

Reaction mechanisms and cracking performance of CH₄ provoked by non-equilibrium plasma

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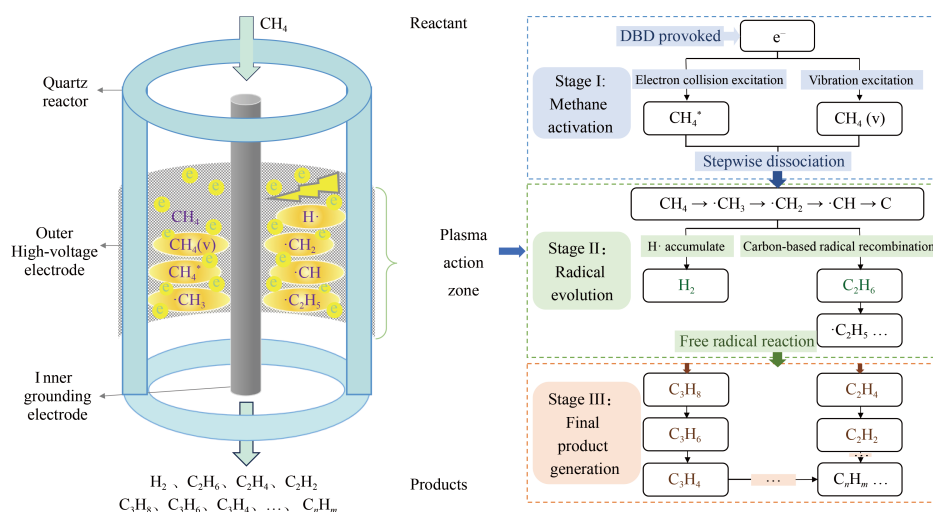
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Abstract: Methane cracking driven by electric power holds significant promise in the context of the rapid development of renewable energy. The effects of carrier gas ratio, input power, and inlet gas flow rate on CH₄ cracking performance were systematically investigated in a dielectric barrier discharge (DBD)



reactor. The variation of temperature distribution and reaction energy intensity were also examined. The experimental results indicate that CH₄ conversion and gaseous product formation are promoted by increasing the DBD input power or decreasing the inlet gas flow rate. At an input power of 90 W and an inlet gas flow rate of 200 mL/min, the single-pass CH₄ conversion reach 46.6%, with an H₂ yield of 23.3%, demonstrating that CH₄ cracking is governed by electron induced. While the Joule heating from the inner and outer electrodes is relatively limited. The reaction energy intensity increases as the CH₄ conversion decreases. When the inlet gas flow rate increases from 200 to 800 mL/min, the energy intensity rises by approximately 2.8 times, indicating that higher inlet gas flow rates enhance the convective heat transfer and shorten the gas residence time, thereby suppressing deep CH₄ cracking. Moreover, BOLSIG+ calculations further reveal that CH₄ activation is dominated by electron induced vibrational excitation, in which stepwise energy accumulation drives C–H bond dissociation. The energy transfer and species transformation pathways of overall CH₄ cracking process, which comprises electron energy injection, vibrational excitation, stepwise dissociation, radical chain extension, and final product formation, can be summarized into three stages, i.e. methane activation, radical evolution, and product formation.

Key words: methane cracking; non-equilibrium plasma; reaction performance; mechanism exploration

Methane (CH₄), the main component of natural gas, coalbed methane, shale gas, combustible ice, and biogas,

attributes as both an energy carrier and a chemical feedstock^[1]. However, CH₄ leakage can cause a severe greenhouse

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effect^[2]. Therefore, the efficient conversion and utilization of CH₄ have always been a research hotspot in the fields of energy and chemical engineering^[3–12]. Currently, industrial CH₄ conversion mainly involves steam reforming to produce syngas (a mixture of carbon monoxide and hydrogen), which is then further converted into liquid fuels or chemicals^[12–13]. Numerous studies^[14–19] have explored partial oxidation of CH₄ to produce syngas, as well as thermal cracking of CH₄ to produce high-value products like hydrogen and carbon materials. However, CH₄ molecules are chemically stable due to a non-polar structure and a relatively high C–H bond dissociation energy of approximately 439.3 kJ/mol at 298.15 K and 101 kPa^[1], making thermal cracking typically under high temperatures and in the presence of catalysts^[20].

Non-Equilibrium Plasma (NEP) refers to a system where the electron temperature is significantly higher than that of heavy particles during the discharge process^[10]. Due to the overall low gas temperature, even close to room temperature, NEP is often referred to as a non-thermal plasma, characterized by the ability to directly activate molecules under mild conditions using high-energy electrons to produce particles such as atoms, ions, free radicals, and active species. These particles undergo dissociation, excitation, and chain reactions, enhancing the molecular activity and accelerating the reaction rates, thus overcoming the dependence on high temperatures in traditional thermal catalytic reactions^[10]. In the past decade, with the rapid development of intermittent renewable energy sources such as wind and solar power^[21], renewable electricity-driven chemical conversions have gradually become a potential alternative to traditional thermochemical processes^[22–24]. NEP has attracted widespread attention in the fields such as the high-value utilization of carbon resources^[25–27] and is of significant importance for greenhouse gas treatment.

To date, the main methods for generating NEP include dielectric barrier discharge (DBD), corona discharge, and gliding arc discharge^[10]. Among these, DBD offers advantages such as simple equipment, stable discharge, scalable structure, and ease of continuous reactions^[27–28]. In the past decade, many studies^[29–39] have been conducted on experiments and numerical simulations on DBD induced CH₄ conversion. For instance, Xu et al.^[34] used a DBD reactor to directly convert CH₄ to C₂–C₄ hydrocarbons and hydrogen under ambient temperature and pressure. The results showed that CH₄ in DBD reactor exhibited a filamentary discharge mode, with residence time having the most significant impact on CH₄ conversion and hydrogen yield. While the effect of frequency was negligible. Wang et al.^[35] employed a miniature DBD reactor to directly synthesize high-carbon hydrocarbons from CH₄. The effects of input power, residence time, discharge gap, and outer electrode length on CH₄ conversion and product selectivity were studied, highlighting the positive correlation between input power or residence time and CH₄ conversion. Konno et al.^[36] investigated the impact of electrode structure on

CH₄ conversion in a DBD reactor, revealing the critical role of reactor geometry in plasma conversion efficiency. Moreover, Li et al.^[37] simulated methane-air plasma discharge characteristics, analyzing the spatiotemporal distribution of key active radicals such as ·CH₃ and O·, providing a microscopic kinetic perspective on plasma discharge. Chen et al.^[38] compared the kinetic roles of CO₂ and O₂ additives in plasma activated CH₄ conversion, finding that O₂, due to its lower ionization energy, more easily promoted the CH₄ oxidation. Whereas CO₂ favored the formation of syngas and C₂ hydrocarbons. Gadkari et al.^[39] simulated the effects of dielectric constant, voltage, and frequency on discharge characteristics in a coaxial DBD reactor, clarifying the regulatory mechanism of operating parameters. The above research revealed the potential application of non-equilibrium plasma in the high-value conversion of CH₄ from the aspects of discharge mode, reactor structure, operating parameters, and numerical simulation, using a continuous flow DBD reactor combined with online gas chromatography for quantitative analysis of product composition, or based on fluid scale simulation and microscopic reaction kinetics analysis. However, most of the existing research focused on conversions, yields, energy efficiency, and device optimization. The reaction pathway of CH₄ from electronic vibration excitation to stepwise dissociation in DBD reactor remains to be better understood, and the impact of the temperature field distribution on the CH₄ cracking has yet to be systematically analyzed.

Building on previous investigations into the effects of pulse mode, cooling method, and packed bed on CO₂ splitting performance in a DBD reactor^[40], the synergistic effects of manganese-based composite catalysts on the reaction between toluene and CO₂ induced by DBD were explored^[41], followed by a recent examination of how the temperature field in the DBD reactor influences the discharge characteristics and reaction performance during CO₂ reforming of CH₄^[3]. This work focuses on the characteristics and reaction mechanisms of CH₄ cracking in a DBD reactor. Moreover, the influence of variations in the temperature field on the reaction performance is examined.

1 Experimental

Figure 1 illustrates the schematic of the experimental setup for DBD provoked CH₄ cracking, which consists of four main parts, i.e. the DBD reactor, plasma generator, gas inlet unit, and detection unit. The DBD reactor uses a quartz tube with an inner diameter of 20 mm and a wall thickness of 2.5 mm as the discharge barrier medium. The inner and outer electrodes are made of stainless steel rods with a diameter of 16 and a 150 mm long stainless steel wire mesh wrapped around the outer surface of the quartz tube. The plasma generator consists of a high-frequency, high-voltage power supply (Corona Lab CTP-2000K) and a voltage regulator. The power supply outputs a sinusoidal AC signal with a voltage range of 0–30 kV and a frequency range of

5–20 kHz. The gas inlet unit includes gas cylinders, mass flow meters, and a gas mixer. The detection unit consists of an oscilloscope (Tektronix TBS2000B), infrared thermal imager (FLIR A6750), soap film flowmeter (Beilao BL1000), and gas chromatograph (Shimadzu GC-2014) to measure discharge current and voltage, reaction temperature, outlet gas flow rate and gas composition and concentration after the reaction, respectively.

Before each experiment, N₂ with 99.99% purity is introduced into the reaction system at a flow rate of 100 mL/min for about 30 min to ensure that no O₂ is detected at the outlet using a gas chromatograph. CH₄ and N₂ are then mixed in a ratio of 10:90 by mass flow controllers. Following thorough mixing, the mixture is introduced into the DBD reactor. The addition of 90% N₂ is used to dilute the CH₄ gas, stabilize the discharge process, and improve the accuracy of gas chromatographic measurements. The applied voltage and frequency of the DBD reactor are adjusted using the voltage regulator and high-frequency high-voltage power supply. The input voltage and current are displayed on the power supply panel, and the discharge voltage and current are monitored and recorded in real time on the oscilloscope. After stable discharge in the DBD reactor for about 50 min, the temperature in the reactor reaches a near equilibrium state. The real-time temperature is recorded using the infrared thermal imager. The outlet gas flow is measured using the soap film flow meter, and the gas composition and concentration are analyzed online by gas chromatograph. The experiments are conducted at ambient temperature and pressure. The performance of the CH₄ cracking is characterized by single-pass CH₄ conversion (x_{CH_4}), gas products yields (Y_{H_2} , $Y_{\text{C}_2\text{H}_6}$, $Y_{\text{C}_2\text{H}_4}$, $Y_{\text{C}_3\text{H}_8}$, $Y_{\text{C}_3\text{H}_6}$, $Y_{\text{C}_2\text{H}_2}$, $Y_{\text{C}_3\text{H}_4}$) and reaction energy intensity (EI). Each experiment is repeated for three times to calculate the average value and standard deviations. Moreover, the reaction pathways and the underlying mechanisms are explored by combining the electron collision rate coefficients and energy loss fractions for CH₄ calculated by BOLSIG+.

The CH₄ conversion is calculated as:

$$x_{\text{CH}_4} = \frac{n_{(\text{CH}_4 \text{ reacted})}}{n_{(\text{CH}_4 \text{ input})}} \times 100\% \quad (1)$$

The gas product yield is derived from:

$$Y_{\text{H}_2} = \frac{n_{(\text{H}_2 \text{ produced})}}{2n_{(\text{CH}_4 \text{ input})}} \times 100\% \quad (2)$$

$$Y_{\text{C}_x\text{H}_y} = \frac{x \cdot n_{(\text{C}_x\text{H}_y \text{ produced})}}{n_{(\text{CH}_4 \text{ input})}} \times 100\% \quad (3)$$

where n refers to the number of moles of reactants or products, and the “reacted”, “input”, and “produced” stand for the reacted, input, and produced substances, respectively. The “ x ” and “ y ” are the numbers of carbon and hydrogen atoms in the molecule.

The reaction energy intensity (EI) is calculated as:

$$\text{EI}(\%) = \frac{(\sum \Delta_f H_m^\circ (\text{product}) \times n_{\text{product}}) - (\Delta_f H_m^\circ (\text{CH}_4) \times n_{\text{CH}_4 \text{ reacted}})}{\int P dt} \times 100\% \quad (4)$$

where n represents the number of moles of the substance, $\Delta_f H_m^\circ$ is the standard molar enthalpy of formation of the substance, P represents the discharge power and t is the gas residence time.

The discharge power (P) is calculated using the classic Lissajous figure method^[42]:

$$P = f \times C_m \times A \quad (5)$$

where f is the frequency of the plasma AC power supply, C_m refers to the sampling capacitance and A represents the area of the Lissajous figure.

The principle of the Lissajous figure method is that when discharge occurs, the capacitor C_m measures the amount of charge Q transported by the discharge. The current flowing through the circuit is as following:

$$I = \frac{dQ}{dt} = \frac{d(C_m V_m)}{dt} = C_m \frac{dV_m}{dt} \quad (6)$$

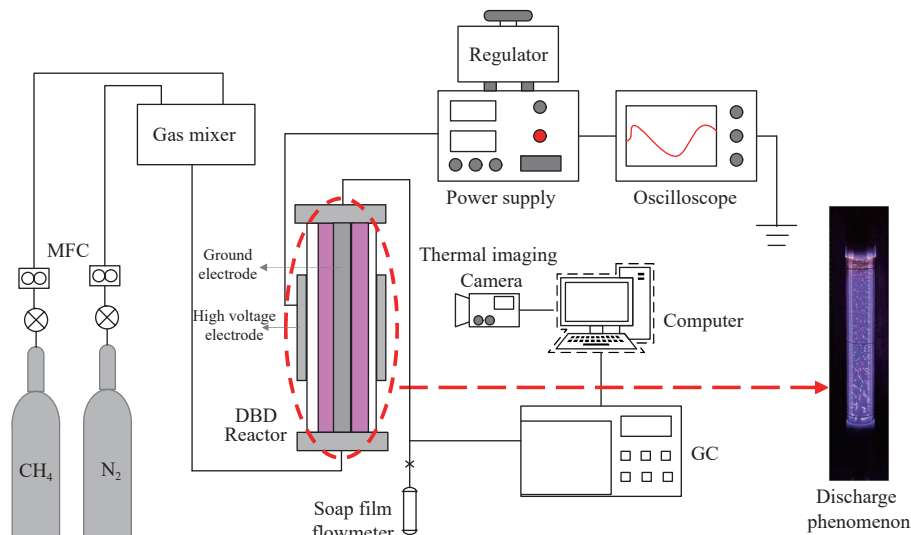


Fig. 1 A schematic of the experimental setup for DBD provoked CH₄ cracking

where I is the discharge circuit current, V_m refers to the voltage across the measuring capacitor C_m , and V_m represents proportional to the charge Q on the measuring capacitor. Consequently, the discharge power is:

$$P = \frac{1}{T} \int_0^T V I dt = \frac{C_m}{T} \int_0^T V \frac{dV_m}{dt} dt = f C_m \int V dV_m \quad (7)$$

where V is the output voltage of the power supply, T refers to the period, output frequency $f=1/T$. Applying V and V_m to the x-y axes of the oscilloscope yields a closed curve, i.e. the Q - V Lissajous figure. The area of the closed curve is proportional to the discharge power P .

2 Results and discussion

2.1 Methane cracking characteristics

This section specifically examines the effects of carrier gas ratio, input power, and inlet gas flow rate on the reaction performance, temperature distribution, and reaction energy intensity.

2.1.1 Effect of gas carrier ratio

Figure 2 shows the Lissajous figures under pure N_2 and

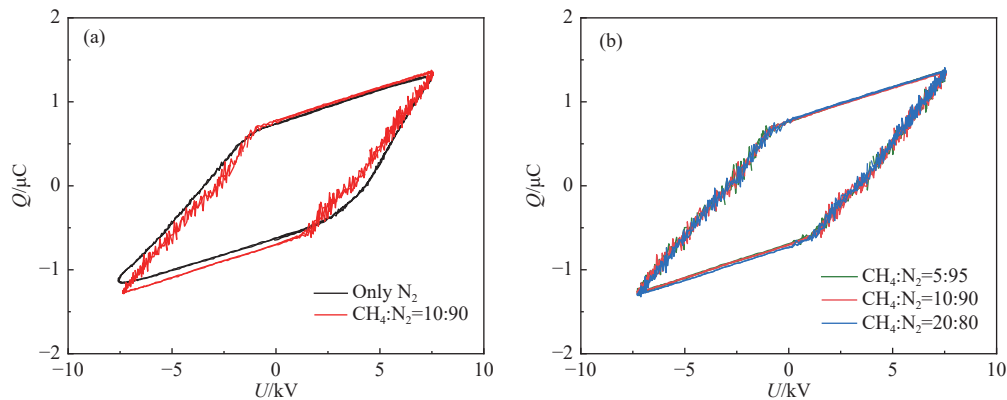


Fig. 2 Lissajous figures of pure N_2 and different CH_4/N_2 ratios under DBD at 8 kHz frequency, 500 mL/min inlet flow gas rate, and 60 W input power

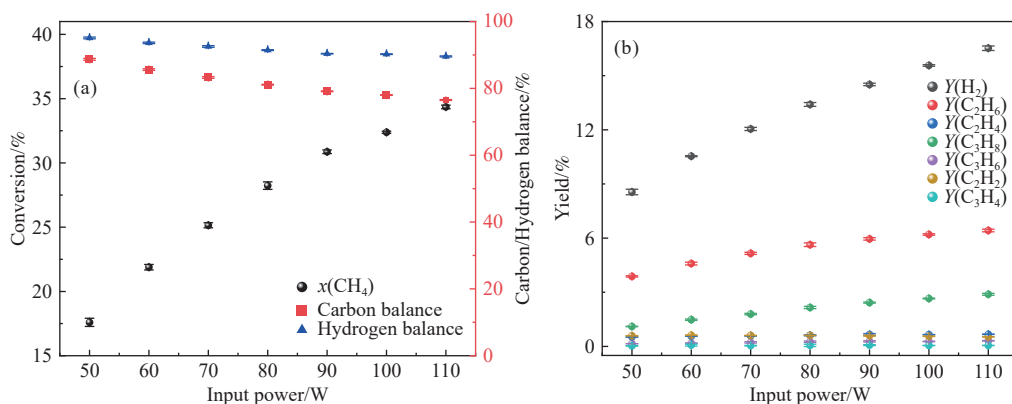


Fig. 3 Effect of input power on CH_4 conversions (a) and product yields (b) at 8 kHz frequency and 500 mL/min

different CH_4/N_2 ratios. It can be observed that when the CH_4 concentrations are 0, 5%, 10% and 20%, the discharge power is 49.5, 49.1, 49.0 and 48.9 W, respectively, with a maximum difference of less than 1.2%. Although there are slight differences in the Lissajous curves of pure N_2 and CH_4/N_2 mixture discharge (Figure 2(a)), the CH_4 concentration has minimal impact on discharge characteristics (Figure 2(b)). Therefore, 90% N_2 concentration is selected as the carrier gas which not only improves the accuracy of gas chromatographic measurements but also stabilizes the CH_4 cracking in DBD reactor. Mohsenian et al.^[43] also confirmed that N_2 helps maintain stable plasma operation.

2.1.2 Effect of input power

Figure 3 illustrates the CH_4 conversion and its main gaseous product yields at different input powers. The results indicate that when the input power increases from 50 to 110 W, the CH_4 conversion increases from 17.6% to 34.4% (Figure 3(a)), with the main gaseous products being H_2 , C_2H_6 , C_3H_8 , C_2H_4 , C_2H_2 , C_3H_6 , C_3H_4 . The yields of H_2 , C_2H_6 , C_3H_8 , C_2H_4 and C_3H_6 increase with the increase of input power (Figure 3(b)), from 8.6%, 3.9%, 1.1%, 0.5%, 0.2% to 16.5%, 6.4%, 2.9%, 0.7%, 0.3%. While that of C_2H_2 decreases from 0.6% to 0.5%.

This reveals that as the input power increases, the electric field intensity in the DBD reactor also increases, leading to an increase in the energy of electrons, the number of high-energy electrons and the active radicals^[39]. As a result, CH₄ molecules in the discharge area have an increased probability of being dissociated by high-energy electron collisions. Simultaneously, the energy density in the DBD reactor also increases, promoting the CH₄ cracking and benefiting the gaseous product generation. The decrease in C₂H₂ yield may due to that the consumption rate of C₂H₂ exceeds its formation rate.

To explore the mechanism of DBD provoked CH₄ cracking, Figure 4 presents the temperature distribution under different input powers. As the input power increases from 60 to 100 W, the maximum temperature increases from 481 to 561 K. This is primarily because of the Joule heating loss from the DBD electrodes^[24] and energy loss from the collision of active radicals against the dielectric wall. However, the temperature is still significantly lower than that required for traditional CH₄ thermal cracking^[44], indicating that the process is primarily driven by high-energy electron collisions.

2.1.3 Effect of Inlet gas flow rate

Figure 5 shows the CH₄ conversion and the main gaseous product yields at different inlet gas flow rates. When the gas flow rate increases from 200 to 800 mL/min, the residence time of the reaction gas in the discharge region decreases from 5.1 to 1.3 s. The CH₄ conversion decreases from 46.6% to 24.6% (Figure 5(a)). The main gaseous products are H₂, C₂H₆, C₃H₈, C₂H₄, C₂H₂, C₃H₆, C₃H₄, with the yields of H₂, C₂H₆, C₃H₈, C₃H₆ decreasing from 23.3%, 7.0%, 3.6%, 0.3% to 12.2%, 4.7%, 1.7%, 0.2% (Figure 5(b)). While those of C₂H₄ and C₂H₂ increase from 0.6% and 0.5% to 0.7% and 0.8%, respectively. This suggests that the decreases in residence time of CH₄ reduce the collision probability between gas molecules and high-energy electrons or active radicals. At the same time, the energy density also decreases, which is unfavorable for CH₄

cracking. The increase in C₂H₄ and C₂H₂ yields may due to the decreasing residence time of intermediate radicals ($\cdot\text{CH}_3$, $\cdot\text{CH}_2$, $\cdot\text{CH}$), limiting the coupling reactions to form saturated hydrocarbons and promoting the formation of unsaturated hydrocarbons through recombination.

Figure 6 presents the temperature distribution in the DBD reactor at different inlet gas flow rates. As the gas flow rate increases from 200 to 800 mL/min, the maximum temperature decreases slightly from 549 to 540 K, i.e. increasing the inlet gas flow rate strengthens the convective heat transfer, causing more rapidly removing of the heat generated by the DBD electrodes Joule heating and discharge. Additionally, the discharge maintenance time per unit volume of gas is shortened, reducing the accumulation of energy and leading to decline in the overall temperature field. Similar to the effect of input power, CH₄ cracking are also dominated by electronic collision excitation.

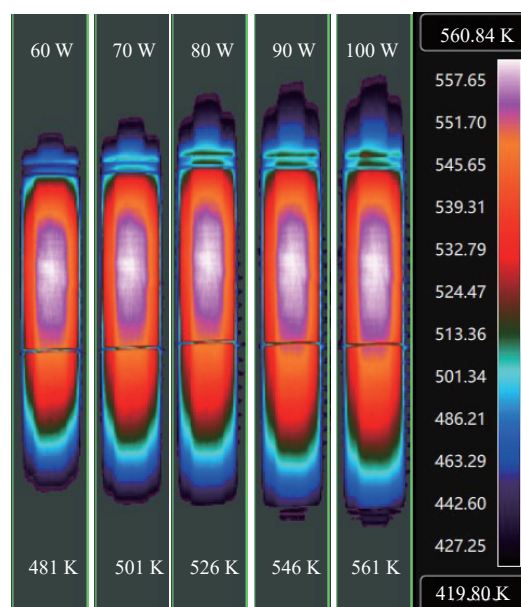


Fig. 4 Effect of input power on temperature distribution in DBD reactor at 8 kHz frequency and 500 mL/min inlet flow gas rate

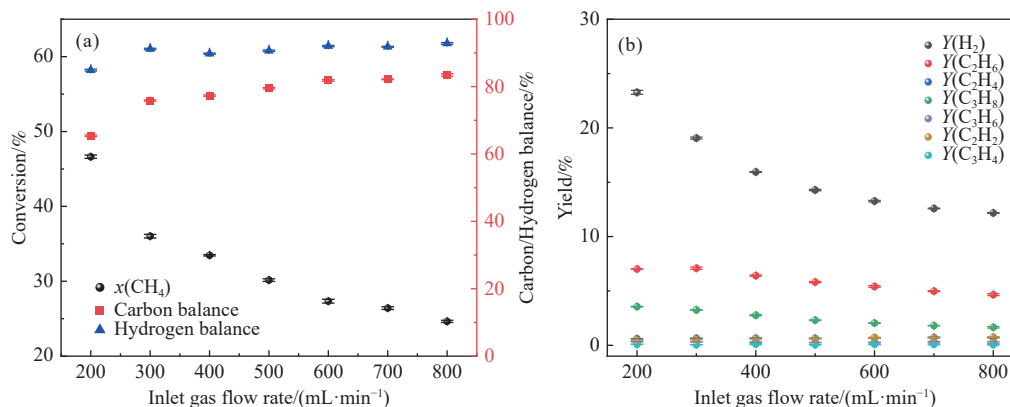


Fig. 5 Effect of inlet gas flow rate on CH₄ conversions (a) and product yields (b) at 8 kHz frequency and 90 W input power

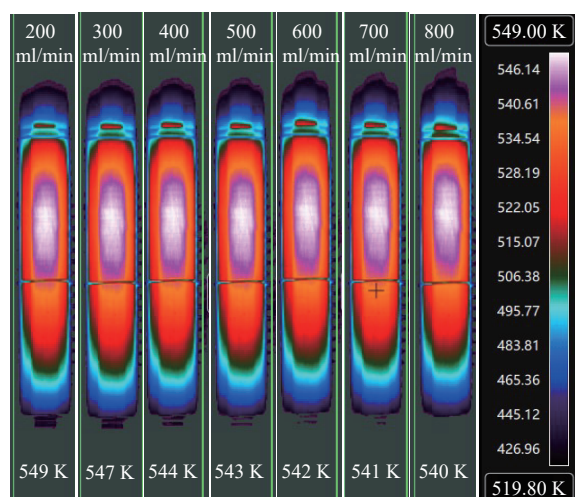


Fig. 6 Effect of inlet gas flow rate on temperature distribution in DBD reactor at 8 kHz frequency and 60 W input power

2.1.4 Reaction energy intensity

Reaction energy intensity (EI) is one of the key indicators for evaluating the economic viability of the DBD system^[45]. To assess the CH_4 cracking performance, EI is defined as the ratio of the enthalpy change of the target reaction to the discharge energy of the DBD reactor^[3]. Figure 7 shows the discharge power and reaction energy intensity under different input powers and inlet gas flow rates. It can be found that the discharge power of CH_4 cracking increases with increasing of input power. While the reaction energy intensity shows a decreasing trend with increasing input power (Figure 7(a)), i.e. when the input power increases from 50 to 110 W, the discharge power increases from 41.3 to 98.2 W. While the energy intensity decreases from 5.1% to 4.1%. This demonstrates that although higher energy input favors the generation of more high-energy electrons, which collide with CH_4 molecules to generate more active radicals, enhancing the discharge and increasing the conversion and major product yields. It also increases the thermal losses during discharge and energy losses from the dielectric, resulting in a decrease in reaction energy intensity. Within the experimental range, reaction energy

intensity increases with the increase in inlet gas flow rate (Figure 7(b)). When the gas flow rate increases from 200 to 800 mL/min, the discharge power decreases from 82.9 to 77.4 W. Whereas the reaction energy intensity increases from 2.4% to 6.8%. This indicates that the DBD discharge remain relatively stable, revealing that the total number of high-energy electrons and active radicals in the discharge gap is relatively less affected by the inlet gas flow rate, but mainly influenced by input power and reactor characteristics. Simultaneously, the increase in inlet gas flow rate shortens the gas residence time, suppressing the deep cracking of CH_4 , thus increasing the reaction energy intensity.

2.2 Reaction mechanism exploration

This section explores the activation process of CH_4 in DBD reactor based on the discharge characteristics and clarifies the CH_4 cracking reaction network.

2.2.1 CH_4 discharge characteristics

Figure 8 shows the discharge voltage and current under different input powers, with corresponding discharge phenomena illustrated in Figure 9. The results indicate that under the applied sinusoidal voltage, the discharge current shows a nearly sinusoidal waveform. In each half-period of the applied voltage, current pulse peaks are observed which are caused by CH_4 filamentary discharges and are randomly distributed in time and space in the discharge gap. Theoretically, the duration of a single micro-discharge pulse is only 10–100 ns^[46–48], whereas the free electrons in the gap can still be accelerated to form high-energy electrons, which collide with CH_4 molecules to generate $\text{CH}_4(v_i)$, $\cdot\text{CH}_3$, $\text{H}\cdot$, and other active radicals. This process continues until the electron density in the space exceeds the critical value and the Paschen breakdown voltage is reached, at which point many micro-discharge filaments are formed between the inner and outer electrodes, resulting in a luminescent phenomenon in the reactor.

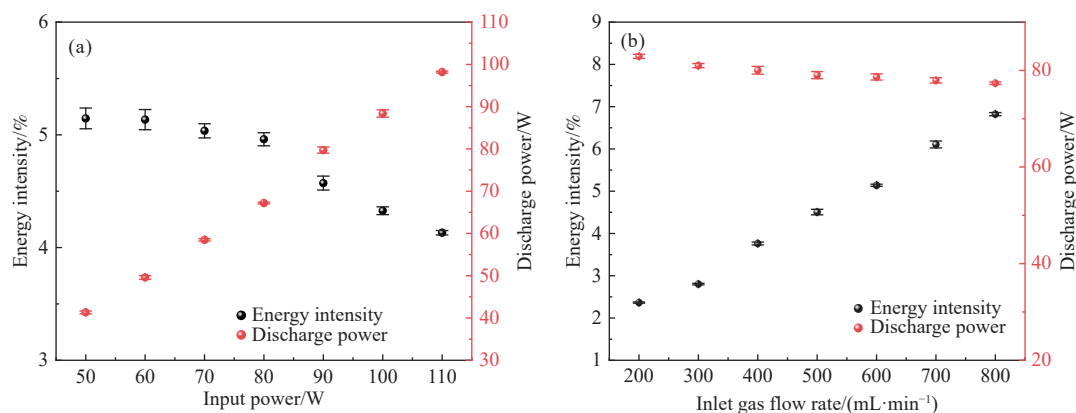


Fig. 7 Effect of (a) input power, and (b) inlet gas flow rate on the DBD discharge power and reaction energy intensity at 8 kHz frequency, 500 mL/min inlet flow gas rate, or 60 W input power

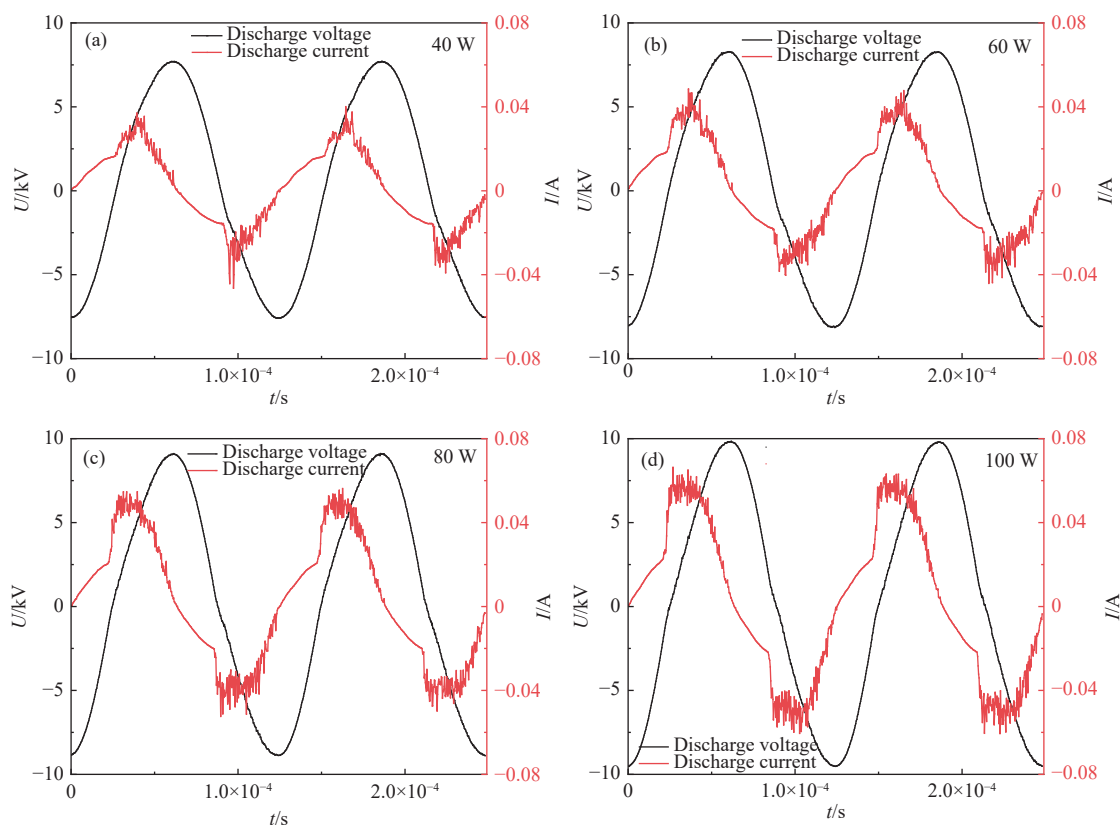


Fig. 8 Representative photographs showing the effect of input power on time-resolved discharge voltages and currents during DBD provoked CH_4 cracking at 8 kHz frequency and 500 mL/min inlet flow gas rate

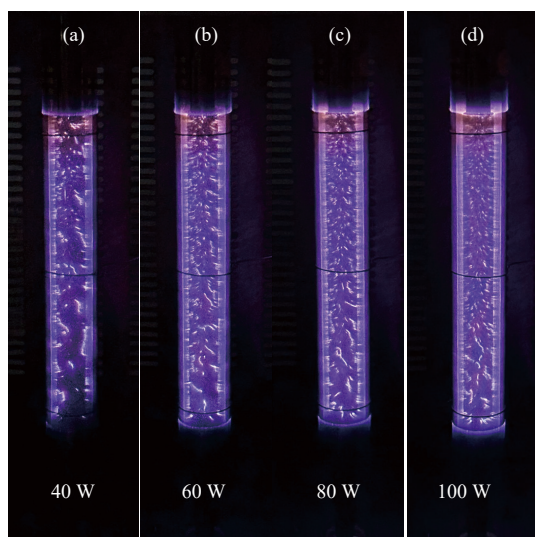


Fig. 9 Representative photographs showing the effect of input power on plasma discharge phenomena during DBD provoked CH_4 cracking at 8 kHz frequency and 500 mL/min inlet flow gas rate

As the input power increases from 40 to 100 W, both the discharge brightness and the number of micro-discharge filaments increase, and individual discharge filaments become more prominent (Figure 9). Although it is difficult to quantitatively measure the total number of micro-discharge filaments and their energy in the reactor, Figure 8 clearly reveals that higher input power leads to more current

pulses and higher current peaks in each half-period. This is consistent with the enhanced discharge phenomena observed in the discharge photographs (Figure 9). Theoretically, the number and energy of micro-discharge filaments in each cycle directly determine the electron density and electron temperature in the discharge region^[49]. Therefore, changes in discharge characteristics will further affect the CH_4 conversion and the product formation.

2.2.2 CH_4 activation process

To quantitatively describe the collision dynamics between electrons and CH_4 molecules in the DBD reactor, BOLSIG+^[50–52] is used to calculate the electron energy distribution function (EEDF). BOLSIG+ is a numerical solver based on the Boltzmann equation to solve the electron transport behavior under steady-state approximation and one-dimensional isotropic assumptions. It has been widely applied in the study of electron transport parameters and collision reaction rates in non-equilibrium plasma systems. For the series of electron collisions with CH_4 molecules, including elastic collisions, attachment dissociation, vibrational excitation, dissociative excitation, and ionization, this work calculates the rate coefficients and energy loss fractions based on the electron collision reactions involved in the CH_4 cracking. The electron energy distribution function f_0 under steady-state conditions is given by the following one-dimensional isotropic

Boltzmann equation:

$$\frac{\partial f_0}{\partial t} + \mathbf{v} \cdot \nabla f_0 - \frac{e}{m} \mathbf{E} \cdot \nabla_{\mathbf{v}} f_0 = C[f_0] \quad (8)$$

where, the left side describes the free movement of particles, including the time evolution term, space convection term, and external force term. f_0 is the electron energy distribution function, $\mathbf{v}$ refers to the velocity coordinate, e is the elementary charge, m represents the electron mass, $\mathbf{E}$ is the electric field strength, and $\nabla_{\mathbf{v}}$ stands for the velocity gradient operator. The right side represents the collision term, which characterizes the interaction between particles, and C is the rate of change of f_0 due to collisions.

Subsequently, based on the electron energy distribution function f_0 , the rate coefficients k_i for various complex reactions i involved in CH_4 activation, such as elastic collisions, attachment dissociation, vibrational excitation, dissociative excitation, and ionization (shown in Table 1), are calculated as:

$$k_i = \gamma \int_0^{\infty} \varepsilon \sigma_i f_0 d\varepsilon \quad (9)$$

where γ is a constant coefficient, $\gamma = (2e/m_e)^{1/2}$, ε refers to the electron energy, and σ_i is the collision cross-section for the reaction i .

The energy loss fraction for reaction i is obtained by calculating the ratio of the energy loss from reaction i to the sum of energy losses from all reactions:

$$\eta_k = \frac{k_i \Delta \varepsilon_i}{\sum_j k_j \Delta \varepsilon_j} \quad (10)$$

where $\Delta \varepsilon_j$ is the average energy loss per collision for reaction i .

The reduced electric field (denoted as E/N) is defined as the ratio of the electric field strength to the gas particle density, with units in Td (Townsend) determined by the input power and inlet gas flow rate. Figure 10 shows the rate coefficients and energy loss fractions for the major CH_4 activation reactions under different E/N conditions. The results indicate that the rate coefficient for CH_4 elastic collisions E3 is the highest (Figure 10(a)), suggesting that elastic collisions between electrons and CH_4 molecules are frequent. However, this process causes almost no chemical reactions, only leading to minor energy dissipation. The rate coefficients for CH_4 vibrational excitation E4 and E5 are significantly higher than other pathways in the E/N range of 98.5–123.9 Td, indicating that electron vibrational excitation is a key driving force for CH_4 activation and dissociation. This is primarily due to high-energy electrons can stepwise excite the vibrational energy levels of the C–H bond in CH_4 molecules. After multiple accumulations, the C–H bond breaks, generating active intermediates such as $\cdot\text{CH}_3$, which then experience subsequent chain cleavage reactions.

At lower E/N (<79 Td), vibrational excitation processes E4 and E5 are the major energy loss pathways (Figure 10(b)), revealing that at this stage, the average electron energy is lower, and most of the energy is used to excite the

vibrational modes of CH_4 . As E/N increases, the energy loss fraction for the dissociative excitation E6 gradually increases, reflecting that with an increase in the number of high-energy electrons, there is an increase in the directly induction of C–H bond breaking. When E/N is in the range of 98.5–123.9 Td, E5 and E6 are the main energy loss pathways, with vibrational excitation and dissociative excitation both contributing to the energy loss in CH_4 cracking. Additionally, the energy loss fraction for elastic collisions E3 is very small and can be neglected. Therefore, the core pathway for CH_4 cracking is the stepwise energy accumulation leading to bond breakage, driven by electron vibrational excitation.

Table 1 Electron collision reactions during DBD provoked CH_4 cracking^[53–55]

Number	Reaction equations	Reaction type
E1	$\text{e}^- + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}^-$	dissociation attachment
E2	$\text{e}^- + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_2^-$	dissociation attachment
E3	$\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_4$	elastic
E4	$\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_4$ (v24) (0.162 eV)	vibrational excitation
E5	$\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_4$ (v13) (0.361 eV)	vibrational excitation
E6	$\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_4^*$ (9 eV-dissoc)	dissociation excitation
E7	$\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_4^*$ (10 eV-dissoc)	dissociation excitation
E8	$\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_4^*$ (11 eV-dissoc)	dissociation excitation
E9	$\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_4^*$ (12 eV-dissoc)	dissociation excitation
E10	$\text{e}^- + \text{CH}_4 \rightarrow 2\text{e}^- + \text{CH}_4^+$	ionization
E11	$\text{e}^- + \text{CH}_4 \rightarrow 2\text{e}^- + \text{H} + \text{CH}_3^+$	dissociation ionization

2.2.3 Main reaction pathways for CH_4 cracking

In the DBD reactor, the CH_4 cracking process involves a series of complex reactions, including methane activation, free radical recombination, intermediate formation, and product generation. Based on the experimental results from Section 2.1 and the calculations in Section 2.2.2, it can be observed that the maximum temperature in the DBD reactor is approximately 560 K, which is much lower than that required for traditional CH_4 thermal cracking^[44]. However, the high-energy electrons generated during the discharge process can effectively drive stepwise CH_4 molecules excitation to form a radical chain reaction, thus achieving stepwise activation and cracking. The result reflects the non-equilibrium plasma characteristic of CH_4 cracking provoked by DBD, where the electron temperature is much higher than the gas temperature^[25].

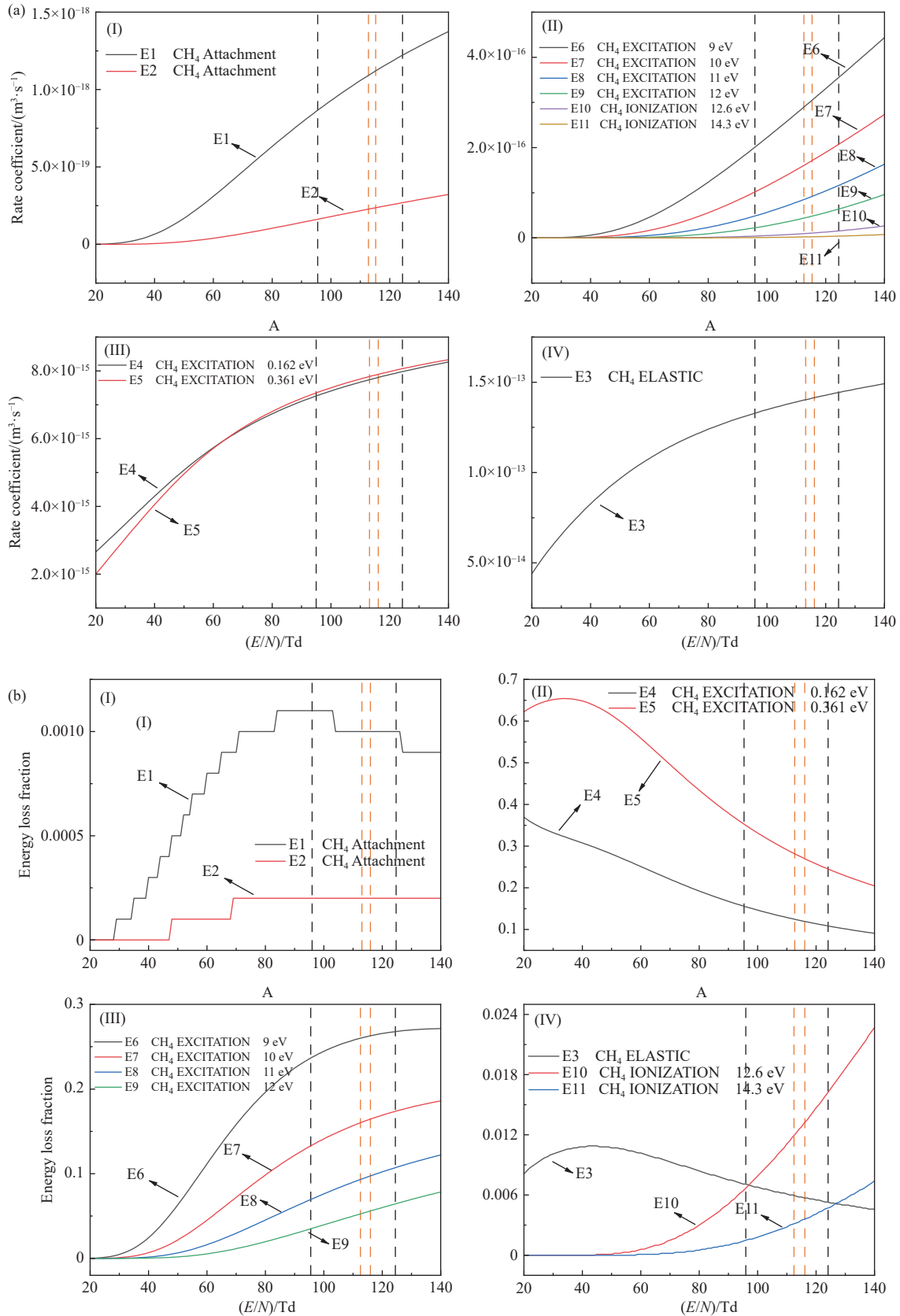


Fig. 10 Effect of E/N on the rate coefficient and energy loss fraction during DBD provoked CH_4 cracking (Black dashed: range of varying input power; Yellow dashed: range of varying inlet gas flow rate)

From a mechanistic perspective, on the one hand, the vibrationally excited $\text{CH}_4(v_i)$ is a key intermediate, with

dissociation threshold significantly lower than that of ground-state CH_4 . Therefore, higher electron temperatures

are favorable for continuously exciting the vibrational energy levels. On the other hand, the lower gas temperature slows down the relaxation loss of vibrational energy, thus prolonging the lifetime of the vibrationally excited $\text{CH}_4(\text{v}_i)$. The combination of high electron temperature and low gas temperature provides favorable conditions for CH_4 molecules to follow a stepwise accumulation to ladder type vibrational excitation dissociation pathway.

From a reactor perspective, Joule heating generated by the electrodes during discharge causes the increased temperature of the reaction zone (Figures 4 and 6). This suggests that the electrical energy input not only maintains the discharge but also partially transfers to the reaction system in the form of heat, raising the reaction temperature which enhances the thermal motion rate of neutral particles and free radicals, thereby increasing the collision frequency and energy between neutral-neutral particles and neutral-radical species, further promoting the CH_4 cracking.

The thermal effect of the DBD discharge process indirectly influences the CH_4 cracking pathway by affecting transport characteristics. However, the reaction is still mainly driven by collisions between high-energy electrons and CH_4 as well as the intermediates. The vibrationally excited $\text{CH}_4(\text{v}_i)$, induced by electron collisions, plays a key role in enhancing the cracking activity. The vibrationally excited $\text{CH}_4(\text{v}_i)$ includes asymmetric stretching vibration and bending vibration, which respectively reduce the bond energy by weakening the C–H bond strength and altering the molecular configuration, thereby increasing the probability of bond breaking. Under non-equilibrium plasma conditions, high-energy electrons preferentially excite the molecular vibrational degrees of freedom, concentrating the energy in the C–H bonds, creating a favorable environment for selective bond breaking. Additionally, the CH_4 cracking induced by the vibrational excitation pathway has a lower activation barrier than direct dissociation. Moreover, the vibrational energy levels serve as a stepwise energy accumulation channel, further promoting CH_4 cracking during subsequent electron-molecule collisions. The non-equilibrium plasma effectively suppresses the rapid relaxation of vibrational energy, maintaining a higher concentration of vibrationally excited states. The combined effect of these factors significantly enhances the activity of CH_4 cracking by electron driven vibration excitation-stepwise dissociation mechanism.

In summary, the DBD provoked CH_4 cracking process can be divided into three stages, i.e. methane activation, radical evolution, and product formation, as summarized in Table 2.

It should be noted that the CH_4 cracking in the DBD reactor include a total of 13 key reactions. In this work, it is also observed that there is certain degree of carbon deposition (or coking) on the surface of the metal inner electrode and the inner surface of quartz tube (Figure 11). The middle section of the quartz tube is relatively clean, while carbon deposition is mainly on the metal electrode surface and the reactor tail region.

Table 2 Reaction pathway during DBD provoked CH_4 cracking

Stage	Reaction equation	Number
I Methane activation	$\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_4(\text{v}_i)$	R1
	$\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \text{CH}_4^*$	R2
	$\text{e}^- + \text{CH}_4 \rightarrow \text{e}^- + \cdot\text{CH}_3 + \text{H}\cdot$	R3
	$\text{e}^- + \text{CH}_3 \rightarrow \text{e}^- + \cdot\text{CH}_2 + \text{H}\cdot$	R4
	$\text{e}^- + \text{CH}_2 \rightarrow \text{e}^- + \cdot\text{CH} + \text{H}\cdot$	R5
II Radical evolution	$\text{H}\cdot + \text{H}\cdot + \text{M} \rightarrow \text{H}_2 + \text{M}$	R6
	$\cdot\text{CH}_3 + \cdot\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	R7
	$\text{C}_2\text{H}_6 + \text{e}^- \rightarrow \cdot\text{C}_2\text{H}_5 + \text{H}\cdot + \text{e}^-$	R8
	$\cdot\text{C}_2\text{H}_5 + \text{e}^- \rightarrow \text{C}_2\text{H}_4 + \text{H}\cdot$	R9
	$\text{C}_2\text{H}_4 + \text{e}^- \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 + \text{e}^-$	R10
III Final product formation	$\cdot\text{C}_2\text{H}_5 + \cdot\text{CH}_3 \rightarrow \text{C}_3\text{H}_8$	R11
	$\text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2$	R12
	$\text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_4 + \text{H}_2$	R13

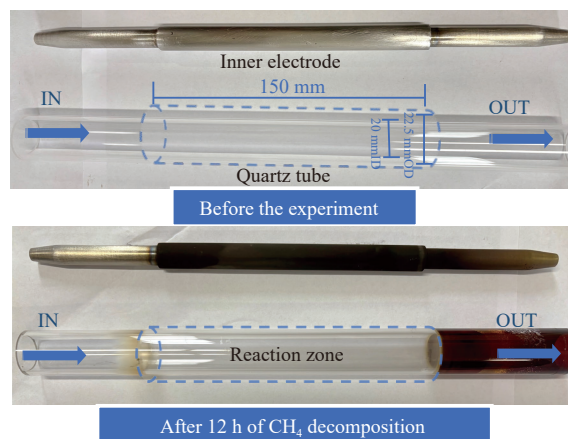


Fig. 11 Carbon deposition in the inner electrode and quartz tube before and after CH_4 cracking

This phenomenon may be due to the higher electric field strength in the middle section and that the metal electrode surface is more likely to induce adsorption and deposition of carbon-based radicals. Meanwhile, at the tail region, where the temperature is relatively lower, radicals and unsaturated hydrocarbons are more likely to form solid-phase carbon deposits. This can alter the surface roughness and local properties of the electrode and dielectric, leading to changes in discharge uniformity and affecting the stability of the operation^[56]. However, the deposited product has potential as a high-value material^[57].

The reaction system (R1–R13) can be summarized in Figure 12. Stage I involves methane activation, primarily driven by high-energy electrons, inducing vibrational excitation and energy level accumulation, followed by stepwise dissociation. As shown in Figure 10, during this stage, high-energy electrons in the discharge area transfer the energy to CH_4 molecules (R1 and R2), forming

vibrationally excited states and electronic excited states. Compared to traditional CH₄ thermal cracking, this significantly reduces the energy barrier required for C–H bond breaking. The system then enters typical stepwise dissociation, generating active radicals such as H·, ·CH₃, ·CH₂ and ·CH (R3–R5), forming a radical-dominated non-equilibrium plasma environment and achieving energy conversion from electrical energy to chemical energy.

Stage II is the radical evolution process, primarily manifested as reactions among the radicals through recombination, rearrangement, and electron collisions. From the experimental results (Figures 3 and 5), possible intermediates or products like $\cdot\text{C}_2\text{H}_5$, H_2 , C_2H_6 , C_2H_4 , C_2H_2 are generated. With increasing input power, the degree of CH_4 cracking deepens, and the reaction system gradually evolves from being dominated by C_2 saturated hydrocarbons to coexistence of various saturated and unsaturated C_2 – C_3 hydrocarbons. With increasing inlet gas flow rate, the reaction system shifts from a mode characterized by deep cracking and sufficient radical coupling to a mode characterized by short residence time and rapid radical recombination, increasing the proportion of unsaturated hydrocarbons (e.g. C_2H_4 and C_2H_2) in the product. Combined with the calculation results in Figure 10, it is explained that $\text{H}\cdot$ radical recombination and its collision with a third species M (typically CH_4 or inert carrier gas molecules) generate hydrogen (R6). Theoretically, this is the main source for hydrogen. Simultaneously, dehydrogenation of hydrocarbon products also produces a small amount of hydrogen (R10, R12, R13). Additionally, small amounts of methyl radicals undergo coupling reactions to form ethane (R7) and subsequent stepwise dehydrogenation to generate $\cdot\text{C}_2\text{H}_5$ (R8), ethylene (R9), acetylene (R10), etc.

Stage III is the product generation process, characterized by the further coupling of radicals and other intermediates generated in the first and second stages to form saturated and unsaturated C₃ and higher hydrocarbons (Figure 3 and 5). This indicates that the products mainly include H₂, C₂H₆, C₃H₈, C₂H₄, C₂H₂, C₃H₆, C₃H₄ and a small amount of carbon deposits and medium or long-chain hydrocarbons. Among them, propane may originate from the coupling of ·CH₃ and ·C₂H₅ radicals (R11). Propylene and propyne are speculated to be formed via stepwise dehydrogenation of propane (R12 and R13), respectively.

Comprehensively considering the product distribution and the microscopic electron activation processes obtained from BOLSIG+ calculations, Figure 12 illustrates the evolution of energy transfer and reactive species transformation during the DBD provoked CH_4 cracking, encompassing electron energy injection, vibrational excitation, stepwise dissociation, radical chain extension, and product formation. This is summarized as three stages, i.e. methane activation, radical evolution, and product formation.

3 Conclusion

Increasing input power or decreasing inlet gas flow rate promotes CH₄ cracking and gaseous product generation. At an input power of 90 W and an inlet gas flow rate of 200 mL/min, the single-pass CH₄ conversion is 46.6% with H₂ yield of 23.3%. The CH₄ cracking is dominated by electron driven reactions, with the Joule heat produced by the electrodes having a limited contribution.

The reaction energy intensity shows an inverse relationship with CH_4 conversion. It increases with decreasing input power or increasing inlet gas flow rate. When the inlet gas flow rate increases from 200 to 800 mL/min, the reaction energy intensity increases by approximately 2.8 times, indicating that a higher inlet gas flow rate enhances the convective heat transfer and shortens the gas residence time, thereby inhibiting deep CH_4 cracking.

Combining the CH₄ electronic collision reaction rate coefficients and energy loss fractions obtained from BOLSIG+ calculations, the electron vibrational excitation is the main pathway for CH₄ activation, mainly induced by the accumulation of high-energy electrons through stepwise vibration to induce C–H bond breaking and promote the subsequent free radical reactions.

The DBD provoked CH₄ cracking involves electron energy injection, vibrational excitation, stepwise dissociation, radical chain extension, and product generation. The energy transfer and species transformation pathways can be summarized into three stages, i.e. methane activation, free radical evolution, and product formation.

Declaration of Competing Interest

The authors declare no conflict of interest.

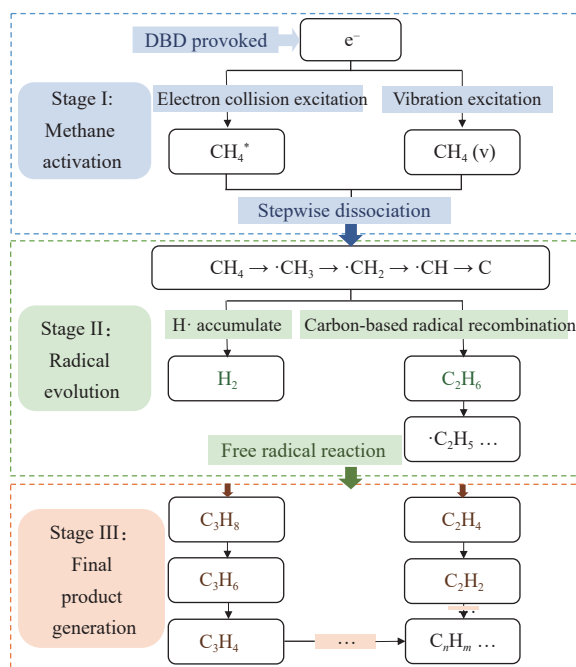
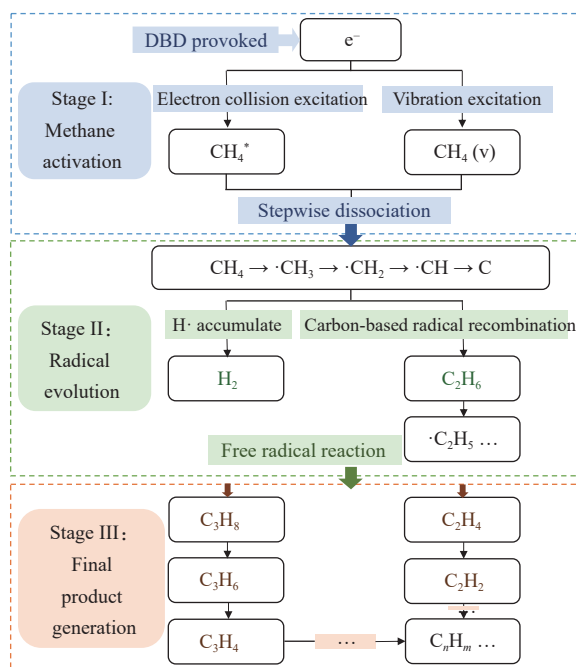


Fig. 12 Proposed main reaction paths during DBD provoked CH_4 cracking



References

- [1] MENG X, CUI X, RAJAN N P, et al. Direct methane conversion under mild condition by thermo-, electro-, or photocatalysis[J]. Chem, 2019, 5(9): 2296–2325.
- [2] FILONCHYK M, PETERSON M P, ZHANG L, et al. Greenhouse gases emissions and global climate change: Examining the influence of CO₂, CH₄, and N₂O[J]. Sci Total Environ, 2024, 935: 173359.
- [3] SUN Y, ZHANG K, QI N, et al. Reaction performance of non-thermal plasma induced CO₂ reforming of CH₄ for landfill gas treatment[J]. Waste Manag, 2025, 200: 114751.
- [4] ZHENG Y, WANG Y, LI R, et al. CO₂-free hydrogen production from solar-driven photothermal catalytic decomposition of methane[J]. Chin J Catal, 2025, 73: 289–299.
- [5] FIDALGO B, FERNÁNDEZ Y, ZUBIZARRETA L, et al. Growth of nanofilaments on carbon-based materials from microwave-assisted decomposition of CH₄[J]. Appl Surf Sci, 2008, 254(11): 3553–3557.
- [6] FAN Z, WENG W, ZHOU J, et al. Catalytic decomposition of methane to produce hydrogen: A review[J]. J Energy Chem, 2021, 58: 415–430.
- [7] LIANG H, ZHANG R, YE R, et al. Study on optimization of influencing factors of anaerobic methane coupling catalyzed by dielectric barrier discharge plasma[J]. Low-Carbon Chem Chem Eng, 2025, 50(11): 1–11.
- [8] FACAS G G, CALABRESE G, SCHÜLLER N, et al. Hydrogen production by microwave plasma CH₄ pyrolysis: Characterization via optical emission spectroscopy and response surface methodology[J]. Int J Hydrogen Energy, 2025, 157: 150436.
- [9] HUANG Hui-min, ZHOU Yun-xiao, ZHANG Kui-kui, et al. Research progress on methane pyrolysis process for hydrogen and carbon materials[J]. Low-Carbon Chem Chem Eng, 2024, 49(9): 1–11.
- [10] BAIG S, SAJJADI B. Non-thermal plasma enhanced catalytic conversion of methane into value added chemicals and fuels[J]. J Energy Chem, 2024, 97: 265–301.
- [11] BAI F, XU X, LIU D, et al. Research progress on methane conversion to ethylene technology[J]. Ind Catal, 2023, 31(12): 16–24.
- [12] ORANGIAN M, ALAVI S M, REZAEI M, et al. Combined dry and steam reforming of CH₄ over the nanocrystalline Ni/Al₂O₃ catalysts fabricated by various synthesis methods: Influence of nickel content and processing factors[J]. Fuel, 2026, 405: 136555.
- [13] FROM T N, RAUTENBACH M, PARTOON B, et al. Understanding the dynamic interplay of CH₄/CO₂ ratio in electrified reforming of biogas to renewable methanol production: A pilot plant story[J]. Chem Eng J, 2025, 518: 164662.
- [14] GUAN Y, SONG G, LI C, et al. Ni-based core-shell structured catalysts for efficient conversion of CH₄ to H₂: A review[J]. Carbon Capture Sci Technol, 2024, 11: 100200.
- [15] HUANG X, JIAO X, LIN M, et al. Research progress in the direct nonoxidative dehydroaromatization of methane to aromatics[J]. J Fuel Chem Technol, 2018, 46(9): 1087–1100.
- [16] LI J, WANG X, ZHANG B, et al. Kinetic study of the decomposition of methane over Ni-Mg composite catalyst for hydrogen production[J]. J Fuel Chem Technol, 2017, 45(2): 249–256.
- [17] RIVAS M E, HORI C E, FIERRO J L G, et al. H₂ production from CH₄ decomposition: Regeneration capability and performance of nickel and rhodium oxide catalysts[J]. J Power Sources, 2008, 184(1): 265–275.
- [18] PRABOWO J, LAI L, CHIVERS B, et al. Solid carbon co-products from hydrogen production by methane pyrolysis: Current understandings and recent progress[J]. Carbon, 2024, 216: 118507.
- [19] ZHANG S, YEO J Y J, SUNARSO J, et al. Robust ceramic hollow fiber membrane reactor for dual syngas in-tandem production by coupling of CO₂-H₂O co-decomposition with CH₄ partial oxidation[J]. Chem Eng J, 2025, 512: 162553.
- [20] MCCONNACHIE M, KONAROVA M, SMART S. Literature review of the catalytic pyrolysis of methane for hydrogen and carbon production[J]. Int J Hydrogen Energy, 2023, 48(66): 25660–25682.
- [21] ZHAO W, WANG X, YAN Y. The substitution of fossil fuels for renewables in the electricity mix of China: From the perspectives of generation, capacity, and demand[J]. Energy, 2025, 315: 134364.
- [22] GITELMAN L, KOZHEVNIKOV M, DITENBERG M. Electrification as a factor in replacing hydrocarbon fuel[J]. Energy, 2024, 307: 132800.
- [23] GIRSHEVICH S, BAJEC D, YAKUSHKIN S, et al. Electrification of catalytic methane decomposition to hydrogen and nanostructured carbonaceous materials[J]. Int J Hydrogen Energy, 2025, 160: 150466.
- [24] CUI G, JIANG G, XU C, et al. Joule heat catalysis[J]. Sci Sin: Chim, 2025, 55(2): 462–471.
- [25] HEGEMANN D, NAVASCUES P, SNOECKX R. Plasma gas conversion in non-equilibrium conditions[J]. Int J Hydrogen Energy, 2025, 100: 548–555.
- [26] MIERCZYNSKI P, MIERCZYNSKA-VASILEV A, SZYNKOWSKA-JOZWIK M I, et al. Plasma-assisted catalysis for CH₄ and CO₂ conversion[J]. Catal Commun, 2023, 180: 106709.
- [27] LI L, CHEN X, BELLA, et al. Dielectric barrier discharge plasma catalysis for CO₂ conversion: Recent progress and perspectives[J]. Carbon Capture Sci Technol, 2025, 16: 100485.
- [28] VADIKKEETIL Y, SUBRAMANIAM Y, MURUGAN R, et al. Plasma assisted decomposition and reforming of greenhouse gases: A review of current status and emerging trends[J]. Renewable Sustainable Energy Rev, 2022, 161: 112343.
- [29] KHALIFEH O, TAGHVAEI H, MOSALLANEJAD A, et al. Extra pure hydrogen production through methane decomposition using nanosecond pulsed plasma and Pt-Re

- catalyst[J]. *Chem Eng J*, 2016, 294: 132–145.
- [30] NISHIDA Y, CHIANG H, CHEN T, et al. Efficient production of hydrogen by DBD type plasma discharges[J]. *IEEE Trans Plasma Sci*, 2014, 42(12): 3765–3771.
- [31] SRIBALA G, MICHIELS D, LEYS C, et al. Methane reforming to valuable products by an atmospheric pressure direct current discharge[J]. *J Cleaner Prod*, 2019, 209: 655–664.
- [32] De BIE C, JAN VAN D, BOGAERTS A. The dominant pathways for the conversion of methane into oxygenates and syngas in an atmospheric pressure dielectric barrier discharge[J]. *J Phys Chem C*, 2015, 119(39): 22331–22350.
- [33] NISHIDA Y, CHIANG H, CHEN T, et al. Hydrogen production from hydrocarbons using plasma: Effect of discharge pulsewidth on decomposition[J]. *IEEE Trans Plasma Sci*, 2015, 43(10): 3500–3506.
- [34] XU C, TU X. Plasma-assisted methane conversion in an atmospheric pressure dielectric barrier discharge reactor[J]. *J Energy Chem*, 2013, 22(3): 420–425.
- [35] WANG B, YAN W, GE W, et al. Methane conversion into higher hydrocarbons with dielectric barrier discharge micro-plasma reactor[J]. *J Energy Chem*, 2013, 22(6): 876–882.
- [36] KONNO K, ONOE K, TAKIGUCHI Y, et al. Conversion of methane by an electric barrier-discharge plasma using an inner electrode with discharge disks set at 5 mm intervals[J]. *Chem Eng Res Des*, 2015, 95: 144–149.
- [37] LI G, QIAN M, LIU S, et al. A numerical simulation study on active species production in dense methane-air plasma discharge[J]. *Plasma Sci Technol*, 2018, 20(1): 23–31.
- [38] CHEN Q, SUN J, ZHANG X. Kinetic contribution of CO₂/O₂ additive in methane conversion activated by non-equilibrium plasmas[J]. *Chin J Chem Eng*, 2018, 26(5): 1041–1050.
- [39] GADKARI S, GU S. Numerical investigation of co-axial DBD: Influence of relative permittivity of the dielectric barrier, applied voltage amplitude, and frequency[J]. *Phys Plasmas*, 2017, 24: 053517.
- [40] SANTOSO J, ZHU M, ZHANG D. Burst mode in a cooled packed-bed dielectric barrier discharge reactor for CO₂ splitting[J]. *Plasma Res Express*, 2021, 3: 25009.
- [41] XIAO K, LI X, SANTOSO J, et al. Synergistic effect of dielectric barrier discharge plasma and Mn catalyst on CO₂ reforming of toluene[J]. *Fuel*, 2021, 285: 119057.
- [42] DAI Y, WAN L, WAN J, et al. Study on output power calculation of modulated pulse coaxial double dielectric barrier discharge[J]. *Appl IC*, 2020, 37(11): 4–7.
- [43] MOHSENIAN S, NAGASSOU D, ELAHI R, et al. Carbon dioxide conversion by solar-enhanced microwave plasma: Effect of specific power and argon/nitrogen carrier gases[J]. *J CO₂ Util*, 2019, 34: 725–732.
- [44] SLAETS J, LOENDERS B, BOGAERTS A. Plasma-based dry reforming of CH₄: Plasma effects vs. thermal conversion[J]. *Fuel*, 2024, 360: 130650.
- [45] WANTEN B, VERTONGEN R, DE MEYER R, et al. Plasma-based CO₂ conversion: How to correctly analyze the performance?[J]. *J Energy Chem*, 2023, 86: 180–196.
- [46] LIU Y, HE X, MA F. Analysis and simulation of dielectric barrier discharge and atmospheric pressure glow discharge[J]. *High Voltage Eng*, 2005, 31(6): 55–58.
- [47] KUNHARDT E E. Generation of large-volume, atmospheric-pressure, nonequilibrium plasmas[J]. *IEEE Trans Plasma Sci*, 2000, 28(1): 189–200.
- [48] SHAO T, ZHANG C, YU Y, et al. Discharge characteristic of nanosecond-pulse DBD in atmospheric air using magnetic compression pulsed power generator[J]. *Vacuum*, 2012, 86(7): 876–880.
- [49] ZHANG Z, SHAO X, ZHANG G, et al. One-dimensional simulation of dielectric barrier glow discharge in atmospheric pressure Ar[J]. *Acta Phys Sin*, 2012, 61(4): 45205.
- [50] YE Y, WEI X, ZHANG L, et al. Sustainable nitrogen fixation by bubble discharge plasma: Performance optimization and mechanism[J]. *J Energy Chem*, 2024, 98: 692–701.
- [51] SUN Y, DONG K, XU Z, et al. Experiment and simulation calculation of micro-cavity dielectric barrier discharge[J]. *Results Phys*, 2018, 11: 999–1003.
- [52] RISTIC M M, VOJNOVIC M, POPARIC G B, et al. Rate coefficients for electron impact excitation of the a³π state of CO[J]. *Chem Phys*, 2012, 405: 16–21.
- [53] SONG M, YOON J, CHO H, et al. Cross sections for electron collisions with methane[J]. *J Phys Chem Ref Data*, 2015, 44(2): 23101.
- [54] MORGAN W L. A critical evaluation of low-energy electron impact cross sections for plasma processing modeling. II: Cl₄, SiH₄, and CH₄[J]. *Plasma Chem Plasma Process*, 1992, 12(4): 477–493.
- [55] BOUWMAN D, MARTINEZ A, BRAAMS B J, et al. Neutral dissociation of methane by electron impact and a complete and consistent cross section set[J]. *Plasma Sources Sci Technol*, 2021, 30(7): 75012.
- [56] GARCÍA-MONCADA N, VAN ROOIJ G, CENTS T, et al. Catalyst-assisted DBD plasma for coupling of methane: Minimizing carbon-deposits by structured reactors[J]. *Catal Today*, 2021, 369: 210–220.
- [57] TURACZY K K, XIE Z, CHEN J G, et al. DBD plasma-thermal tandem reactors for converting biogas to carbon nanofibers[J]. *EES catal*, 2025, 3(4): 756–762.

非平衡等离子体作用下 CH₄ 裂解特性及其反应机理分析

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摘 要: 系统研究了介质阻挡放电(DBD)反应器内载气比例、输入功率和进气流量对 CH₄ 裂解性能、温度分布特征以及反应能量强度影响行为。结果表明, DBD 输入功率增大或原料气进气流量减小有利于 CH₄ 裂解和气态产物生成。当输入功率 90 W 和进气流量 200 mL/min 时, CH₄ 单程转化率为 46.6 %, H₂ 产率为 23.3 %, 表明 CH₄ 裂解以电子驱动的反应为主导, 而电极产生的焦耳热作用有限。反应能量强度随着 CH₄ 转化率减小而增强, 进气流量从 200 mL/min 增大到 800 mL/min 时提高约 2.8 倍, 表明进气流量增大有利于对流传热并缩短气体停留时间, 从而抑制了 CH₄ 深度裂解。BOLSIG+计算结果揭示了 DBD 诱导 CH₄ 活化以电子振动激发驱动的梯级能量累积主导 C-H 断键, CH₄ 裂解过程所经历的电子能量注入、振动激发、逐级解离、自由基链式扩展到最终产物生成的完整能量传递与物质转化路径归纳为甲烷活化、自由基演变和最终产物形成三个阶段。

关键词: CH₄ 裂解; 非平衡等离子体; 反应特性; 机理探索

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