The effect on hydrogen selectivity of quenching gas in the methane pyrolysis process using triple thermal plasma

Y. H. Lee[1], J.-H. Oh[2] and S. Choi[1]

[1]*Faculty of Applied Energy System, Jeju National University, Jeju, Republic of Korea*
[2]*Electric Energy Center, Jeju National University, Jeju, Republic of Korea*

Abstract: The methane (CH_4) pyrolysis process using thermal plasma is recently to be notable because it can produce hydrogen (H_2) without emitting carbon dioxide (CO_2). Nevertheless, it is necessary to enhance the efficiency of the process to prepare a massive H_2 economically. Therefore, we applied the triple thermal plasma to the process and investigated the effect of the quenching conditions. At the plasma power of 30 kW and CH_4 flow rate of 50 L/min, the CH_4 conversion rate was 97%, a higher value of about 7% than the previous work. Furthermore, the energies to produce H_2 of 1 kg showed the lowest value of 37.5 kWh/kg-H_2 compared with other works applying thermal plasma.

Keywords: Methane pyrolysis, triple thermal plasma, H_2 production, Quenching.

1. Introduction

The methane (CH_4) pyrolysis process converts CH_4 into hydrogen (H_2) and solid carbon. Large amounts of energy of 75.6 kJ/mol are required to decompose CH_4. As a technology to supply this energy, studies on applying a thermal plasma to the CH_4 pyrolysis process have been conducted, of which the primary purpose is increasing the efficiency of the process.

The variable hydrocarbons, such as acetylene (C_2H_2), ethylene (C_2H_4), and polycyclic aromatic hydrocarbons (PAHs), are produced in the process. It is essential to increase the H_2 selectivity by cracking these hydrocarbons into H_2 and solid carbon to enhance the efficiency of the process. The quenching condition is a significant factor in increasing the H_2 selectivity. Fincke *et al.* [1] changed the quenching condition by adapting the conversing-diverging nozzle and finally increased H_2 and C_2H_2 selectivity. However, the limitation of the study is that it focused on C_2H_2 production. The effect of the quenching condition on the solid carbon and H_2 selectivity has been hardly investigated.

According to Meriaudeau's work [2], it was identified that the conversion of C_2H_2 into benzene (C_6H_6) is actively achieved at the surface of the solid by the catalytic effect. As C_6H_6 is the component of PAHs, which is known as the precursor of solid carbon, the catalytic effect means that C_2H_2 can be converted into H_2 and solid carbon at the surface of the solid. Furthermore, it was confirmed that the activation energy for CH_4 decomposition over the activated carbon is about 117 to 185 kJ/mol, which is lower than the C-H bond energy of CH_4 of 440 kJ/mol [3]. Such works indicate that the inhomogeneous effect at the surface easily splits H_2 from hydrocarbon species.

Therefore, the present work is about the CH_4 pyrolysis process applying triple thermal plasma and investigates the effect on the H_2 selectivity of the quenching conditions. Furthermore, we injected the carbon powder with the quenching gas and analyzed its effect.

2. Experimental method

Fig. 1 (a) indicates a schematic of the CH_4 pyrolysis process used in this study. The process consisted of triple DC torches, power supplies, and reaction and filtration chambers. Each torch was arranged with a horizontal angle of 120°. The plasma jets emitted from each torch were merged to the same position, where CH_4 was injected through an injector. The two structures made by the graphite were located inside the reaction chamber to confine the plasma jets and CH_4 and enable CH_4 to react with the plasma jets actively.

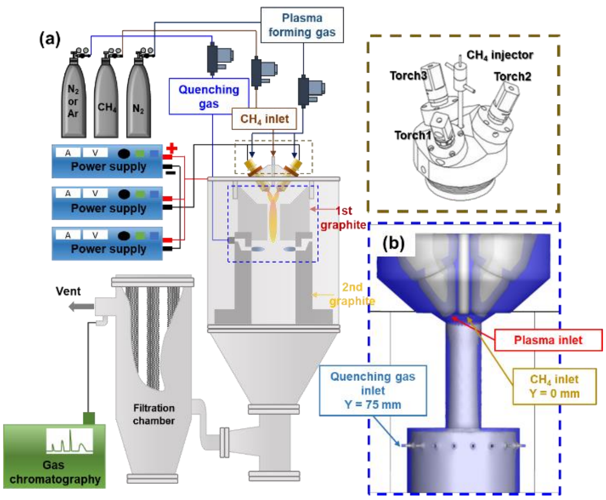

Fig. 1. (a) Experimental setup of the CH_4 pyrolysis process applying the triple DC thermal plasma system. (b) The three-dimensional geometry information for computational fluid dynamics (CFD) simulation conducted in this work with the boundary conditions of plasma, CH_4, and quenching gas inlets.

The quenching gas was injected 10 mm from the first graphite exit. As shown in Fig. 1 (b), the position of the quenching gas inlet was 75 mm from the position of the CH_4 inlet along with the y-axis. In addition, the quenching gas was injected counter to the downstream flow. The carbon powder was included with the quenching gas injected into the counter flow. The experimental conditions for this work are summarized in Table 1.

Table 1. Operating conditions for the CH_4 pyrolysis process conducted in this work

No.	1	2	3	4
Plasma-forming gas flow rate (L/min)	15 per torch (N_2)			
Input power (kW)	29.3			
CH_4 flow rate (L/min)	50	60	70	80
Quenching gas flow rate (L/min)	100		100, 150, 200	100

3. Results and discussion

The CH_4 conversion rate with varying the CH_4 flow rate and quenching gas flow rate is indicated in Fig. 2 (a) and (b), respectively. The maximum conversion rate was about 97% at 50 L/min of CH_4 flow rate and 100 L/min of quenching gas flow rate. At the condition, the energy supplied to CH_4 of 1 mol was about 500 kJ. When compared with the conversion rate by other work at the similar supplied energy [4], it is higher by about 7%. It seems that this high conversion rate was attributed to the easy penetration of CH_4 into the region where the plasma jets are merged inside the first graphite.

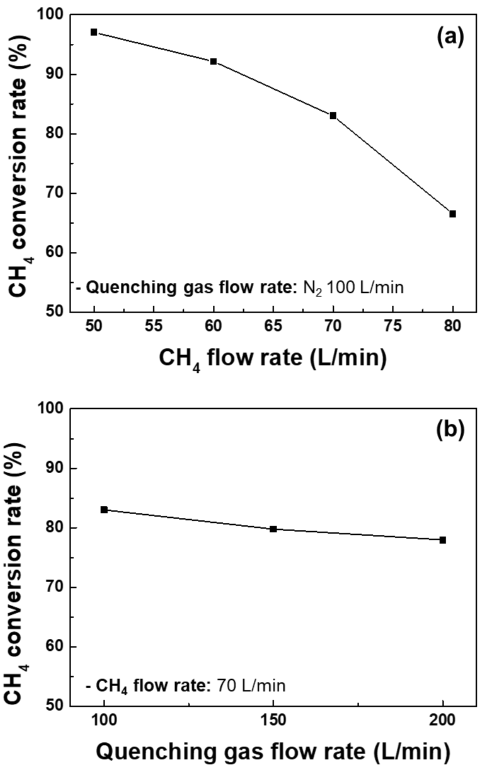

Fig. 2. (a) CH_4 conversion rate as a function of CH_4 flow rate with quenching conditions using N_2 quenching gas and 100 L/min quenching gas flow rate. (b) CH_4 conversion rate as a function of quenching gas flow rate and type of quenching gas at fixed 70 L/min of CH_4 flow rate.

The H_2 and selectivity with varying CH_4 flow rates and quenching conditions are shown in Fig. 3 (a) and (b), respectively. The H_2 selectivity depending on CH_4 flow rates and quenching gas flow rate was mildly changed in the 70-80% range. The quenching rate estimated by the CFD work increased above two times when changing the quenching gas flow rate from 100 to 200 L/min. This finding indicates that it is challenging to enhance the H_2 selectivity by only adjusting the quenching gas flow rate.

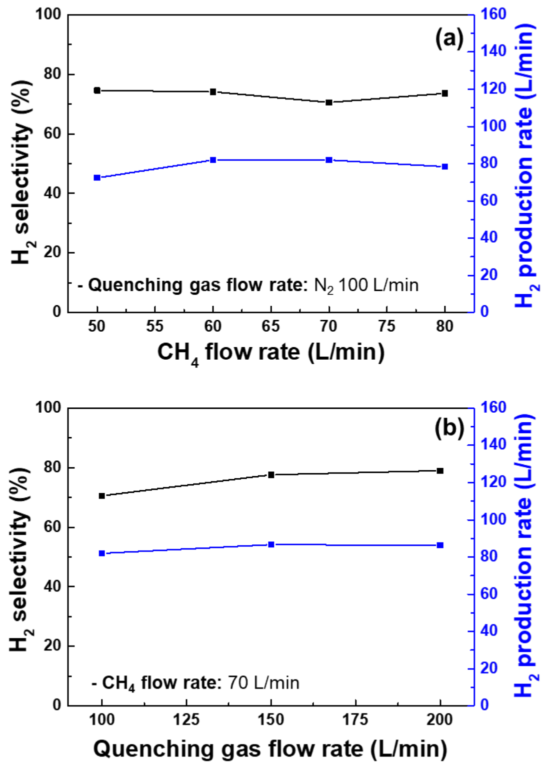

Fig. 3. (a) H_2 selectivity and production rate as a function of CH_4 flow rate using N_2 as the quenching gas and 100 L/min quenching gas flow rate. (b) H_2 selectivity and production rate as a function of quenching gas flow rate and type of quenching gas at fixed 70 L/min CH_4 flow rate.

The results without the carbon powder were compared with other works to analyze the performance of the present work, as shown in Table 2. Although Fincke *et al.* [5] showed the possibility of decreasing SER (Specific Energy Requirement) by supplying substantially more CH_4, succeeding research has not been reported. Maslani *et al.* [4] dealt with the most considerable amount of CH_4 of up to 500 L/min by using H_2O as the plasma-forming gas. However, the formation of CO and CO_2 was inevitable owing to the existence of H_2O. The process used in this study achieved the lowest value of SER compared to other works, indicating that the system used here has acceptable performance for H_2 production without emitting CO_2.

Table. 2. Comparison of the process enthalpy, CH_4 conversion rate, and SER per 1 kg of H_2 for various CH_4 pyrolysis process applying thermal plasma.

	Plasma type (Plasma forming gas)	Process enthalpy (kJ/mol)	CH_4 conversion rate (%)	SER (kWh/kg-H_2)
Finke, 2002	DC plasma ($Ar+H_2$)	896	99.4	61.40
Maslani, 2021	DC plasma ($Ar + H_2O$)	508	80	51.53
		338	76	40.71
This work	DC plasma (N_2)	354	80	39.44

4. Conclusion

The triple thermal plasma was applied to the CH_4 pyrolysis process. When supplying the energy of 500 kJ to CH_4 of 1 mol, the conversion rate was about 97%, which is higher than the previous work applying other types of thermal plasma. It seems that the structure with triple thermal plasma contributed to the active decomposition of CH_4.

The effect of the quenching condition on the H_2 selectivity was investigated. According to the quenching rate calculated by the CFD work, it was identified that the quenching condition was insignificant on the H_2 selectivity. This finding implies that the quenching operation would prevent hydrocarbons from converting into H_2 and solid carbon. Nevertheless, compared to previous studies, applying triple thermal plasma indicated an outstanding performance in terms of the SER. Although the optimal conditions remain unknown, the distinguishable performance could originate from the advantage of the triple thermal plasma system.

5. References

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