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Steam reforming of methane in a temperature-controlled dielectric barrier discharge reactor: The role of electron-induced chemistry vs thermochemistry

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Abstract

While classic reforming processes rely on heat and chemical equilibrium, plasma-based reforming processes possess the ability to induce non-equilibrium and reactive chemistry at low temperatures using high energy electrons. To better understand the distinctive roles of both electron-induced chemistry and thermochemistry during plasma-assisted fuel reforming, we previously developed a temperature-controlled dielectric barrier discharge (DBD) reactor, which controlled the gas temperature and the electron temperature independently. Here, we investigate plasma-assisted steam reforming of methane using the temperature-controlled DBD reactor and electron-kinetics calculations. We investigated the individual effects of the determining factors for electron-induced chemistry (i.e., reduced electric field intensity and discharge power) and for thermochemistry (i.e., background gas temperature) by varying the discharge power, gas temperature, and pressure inside the reactor. As a result, we found that both the electron-induced chemistry and thermochemistry governed the reactant conversions. Thermochemistry positively affected the methane conversion in particular, but negatively affected the water conversion as the gas temperature increased. The electron-induced chemistry weakly affected the product distribution, while the background temperature (thermochemistry) strongly influenced the product selectivity and composition by altering the chemical pathways involving the plasma-generated reactive species at the given temperature.

Keywords: plasma reforming, electron-induced chemistry, thermochemistry, steam reforming, methane

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1. Introduction

Plasma-assisted fuel reforming techniques for producing hydrogen-enriched syngas have been studied since two decades ago [1-3] stimulated by the hydrogen economy. Recently, the plasma-assisted reforming processes have attracted increased attention from both the energy and environmental sectors [4-6]. Dry reforming of methane, which uses carbon dioxide as the reaction partner of methane, has become especially popular because carbon dioxide is a major greenhouse gas, methane is an underutilized source of carbon, and both are major constituents of biogas and landfill gas. Plasma processes, e.g., corona discharge [7], dielectric barrier discharge (DBD) [8], spark [9], gliding arc [3], and thermal arc plasma [2], have been widely investigated, proposing efficient and handy reforming techniques as compared to the conventional thermocatalytic processes. However, the central research effort in this area is currently focused on studying the fundamental chemical aspects of the plasma rather than creating a new concept for a technical apparatus. It is a plausible transition for the plasma reforming study to advance related technology based on solid scientific understandings.

Previous studies on the partial oxidation [3] and the dry reforming [10] of methane, using a rotating glide arc and an elongated arc jet, respectively, showed higher efficiencies than those with corona discharges [4] and DBD [5]. Particularly, the conversion of methane and the selectivity of hydrogen from the partial oxidation of methane via the rotating glide arc were found to reach almost 100 % at the energy density $\sim 5\text{kJ/L}$ [3]. These studies indicated that *hotter* plasmas in terms of gas temperature were better than *colder* plasmas, such as corona and DBD [5, 9, 11, 12], in fuel reforming processes, although the *hotter* and *colder* plasmas can be generally categorized as non-thermal plasmas.

In DBDs, which selectively transfer electrical energy into highly energetic electrons at room temperature, reactive species are generated through electron-impact reactions, and these reactive species induce the necessary cascade reactions to produce the final products [13, 14]. A modelling study of the methane dry reforming in a DBD at 300 K showed that the electron-induced reactions were dominant in

the plasma chemistry, highlighting the importance of the plasma parameters [13]. In addition, the discharge power, i.e., the specific energy input, always determined the reactant conversion in colder plasmas [15, 16].

In our previous works, we introduced a temperature-controlled DBD reactor in which the plasma parameters and background temperature were controlled independently [11, 17]. Using this system, we carried out experimental studies on the dry reforming and partial oxidation of methane, aimed at deciphering the important but different roles of the electron-induced chemistry and thermochemistry during the reforming processes [11, 17]. For dry reforming in temperature-controlled DBD plasma, we found that the electron-induced chemistry governed the reactant conversions, while the thermochemistry at a given gas temperature strongly affected the product distribution [11]. However, with the partial oxidation of methane using the same DBD plasma, the conversions of methane and oxygen were not only affected by the electron-induced chemistry but also by the thermochemistry, exhibiting an increased consumption of the reactants either with reduced field intensity or with elevated gas temperature [17]. Meanwhile, the product distribution was still solely influenced by the thermochemistry at a given temperature.

The other major fundamental methane reforming method, besides dry reforming and partial oxidation, is steam reforming. To obtain a comprehensive picture of the three main reforming methods via plasma chemistry, methane steam reforming in terms of electron-induced chemistry and thermochemistry should be properly addressed in systematic experiments. These data will be an essential validation reference for modeling efforts. In the present work, we investigate the steam reforming of methane in the same temperature-controlled DBD reactor used in the previous dry reforming and partial oxidation studies [11, 17]. We explore the roles of electron-induced chemistry and thermochemistry in the steam reforming by varying the discharge power, the pressure inside the reactor, and the gas temperature.

To support the experimental data and obtain better insight into the electron-induced chemistry, we also performed numerical calculations based on the Boltzmann equation.

2. Experimental and numerical methods

2.1. Experiment

Figure 1. Schematic diagram of the experimental setup.

The experimental setup consisted of a temperature-controlled DBD reactor, a reactant feeding system, a high-voltage supply, and analytical systems (figure 1). The temperature-controlled DBD reactor, which was introduced in our previous works [11, 17], consisted of an electrically heated furnace and a DBD section made from a quartz tube installed inside the furnace. The quartz tube had a 630 mm long straight section with an inner diameter of 45 mm that allowed the gas mixture to reach a target temperature

before the tube narrowed to accommodate the DBD section. A 45 mm long stainless-steel mesh serving as a ground electrode surrounded the narrow section of the quartz tube (20 mm inner and 25 mm outer diameter). A 17.5 mm thick stainless-steel circular rod was inserted into the center of the contracted quartz tube as a high-voltage electrode, forming a 1.25 mm gas gap between the rod electrode and the quartz tube.

A high-voltage supply (30/20 A, Trek) amplified a sinusoidal waveform from a function generator (AFG 3021B, Tektronix), whose amplitude and frequency could be adjusted, to operate the DBD. The voltages applied to the high-voltage electrode and across a sampling capacitor (10 nF), which was installed in the ground electrode to collect charges for the estimation of discharge power, were monitored by voltage probes (P6015A and TPP1000 Tektronix, respectively) with a digital oscilloscope (DPO 4140B, Tektronix). Five thousand cycles of the voltage waveforms were averaged for each tested condition to estimate the power. As indicated in figure 2, the Lissajous diagram for an applied peak-to-peak voltage (U_p) of 20 kV was used to calculate the discharge power, P_{dis} , based on the internal area of the parallelogram multiplied by the operating AC frequency, f_{ac} . An onset voltage (U_{on}) and the effective capacitances of the barrier (C_d) and a total system (C_{tot}) were also deduced from the Lissajous diagram and, as a consequence, the capacitance of the gas gap (C_g), the breakdown voltage (U_b) across the gas gap, and the reduced field intensity, E/N , were determined from $C_g = C_d C_{tot} / (C_d - C_{tot})$, $U_b = U_{on} / (1 + C_g / C_d)$, and $E/N \approx U_b / (dN)$, respectively, where d is the gas-gap distance in the DBD, N is the gas number density, and E is the averaged electric field in the gas gap.

Figure 2. V-Q Lissajous diagram for an applied peak-to-peak voltage of 20 kV and $f_{ac} = 3.3$ kHz at 473 K and 1 atm. Calculated power was $P_{dis} = 10$ W.

To prepare a gas mixture for the steam reforming of methane ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$), equal amounts of methane and water vapor were considered, with nitrogen as a diluent. The mixture composition was $\text{CH}_4 : \text{H}_2\text{O} : \text{N}_2 = 1 : 1 : 8$ in volume, and the total flow rate of the mixture was fixed at 200 ml min^{-1} , calculated at 293 K and 1 atm. The flow rate was the same as the one used in a previous study [11] on dry reforming of methane with $\text{CH}_4 : \text{CO}_2 : \text{N}_2 = 1 : 1 : 8$. The input flow rates of methane (20 ml min^{-1} with purity of 99.999%) and nitrogen (160 ml min^{-1} with purity of 99.999%) were maintained using mass flow controllers (SLA5850, Brooks Instrument); the amount of water was controlled by a syringe pump (KDS 100, KD Scientific). An evaporator fully vaporized the water feed (with TOC < 5 ppb). To avoid water condensation, the temperature of the flow section from the outlet of the evaporator to the inlet of the temperature-controlled DBD reactor was maintained at around 400 K. The electrically heated furnace controlled the target mixture temperature (background temperature), and a vacuum pump (BA series, Iwaki) installed downstream of the reactor maintained the pressure in the reactor at 0.47 – 1 atm. Varying the pressure allowed E/N to change, which allowed comparisons with results having similar E/N caused by variations in the background temperature.

To analyze product composition, we collected samples after 2 hours of a dummy operation of the reactor, turning on the DBD with the $\text{CH}_4/\text{H}_2\text{O}/\text{N}_2$ mixture. The gaseous products were analyzed by an online gas chromatograph (GC 7890A, Agilent). In order to dry the gaseous products and to collect the liquid components, the produced gas passed through a cold trap (273 K) before entering GC. Since nitrogen can be considered chemically inert during plasma reactions, it was used as the internal standard gas to quantify the methane, carbon monoxide, carbon dioxide, and C1 to C5 hydrocarbons. In addition, helium was fed into the products to quantify the hydrogen. The collected liquid samples were injected into a gas chromatography mass spectrometer (GC-MS/FID 7890A-5975C, Agilent) and separated in a capillary column (DB-5MS, Agilent). An external standard method was adopted to analyze the concentrations of alcohols (methanol, ethanol, and propanol), and the remaining products were analyzed using their effective carbon numbers [18]. Note that nitrogen is not completely inert in plasma, but its conversion can be ignored because only tens ppm of nitrogen containing species were found in the condensed liquid.

To characterize the steam reforming of methane, the conversion of the reactant and the selectivity of the product were defined based on measured data using analytical tools. The conversion of the reactant (X_x) was calculated based on the net consumption of component x as

$$X_x(\%) = \left(\frac{\dot{n}_x^{\text{in}} - \dot{n}_x^{\text{out}}}{\dot{n}_x^{\text{in}}} \right) \times 100, \quad (1)$$

where $\dot{n}_x$ denotes the molar flow rate of component x , and the superscripts *in* and *out* indicate the inlet and outlet conditions of the DBD reactor, respectively. The outlet molar flow rate of component x can be obtained from the measured outlet concentration of x corrected by nitrogen, which has a known inlet molar flow rate; thus, $\dot{n}_{\text{CH}_4}^{\text{out}}$ can be expressed as $C_{\text{CH}_4}^{\text{out}} \cdot (\dot{n}_{\text{N}_2}^{\text{in}} / C_{\text{N}_2}^{\text{out}})$, where $C_{\text{CH}_4}^{\text{out}}$ and $C_{\text{N}_2}^{\text{out}}$ denote the concentrations of methane and nitrogen in the produced gas, respectively. Then, equation 1 can be rewritten as

$$X_{CH_4}(\%) = \left(1 - \frac{\dot{n}_{N_2}^{in}}{\dot{n}_{CH_4}^{in}} \cdot \frac{C_{CH_4}^{out}}{C_{N_2}^{out}} \right) \times 100. \quad (2)$$

On the other hand, calculating the conversion of water vapor (X_{H_2O}) is not as straightforward. The concentration of water vapor in the gas phase cannot be measured using the current analytical tools. Therefore, an indirect estimation of the water consumption was adopted based on the oxygen balance, i.e., $\dot{n}_{H_2O}^{in} - \dot{n}_{H_2O}^{out} = \sum c \cdot \dot{n}_{C_aH_bO_c}^{out}$. In the gas phase, carbon monoxide and carbon dioxide were the only two detected species containing oxygen, and non-negligible amounts of alcohols were found in the condensed liquid. Therefore, the conversion of water is expressed as

$$X_{H_2O}(\%) = \left(\frac{\dot{n}_{N_2}^{in} \cdot \left(\frac{2C_{CO_2}^{out} + C_{CO}^{out}}{C_{N_2}^{out}} \right) + \dot{n}_{alcohols}^{out}}{\dot{n}_{H_2O}^{in}} \right) \times 100, \quad (3)$$

where $\dot{n}_{alcohols}^{out}$ indicates the molar flow rate of alcohols detected in the liquid products, defined as

$$\dot{n}_{alcohols}^{out} = \dot{n}_{liquid}^{out} \cdot (C_{CH_3OH}^{liquid} + C_{C_2H_5OH}^{liquid} + C_{C_3H_7OH}^{liquid}). \quad (4)$$

Here, $C_{CH_3OH}^{liquid}$, $C_{C_2H_5OH}^{liquid}$, and $C_{C_3H_7OH}^{liquid}$ denote the concentrations of methanol, ethanol, and propanol in the liquid products. Due to difficulties in direct measurement, the outlet molar flow rate of the liquid products, $\dot{n}_{liquid}^{out}$, can only be estimated. In the liquid product, non-negligible amounts of alcohols (methanol, ethanol, and propanol) were measured, while only a few tens of ppm of the other oxygen-containing liquid products, such as butanone and acetic acid, were detected; therefore, $\dot{n}_{liquid}^{out}$ can be reasonably calculated based on the oxygen balance:

$$\dot{n}_{liquid}^{out} \approx \dot{n}_{H_2O}^{out} + \dot{n}_{alcohols}^{out} = \dot{n}_{H_2O}^{in} - \dot{n}_{N_2}^{in} \cdot \left(\frac{2 \cdot C_{CO_2}^{out} + C_{CO}^{out}}{C_{N_2}^{out}} \right). \quad (5)$$

Meanwhile, a carbon-based selectivity was used to analyze the product selectivity, such that

$$S_{C_aH_bO_c}(\%) = \left(\frac{a \times \text{moles of } C_aH_bO_c \text{ produced}}{\text{moles of } CH_4 \text{ converted}} \right) \times 100. \quad (6)$$

Similar to the above conversion equations, the selectivities of carbon monoxide (S_{CO}), carbon dioxide (S_{CO_2}), ethane ($S_{C_2H_6}$), and methanol (S_{CH_3OH}) were calculated via the following equations:

$$S_{CO}(\%) = \left(\frac{\dot{n}_{N_2}^{in}}{\dot{n}_{CH_4}^{in} \cdot X_{CH_4}} \cdot \frac{C_{CO}^{out}}{C_{N_2}^{out}} \right) \times 100, \quad (7)$$

$$S_{CO_2}(\%) = \left(\frac{\dot{n}_{N_2}^{in}}{\dot{n}_{CH_4}^{in} \cdot X_{CH_4}} \cdot \frac{C_{CO_2}^{out}}{C_{N_2}^{out}} \right) \times 100, \quad (8)$$

$$S_{C_2H_6}(\%) = \left(\frac{\dot{n}_{N_2}^{in}}{\dot{n}_{CH_4}^{in} \cdot X_{CH_4}} \cdot \frac{2C_{C_2H_6}^{out}}{C_{N_2}^{out}} \right) \times 100, \text{ and} \quad (9)$$

$$S_{CH_3OH}(\%) = \left(\frac{\dot{n}_{liquid}^{out} \cdot C_{CH_3OH}^{liquid}}{\dot{n}_{CH_4}^{in} \cdot X_{CH_4}} \right) \times 100. \quad (10)$$

Hydrogen selectivity (S_{H_2}) was calculated based on a hydrogen balance using the known amount of helium injected after DBD reactor as the internal standard:

$$S_{H_2}(\%) = \left(\frac{\dot{n}_{He}^{out}}{2 \cdot \dot{n}_{CH_4}^{in} \cdot X_{CH_4} + \dot{n}_{H_2O}^{in} \cdot X_{H_2O}} \cdot \frac{C_{H_2}^{out}}{C_{He}^{out}} \right) \times 100. \quad (11)$$

2.2. Electron-induced chemistry analysis

DBD plasmas are known to have minimal temperature increase because most of the electrical input energy is dissipated into dissociation, excitation, and ionization of molecules via energetic electrons. Hence, when the DBD operates in sufficiently low temperature, where no conversion of the reactant is

found without discharges, the most important step to initiate the reaction is the production of chemically reactive species via electron-impact reactions [13]. The coefficients of these electron-impact reactions are governed by the electron-energy distribution, which depends on E/N [19]. To investigate the effects of electrons on the chemistry inside the DBD reactor, we solved the Boltzmann equation with a temporal growth model, as described in the work of Hagelaar and Pitchford [20]. By taking cross-sections of the electron collisions into account, the collision and energy loss coefficients at a specific E/N can be calculated. From these data, the required energy (EC_R) to convert (dissociate or ionize) one target molecule—methane or water in this study—through electron-impact reactions can be obtained using the following equation:

$$EC_R = \frac{EC_{total}^{Loss}}{kn_e N_R} = \frac{\sum \sum k^{ECloss}}{k}, \quad (12)$$

where n_e and N_R represent the electron density and the number density of a target molecule, respectively, EC_{total}^{Loss} is the total energy loss calculated by summation of all the electron-collisional processes, and k and k^{ECloss} are the collision and energy loss coefficients, respectively. The amount of methane and water being dissociated and ionized by electron-impact reactions can be determined for a given P_{dis} from the EC_R of methane and water. Finally, the electron-induced conversion of methane and water can be evaluated from

$$X_R^{EC} = \frac{P_{dis}}{EC_R} \cdot \frac{1}{\dot{n}_R^{in}}, \quad (13)$$

where $\dot{n}_R^{in}$ is the molar flow rate of the methane or water being fed into the plasma. In the present calculations, we considered the same mixture of methane, water vapor, and nitrogen with a molar ratio of $CH_4:H_2O:N_2=1:1:8$, and a total molar flow rate of 8.9 mmol/min as in the experiment. The cross-sections of the electron impact were collected from various sources [21-24]: nitrogen [21, 23], methane [22, 23], water [24].

Table 1 shows the relevant electron-impact reactions (only dissociation and ionization) for the generation of reactive species from methane and water. The calculations only provided the amounts of reactants dissociated or ionized through electron-impact reactions and cannot be considered representative of the total conversion because they do not include all the chemical reactions that typically occur in the plasma. For example, the calculations do not take into account any backward recombination reactions or the dissociation and ionization reactions with other reactive species. Although we understand the importance of those omitted reactions, which can significantly influence the conversions in the plasma chemistry, we regretfully note that the temperature dependencies of most of these reactions were unknown. This is probably one reason that most modeling studies in literature have been performed at room temperature [25]. Nevertheless, looking at the effects of the abovementioned parameters, such as E/N and P_{dis} for a given mixture composition, on the electron-impact dissociation and ionization, we find valuable connections with the experimental data. In this study, the calculations were performed simply to support the experimental observations regarding the influence of different plasma parameters; therefore, descriptions of the entire underlying plasma chemistry were out of scope. The important implication is that we only evaluate the results of the calculations based on their trends and not their absolute values.

Table 1. Electron-impact reactions for reactive species generation from methane and water.

	$e+\text{CH}_4$		$e+\text{H}_2\text{O}$
Dissociation	$\rightarrow \cdot\text{CH}_3 + \cdot\text{H} + e$ [24] $\rightarrow \cdot\text{CH}_2 + 2\cdot\text{H} + e$ [23] $\rightarrow \cdot\text{CH}_2 + \text{H}_2 + e$ [21]		$\rightarrow \cdot\text{H} + \cdot\text{OH} + e$ [24] $\rightarrow \text{H}_2 + \cdot\text{O} + e$ [24] $\rightarrow \text{H} + \cdot\text{OH}$ [24] $\rightarrow \cdot\text{H} + \text{OH}^\cdot$ [24] $\rightarrow \text{H}_2 + \text{O}^\cdot$ [24]
Ionization	$\rightarrow \text{CH}_4^+ + 2e$ [22] $\rightarrow \text{CH}_3^+ + \cdot\text{H} + 2e$ [19] $\rightarrow \text{CH}_2^+ + 2\cdot\text{H} + 2e$ [21]		$\rightarrow \text{H}_2\text{O}^+ + 2e$ [24]

3. Results and discussion

3.1. Effect of discharge parameters on the steam reforming

We investigated the steam reforming of methane with various discharge parameters, such as f_{ac} and P_{dis} . As a result of varying f_{ac} and P_{dis} , E/N was also varied during the discharge, due to the change in breakdown voltage (as shown in Table 2). Thus, the effects of E/N on the process could be indirectly investigated for a given background temperature and pressure. The reduced field intensity and the discharge power are key parameters for electron-impact reactions, because they govern both the temperature and the density of electrons.

First, we varied f_{ac} while maintaining P_{dis} at 10 W. Table 2 shows the related discharge parameters, such as C_d , C_g , U_{on} , U_b , and estimated E/N . Those parameters were determined by the V-Q diagram (explained in the experimental section) for a background temperature of 473 K and a reactor pressure of 1 atm. The reduced field intensity monotonically decreased as f_{ac} increased, due to the decreased U_b , as shown in the table ($E/N = 176$ Td and 146 Td at $f_{ac} = 1.5$ kHz and 3.4 kHz, respectively).

Table 2. DBD discharge parameters at various f_{ac} determined by the V-Q plots by fixing $P_{dis} = 10$ W.

f_{ac} (kHz)	C_d (pF)	C_g (pF)	U_{on} (kV)	U_b (kV)	E/N (Td)
1.5	49.5	15.2	4.5	3.4	176
2.4	49.0	14.8	4.2	3.2	165
2.8	42.6	15.4	4.0	3.0	153
3.1	42.1	15.1	4.0	2.9	151
3.3	38.9	15.2	3.9	2.8	147
3.4	40.3	15.2	3.9	2.8	146

We found that the reactant conversion and product selectivities were not significantly affected by the f_{ac} applied to the DBD, as long as P_{dis} remained the same (figure 3). The result also implied that the applied voltage insignificantly influenced the conversion; we had to modify the applied voltage to keep

$P_{\text{dis}} = 10$ W for a range of tested f_{ac} . Figure 3 also illustrates the effect of changing E/N by varying f_{ac} on the reactant conversion and product selectivities. The conversions of methane and water were around 4.8 and 1.4 %, respectively, irrespective of f_{ac} . Meanwhile, the selectivities of hydrogen, ethane, methanol, carbon monoxide, and carbon dioxide remained at about 50, 27, 6, 18, and 2 %, respectively. Without plasma, no reaction was observed at 473 K, indicating that the electron-impact reactions through DBD initiated the observed chemical reactions.

In order to further investigate the insensitive experimental result of the conversions responding to varying E/N in the range of 146–176 Td, we calculated the electron-impact dissociation and ionization of methane and water via equation 13, based on the corresponding E/N of each tested f_{ac} , as shown in Table 2. The dissociation reactions were dominant over the ionization for the calculated range of E/N . The calculated conversions, including electron-impact dissociation and ionization of methane and water, showed similar quantitative behaviors to the conversions with various f_{ac} (co-plotted in figure 3a). This is mainly attributed to the weak influence of E/N on electron-impact dissociation, which was a dominant contributor to the methane and water conversions. As calculated via equation 12, the energy required to dissociate or ionize one molecule of methane through electron-impact reactions was much lower than required for water, explaining the higher conversion of methane than of water in the present study. Theoretically, this is due to the effects of water having smaller cross-sections of dissociation and ionization than methane, and the high bond energy of O–H compared to C–H, which respectively exist in water and methane. The dashed lines in figure 3b indicate trends from the experimental data; the calculations do not capture an overall picture of the plasma chemistry.

Figure 3. Effect of f_{ac} and E/N on (a) conversions of methane and water (data points indicate experiment and solid lines represent calculation) and (b) selectivities of carbon monoxide, carbon dioxide, ethane, methanol and hydrogen (dashed lines indicate trend lines based on experiment). P_{dis} was maintained at 10 W.

Table 3. DBD discharge parameters at various P_{dis} by changing the applied voltage while keeping $f_{ac} = 3.3$ kHz.

P_{in} (W)	C_d (pF)	C_g (pF)	U_{on} (kV)	U_b (kV)	E/N (Td)
6.7	36.2	15.2	3.6	2.6	132
10.0	38.9	15.2	3.9	2.8	147
12.9	41.6	15.2	4.0	3.0	155
17.3	49.3	15.7	4.0	3.2	168

Secondly, to investigate the effect of P_{dis} on the steam reforming of methane, we varied P_{dis} from 6.7 to 17.3 W by changing the applied voltage, and maintained $f_{ac} = 3.3$ kHz and a background temperature of 473 K. The detailed parameters for each power condition are listed in Table 3. With increasing P_{dis} , E/N increased from 132 to 168 Td. This range of E/N was similar to the previous cases shown in Table 2; hence, we assumed that E/N had no distinct effect on the test conditions shown in Table 3. On the other hand, we expected a linear increase of the conversions with increased P_{dis} due to increased electron density. We observe this trend in figure 4a. The calculated electron-impact dissociation and ionization of methane and water show reasonably similar trends to the experimental conversions. This indicates that the electron-

induced chemistry is highly dependent on P_{dis} and plays a determining role in the reactant conversions for low gas temperatures at which no conversion can occur without discharges.

Figure 4b illustrates the selectivities of hydrogen, ethane, methanol, carbon monoxide, and carbon dioxide at various P_{dis} . Similar to figure 3b, each selectivity appears insensitive to P_{dis} . This indicates that electron-induced chemistry governs the conversion of the reactants, while the reaction pathways to the final product during steam reforming are not significantly affected by the plasma parameters P_{dis} , f_{ac} , or E/N . This result is consistent with the previously reported results for dry reforming and partial oxidation of methane [11, 17].

Figure 4. Effect of P_{dis} on (a) conversions of methane and water (data points indicate experiment and solid lines represent calculation) and (b) selectivities of carbon monoxide, carbon dioxide, ethane, methanol and hydrogen (dashed lines indicate trend lines based on experiment). f_{ac} was maintained at 3.3 kHz, while varying applied voltage controlled P_{dis} .

3.2. Effect of background temperature on the steam reforming

In general, plasma-chemical reactions are initiated by electron-impact reactions that produce chemically reactive species. These reactive species ($\cdot\text{H}$, $\cdot\text{OH}$, $\cdot\text{CH}_3$, CH_4^+ , and H_2O^+ in the steam reforming of methane) induce further thermochemical reactions to form the final products. Unlike electron-impact reactions, the radical- and ion-induced thermochemical reactions are less likely to be affected by an electrical field. Instead, the reactions are determined by temperature, as expressed in the

Arrhenius equation. To investigate the role of thermochemistry in steam reforming, we varied the background temperature from 443 to 673 K at 1 atm. The discharge power was fixed at 10 W by maintaining the applied voltage of 10 kV (peak voltage in the sinusoidal wave). Then, f_{ac} was adjusted to achieve $P_{dis} = 10$ W.

Figure 5 shows the temperature dependencies of the reactant conversions and product selectivities. The measured methane conversion gradually increased from 4.5 % at 443 K to 6.4 % at 623 K, followed by an abrupt decrease. The conversion of water decreased monotonically with increasing background temperature. Similar trends for methane conversion were observed in previous studies on the dry reforming and partial oxidation of methane [11, 17], which could be attributed to the increase in dielectric loss above a certain temperature [26]. Figure 5a compares the measured conversion and the calculated conversions considering only electron-impact dissociations and the ionizations of methane and water based on E/N from Table 4. The calculation of the electron-impact reactions depended only on E/N and had nothing to do with temperature. The reason we found a wider range of E/N than in previous cases is because the temperature change caused a large variation in the gas number density. The calculated methane conversion showed a similar trend to the measured methane conversion for background temperatures below 623 K. The calculated water conversion, on the other hand, had a slightly increasing trend, whereas the measured water conversion was slowly decreasing. This might indicate that the electron-impact dissociation and ionization reactions of water were not sufficient to describe the water conversion obtained experimentally at elevated temperatures (or increased E/N ; see discussion regarding pressure variation below), and the reactive species created by the electron-induced chemistry played an important role at these temperatures via thermochemical water consumption and formation.

As shown in figure 5b, the selectivities of carbon monoxide, ethane, and hydrogen were strongly affected by the background temperature, while the other components were not. As the background

temperature became higher, the ethane selectivity increased to make up for the decreases in the carbon monoxide and hydrogen selectivity.

Figure 5. Effect of temperature on (a) conversions of methane and water (data points indicate experiment, and solid lines represent calculation) and (b) selectivities of carbon monoxide, carbon dioxide, ethane, methanol, and hydrogen (dashed lines indicate trend lines based on experiments). The applied peak voltage was fixed at 10 kV, while f_{ac} was adjusted to maintain $P_{dis} = 10$ W.

Table 4. DBD discharge parameter for various temperatures. The applied peak voltage was fixed at 10 kV, while f_{ac} was adjusted to maintain $P_{dis} = 10$ W. The pressure inside the reactor was 1 atm.

T (K)	C_d (pF)	C_g (pF)	U_{on} (kV)	U_{break} (kV)	E/N (Td)
443	36.8	15.3	3.9	2.7	132
473	38.9	15.2	3.9	2.8	147
523	39.8	15.0	3.9	2.8	162
573	42.1	14.7	4.0	2.9	184
598	41.6	14.8	4.0	2.9	192
623	42.4	14.7	4.4	3.3	222
648	45.0	13.7	5.0	3.8	271
673	51.5	12.1	6.2	5.3	369

The background temperature should have a strong impact on the results above, but we noticed that a significant increase in E/N that was caused by a lower number density due to temperature increase. In the previous sections, the variation in E/N was less than 30 %. In this case, it was around 300 % (Table 4). Therefore, to clearly identify the distinct roles of the electron-induced chemistry and the

thermochemistry, we varied E/N by changing the operating pressure from 0.47 atm to 1 atm at a fixed background temperature of 473 K (see Table 5).

Table 5. DBD discharge parameters for various pressures. The applied peak voltage was fixed at 10 kV, while f_{ac} was adjusted to maintain $P_{dis} = 10$ W. The background temperature was maintained at 473 K.

p (bar)	C_d (pF)	C_g (pF)	U_{on} (kV)	U_{break} (kV)	E/N (Td)
1.00	38.9	15.2	3.9	2.8	147
0.86	48.3	18.1	3.7	2.7	160
0.77	50.1	18.3	3.6	2.7	179
0.68	51.7	19.2	3.5	2.5	193
0.56	54.8	17.7	3.4	2.5	233
0.47	58.5	16.6	3.4	2.5	276

In figure 6, the reactant conversions and product selectivities as a function of E/N are compared for two conditions, one with varying background temperatures at 1 atm (figure 5) and one with varying pressures at 473 K. For the conversion of water (figure 6a), no significant difference was found between the two tested conditions. This indicates the importance of E/N (and, thus, electron temperature) for the water conversion; it seems to be mainly dependent on the electron-impact reactions. The conversion of methane, however, is higher with increased temperature than with decreased pressure for similar E/N . This could be attributed to the thermochemistry occurring with reactive species such as $\cdot H$ and $\cdot OH$, indicating that both the electron-induced chemistry and the thermochemistry are important for the conversion of methane. The thermochemical radical reactions lead to further methane dissociation and enhance the overall methane conversion for the cases with increased temperature at a constant pressure.

For the cases where pressure varied but temperature remained the same, the product selectivities (figure 6b) showed a weaker dependence on E/N than those where temperature was varied. For example, the selectivity of ethane remained about 27 % when the pressure was varied, while it increased from 27 %

to 38 % with elevated background temperatures. This implies that the background temperature (thermochemistry) had a strong effect on the underlying chemical-reaction pathways to the final products.

Figure 6. Effect of E/N on (a) conversions of methane and water; (b) selectivities of carbon monoxide, carbon dioxide, ethane, methanol, and hydrogen when the background temperature is varied at 1 atm (CP: constant pressure); selectivities when the pressure is varied at 473 K (CT: constant temperature).

3.4. Potential thermochemistry affecting the conversions of methane and water

In plasmas, chemically reactive species are mainly produced through electron-impact reactions. Then, they are rapidly consumed to form intermediates and final products [27, 28]. Thus, the electron-impact reactions are important not only for the consumption of the reactants, but especially for the generation of reactive species, which are the key components in thermochemical reactions. As listed in Table 1, the main reactive species produced from our initial mixture via electron-impact reactions were $\cdot H$, $\cdot OH$, and $\cdot CH_3$.

Figure 7. Reaction constants of the reactions relating to conversions of (a) methane and (b) water induced by the main reactive species produced by the electrons impact reactions.

To investigate the temperature dependence of elementary reactions involving those radicals, we investigated eight of the reactions induced by reactive species for the mixture under study. The reaction constants obtained from the NIST database [29] are illustrated in figure 7 as a function of temperature. The main methane-consumption reactions caused by radicals should be R1 and R2, while the main recombination reactions forming methane are R3, R4, and R5. For easy comparison, figure 7a illustrates only methane-related reactions (R1–R5).

Comparing the role of hydrogen radicals in R1 and R3, the radical-recombination reaction constant to form methane (R3) is larger than that of methane dissociation (R1) in the tested range of temperatures. Since R1 increases with temperature and R3 decreases, methane conversion by hydrogen radicals will be promoted by high temperatures. The dissociation of methane via hydroxyl radicals (R2) and the recombination of methyl and hydroxyl radicals to produce methane (R4) are also enhanced by increasing

the reaction temperature. However, the reaction rate of hydroxyl involved methane dissociation (R2) is more than two orders of magnitude higher than that of recombination (R4). This indicates that an overall hydroxyl radical reaction is more favorable for enhancing methane conversion with increased temperature. The methane production reaction R5 is a very slow reaction in the studied temperature range; thus, its influence should be negligible.

Considering the radical reactions for water consumption and formation, we examined the dissociation (R6) and formation (R2, R7, and R8) of water (shown in figure 7b). The reaction constant of water consumption (R6) is negligibly small, particularly in the tested range of temperatures, indicating that thermochemistry caused no significant conversion of water. On the other hand, the water formation reactions (R2, R7, and R8) were significant under the present conditions. The hydroxyl radical reactions with methane and methyl radicals (R2 and R7) that result in water formation were faster with increased temperature; the recombination of hydrogen radicals and hydroxyl radicals decreased with the temperature. It is difficult to conclude that which reaction produced the most water, partly because the water formation reactions (R2, R7, and R8) showed no clear direction for the water, and partly because the result in figure 6a shows no discernable difference between the two cases, i.e., constant pressure and constant temperature.

However, considering the difference between the calculated and measured conversions at increased temperatures (figure 5a), there should be non-negligible radical reactions resulting in a net production of water. Furthermore, since increased E/N gradually decreased water conversions (figure 6a), the overall radical reaction for water seems to produce water when E/N becomes stronger. This can be attributed to the increased concentrations of radicals ($\cdot\text{H}$ and $\cdot\text{OH}$) caused by the augmented electron-impact dissociation of reactants with a stronger E/N . In addition, the increased concentrations of $\cdot\text{H}$ and $\cdot\text{CH}_3$ due to increased methane conversion with high temperatures (figure 5a) also indicated the same direction of water formation via R8 and R7.

As a result, we hypothesized that, in the tested range of temperatures, water consumption is mainly controlled by electron-impact reactions that are dependent on E/N . Overall, the water-formation reaction constant with radicals was somewhat insensitive to temperature, but the reaction produced more water from the increased number of radicals caused by a stronger E/N and methane dissociation. Thus, water conversion deteriorated with higher E/N .

In this regard, to fully understand the comprehensive effects of the electron-impact reactions and radical reactions that occur during methane steam reforming, an extensive numerical study should be performed. That study should include detailed chemical kinetics based on both electron-induced and thermochemistry. However, due to insufficient kinetics data for a wide range of temperatures, it is not currently feasible to accurately perform such a numerical study. In this regard, solid fundamental data on the thermochemical reactions in a range of 300–800 K is urgently required.

4. Conclusions

We investigated the steam reforming of methane in a temperature-controlled dielectric barrier discharge (DBD) reactor, and performed systematic experiments by varying gas temperature, discharge power, and reduced field intensity. The main objective was to obtain a better understanding of the plasma chemistry during the steam reforming of methane, addressing respective and distinctive role of both electron-induced chemistry and thermochemistry. We found that, as long as P_{dis} and the gas temperature were constant, applied voltage and applied AC frequency showed negligible effects on the reactant conversions and product selectivities. The product selectivities (i.e., product composition) seemed to be mainly controlled by the gas temperature up to 673 K, irrespective of P_{dis} but weakly depending on E/N . This indicates the importance of thermochemistry on the product composition.

On the other hand, the reactant conversions were affected by both the electron-induced chemistry and thermochemistry. Electron-impact dissociation of methane and water initiated the process and produced $\cdot\text{H}$, $\cdot\text{CH}_3$, and $\cdot\text{OH}$ radicals, thus increasing the electron density ($\sim P_{\text{dis}}$) and the electron energy ($\sim E/N$) within the tested ranges ($P_{\text{dis}} < 18 \text{ W}$ and $130 < E/N < 370 \text{ Td}$) should have positively affected the reactant conversions. However, due to the increased consumption of methane and increased production of water caused by $\cdot\text{H}$ and $\cdot\text{OH}$ radicals (methyl and $\cdot\text{OH}$ radicals) at elevated gas temperatures, methane conversion was enhanced and water conversion deteriorated.

These results together with those of our previous studies for the partial oxidation [17] and the dry reforming [11] of methane contribute experimental data for methane/oxygen/nitrogen ($\text{CH}_4/\text{O}_2/\text{N}_2$), methane/carbon dioxide/nitrogen ($\text{CH}_4/\text{CO}_2/\text{N}_2$), and methane/water/nitrogen ($\text{CH}_4/\text{H}_2\text{O}/\text{N}_2$) mixtures with various gas temperatures, reduced field intensities, and discharge powers. Future efforts should be collaborative works with modeling experts to develop comprehensive chemical kinetic data and their validation through fundamental experiments.

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