

Temperature-Dependent Selectivity between Plasma and Homogeneous Reaction Chemistry of Methane DBD Plasmas

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Abstract: It has been previously observed that methane (CH₄) conversion in dielectric barrier discharges (DBDs) is inhibited at higher temperatures, greater than 600 °C. In this work, we use ZDPlasKin and FTIR-AS in a CH₄ DBD to understand the temperature-dependent chemistry of these systems. Findings show a temperature-dependent change from higher to single order carbon-carbon coupling that potentially leads to CH₄ conversion inhibition.

1. Introduction

The conversion of light hydrocarbons into valuable chemistries, specifically methane (CH₄), using plasmas offers a promising pathway for decarbonization and a shift towards the utilization of renewable energy to produce value-added products [1]. Previous work has shown a sensitivity of CH₄ conversion to the bulk reaction temperature in a dielectric barrier discharge (DBD) reactor, resulting in inhibited conversion at reaction temperatures above 600 °C [2]. Understanding the interplay between plasma chemistry and thermal homogeneous reactions at these elevated temperatures is imperative for optimizing the conversion process and reactor design.

In this work, we utilize the chemical kinetic modeling software ZDPlasKin [3] to investigate the decomposition products of the gas-phase effluent in CH₄ DBD plasmas at various bulk reaction temperatures and gas compositions. We validate the simulated results with a model DBD reactor using Fourier transform infrared (FTIR) absorption spectroscopy (AS).

2. Methods

A DBD reactor with the same configuration as described by Akintola et. al. in [2] was used. Total gas flow at 50 sccm and power at 20 W were kept constant and gas compositions consisted of pure CH₄, 1-1 CH₄/Ar, and 9-1 CH₄/Ar mixtures. FTIR-AS measurements were collected downstream of the DBD reactor in a cell chamber at a constant pressure of 16 Torr.

For simulation conditions, a reduced electric field E/N of 100 Td was estimated from the experimental reactor geometry and an electron density N_e of $5 \times 10^{13} \text{ cm}^{-3}$ was estimated from electrical measurements of the total current per half cycle. E/N and N_e were pulsed every 25 μs with a 60% duty cycle for a total simulation time of 1 ms to model the experimental DBD frequency of approximately 20 kHz and filamentary behavior of the plasma.

3. Results and Conclusion

Figure 1 shows the distribution of simulated C₂H_x products, acetylene (C₂H₂), ethylene (C₂H₄), and ethane (C₂H₆), as a function of bulk reaction temperature from 200 to 700 °C. Results show a monotonic decrease in the distribution of C₂H₂ and increase in the distribution of C₂H₆. There is a non-monotonic change in the distribution

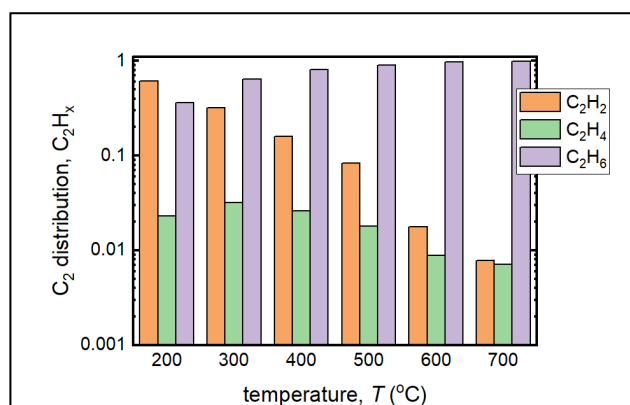


Fig. 1. Simulated C₂H_x species product distribution of 1-1 CH₄/Ar DBD as bulk reaction temperature increases.

of C₂H₄, with an overall decrease at temperatures higher than 400 °C.

These results demonstrate a change in the distribution of products from a higher order carbon-carbon coupling (C≡C) at lower temperatures to single order carbon bonding at higher temperatures. Observed changes in product distribution suggest a shift in the selectivity of reaction pathways from plasma-driven reaction chemistry at lower temperatures, enabling more complex product formation, to homogeneous reaction chemistry at higher temperatures, resulting in single carbon-carbon coupling that potentially inhibit CH₄ conversion into other products.

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References

- [1] T. Nozaki et al., Jpn. J. Appl. Phys., **63**, 6749-6798 (2024)
- [2] I. Akintola et al., Plasma Chem. Plasma Process., **43**(6), 1999-2016 (2023)
- [3] S. Pancheshnyi et al., Bull. Am. Phys. Soc., **53** (2008)