, **77**, 181 (2002).
17. J. R. Hufton, S. Mayorga and S. Sircar, *AIChE J.*, **45**, 248 (1999).
18. Z. Zhang, X. E. Verykios, S. M. MacDonald and S. Affrossman, *Journal of Physical Chemistry*, **100**, 744 (1996).
19. J. Snoeck, G. Froment and M. Fowles, *International Journal of Chemical Reactor Engineering*, **1**, A7, 1 (2003).
20. O. González, J. Lujano, E. Pietri and M. Goldwasser, *Catalysis Today*, **107**, 436 (2005).
21. M. V. Twigg, *Catalyst handbook*, Wolfe, London (1989).
22. Y. S. Seo, A. Shirley and S. T. Kolaczowski, *Journal of Power Source*, **108**, 213 (2002).
23. K. M. Hardiman, T. T. Ying, A. A. Adesina, E. M. Kennedy and B. Z. Dlugogorski, *Chemical Engineering Journal*, **102**, 119 (2004).
24. J. R. Rostmp-Nielsen, J. R. Anderson and M. Boudart, *Catalysis Science and Technology*, **5**, 1 (1984).
25. I. Alstrup, *J. Catal.*, **109**, 241 (1988).