Role of thermal activation for partial oxidation of methane in plasma reforming

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Abstract: The plasma-reforming process has been widely studied for over a decade, with focus on diverse fuel and plasma parameters in order to determine the most effective parameters for the reforming process. This study evaluates the effect of thermal activation on the chemistry and energy efficiency of the reform process. Based on empirical evaluation, a proportional relationship between the methane conversion rate and the reactant temperature, and correlation between the change of chemistry and the plasma power as well as the reactant temperature were confirmed. Remarkably, the pattern of the plasma chemistry did not change with the reactant temperature within the range evaluated. It was also found that the ratio of plasma to heating input power is an important parameter for enhancing the efficiency of the partial oxidation of methane.

Keywords: plasma reforming, methane, partial oxidation, reaction chemistry

1. Introduction

Plasma comprises diverse types of chemically active species such as high-energy electrons, ions, and excited gas molecules, and is expected to achieve chemical activation even at room temperature [1]. As one of active applications, plasma-reforming processes have been actively developed for possible utilization in mobile systems including emission control and generation of small-scale distributed synthesis gas (or hydrogen) that can be cost-effective as compared to the existing steam-reforming process that is suitable only for large-scale process [2-4].

Because thermal plasma generation requires a very high temperature reaction field (and thus a high cost of operation), a non-thermal plasma source has been widely studied for plasma-reforming processes [5, 6]. Despite the efforts, the fuel conversion rate and energy efficiency using plasma operated at room temperature are ineffective to compete with the existing plasma-reforming systems.

Recently, Lee et al. performed a study on the partial oxidation of methane using a rotating arc source and reported that the thermal parameter is important for controlling the relative contributions between plasma chemistry and thermochemistry. In addition, Gutsol et al. compared various plasma systems for fuel conversion applications and suggested that relatively high local temperature, the so called “warm plasmas,” are optimal for large-scale fuel processing because of the stepwise ionization and reduced heat loss. Both these studies indicate the importance of the thermal environment in plasma-reforming processes; however, studies related to thermal effects have not yet determined how thermal activation affects the reaction chemistry and energy efficiency. The objective of the present study is to investigate the effects of gas temperature on the chemistry and energy efficiency of plasma-mediated partial oxidation of methane. The temperature of the reactant supplied into the rotating arc reactor is considered as a variable for determining the thermal condition.

2. Experiment

The experimental setup consists of a plasma reactor, a furnace, a power supply system, flow controllers, and measurement systems (Fig. 1). The plasma reactor comprises a cone-shaped inner electrode (connected to a high voltage source) placed inside a circular cylinder (inner diameter: 25 mm; length: 400 mm), which serves as a ground electrode. The inner and outer electrodes are made of copper and stainless steel, respectively. The minimum gap between the electrodes is designed to be 1.5 mm for the initial ignition of the arc channel. The circular cylinder is covered with 30-mm thick ceramic wool to minimize heat loss through the cylinder wall.

Fig. 1 Schematic diagram of experimental setup.
A commercially pure grade of methane was used as fuel. Oxygen and nitrogen were separately used to adjust the composition of the air. The flow rates of the gases were controlled by using mass flow controllers (Brooks, 5850E-series). In order to obtain a designated gas inlet temperature, a mixture of fuel and air was preheated by passing it through the furnace. An AC power supply (maximum power = 2 kW) with a high-voltage transformer was used to generate a rotating arc. The electrical power delivered to the reactor was measured by an oscilloscope (Tektronix, TDS5104B) with a 1000:1 high-voltage probe and a current probe (Tektronix, TCP 202 current probe). The dry compositions of the gaseous products were analyzed using a GC (gas chromatograph, HP 6890-series). The total flow rate was 10 lpm, and the flow rates of fuel and air were adjusted to an O₂/C ratio of 0.5, which is the stoichiometric condition for partial oxidation of methane. As a selected variable, the inlet gas temperature, Tin, was measured near the minimum gap of the electrodes, and all experiments were performed when the inlet gas temperature was stabilized at the designated values. The methane conversion rate and selectivity for C₂H₂ and C₂H₆ species are defined as in Eqs. (1)–(3).

\[
\text{Conversion (CH}_4\text{)} = \frac{\text{mole (converted CH}_4\text{)}}{\text{mole (supplied CH}_4\text{)}} \times 100 \% \quad (1)
\]

\[
\text{Selectivity (CH}_2\text{)} = 2.0 \times \frac{\text{mole (produced CH}_2\text{)}}{\text{mole (converted CH}_4\text{)}} \times 100 \% \quad (2)
\]

\[
\text{Selectivity (C}_2\text{H}_6\text{)} = 2.0 \times \frac{\text{mole (produced C}_2\text{H}_6\text{)}}{\text{mole (converted CH}_4\text{)}} \times 100 \% \quad (3)
\]

3. Result and discussion

3.1 Thermal activation on methane conversion

The experimentally determined methane conversion rates under stable operation are shown in Fig. 2. From the results obtained at room temperature (Tin = 300 K), we confirmed that the methane conversion rate increases with increasing specific energy density (SED, electrical energy per unit volume of reactant). This result can be explained in terms of an enlarged reaction volume resulting from the elongation of the arc column due to an increase in the electric power. Analysis of the conversion rate with increasing reactant temperature shows two different trends, as indicated in regions [A] and [B] of Fig. 2. Region [A] shows no noticeable difference in the conversion rate even though the reactant temperature increases. In other words, the controlling parameter for the reaction in region [A] is plasma chemistry because the thermal environment was not sufficiently active to induce any meaningful. However, once the SED exceeded a certain value (region [B]), the increase in the reactant temperature resulted in a noticeable change in the conversion rate. This result can be explained as the elongation of the arc string, thereby generating an increased reaction volume. This induces an increase in the temperature, which is beneficial for sustaining a stable arc discharge due to reduced heat loss. And, the exothermic reaction concomitantly affects the discharge, thereby reducing the gas density. The synergistic effect derived from the reduced gas density and the generation of hydrogen because of the increase in methane conversion makes the environment amenable for sustaining the discharge.

As shown in Fig. 2, the thermal equilibrium compositions for each experimental condition were calculated (see http://www.gaseq.co.uk) under the assumption that all of the electric power used to generate the arc is converted to the thermal energy of the reactant. Similar to the experimental results, the conversion rate at equilibrium increases on increasing the reactant temperature; however, complete conversion of methane is accomplished irrespective of the temperature after a certain SED (region [C]) because the thermal energy is sufficient to convert all of the supplied methane.

However, under the experimental conditions, at a lower SED, varying the reactant temperature definitively results in different conversion characteristics. If the SED could be simply converted into thermal energy, the experimental results (region [A]) should be typified by a difference in the conversion. However, as shown in Fig. 2, the empirical results exhibit somewhat inverse behavior to that derived from the equilibrium calculation. This reasoning is clearly illustrative of the status of the plasma chemistry. Regime [C] is characterized by a highly thermal environment, where the effect of plasma chemistry is almost overwhelmed by thermal activation. Notably, the difference in the chemistry operative in each regime results in a different product selectivity. In fact, when a reaction is controlled only by thermal activation, the product selectivity is determined solely by the thermal equilibrium. However, when plasma chemistry becomes operative, this enables to overcome the thermal equilibrium, which is one of the virtues of using plasma in the reforming pro-
cess.

3.2 Effect on chemistry
The present study focused on C2H2 and C2H6 to estimate the dependence of methane conversion on thermo-chemistry with the help of reactant gas temperature. The selectivity for C2H2 and C2H6 is shown in Fig. 3. The variation of the selectivity based on the SED is in accordance with the result of a previous study [7] that describes the C2H2 and C2H6 selectivity in detail. The selectivity for C2H2 increases as the reactant temperature is varied, which can be explained by thermal dehydrogenation of C2H2 and C2H6. Notably, the selectivity for C2 species simply shifts in the direction of low SED without any change in the shape of the correlation profile. This means the role of plasma-dominated chemistry is still crucial, typified by a change in the behavior solely with respect to SED before the reaction confronts extreme thermal conditions sufficient to change the current reaction pathways.

![Fig. 3 C2H2 and C2H6 selectivity with variation of gas temperature.](image)

3.3 Power evaluation for optimization
The energy cost is a major concern in plasma-reforming processes. Based on the experimental data, it is confirmed that there is a correlation between the SED as well as the temperature of the reactant and the methane conversion rate and the overall chemistry. Thermal efficiency is defined as the energy available in the product relative to that in the reactant. In this study, the heating values of H2, CO, C2H2, C2H4, and C2H6 are confined to products for available energy, whereas the heating value of CH4, electric power for plasma generation, and heating input power required to elevate the reactant temperature are considered as the available input energy. The efficiency is expressed by Eq. (4)

\[
\text{Efficiency } (\eta_{\text{th}}) = \sum_{\text{products}} \frac{\text{LHV}_i \cdot \dot{n}_i}{P_p + P_h + (\text{LHV} \cdot \dot{n})_{\text{CH}_4}} \times 100 \text{ [%]} \quad (4)
\]

where, \(P_p\) and \(P_h\) are the plasma and heating input power, respectively. LHV is the lower heating value and \(n_{\text{dot}}\) is the molar flow rate.

![Fig. 4 Efficiency evaluation based on total power (plasma + heating input power) and comparison of power at the same efficiency of 30%](image)

Figure 4 shows variation in the determined efficiency with respect to the total input power, which is the sum of the electric power (for generation of the plasma) and the heating input power. As expected, the efficiency is proportional to the total input power; however, there is a variation in the results obtained for the different reactant temperatures. As the total input power increases, the efficiency becomes much higher in the case of the heated reactant than that obtained with relatively low temperature.

Another point of interest emerges from the comparison of the relative amount of electric power and heating power required to achieve the same thermal efficiency for each evaluated reactant temperature. The bar graph in Fig. 4 shows the electric power and heating power required to reach a thermal efficiency of 30%. As the reactant temperature increases, the total input power required to reach the efficiency of 30% decreases and the ratio of heating to plasma power increases. In other words, the data indicate that a portion of the plasma power can be replaced with the power required for heating the reactant, and the ratio of heating to plasma input power is an important parameter for enhancing the efficiency of the reforming process.

4. Conclusion
The effect of temperature on the plasma-mediated partial oxidation of methane was investigated by focusing on the variation of the reaction chemistry and energy efficiency based on the reactant temperature. The experimental results indicate that the methane conversion rate increases with increasing reactant temperature. The re-
sults of the production of C2 species show that the reaction path of the process is primarily determined by the plasma power. Evaluation of the power consumption during the process by comparing the thermal efficiency of various reactant temperatures revealed a correlation between the efficiency and the plasma and heating input power; the ratio of plasma to heating input power was determined to be an important parameter for optimizing the process.

5. Acknowledgements

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6. References