

Longevity Demonstration of Methane to C2 via a Nonthermal Plasma Microreactor

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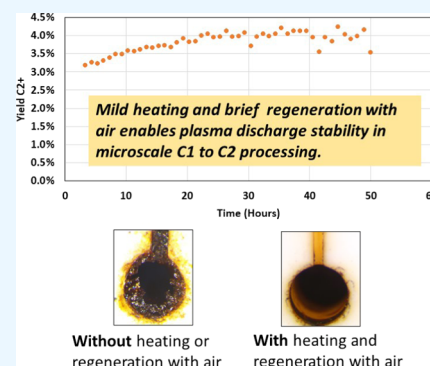


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ABSTRACT: Hydrocarbon processing using plasmas has tremendous potential, yet there still exist many uncertainties pertaining to practical operation over long durations. Previously, it has been demonstrated that a nonthermal plasma operating in a DC glow regime can transform methane into C2 species (acetylene, ethylene, ethane) in a microreactor. Using a DC glow regime in a microchannel reactor allows for lower power consumption, at the expense of greater consequence of fouling. Since biogas can be a source of methane, a longevity study was undertaken to understand how the microreactor system would change over time with a feed mixture of simulated biogas (CO₂, CH₄) and air. Two different biogas mixtures were used, one of which contained 300 ppm H₂S, while the other had no H₂S. Potential difficulties observed from previous experiments included carbon deposition on the electrodes, which could interfere with the electrical characteristics of the plasma discharge as well as material deposition in the microchannel, which could affect gas flow. It was found that raising the temperature of the system to 120 °C helped prevent hydrocarbon deposition in the reactor. Purging the reactor periodically with dry air was also found to have positive effects as it removed carbon buildup on the electrodes themselves. Successful operation over a 50 h time period without any significant deterioration was demonstrated.



INTRODUCTION

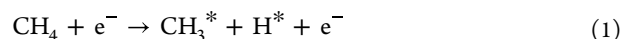
Methane is a significant waste product that is commonly emitted from cattle farms, landfills, and activities related to fossil fuel extraction. Landfills and livestock accounted for approximately half of the U.S. methane emissions in 2017.¹ From previous work,² it has been found that a nonthermal plasma discharge can turn this methane into longer hydrocarbons, which may be more viable to bring to market from these stranded methane sources.

In nonthermal plasmas, electrons are accelerated through an electric field to cause reactions. This means that the gas molecules themselves can be at a relative temperature as thermal collisions are not needed to initiate reactions. Because the molecules and the electrons are not at the same temperature, the system is not in thermal equilibrium.³ However, radical species formed from methane can deposit on a surface. Carbon deposition is a commonly referenced problem of methane discharges. This deposited carbon can interfere with the emission of electrons from the surface electrodes and threaten the stability of the discharge.^{4–8} The aim of this study is to find ways to mitigate this deposition so that the plasma microreactor can operate for a long time with limited maintenance.

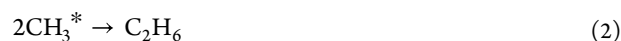
Operating a nonthermal plasma in a microreactor allows for the use of smaller length scales, which reduces the voltage requirements of the plasma. The microreactor for this study

used an electrode gap distance of 500 μm, which required approximately 550 volts for a plasma discharge. Less than 4 watts was needed to power the plasma at a steady state. This contrasts to other similar studies that usually required more than 10 watts for the plasma.^{6,9,10}

The key reaction for methane in the plasma is a collision between the molecule and an electron. This can create methyl radicals as seen in eq 1.



Two methyl radicals can then recombine to make an ethane molecule as seen in eq 2.



Similar products such as C₂H₂ and C₂H₄ can also be formed from this process. Synthesis gas (H₂ and CO) has been commonly made in nonthermal plasmas with methane as a key reactant along with air or carbon dioxide. Although syngas production has been the goal of much of this research,^{4,5,9–15}

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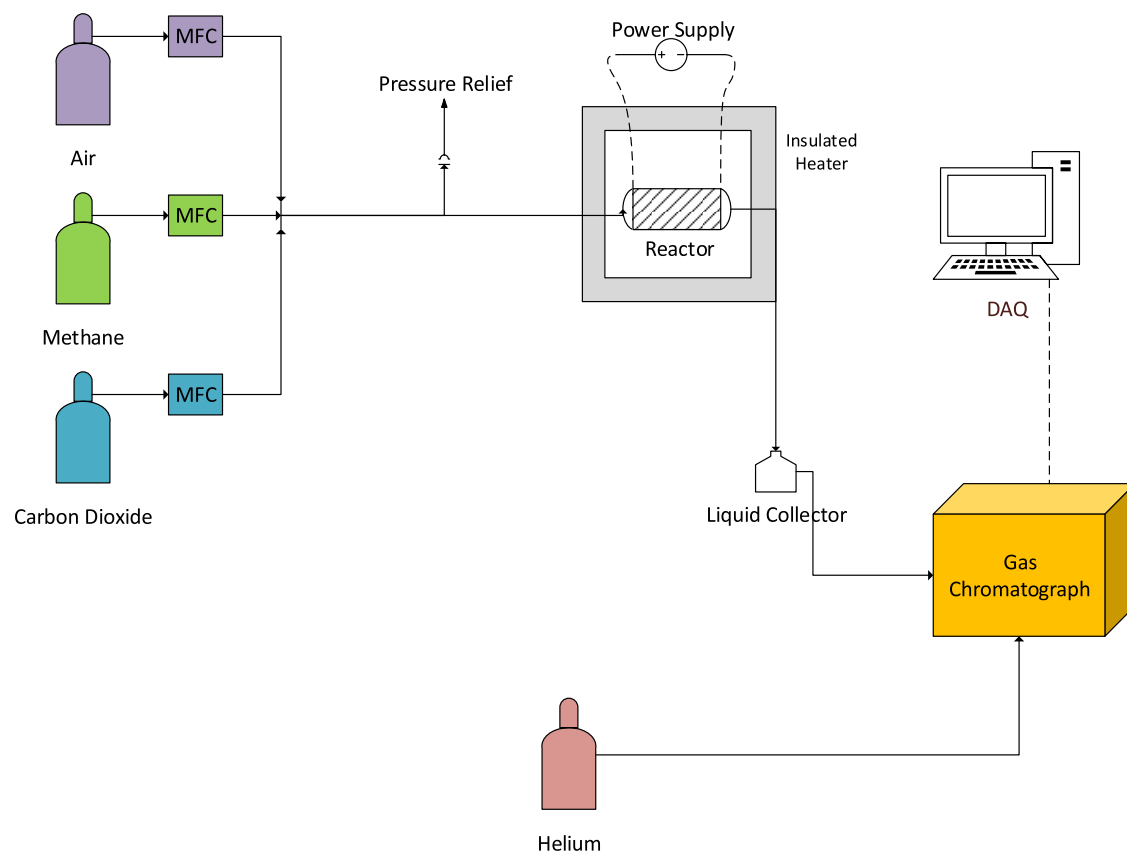


Figure 1. Experimental apparatus setup for conversion of methane in a nonthermal plasma microreactor over longer timescales.

there have also been studies focused on making larger hydrocarbons from methane.^{16,17} In previous work at OSU,^{2,18,19} carbon deposition on the electrodes over time harmed the operation of the reactor by making discharges unstable over time. At high methane fractions (>50% by mole), the discharge would short on the order of seconds to a minute. Low methane fraction (~15%) discharges with an oxidizer such as CO₂ present could last for hours without cleaning. This is similar to the findings of Li et al. who found that ratios of CH₄/CO₂ of 2:1 greatly increased the amount of deposited carbon, especially at the cathode.⁶ They concluded that the carbon deposition was primarily from methane decomposition as opposed to the decomposition of CO as carbon deposition increased with increasing amounts of methane. Long et al. found increasing water content in the product at these higher methane concentrations.²⁰ They theorized that the oxygen dissociated from CO₂ was taken up by hydrogen broken off from the methane, and oxygen radicals were not available to react with the solid carbon formed greatly increasing the carbon deposition. Some work has been done to characterize this carbon.

Carbon particles can form within the plasma itself. This phenomenon is known as a dusty plasma.²¹ In this process carbon can be made within the plasma, for example, by a methane molecule losing all of its surrounding hydrogen by electron bombardment. These carbon atoms or ions can then agglomerate into grains or react with molecules or radicals to grow larger particles.²² Gravity can have a significant effect on larger particles, while the electric field from the electrodes can dominate smaller charged particles, especially if they are closer to the electrodes.²¹ For this case, this means that charged

particles of carbon can be attracted to the electrodes, allowing deposition to occur depending on the charge of the particle.

Tu et al. used a transmission electron microscope (TEM) to find that this carbon could be spherical particles, amorphous, or carbon nanotubes.¹⁰ While physically cleaning this deposited carbon is possible, an operational solution to prevent coke and clean without opening the reactor would be desirable.²³ The objective of this experimental study was to examine how the performance of the reactor changed over time and identify mitigating steps that could be taken to extend the performance life of the plasma reactor, such as regularly decoking the system with air.

The addition of air to the mixture is expected to allow for the oxidation of methane to CO and CO₂ via the oxygen. Some studies have been carried out and found that methanol could also be made from a plasma, which was improved with catalysts^{24–27} as well as adsorbents.²⁸ With input CO₂ mole fractions of approximately 11%, it is initially unclear whether there will be a net creation of CO₂ by oxidizing methane or a net consumption by dry reforming.

Pham et al. used a La₂O₃/γ-Al₂O₃ catalyst within a dielectric barrier discharge reactor to make larger hydrocarbons from methane and CO₂.²⁹ They found that higher temperatures improved the carbon balance, which implied that less carbon was lost to coking. Pham et al. reasoned that the higher temperature improved the rate of oxidation of deposited carbon. They also found that selectivity to C3 and C4 were decreased at the higher temperatures as well.

In contrast, carbon deposition can also be controlled by changing the gas composition. Kameshima et al. used a pulsed flow system with a constant flow of CO₂ and an intermittent

flow of methane to reduce carbon deposition.³⁰ Carbon would build up, while methane was in the feed. Coke would then be burned off when methane was not in the feed, as CO₂ would react with the solid carbon to form CO.

Few studies have looked at the long-term operation of a plasma with methane as a feed gas. One study by Redondo et al.⁸ found that their mixture of methane and helium could last about 100 min with stainless-steel electrodes. Failure then occurred due to carbon deposition on the electrodes. They then plated their electrodes with gold and found that they could increase their longevity to about 200 min before conversion of methane dropped. They theorized that the inert quality of gold helped prevent polymerization of ethylene and acetylene on the electrodes, which therefore increased the lifetime of the process.

Rather than pulsing the gases like Kameshima et al.,³⁰ Delikonstantis et al. worked with a pulsed plasma system to convert methane into hydrocarbons where electricity was pulsed.^{7,17} They theorized that pulsing the discharge would cause fewer methane molecules to be hit multiple times by electrons, thus reducing secondary reactions to species such as solid carbon. They also added hydrogen to help mitigate carbon deposition.

To summarize the literature, it is apparent that coking/clogging/deactivation of plasma reactors for hydrocarbon processing is fraught with challenges. In the work presented here, the goal was to determine whether or not low power, microchannel glow discharges can withstand extended operation of appreciable duration. As deposition of solids and liquids will be increasingly damaging as dimensions get smaller, the lower power microscale approach taken here represents a considerable technology risk for practical development. Therefore, the objective of this study was to determine if a microchannel discharge could reliably produce C₂ from C₁ over long durations. To derisk the concept, a target duration of 50 h was chosen. If the performance suffered, the aim was to manage the conditions to be more conducive of long-term operation. In this work, only single discharge was studied. The reactor was not optimized for performance, as a multidischarge reactor would be needed to reach higher conversions.

EXPERIMENTAL MATERIALS AND METHODS

Reactor Design. Two different ceramics were used for the nonthermal plasma microreactor body material in these experiments: Mykroy ceramic and MACOR ceramic. These ceramics were chosen based on their maximum operational temperature of 500 °C³¹ and low electrical conductivity. The electrode material chosen was thoriated tungsten. Thoriated tungsten has a relatively low work function of approximately 3.4 eV³² compared to pure tungsten (4.54 eV).³³ This increases the chance of an electron being emitted via an ion impact with the surface, reducing voltage requirements to initiate a discharge. A channel 500 μm wide and 500 μm long was milled into the ceramic for gas flow. A figure for this reactor channel can be found in previous work² (Figure 1). Five electrode pairs also had channels milled such that they could be placed perpendicular to the flow channel. On top of the ceramic, borosilicate glass was used to seal the surface, which allowed the plasma to be observed visually.

Experimental Platform. A diagram of the experimental platform used can be seen in Figure 1. Gases of interest were fed to the reactor using individual mass flow controllers

(MFCs). The gases for this experiment included methane, carbon dioxide, and air. The nitrogen present in air was used for analytical purposes as an internal standard to account for potential changes in the total number of molecules. It was assumed that the conversion of nitrogen would be relatively small due to its strong triple bond. After the gas mixture exited the reactor, it passed through a room-temperature cold trap (liquid collector), which allowed any large hydrocarbons formed to be removed from the stream before reaching the gas chromatograph. The gas chromatograph (GC) took samples of the gas stream via a flow-through 0.25 mL sample loop activated by a sampling valve.

Light gases (H₂, O₂, N₂, CO) were separated using a molecular sieve column, while hydrocarbons and carbon dioxide were separated using a HAYESE-PD column. A DC power supply with a maximum current of 12 mA and a maximum voltage of 5 kV was used to power the plasma microreactor. An insulated hot box capable of controlling the reactor temperature was placed around the reactor. The reactor was heated to keep longer chain products in the gas phase, which helped prevent deposition of materials in the reactor.

Methods. Gas flow rates were maintained by the MFCs. Unreacted gas was first sampled before initiating the discharge with the DC power supply. The plasma discharge was initiated after this GC sampling was completed by raising the power supply voltage and then setting the current to the desired amperage. As the voltage is determined by the gas composition, pressure, and the distance between electrodes, voltage across the discharge gap was not a controlled variable. Once the desired current was reached, samples of gas were taken once every hour.

A 200 kΩ ballast resistance was placed in series with the discharge along with a smaller 1 or 50 kΩ resistor as seen in Figure 2. This helped control the current in the system. By

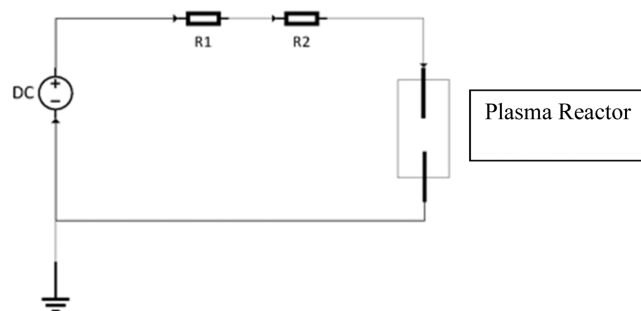


Figure 2. Circuit diagram of the direct current plasma system.² R1 and R2 are resistors of 200 and 1 kΩ, respectively, for studies with no reactor heating and 200 and 50 kΩ, respectively, for heated reactor studies. Reprinted (adapted or reprinted in part) with permission from I. Reddick et al., “Parametric Study of Hydrocarbon Chain Growth from Methane via a Nonthermal Plasma Discharge Microreactor,” *Ind. Eng. Chem. Res.*, vol. 61, no. 28, pp. 10047–10057, Jul. 2022, doi: 10.1021/ACS.IEER.2C01472. Copyright 2022, American Chemical Society.

measuring the voltage on the smaller resistor, current through the circuit and thus the discharge could be determined. The temperature was controlled using a heater inside a hot box. The voltage to the heater was adjusted by a Variac variable transformer to set a desired temperature. Temperature was measured using a thermometer rather than a thermocouple as

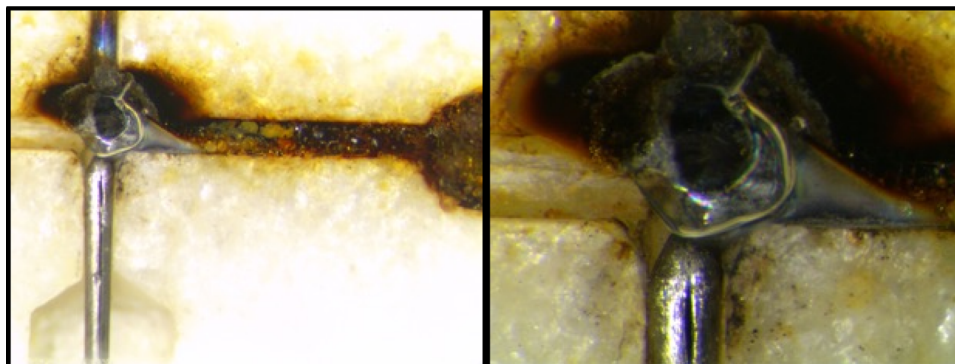


Figure 3. Left: Electrode and channel after 17 h study without H₂S. Right: electrode condition after 17 h. The glass window is present in both pictures. Photograph courtesy of Ian Reddick. Copyright 2023. Free domain.

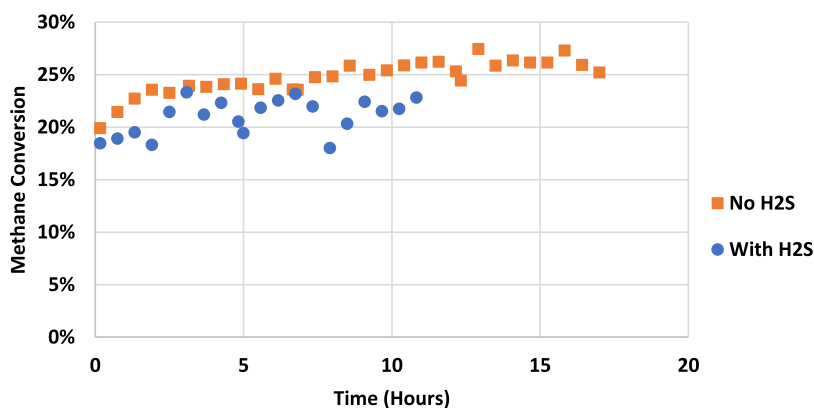


Figure 4. Methane conversion over time with H₂S and without H₂S present in the feed stream. Ambient condition reactor surroundings.

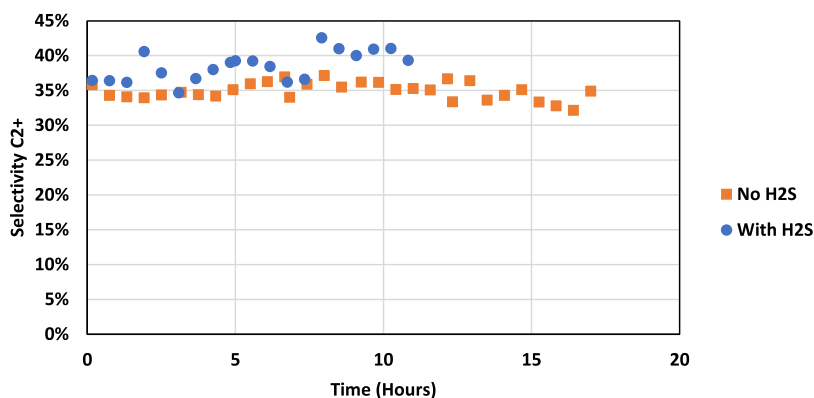


Figure 5. Selectivity to C₂₊ over time with H₂S and without H₂S present in the feed stream. Ambient condition reactor surroundings.

the electrical interference from the plasma affected the thermocouple voltage reading.

Measured Metrics. To study how the products of the reactor could change with time, three metrics were considered. These were the fractional conversion of methane feed, selectivity to larger hydrocarbons (C₂₊), and yield of C₂₊. The metrics were defined by the following equations

$$\text{conversion}_{\text{CH}_4} = \frac{\text{CH}_{4_i} - \text{CH}_{4_o}}{\text{CH}_{4_i}} \quad (3)$$

$$\text{selectivity}_{\text{C}_{2+}} = \frac{\sum nC_n}{\text{CH}_{4_i} - \text{CH}_{4_o}} \quad (4)$$

$$\text{yield}_{\text{C}_{2+}} = \frac{\sum nC_n}{\text{CH}_{4_i}} \quad (5)$$

where CH_{4_i} is the inlet molar flow of methane, CH_{4_o} is the outlet flow of methane, and $\sum nC_n$ is the summation of the flows of product hydrocarbons multiplied by their respective number of carbons n ($n \geq 2$).

RESULTS AND DISCUSSION

Several attempts were made to reach 50 h of operation of a single discharge without manual cleaning of the reactor. The first two attempts were conducted with the reactor surroundings at ambient temperature with a Mykroy reactor body. The feed gas mixture was 60% air and 40% by mole

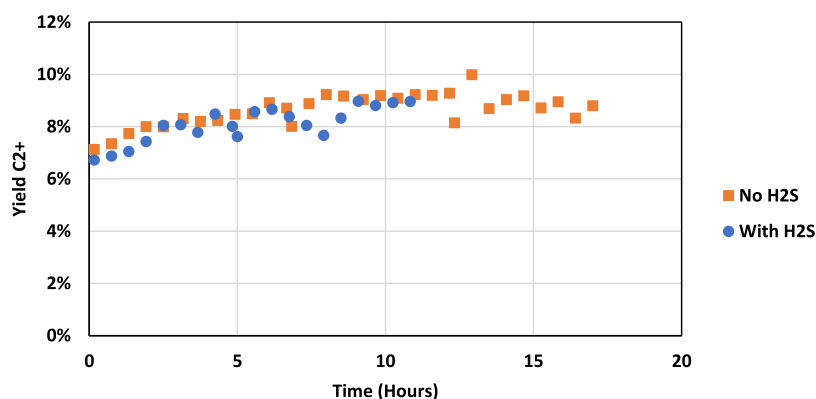


Figure 6. Yield C₂₊ over time with H₂S and without H₂S present in the feed stream. Ambient condition reactor surroundings.

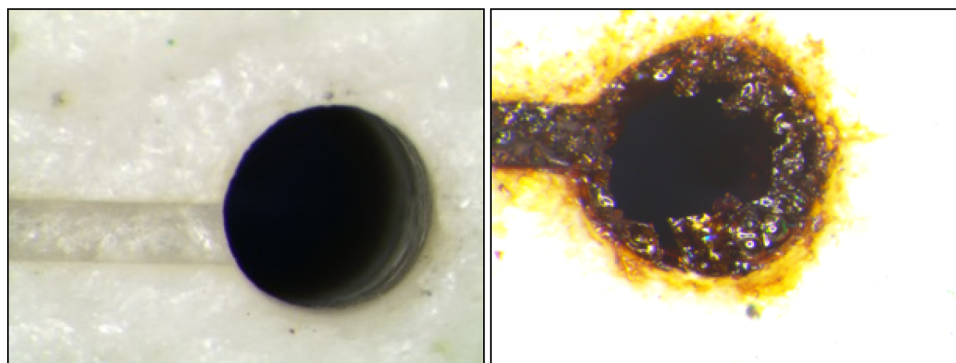


Figure 7. Left: inlet of the reactor. Right: outlet of the reactor, with blockage. Window removed. Photograph courtesy of Ian Reddick. Copyright 2023. Free domain.

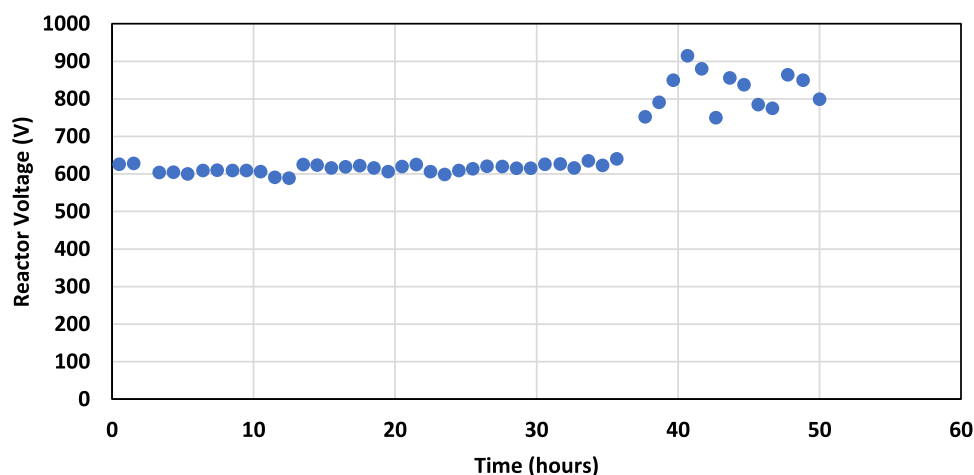


Figure 8. Voltage of the reactor over time with surroundings of 120 °C. No electrode cleaning.

simulated biogas (2:1 CH₄ to CO₂) with a total flow rate of 60 sccm. In one case, the biogas contained 300 ppm H₂S and 1% O₂, while the second case had no H₂S or O₂. The reactor was shut down overnight and then restarted with the same conditions each successive day. The discharge was kept at a current of 5 mA. GC samples were taken approximately every half an hour.

Reactor failure occurred before 50 h in both cases: 17 h without H₂S and 11 h with H₂S. The deposited material in the reactor created a critical flow blockage as shown in Figure 3 that could not be removed without opening and cleaning the reactor. Over that period, conversion of methane and

selectivity to C₂₊ were relatively constant in both cases as seen in Figures 4 and 5. In the study without H₂S, methane conversion increased from 20 to 25% over the first few hours and then roughly stayed constant. Yield of C₂₊ was likewise relatively constant as demonstrated in Figure 6. Due to similar performance between representative biogas with and without H₂S, it was then decided to discontinue the use of H₂S in the experiments that follow.

Due to the deposition of materials in the reactor, future attempts raised the reactor temperature to 120 °C to prevent condensation. The reactor body material was switched to MACOR, which seemed to help prevent deposition when

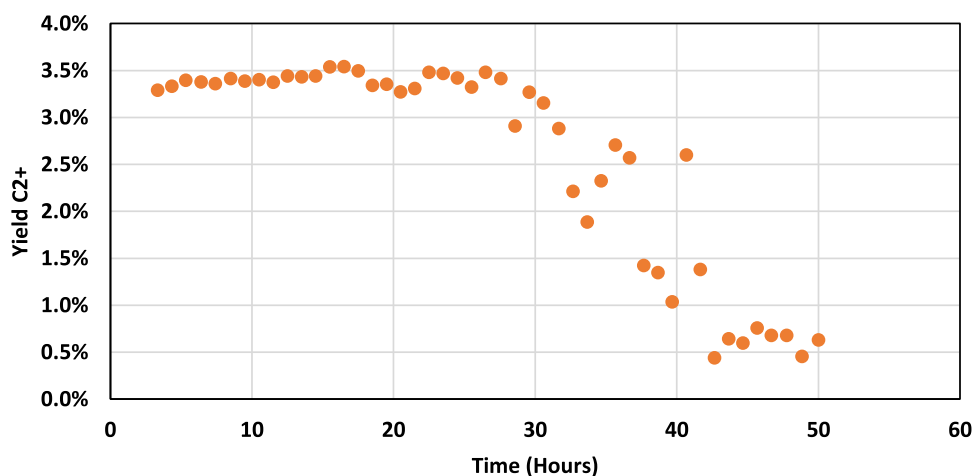


Figure 9. Yield C2+ over time with reactor surroundings of 120 °C. No electrode cleaning.

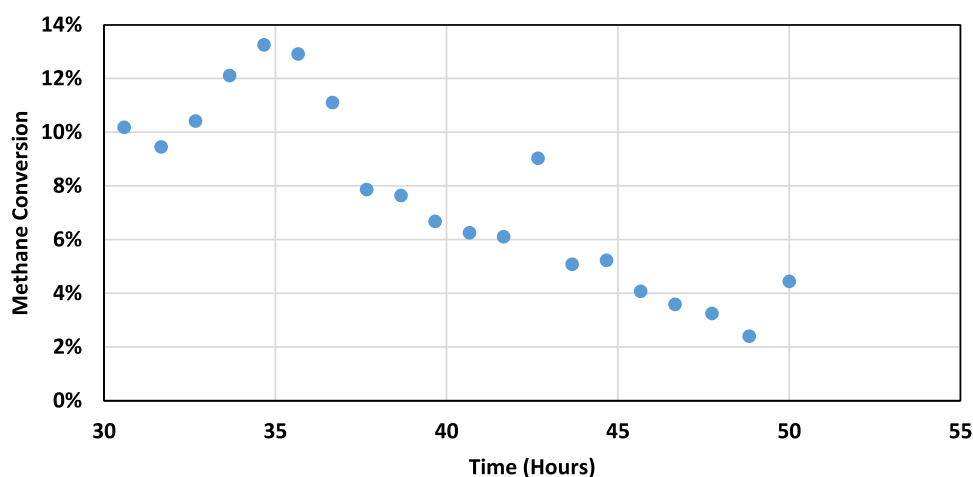


Figure 10. Methane conversion over time with reactor surroundings of 120 °C. No electrode cleaning.

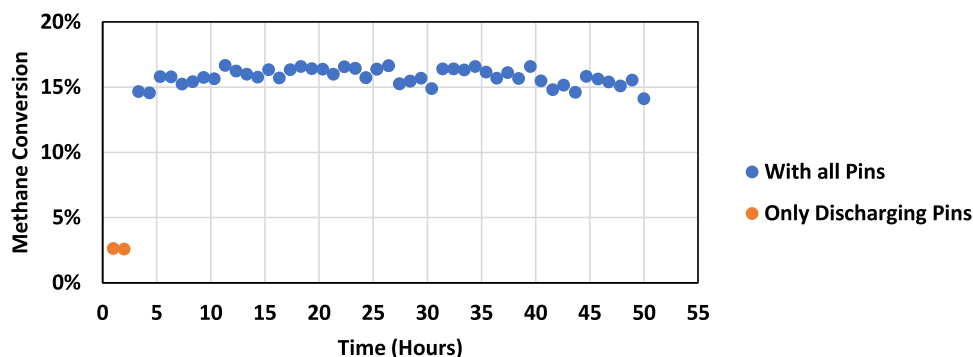


Figure 11. Methane conversion over time with reactor surroundings of 120 °C. Electrode regenerated by pure air for 2 min for every 2 h (i.e., less than 2% of the time).

heated due to the increased hardness and lower surface roughness which prevented deposition.

Current was lowered to 4.5 mA, while the mixture composition was altered to increase the air content to 67% by volume and 33% biogas. The air content was increased to boost the O₂ content. Electrodes were not cleaned during the 50 h of operation. The reactor was also run continuously with no shutdown overnight and with GC samples taken approximately every hour (Figure 7).

The reactor functioned at 4.5 mA for the entire 50 h. Over the first 30 h, the discharge stayed in the glow discharge regime. However, at 30 h, it began transitioning between glow and spark regimes as seen in Figure 8. At 36 h, the discharge was entirely in the spark regime. This can be seen in the reactor voltage increase at 36 h. Yield of C2+ was relatively constant over the first 30 h but dropped from ~3.5 to ~0.5% in the transition from the glow regime to spark regime as seen in Figure 9. The change of electrical regime led to a smaller

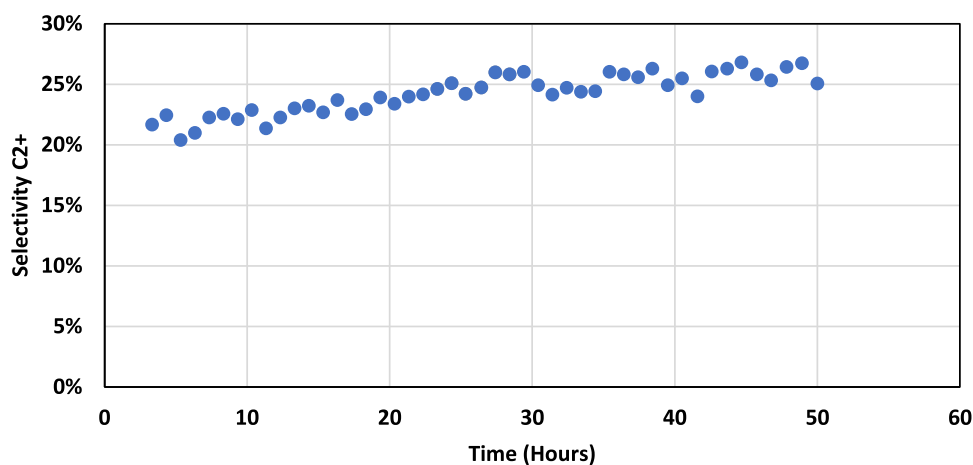


Figure 12. Selectivity C2+ over time with reactor surroundings of 120 °C. Electrode regenerated by pure air for 2 min for every 2 h.

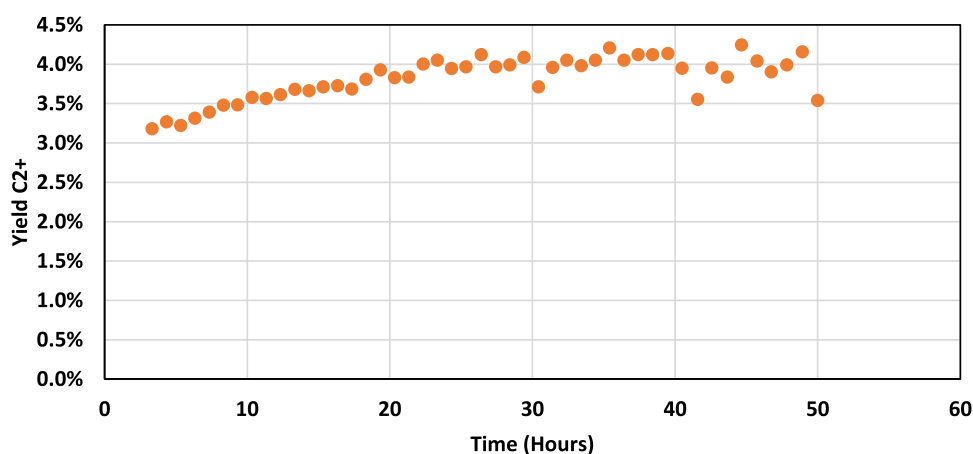


Figure 13. Yield C2+ over time with reactor surroundings of 120 °C. Electrode regenerated by pure air for 2 min for every 2 h.

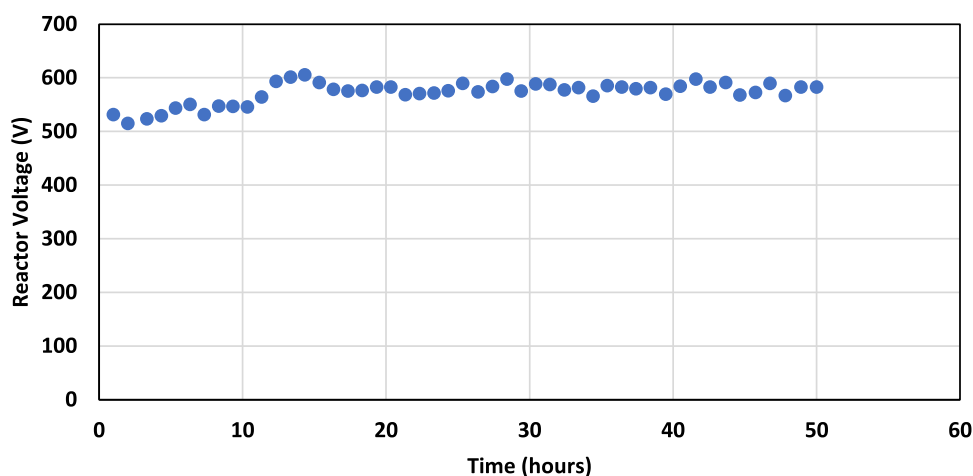


Figure 14. Reactor voltage over time with surroundings of 120 °C. Electrode regenerated by pure air for 2 min for every 2 h.

methane conversion, which caused the drop in C2+ yield- (Figure 10).

It is hypothesized that deposition on the electrodes made it more difficult for electrons to be emitted, which led to the regime shift and unsteady current. A second attempt was made with the heated reactor where every 2 h, dry air was fed to the reactor for 2 min with the discharge still active to remove carbon deposited on the electrodes. All reactor characteristics

were relatively stable over the 50 h after this change was made. Methane conversion was approximately 16% throughout the 50 h as seen in Figure 11. Selectivity increased slightly from 20 to 25% with an accompanying increase in yield as seen in Figures 12 and 13. Electrical measurements were also largely constant with no regime change demonstrated by Figure 14.

Comparing the starting clean reactor channel and electrodes as seen in Figure 15 to the reactor channel after 50 h seen in

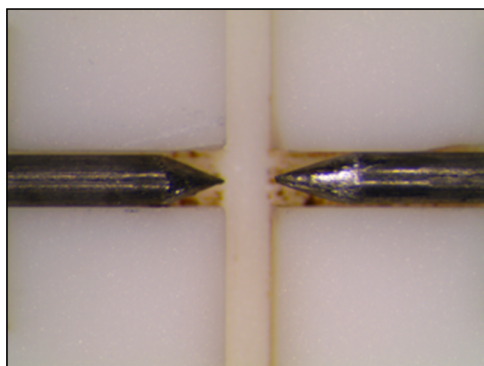


Figure 15. Electrode condition before the start of longevity study for the heated reactor. Photograph courtesy of Ian Reddick. Copyright 2023. Free domain.

Figure 16, some material was deposited in the channel after the discharge and in the electrode region. However, compared to

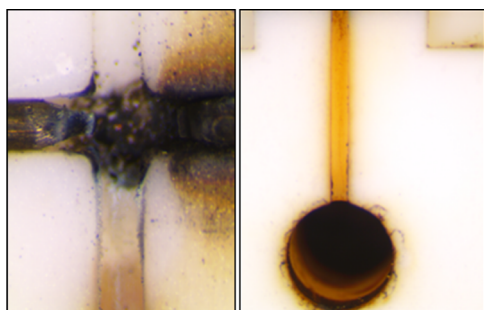


Figure 16. Left: electrode condition after 50 h with regular regeneration and 120 °C surroundings. Right: outlet condition after 50 h. Unlike the study without heat and regeneration, no blockage occurred over 50 h in the reactor. Photograph courtesy of Ian Reddick. Copyright 2023. Free domain.

the first attempt without heating and regular air-cleaning, the channel was not plugged with the material. The coating of the material in this case was much thinner and nowhere close to filling the channel three-dimensionally.

Conversion was artificially low for the first 2 h as only the active discharge pins were present in the reactor. After this was noted, the other four pairs of electrodes were inserted into the reactor after a brief shutdown. After this, conversion climbed from 2.5 to 15%. It is hypothesized that the other electrodes helped push flow through the channel and helped prevent bypass between the glass and ceramic piece. With more flow through the discharge, conversion would increase.

CONCLUSIONS

The long-term operation of a direct current plasma discharge microreactor with significant amounts of input methane was studied. It was found that long-term operation could deposit larger hydrocarbons in the reactor and thus clog the flow path. Heating the reactor to 120 °C mitigated this operational problem. Carbon deposition, a problem from previous studies, could be removed using pure air inside the plasma system. By regularly cleaning the reactor with air every two hours for two minutes and heating the reactor to 120 °C, it was possible to keep the reactor in a stable glow regime for 50 h, while in the glow regime, no significant deterioration in conversion or selectivity to higher hydrocarbons was noted. Future work

could include an investigation into other antideposition mechanisms, such as surface functionalization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c07265>.

Gas chromatography, power input, conversion and selectivity data (PDF)

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<https://pubs.acs.org/10.1021/acsomega.2c07265>

Author Contributions

Dr. N.A., Dr. G.N.J., and Dr. A.Y. assisted with initial reactor design ideas and were strongly involved with steering this research including advice on design of experiments, experimental platform design, and data analysis. Dr. A.V.J. was greatly involved in the initial design of the power system. Dr. J.P. helped build and test a prototype platform and reactor for this process. Dr. M.C. helped review the design of the reactor and assisted with acquisition of supporting equipment for the reactor. He was also involved in the initial testing of new reactor designs. O.M. was very involved in reactor troubleshooting and in carrying out long-term experiments as well as finding ways to improve reactor manufacturing.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) EPA Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2020. EPA 430-R-22-003, 2022. <https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2020>
- (2) Reddick, I.; Shareghi, A.; Miao, Y.; Pommerenck, J.; Coblyn, M.; Yokochi, A.; Jouanne, A. Von.; Jovanovic, G.; AuYeung, N. Parametric Study of Hydrocarbon Chain Growth from Methane via a Nonthermal Plasma Discharge Microreactor. *Ind. Eng. Chem. Res.* **2022**, *61*, 10047–10057.
- (3) Meichsner, J.; Schmidt, M.; Schneider, R.; Wagner, H.-E. *Nonthermal Plasma Chemistry and Physics*; Taylor & Francis Group: Boca Raton, 2013.
- (4) Yang, Y. Methane Conversion and Reforming by Nonthermal Plasma on Pins. *Ind. Eng. Chem. Res.* **2002**, *41*, 5918–5926.
- (5) Tao, X.; Bai, M.; Li, X.; Long, H.; Shang, S.; Yin, Y.; Dai, X. CH₄-CO₂ Reforming by Plasma - Challenges and Opportunities. *Prog. Energy Combust. Sci.* **2011**, *37*, 113–124.
- (6) Li, M.-w.; Xu, G.; Tian, Y.; Chen, L.; Fu, H. Carbon Dioxide Reforming of Methane Using DC Corona Discharge Plasma Reaction. *J. Phys. Chem. A* **2004**, *108*, 1687–1693.
- (7) Delikonstantis, E.; Scapinello, M.; Stefanidis, G. D. Low Energy Cost Conversion of Methane to Ethylene in a Hybrid Plasma-Catalytic Reactor System. *Fuel Process. Technol.* **2018**, *176*, 33–42.
- (8) Beloqui Redondo, A.; Troussard, E.; Bokhoven, J. A. Van. Non-Oxidative Methane Conversion Assisted by Corona Discharge. *Fuel Process. Technol.* **2012**, *104*, 265–270.
- (9) Li, D.; Li, X.; Bai, M.; Tao, X.; Shang, S.; Dai, X.; Yin, Y. CO₂ Reforming of CH₄ by Atmospheric Pressure Glow Discharge Plasma: A High Conversion Ability. *Int. J. Hydrogen Energy* **2009**, *34*, 308–313.
- (10) Tu, X.; Whitehead, J. C. Plasma Dry Reforming of Methane in an Atmospheric Pressure AC Gliding Arc Discharge: Co-Generation of Syngas and Carbon Nanomaterials. *Int. J. Hydrogen Energy* **2014**, *39*, 9658–9669.
- (11) Aziznia, A.; Bozorgzadeh, H. R.; Seyed-matin, N.; Baghalha, M.; Mohamadlilzadeh, A. Comparison of Dry Reforming of Methane in Low Temperature Hybrid Plasma-Catalytic Corona with Thermal Catalytic Reactor over Ni/ γ -Al₂O₃. *J. Nat. Gas Chem.* **2012**, *21*, 466–475.
- (12) Supat, K.; Kruapong, A.; Chavadej, S.; Lobban, L. L.; Mallinson, R. G. Synthesis Gas Production from Partial Oxidation of Methane with Air in AC Electric Gas Discharge. *Energy and Fuels* **2003**, *17*, 474–481.
- (13) Yao, S. L.; Okumoto, M.; Nakayama, A.; Suzuki, E. Plasma Reforming and Coupling of Methane with Carbon Dioxide. *Energy Fuels* **2001**, *15*, 1295–1299.
- (14) Chun, S. M.; Shin, D. H.; Ma, S. H.; Yang, G. W.; Hong, Y. C. CO₂ Microwave Plasma-Catalytic Reactor for Efficient Reforming of Methane to Syngas. *Catalysts* **2019**, *9*, 292.
- (15) Ray, D.; Reddy, M. K.; Subrahmanyam, C. Ni-Mn/ γ -Al₂O₃ Assisted Plasma Dry Reforming of Methane. *Catal. Today* **2018**, *309*, 212–218.
- (16) Park, D.; Kim, J.; Kim, T. Nonthermal Plasma-Assisted Direct Conversion of Methane over NiO and MgO Catalysts Supported on SBA-15. *Catal. Today* **2018**, *299*, 86–92.
- (17) Scapinello, M.; Delikonstantis, E.; Stefanidis, G. D. Direct Methane-to-Ethylene Conversion in a Nanosecond Pulsed Discharge. *Fuel* **2018**, *222*, 705–710.
- (18) Kreider, P. *Applications of Nonthermal Microplasmas in Chemical Reaction Engineering*; Oregon State University, 2015.
- (19) Miao, Y.; Kreider, P.; Reddick, I.; Pommerenck, J.; Collin, R.; AuYeung, N.; von Jouanne, A.; Jovanovic, G.; Yokochi, A. Methane Coupling to Ethylene and Longer-Chain Hydrocarbons by Low-Energy Electrical Discharge in Microstructured Reactors. *Ind. Eng. Chem. Res.* **2021**, *60*, 6950–6958.
- (20) Long, H.; Shang, S.; Tao, X.; Yin, Y.; Dai, X. CO₂ Reforming of CH₄ by Combination of Cold Plasma Jet and Ni/ γ -Al₂O₃ Catalyst. *Int. J. Hydrogen Energy* **2008**, *33*, 5510–5515.
- (21) Ignatov, A. M. Basics of Dusty Plasma. *Plasma Phys. Rep.* **2005**, *31*, 46–56.
- (22) Girshick, S. L. Particle Nucleation and Growth in Dusty Plasmas: On the Importance of Charged-Neutral Interactions. *J. Vac. Sci. Technol. A* **2020**, *38*, 011001_1–011001_6.
- (23) Ozkan, A.; Dufour, T.; Arnoult, G.; De Keyzer, P.; Bogaerts, A.; Reniers, F. CO₂-CH₄ Conversion and Syngas Formation at Atmospheric Pressure Using a Multi-Electrode Dielectric Barrier Discharge. *J. CO₂ Util.* **2015**, *9*, 74–81.
- (24) Chen, L.; Zhang, X.-W.; Huang, L.; Lei, L.-C. Partial Oxidation of Methane with Air for Methanol Production in a Post-Plasma Catalytic System. *Chem. Eng. Process. Process Intensif.* **2009**, *48*, 1333–1340.
- (25) Wang, Y.-F.; Tsai, C.-H.; Shih, M.; Hsieh, L.-T.; Chang, W.-C. Direct Conversion of Methane into Methanol and Formaldehyde in an RF Plasma Environment II: Effects of Experimental Parameters. *Aerosol Air Qual. Res.* **2005**, *5*, 211–224.
- (26) Zhou, L. M.; Xue, B.; Kogelschatz, U.; Eliasson, B. Partial Oxidation of Methane to Methanol with Oxygen or Air in a Nonequilibrium Discharge Plasma. *Plasma Chem. Plasma Process.* **1998**, *18*, 375–393.
- (27) Chawdhury, P.; Wang, Y.; Ray, D.; Mathieu, S.; Wang, N.; Harding, J.; Bin, F.; Tu, X.; Subrahmanyam, C. A Promising Plasma-Catalytic Approach towards Single-Step Methane Conversion to Oxygenates at Room Temperature. *Appl. Catal., B* **2021**, *284*, No. 119735.
- (28) Gorky, F.; Nambo, A.; Carreon, M. L. Cold Plasma-Metal Organic Framework (MOF)-177 Breathable System for Atmospheric Remediation. *J. CO₂ Util.* **2021**, *51*, No. 101642.
- (29) Pham, M. H.; Goujard, V.; Tatibouët, J. M.; Batiot-Dupeyrat, C. Activation of Methane and Carbon Dioxide in a Dielectric-Barrier Discharge-Plasma Reactor to Produce Hydrocarbons - Influence of La₂O₃/ γ -Al₂O₃ Catalyst. *Catal. Today* **2011**, *171*, 67–71.
- (30) Kameshima, S.; Tamura, K.; Ishibashi, Y.; Nozaki, T. Pulsed Dry Methane Reforming in Plasma-Enhanced Catalytic Reaction. *Catal. Today* **2015**, *256*, 67–75.
- (31) Inc., T. P. Mykroy/Mycalex® (Mica) Material Specifications, <https://www.technicalproductsinc.com/pdf/Specs/Mycalex%20Specs%20Comparison.pdf>.
- (32) Rivière, J. C. The Work Function of Thorium. *Proc. Phys. Soc.* **1962**, *80*, 124–129.
- (33) Fridman, A. *Plasma Chemistry*; Cambridge University Press: New York, 2008.