Combined steam and carbon dioxide reforming of methane and side reactions: Thermodynamic equilibrium analysis and experimental application

Won-Jun Jang [a], Dae-Woon Jeong [a], Jae-Oh Shim [a], Hak-Min Kim [a], Hyun-Seog Roh [a,*], In Hyuk Son [b], Seung Jae Lee [c,*]

[a] Department of Environmental Engineering, Yonsei University, 1 Yonseidae-gil, Wonju, Gangwon 220-710, Republic of Korea
[b] Energy Lab., Samsung Advanced Institute of Technology (SAIT), Samsung Electronics Co. Ltd, Gyeonggi-do 443-803, Republic of Korea
[c] Marine Research Institute, Samsung Heavy Industries Co. Ltd, Gyeongsangnam-do 656-710, Republic of Korea

HIGHLIGHTS

- Selected variables have a significant influence on yields of synthesis gas.
- $(CO_2 + H_2O)/CH_4$ affects the temperature which can achieve the maximum conversion.
- Coke is formed at low temperatures even with excess oxidizing agent.
- The occurrence of RWGS becomes critical in real chemical reactions.
- Equilibrium conversions are maintained for 500 h without detectable deactivation.

ARTICLE INFO

ABSTRACT

Thermodynamic equilibrium analysis of the combined steam and carbon dioxide reforming of methane (CSCRM) and side reactions was performed using total Gibbs free energy minimization. The effects of $(CO_2 + H_2O)/CH_4$ ratio (0.9–2.9), $CO_2:H_2O$ ratio (3:1–1:3), and temperature (500–1000 °C) on the equilibrium conversions, yields, coke yield, and H_2/CO ratio were investigated. A $(CO_2 + H_2O)/CH_4$ ratio greater than 1.2, a $CO_2:H_2O$ ratio of 1:2.1, and a temperature of at least 850 °C are preferable reaction conditions for the synthesis gas preparation in the gas to liquid process. Simulated conditions were applied to the CSCRM reaction and the experimental data were compared with the thermodynamic equilibrium results. The thermodynamic equilibrium results were mostly consistent with the experimental data, but the reverse water gas shift reaction rapidly occurred in the real chemical reaction and under excess oxidizing agent conditions. In addition, a long-term stability test (under simulated conditions) showed that the equilibrium conversion was maintained for 500 h and that the coke formation on the used catalyst was not observed.

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1. Introduction

The production of alternative liquid fuel is an important issue because the transport system plays a key role in economy and industry [1]. A gas to liquid (GTL) technology is an attractive technology for the production of transportable liquid fuel using methane [2–5]. Recently, the GTL technology has gained renew interest with regard to the discovery of abundant shale gas reserves [6,7]. In general, GTL technology consists of three steps: reforming, Fischer–Tropsch synthesis, and upgrading. The reforming is an important step in the GTL technology because it is the most expensive process among the three steps and also has the largest part of the energy conversion in the entire process [8,9]. Reforming in GTL technologies is aimed at producing the synthesis gas with an H_2/CO ratio of below 2.0 for Fischer–Tropsch synthesis [10]. Methane can be converted into the synthesis gas via reforming with different oxidizing agents such as H_2O (Eq. (1)), O_2 (Eq. (2)), and CO_2 (Eq. (3)) [11]:

Steam reforming of methane (SRM) : $CH_4 + H_2O \rightarrow CO + 3H_2$,

$\Delta H^0_{298} = 206$ kJ/mol $\qquad\qquad\qquad\qquad\qquad\qquad$ (1)

Partial oxidation of methane (POM) : $CH_4 + 1/2O_2 \rightarrow CO$

$+ 2H_2$, $\Delta H^0_{298} = -38$ kJ/mol $\qquad\qquad\qquad\qquad$ (2)

Carbon dioxide reforming of methane (CDR) : $CH_4 + CO_2 \rightarrow$

$2CO + 2H_2$, $\Delta H^0_{298} = 248$ kJ/mol $\qquad\qquad\qquad$ (3)

The POM can produce synthesis gas with an H_2/CO ratio of 2.0. However, it is difficult to control the process due to the presence of hot spots and the risk of explosions [12,13]. Moreover, the POM requires an air separation unit (ASU), which significantly impacts the costs of a reforming plant [14]. Due to these drawbacks of the POM, combined steam and carbon dioxide reforming of methane (CSCRM), where H_2O is partially substituted by CO_2, has been considered as an alternative method for the production of synthesis gas with an H_2/CO ratio of 2.0 [15–17].

The CSCRM can produce the synthesis gas with flexible H_2/CO ratios. The H_2/CO ratio of the synthesis gas produced via the CSCRM can be controlled by changing the composition of the feed gas (H_2O, CO_2, and CH_4). However, the CSCRM is a complex reaction because two reforming reactions (Eqs. (1) and (3)), secondary reactions (Eqs. (4) and (5)), and coke formation reactions (Eqs. (6) and (7)) occur simultaneously. The reaction pathway of the CSCRM strongly depends on the reaction conditions such as the feed composition, temperature, and pressure. Thus, it is necessary to investigate the effects of reaction conditions on the performance to enable direct use of synthesis gas in downstream applications.

Water gas shift (WGS) : $CO + H_2O \rightarrow CO_2 + H_2$,

$\Delta H^0_{298} = -41$ kJ/mol $\qquad\qquad\qquad\qquad\qquad\qquad$ (4)

Reverse water gas shift (RWGS) : $CO_2 + H_2 \rightarrow CO + H_2O$,

$\Delta H^0_{298} = 41$ kJ/mol $\qquad\qquad\qquad\qquad\qquad\qquad$ (5)

Methane decomposition : $CH_4 \rightarrow C + 2H_2$, $\Delta H^0_{298} = 75$ kJ/mol (6)

Boudouard reaction : $2CO \rightarrow C + CO_2$, $\Delta H^0_{298} = -172$ kJ/mol (7)

Thermodynamic analysis is a useful tool that can serve as a guide for experimental studies [18–20]. In addition, it can offer ideas about the availability of reaction conditions in complex chemical reactions. Hence, numerous studies about the thermodynamic analysis for the reforming of methane have been reported [21–25]. Li et al. conducted the thermodynamic analysis for the autothermal reforming of methane and reported that the rate of coke formation should be taken into consideration to find the

proper reaction conditions [23]. It has been reported that excess steam is effective for inhibiting coke formation, but the excess steam increases the cost of the operating process. Özkara-Aydınoğlu reported that the H_2/CO ratio of synthesis gas can be modified by changing the relative concentration of H_2O and CO_2, the temperature, and the pressure [24]. Jafarbegloo et al. compared results of thermodynamic analysis with experimental data to verify the applicability of simulation results in the CDR reaction [25]. However, previous researches have focused on the positive effect of steam addition or on the relationship between H_2O:CO_2 ratio of reactant gas and H_2/CO ratio of product gas. Thus, the studies have not provided systematic and deep understanding about the prerequisite for the CSCRM reaction. Inhibiting the coke formation and maintaining the H_2/CO ratio of 2.0 should be preferentially taken into account for the stable operation of process and downstream application. Chein et al. claimed the importance of finding carbon free operating condition in the reforming reaction [26]. In addition, measuring the extent of side reaction helps to maximize the yield of target product. From this study, preferable reaction conditions which can maximize conversions and yields in parallel with satisfying prerequisite were determined.

In the present work, thermodynamic analysis of the CSCRM reaction with different $(CO_2 + H_2O)/CH_4$ ratios, CO_2:H_2O ratios, temperatures, and pressures were studied. The results of the CSCRM reaction obtained from thermodynamic analysis were compared with those of side reactions to understand the reaction pathway of CSCRM. Coke yield was analyzed to determine the coke-formed and coke-free regions. The H_2/CO ratio of synthesis gas was investigated for downstream application. The preferable reaction conditions for the production of synthesis gas with the H_2/CO ratio of 2.0 and coke yield of 0% were determined. The wide range of $(CO_2 + H_2O)/CH_4$ ratio was studied to offer practical guidelines which enables the estimation of suitable reaction conditions for considering the amount of excess steam. The simulated conditions are applied to the CSCRM reaction and the experimental data are compared with the thermodynamic equilibrium results.

2. Methodology

2.1. Thermodynamic equilibrium analysis

The spontaneity of a chemical reaction is determined by the Gibbs free energy. The system is thermodynamically favorable when the value of the total Gibbs free energy is at a minimum

Table 1
Summary of thermodynamic equilibrium analysis and experimental conditions.

Description	CH₄		CO₂		H₂O		N₂		$(CO_2 + H_2O)/$ CH₄	CO₂: H₂O	P (atm)
	Molar ratio	Flow rate (mL/min)	Molar ratio	Flow rate (mL/min)	Molar ratio	Flow rate (mL/min)	Molar ratio	Flow rate (mL/min)			
The effect of	1.00	20.05	0.29	5.81	0.62	12.43	3.08	61.70	**0.9**	1.0:2.1	1.0
$(CO_2 + H_2O)/CH_4$	1.00	20.05	0.38	7.62	0.81	16.24	2.80	56.09	**1.2**	1.0:2.1	1.0
ratio	1.00	20.05	0.44	8.82	0.93	18.65	2.62	52.48	**1.4**	1.0:2.1	1.0
	1.00	20.05	0.63	12.63	1.37	27.47	1.99	39.85	**2.0**	1.0:2.1	1.0
	1.00	20.05	0.91	18.25	1.95	39.10	1.13	22.61	**2.9**	1.0:2.1	1.0
The effect of CO₂:H₂O	1.00	20.05	0.89	17.90	0.30	5.98	2.80	56.09	1.2	**3.0:1.0**	1.0
ratio	1.00	20.05	0.81	16.24	0.38	7.62	2.80	56.09	1.2	**2.1:1.0**	1.0
	1.00	20.05	0.60	11.93	0.60	11.93	2.80	56.09	1.2	**1.0:1.0**	1.0
	1.00	20.05	0.38	7.62	0.81	16.24	2.80	56.09	1.2	**1.0:2.1**	1.0
	1.00	20.05	0.30	5.98	0.89	17.90	2.80	56.09	1.2	**1.0:3.0**	1.0
The effect of pressure	1.00	20.05	0.38	7.62	0.81	16.24	2.80	56.09	1.2	1.0:2.1	**1.0**
	1.00	20.05	0.38	7.62	0.81	16.24	2.80	56.09	1.2	1.0:2.1	**3.0**
	1.00	20.05	0.38	7.62	0.81	16.24	2.80	56.09	1.2	1.0:2.1	**5.0**
	1.00	20.05	0.38	7.62	0.81	16.24	2.80	56.09	1.2	1.0:2.1	**10.0**
	1.00	20.05	0.38	7.62	0.81	16.24	2.80	56.09	1.2	1.0:2.1	**20.0**

The bold text indicates the changing variables.