

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

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Abstract—Steam-methane reforming (SMR) reaction was studied using a tubular reactor packed with $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst to obtain synthesis gases with H_2/CO ratios optimal for the production of synthetic diesel fuel from steam-hydrogasification of carbonaceous materials. Pure CH_4 and $\text{CH}_4\text{-CO}_2$ 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_2/CO ratio from 20 to 12. H_2/CO ratio decreased from 16 to 12 with pressure decreasing from 12.8 to 1.7 bars. H_2/CO ratio also decreased from about 11 to 7 with steam/ CH_4 ratio of feed decreasing from 5 to 2, the lowest limit to avoid severe coking. With pure CH_4 as the feed, H_2/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_2/CO ratio for synthetic diesel fuel production could be removed by introducing CO_2 to CH_4 feed to make $\text{CH}_4\text{-CO}_2$ mixtures. This effect can be primarily attributed to the contributions by CO_2 reforming of CH_4 as well as reverse water-gas shift reaction, which led to lower H_2/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_2/CO ratio versus the operation parameters as well as the effect of CO_2 addition to CH_4 feed.

Key words: Steam-methane Reforming, Operation Parameters, CO_2 Addition to CH_4 Feed, ASPEN Simulator, Optimal H_2/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_2 and minimal CO is desirable since fuel cells require H_2 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_2 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_2/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_2/CO ratio of 4-5, because for each mol of CO produced, 2 or 3 mol of H_2 has to be allocated to Fischer-Tropsch reaction and an additional 2 mol of H_2 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_4 ratio optimized to obtain synthesis gas with H_2/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-

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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 H₂/CO ratio for the synthesis gas. In order to resolve this restriction, some researchers have considered adding CO₂ to the reactant mixture to reduce the H₂/CO ratio and prevent coking. Effendi et al. and Hufton et al. found that adding CO₂ to SMR feed could decrease the H₂/CO ratio since the presence of CO₂ not only initiates side reactions, but also affects the chemical equilibrium of the SMR reaction [16,17]. Zhang et al. also showed that CO₂ plays a role in decreasing H₂/CO ratio, by producing additional CO from CO₂-CH₄ reaction noted hereafter as dry reforming reaction [18].



Meanwhile, Snoeck et al. demonstrated by using a simulation model that CO₂ added to SMR feed is consumed by reverse WGS reaction leading to CO production and H₂ consumption, which explains the decrease of H₂/CO ratio for the synthesis gas [19]. As for the CE-CERT process, due to the relatively high CO₂ 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 H₂/CO ratio for the synthesis gas. The use of CO₂ 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/CH₄ ratio and CO₂ addition to CH₄ feed were studied to determine the operating condition of the SMR reaction for obtaining the optimal H₂/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/CH₄ ratio and H₂ 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 cm³ 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

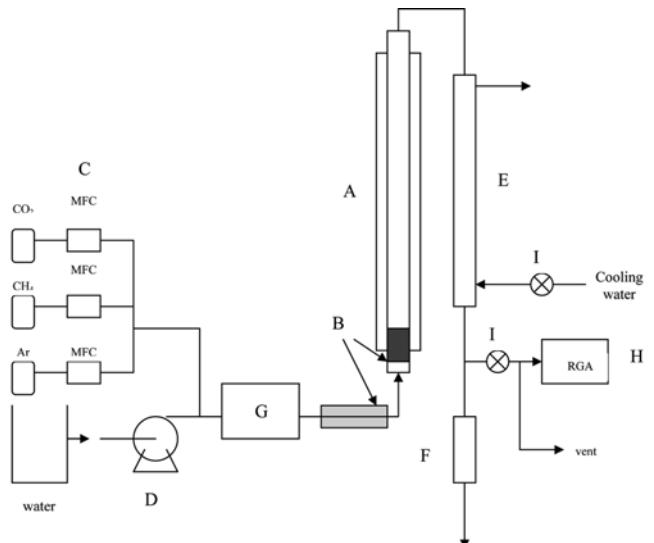


Fig. 1. Schematic diagram of steam-methane reforming reaction system.

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

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 (CH₄, CO₂ and H₂) 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 CH₄ or CH₄-CO₂ mixture was used as reactant, which was mixed with steam in the steam generator and then preheated before entering the reactor. With pure CH₄ 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/CH₄ 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, Stamford 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), CH₄, CO, CO₂, and H₂. To study the effects of temperature, pressure, steam/CH₄ ratio and CO₂ addition to CH₄ 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=

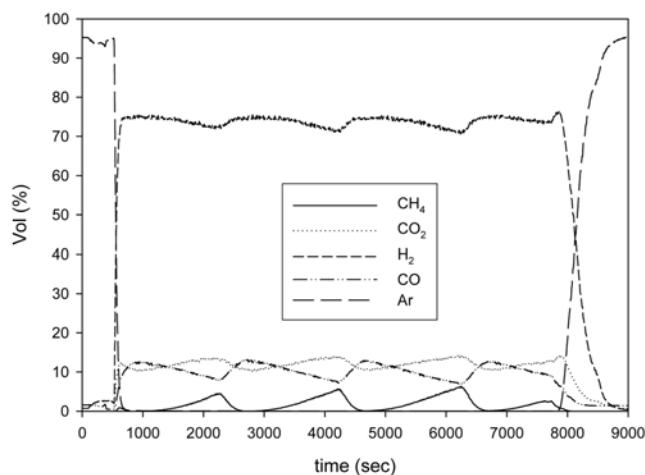


Fig. 2. Real-time composition profile of SMR product gas on a dry basis obtained from pure CH₄ feed at the reference condition.

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 ₄ ratio	5.0	3.0	3.0	3.0	5.0
S.V (ml/g cat·hr)	240	240	240	240	240
H ₂	75.0	72.9	75.3	78.2	73.6
CO	3.6	7.6	10.6	12.8	4.5
CO ₂	16.6	13.5	12.2	9.7	14.8
H ₂ /CO	20.7	9.55	7.09	6.12	16.5
CO/CO ₂	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 H₂/CO and CO/CO₂ 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 CH₄ conversion as temperature increases. In the case of pure CH₄ feed with steam/CH₄ ratio of 3, CH₄ 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 H₂/CO and CO/CO₂ ratios of the product gas versus temperature. With pure CH₄ feed of steam/CH₄=3 at 1.7 bar pressure, H₂/CO ratio decreased from 16 to 7 and CO/CO₂ 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

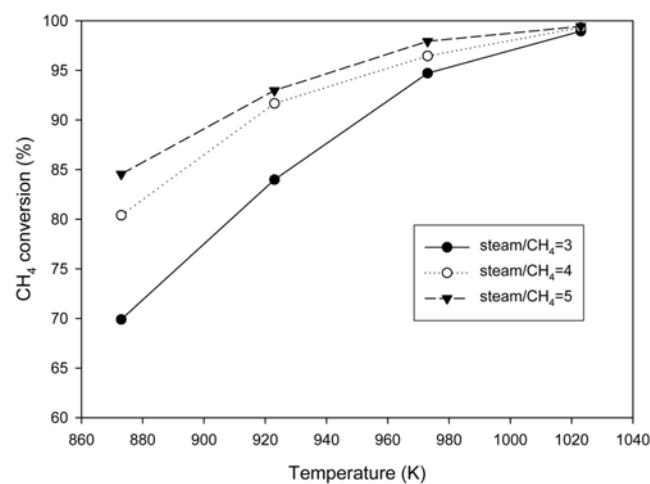


Fig. 3. CH₄ conversion from SMR reaction with the change in temperature (pressure=1.7 bar).

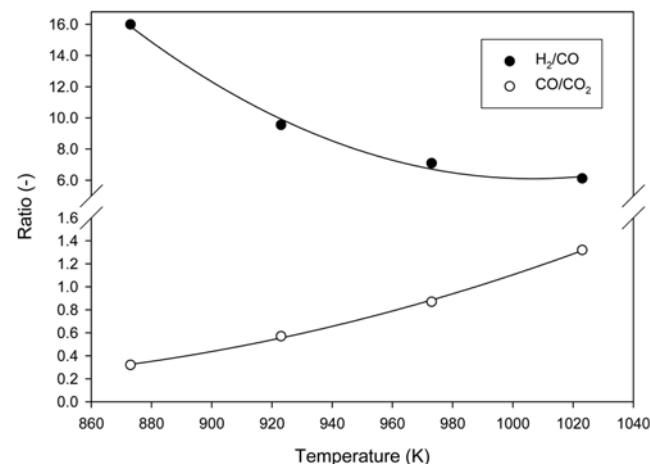


Fig. 4. H₂/CO and CO/CO₂ ratios of SMR product gas with the change in temperature (pressure=1.7 bar, steam/CH₄=3).

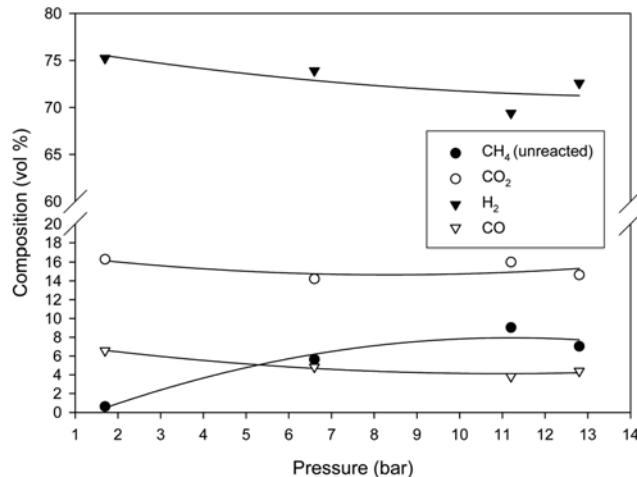


Fig. 5. Product gas composition on a dry basis with the change in pressure (temperature=1,023 K, steam/CH₄=3).

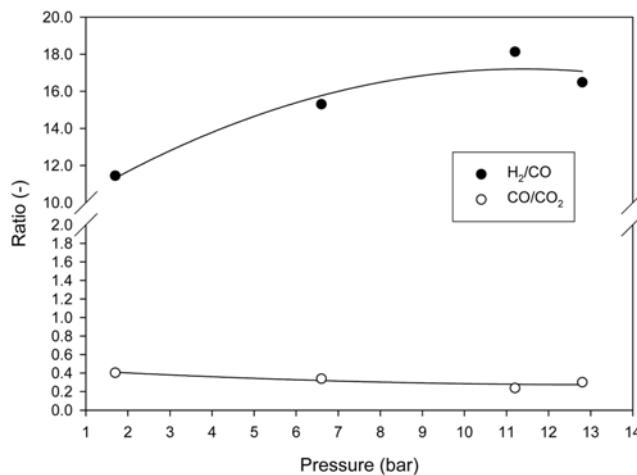


Fig. 6. H₂/CO and CO/CO₂ ratio of SMR product gas with the change in pressure (temperature=1,023 K, steam/CH₄=3).

CO₂ 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 H₂/CO ratio.

3. Effect of Pressure

Fig. 5 shows the effect of reactor pressure on the composition of the product gas. Changes of H₂/CO and CO/CO₂ ratios versus pressure are shown in Fig. 6. The production of H₂ and CO decreased as pressure increased from 1.7 to 12.8 bar, accompanied by the increase of CH₄ slippage. Higher sensitivity of CO versus pressure, relative to other species, gave rise to the increase of H₂/CO ratio and decrease of CO/CO₂ ratio as pressure increased. With pure CH₄ feed of steam/CH₄=5 at 1,023 K, H₂/CO ratio increased from 11.6 to 16.0 and CO/CO₂ 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 H₂/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 H₂/CO ratio and

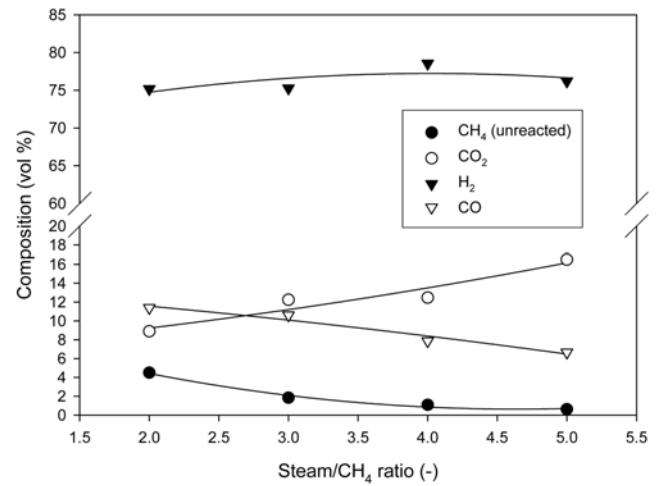


Fig. 7. Product gas composition on a dry basis with the change in steam/CH₄ ratio (temperature=973 K, pressure=1.7 bar).

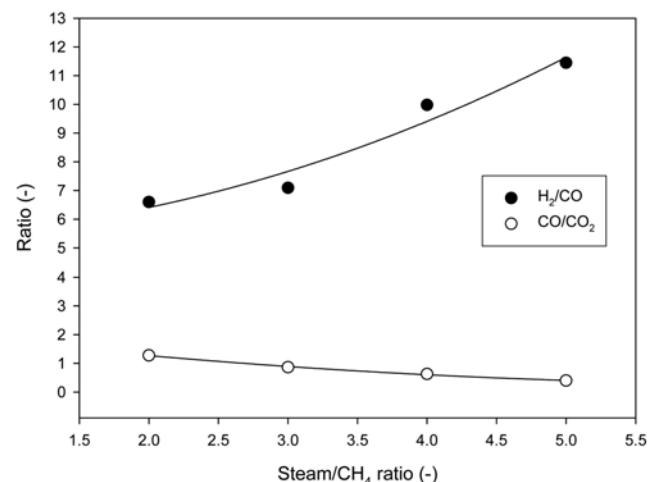


Fig. 8. H₂/CO and CO/CO₂ ratios of SMR product gas with the change in steam/CH₄ ratio (temperature=973 K, pressure=1.7 bar).

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 H₂/CO and CO/CO₂ ratios for pure CH₄ feeds of various steam/CH₄ ratios. H₂ concentration increased and CO concentration decreased as steam/CH₄ 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 H₂ and CO formation; however, the produced CO reacted subsequently with steam to produce CO₂ and H₂ because the equilibrium of WGS reaction also shifted to the right. Therefore, as shown in Fig. 8, the H₂/CO ratio increased from 6.6 to 11.45 and the CO/CO₂ ratio decreased from 1.28 to 0.4 as steam/CH₄ ratio increased from 2 to 5. From this, it is necessary to operate our SMR reactor at lower steam/CH₄ ratio in order to obtain H₂/CO ratio optimal for SDF production, although a steam/CH₄ ratio lower than 2 should be avoided to prevent catalyst coking.

5. Effect of CO₂ Addition

The results described above indicate that variation of the opera-

tion parameters such as temperature, pressure and steam/CH₄ ratio of pure CH₄ feed can adjust the H₂/CO ratio of our SMR product gas to some extent; however, it is difficult to obtain an H₂/CO ratio optimal for Fischer-Tropsch synthesis of the CE-CERT process, i.e., H₂/CO=4.5. Therefore, CO₂ was added to the pure CH₄ feed and its effect upon H₂/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 H₂ and CO mole fractions from them [17].

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

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

where P denotes the total pressure.

Rearranging the above equations gives an equation for H₂/CO ratio as follows:

$$\frac{y_{H_2}}{y_{CO}} = [K_{WGS}] \cdot \frac{[y_{CH_4}]^{0.25} [y_{H_2O}]^{0.5}}{[y_{CO_2}]^{0.25}} \quad (7)$$

From Eq. (5), we can see that H₂ mole fraction decreases as CO₂ mole fraction increases. We can also see from Eq. (6) that CO mole fraction increases as CO₂ mole fraction increases. Therefore, the H₂/CO ratio decreases as the CO₂ mole fraction increases, as explained by Eq. (7). Fig. 9 demonstrates the effect of CO₂ addition to CH₄ feed upon H₂/CO ratio of SMR product gas. Our study shows that the H₂/CO ratio of SMR product gas with CO₂ added to CH₄ (CO₂/CH₄=0.56) is 2.5 times lower than that with pure CH₄, indicating that CO₂ can play a significant role in lowering H₂/CO ratio, owing to the reactions (3) and (4) described above. This result is consistent with the literature: Effendi et al. showed that CO₂ addition to CH₄ (CO₂/CH₄=0.67) resulted in lower H₂/CO ratio of SMR product gas as compared with Hardiman et al.'s work conducted in the absence of CO₂ [16,23]. Compared with these previous works, our study dealt with the effect of CO₂ addition to CH₄ feeds of broader

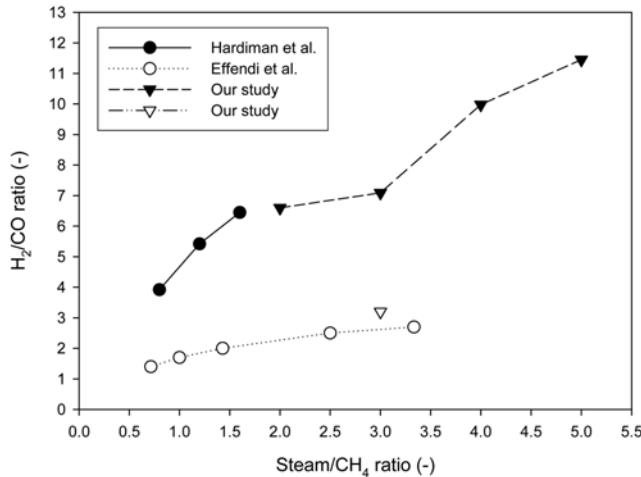


Fig. 9. Comparison of our work with the literature for pure CH₄ and CH₄-CO₂ mixture feeds (●: CO₂/CH₄=0, ○: CO₂/CH₄=0.67, ▼: CO₂/CH₄=0, ▽: CO₂/CH₄=0.5).

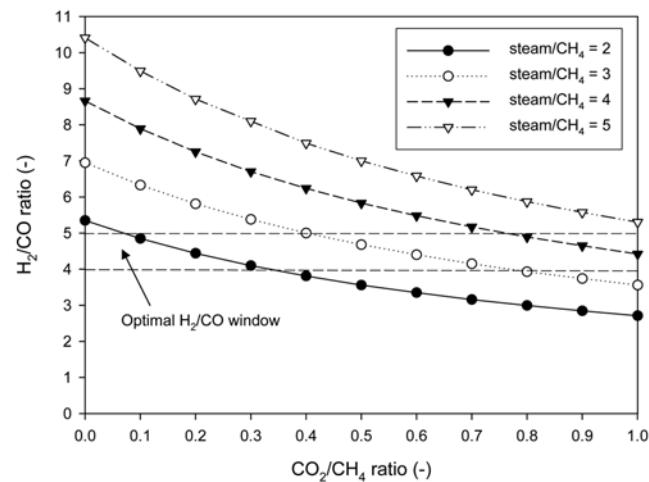


Fig. 10. H₂/CO ratio of SMR product gas with the change in CO₂/CH₄ ratio (temperature=973 K, pressure=1.7 bar, steam/CH₄=2-5).

steam/CH₄ ratios. It should be considered that besides the reverse WGS reaction and the dry reforming reaction, CO₂ can also play a role in reducing H₂/CO ratio by Boudouard reaction (C+CO₂→2CO) [24,25]. Fig. 10 shows the H₂/CO ratio of the SMR product gas versus CO₂/CH₄ ratio as simulated by ASPEN PLUS process simulator. This plot supports the experimental findings: increasing the CO₂/CH₄ ratio of the SMR feed gives birth to lower H₂/CO ratios of the SMR product gas. From these results, we can optimize the CO₂/CH₄ ratio of SMR feed for SDF production.

6. Comparison between Experiments and Simulation

Figs. 11 and 12 illustrate a comparison of the H₂/CO and CO/CO₂ ratios between the experiment and calculation obtained by ASPEN

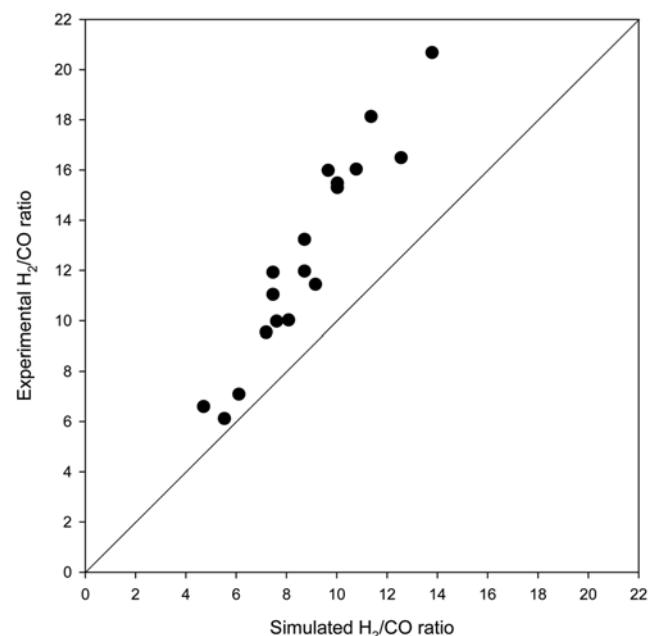


Fig. 11. Comparison of H₂/CO ratio between experiment and simulation for pure CH₄ feeds (temperature: 873-1,023 K, pressure: 1.7-12.8 bar, steam/CH₄: 2-5).

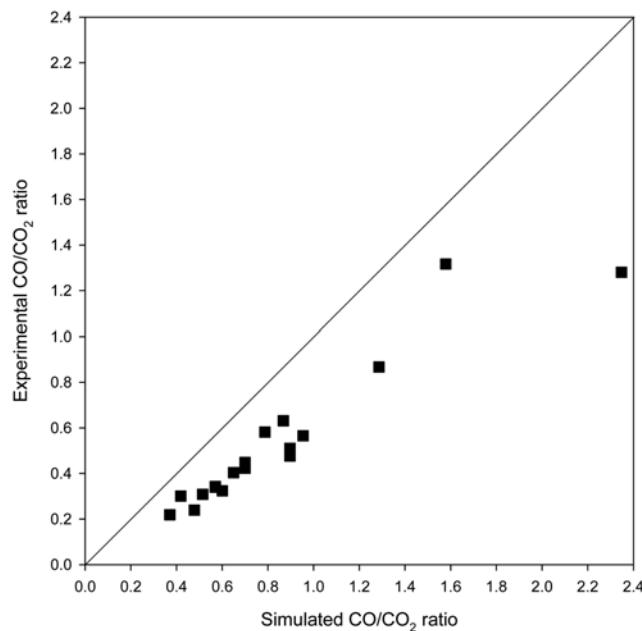


Fig. 12. Comparison of CO/CO₂ ratio between experiment and simulation for pure CH₄ feeds (temperature: 873-1,023 K, pressure: 1.7-12.8 bar, steam/CH₄: 2-5).

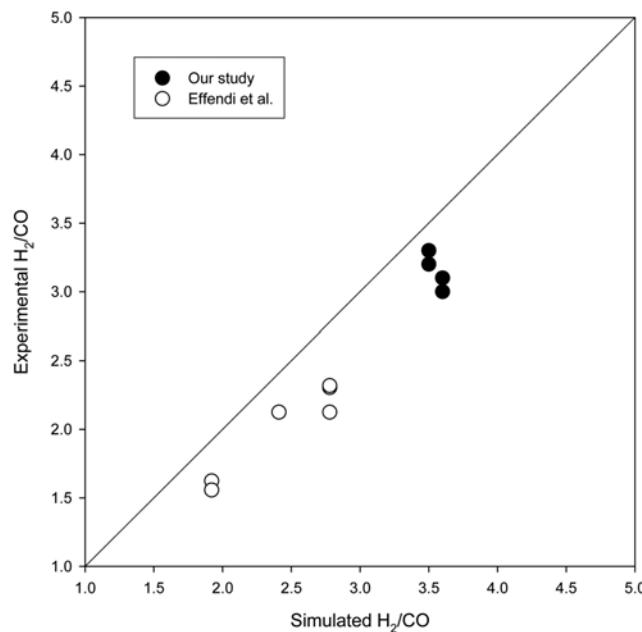


Fig. 13. Comparison of H₂/CO ratio between experiment and simulation for CH₄-CO₂ mixture feeds (temperature: 1,086-1,106 K, pressure: 20.4 bar, steam/CH₄: 2.3-3.1, CO₂/CH₄: 0.36-0.67).

PLUS process simulator for pure CH₄ feed. Fig. 13 shows the comparison for CH₄-CO₂ mixture feed. These figures demonstrate that whereas the experimental H₂/CO and CO/CO₂ ratios are not in good agreement with the simulated ratios for pure CH₄ feed, the addition of CO₂ to CH₄ feed results in improvement of the agreement between the experimental and simulated ratios. This strongly supports our discussion of the experimental results indicating that CO₂

added to CH₄ feed can play a significant role in lowering the overall H₂/CO ratio of SMR product gas.

CONCLUSION

The steam-methane reforming reaction was studied in pure CH₄ and CH₄-CO₂ mixture environments. Experimental results were compared with simulated data obtained by ASPEN PLUS process simulator. The effects of temperature, pressure, steam/methane ratio and CO₂ addition were discussed to obtain the optimal H₂/CO ratio of synthesis gas for SDF production. As the reaction temperature increased from 873 to 1,073 K, the H₂/CO ratio decreased and conversion of CH₄ increased. Meanwhile, as the pressure increased from 1.7 to 12.8 bars, the H₂/CO ratio increased and CO/CO₂ ratio decreased; the same trends were observed when the steam/CH₄ ratio increased. The H₂/CO ratio decreased as CO₂ was added to the SMR feed gas. Experimental and simulated H₂/CO and CO/CO₂ ratios were consistent with each other satisfactorily. With pure CH₄ as the feed, H₂/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/CH₄ ratio. This limitation in optimizing the H₂/CO ratio for synthetic diesel fuel production could be removed by introducing CO₂ to CH₄ feed to make a CH₄-CO₂ mixture. In other words, adding CO₂, we can obtain 4-5 of H₂/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 H₂/CO ratio versus the operating parameters (temperature, pressure and steam/CH₄ ratio) and also verified the effect of CO₂ to CH₄ feed.

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