

Conversion of Methane to Higher Hydrocarbons in AC Nonequilibrium Plasmas

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The effects of plasma chemistry on the conversion of methane were studied using a dielectric barrier discharge reactor at ambient temperatures. A dielectric barrier discharge reactor generates a nonequilibrium plasma when a sufficiently high voltage is applied across the reactor's electrodes. Methane molecules are activated at this temperature and coupled to form C₂ hydrocarbons, higher hydrocarbons, and hydrogen. The study on the effect of voltage, residence time and third bodies on methane conversion and product selectivity shows that methane conversion initially increases with increasing voltage and residence time above the breakdown voltage, and product selectivities are essentially independent of the voltage. Production of hydrogen during the reaction limits olefin production. Methane conversion also increases when helium and ethane are in the feed stream. Helium and ethane both appear to be more easily activated than methane and enhance methane activation and conversion.

Introduction

Commercial technologies for methane conversion are based on multistep reaction processes. These processes start with the transformation of methane and steam into synthesis gas, that is, a mixture of H₂ and CO, via the steam reforming (and water-gas shift) processes. These compounds are then converted either to liquid hydrocarbons via Fischer-Tropsch (FT) synthesis or to methanol.

Direct methane conversion paths, including direct partial oxidation (POM) to methanol and oxidative coupling (OCM) to C₂ hydrocarbons, have been the subject of recent research and development activity. These two reactions are considered potentially more energy-efficient than multistep reaction processes because they bypass the highly energy-intensive step of high-temperature synthesis gas formation.

Another reason for the increased interest in direct methane conversion techniques is that large numbers of natural gas deposits (containing 60–90% methane) are located in very remote areas, precluding any economic means of their transportation to the place of consumption via gas pipeline net-

works. On-site consumption would require small-scale plants that are relatively energy-inefficient due to the high temperatures involved. On-site conversion to liquid products would make transportation of these natural gas deposits much more economical and practical.

Although the presence of oxygen in the dielectric barrier discharge (DBD) environment enhances the conversion of methane, it also tends to further oxidize the desired products, which are produced in intermediate reaction steps, into undesired carbon oxides. Therefore, in almost all of the experiments of this study, only pure methane was fed into the electric discharge environment so that its reaction behavior at steady-state conditions could be monitored in a nonoxidative environment. The purpose of conducting these experiments was to show the achievable degree of direct activation of the methane molecule and the products resulting from such activation. The residence time was varied to determine the effect. Some experiments were also conducted in which helium or ethane was included in the feed along with methane to determine their influence on methane conversion and the product distributions.

Abundant literature can be cited to illustrate the many efforts to develop direct methane conversion processes, partic-

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ularly the POM and OCM reactions (Gesser et al., 1985; Yarlagadda et al., 1987; Zanthoff and Baerns, 1990; McCarty, 1991; Baerns, 1992; Walsh et al., 1992; Periana et al., 1993; Omata et al., 1994; Casey et al., 1994; Chen and Willcox, 1994). Most of these sources indicate that oxygen is required in the reactions to activate the methane molecule. These reactions must be operated at very high temperatures where the desired products (i.e. CH_3OH , C_2H_6 , C_2H_4) tend to be far more reactive than the very stable methane molecule. If oxygen is included in the reaction system, it causes further oxidation of those intermediate, yet desired, products to carbon dioxide (CO_2), water (H_2O), and to a lesser extent carbon monoxide (CO). In order to suppress the deep oxidation reactions and to gain substantial yields from the desired reactions, the introduction of catalysts and the establishment of the proper reaction conditions are required to selectively convert the methane into the desired products. The yields and efficiencies required for a useful process based on thermal/catalytic approaches have not yet been achieved.

Plasmas for methane activation and conversion

Gaseous plasmas are a good source for generating active species, including electrons, ions, and radicals. Research has been conducted on methane conversion using plasmas to initiate the reaction in an oxidative environment (Mallinson et al., 1987; Bhatnager and Mallinson, 1995; Larkin et al., 1998). One important type of plasma is the nonequilibrium plasma. Low gas temperatures and high electron temperatures characterize this type of plasma. In other words, the nonequilibrium plasma consists of electrons that have a much higher energy than the bulk gas species. These electrons may have energies ranging from 1 to 10 eV that correspond to temperatures of about 10,000 to 100,000 K (Rosacha et al., 1993). The nonequilibrium plasma is used in this study. Excited species have short lifetimes because of the low bulk gas temperatures. Therefore, the kinetic chains are short and reactions are rapidly quenched. This behavior allows nonequilibrium product distributions to occur.

The nonequilibrium-type plasma is generated within the gas-filled space between a pair of electrodes. One or both electrodes are covered by a dielectric layer that is commonly made of glass. Previous literature has referred to this kind of discharge, which has long been used in studies on plasma chemical reactions and commercially for the production of ozone, as a "silent electric discharge" (Morinaga and Suzuki, 1961, 1962).

The dielectric is the key for the proper function of the discharge. It enables the system to be operated at atmospheric, or higher, pressures. With the dielectric and the usual application of alternating (about 50 Hz to several kHz frequencies) high voltages, substantial quantities of plasma are created by a large number of so-called "microdischarges" in the gas. These discharges are statistically spread in space and time over the entire electrode area. Once ionization takes place at a location in the discharge gap, the transported charge accumulates on the surface of the dielectric, creating a field opposite to the applied electric field across the gap. After a few nanoseconds, the magnitude of this opposite field counterbalances the applied field and the flow of energetic electrons within the microdischarges across the gap is interrupted.

Throughout the course of application of the sinusoidal high-voltage waveform, the cycle of formation of the microdischarges will be repeated again and again once a sufficiently high field is reached across the gap during each cycle.

In summary, the dielectric serves three functions. The first is to limit the amount of charge transported by a single microdischarge and thereby minimize the chance of arc formation. The second is to distribute the microdischarges over the entire electrode area and gap volume to maximize the chance for each molecule to meet the energetic electrons and be converted into other species. The third is to provide a sufficiently high breakdown potential and consequent electron energy.

The only present commercial utilization of this DBD principle is for the generation of ozone (Eliasson et al., 1987). However, studies on the DBD applications for the destruction of toxic species such as NO_x and SO_x from flue gases, H_2S , NH_3 , and volatile organic compounds have been conducted (Rosacha et al. 1993; Penetrante et al., 1995; Li et al., 1995; Chang et al., 1996). Further studies have been conducted focusing on the partial oxidation of methane to liquid oxygenates (Bhatnager and Mallinson, 1995; Larkin et al., 1998) and the oxidative coupling of methane to higher hydrocarbons (Liu et al., 1996). The role of various catalysts in a nonequilibrium plasma environment is also being studied (Liu et al., 1997).

Experimental Studies

The entire reaction system is shown in Figure 1. This reactor is composed of two metal electrodes made from aluminum plates. A dielectric barrier made of glass covers one side of an aluminum plate. The thickness of the glass plate is 0.23 cm. A Teflon spacer is placed between the dielectric and the other aluminum plate around the periphery to create space for the gas to flow axially along the plates through the discharge zone and to seal the system. The active reaction volume for the electric discharge environment is approximately 200 cm^3 .

The back side of one aluminum plate is contacted with cooling water to absorb heat produced in the reaction zone. Cooling water temperatures between 10°C and 20°C are used in all of the runs to maintain a constant reaction temperature. Two type-K thermocouples are connected to the inlet and outlet cooling lines to measure any temperature change

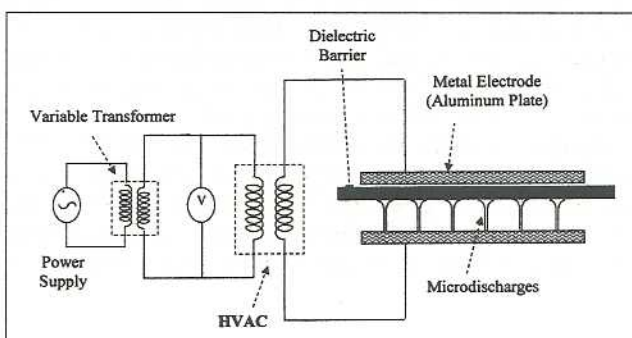


Figure 1. Power equipment and reactor system.

due to the discharge and reactions. However, no significant temperature change can be observed in the cooling water during the experiments, indicating little heat release from the reactor.

Wall current with a voltage of 220 V and a frequency of 50 Hz is sent through a step-down variable transformer that allows the voltage to be varied from 0 to 110 V (the frequency remained at 50 Hz). The output of this variable transformer is connected to a secondary high voltage AC (HVAC) transformer that has a voltage-multiplying factor of 125, developing voltages as high as 15 kV. The high-voltage lines from the HVAC transformer are connected to the reactor for the generation of electric discharges. A voltmeter is connected to the input electrodes of the HVAC transformer to measure the exact voltage supplied to it.

The volumetric flow rate of the gaseous stream both before and during the reaction is measured at the outlet of the reactor by soap bubble flow meters. Mass-flow controllers control individual gas-flow rates. Two liquid traps are placed downstream from the reactor before the gas chromatograph. Both liquid traps are maintained within a temperature range of -20 to -10°C using cool ethanol to collect any liquid products from the reactions. However, no liquid products can be observed when steady-state conditions are reached.

The gaseous product stream exiting the reactor is analyzed with a Perkin-Elmer "Autosystem" Gas Chromatograph. The mole fractions of the gaseous components in the product streams are quantitatively analyzed by correlating their concentrations to their component peak responses (peak area or height) derived from the gas chromatograms based on calibrations of known compositions.

To facilitate the calculations, the following assumptions are made: (1) The pressure in the system is approximately atmospheric ($1.0 \text{ atm} \pm 0.05 \text{ atm}$), and (2) The temperature change due to the reaction is very small and can be considered negligible. All experiments are carried out at ambient temperature ($25^{\circ}\text{C} \pm 5^{\circ}\text{C}$).

Results and Discussion

The first sets of experiments were conducted using a 20 mL/min pure methane feed stream. Product measurements were taken at applied voltages up to 11 kV with a constant frequency of 50 Hz. The feed flow rate was then raised to 40 mL/min and product measurements were made in the same applied voltage range. The effect of varying the applied voltage and total flow rates on methane conversion is illustrated in Figure 2. At both flow rates, the methane conversion is initiated at the same "breakdown" voltage and increases with increasing voltage. As total flow rate increases, however, the methane conversion is always lower because of the lower reactor residence time. As voltage increases, an apparent maximum conversion limit that is higher for longer residence times is approached.

When the external voltage, and consequently the internal electric field, applied across the discharge gap is increased, the density of high-energy electrons within the gap increases. The increase in the number of electrons discharged may result in a higher probability of breaking the bond between the carbon and hydrogen in the methane molecule and thus increase both the degree of methane dissociation and conver-

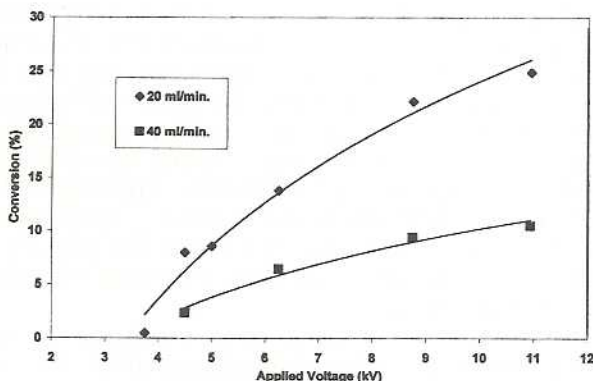


Figure 2. Effect of applied voltage on the methane conversion at two different flow rates.

Frequency = 50 Hz.

sion. Since the energy levels of the electrons that are produced in the field are not equal but rather distributed according to the electron energy distribution function (EEDF) described by the Boltzmann equation, only those collisions between methane molecules and those electrons that have a sufficiently high energy can result in the formation of an active species. When the residence time of the reaction is decreased, the probability that each methane molecule will successfully interact with any of the sufficiently energetic electrons also decreases. For the reactor geometry used in these experiments, the residence time is 10 min. for a flow rate of 20 mL/min and five minutes for a flow rate of 40 mL/min.

The distribution of the product selectivities for these reactions at the two flow rates is plotted vs. the applied voltage in Figure 3. In both cases, increasing the voltage has little effect on the selectivities. Since the yield is the product between the conversion and the selectivity, the yield of each product continues to increase with increasing voltage and conversion even though the selectivities for each product remain nearly constant. Ethane is the major product with smaller amounts of higher hydrocarbons. At longer residence times a higher average carbon number is observed with lower ethane selectivity and higher butane selectivity. Hydrogen formed from methane coupling inhibits olefin formation.

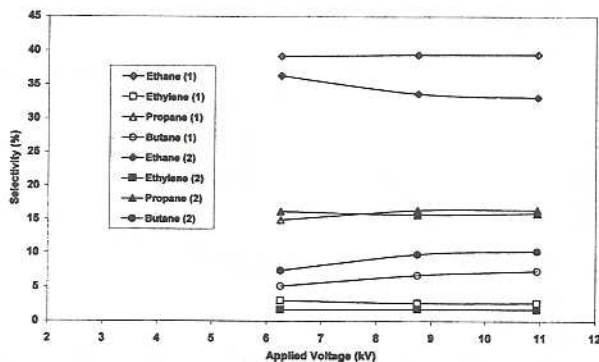


Figure 3. Distribution of product selectivities as a function of the applied voltage at two different flow rates.

(1) 20 mL/min. (2) 40 mL/min. Frequency = 50 Hz.

The leveling off of the methane conversion at higher voltage appears to be due to the establishment of a steady state between the production of C_2 hydrocarbons and their destruction that reforms methane. The substantial hydrogen production that occurs under these conditions may also affect this steady state conversion level. Although the carbon balance for this system closes to 90–99% depending on the methane conversion, the product selectivities systematically sum to substantially less than 1.0. This is due primarily to carbon formation and inadequate accounting of carbon species larger than C_4 .

The conversion and selectivities of this system are very different from those expected at higher temperatures. Mallinson et al. (1992) have shown, consistent with other researchers that little carbon-carbon bond formation is expected at high temperatures and atmospheric pressure under pyrolysis conditions (until very high temperatures, $> 1,000^\circ C$). Instead, cracking reactions dominate. The 900+ reaction model used in the study of Mallinson et al. was thermodynamically consistent at both temperatures and therefore reflects the thermodynamic limitation to chain building at low temperatures. In that modeling study, pyrolysis simulated at low temperatures ($200^\circ C$) did show chain building becoming significant, although this was a large extrapolation from any experimental kinetics results.

Following the experiments using pure methane as a feed, other species were added to the feed stream to determine the effect of third bodies on methane conversion and product selectivity. The initial tests involved adding helium to the methane feed stream. The feed stream first consisted of methane/helium at a 3:1 ratio with a flow rate of 20 mL/min. The applied voltages were varied between 0 and 6.5 kV at 50 Hz. The next set of experiments was conducted using a methane/helium ratio of 1:1 and then 3:1 with the same total flow rate. Figure 4 shows the influence of helium on the reaction of methane. In the case of a 3:1 feed ratio of methane to helium, the methane conversion does not change appreciably. When the methane to helium ratio is lowered to 1:1, however, the methane conversion is greatly enhanced. If helium does not exhibit an interactive effect within the discharge environment, it might be expected to serve only as a diluent and cause a decrease in the conversion by lowering the partial

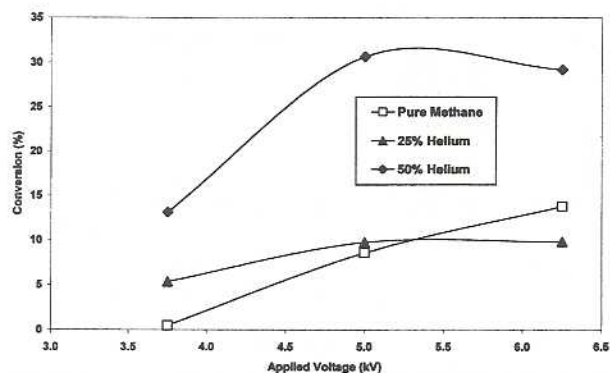


Figure 4. Effect of methane-to-helium ratio on methane conversion as a function of voltage.

Flow rate = 20 mL/min. Frequency = 50 Hz.

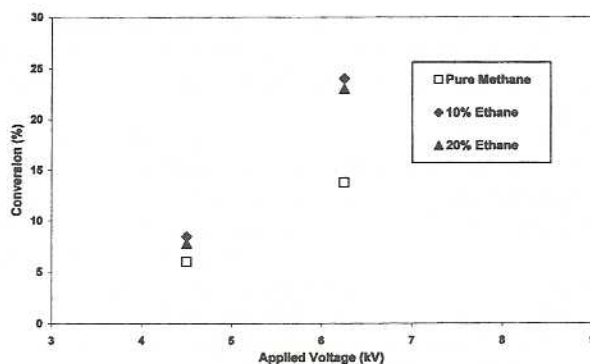


Figure 5. Effect of ethane concentration on the methane conversion at two different applied voltages.

Flow rate = 20 mL/min. Frequency = 50 Hz.

pressure of methane. These experimental results suggest that some of the helium is "activated" by the electric discharge and is able to successfully activate the methane molecules through a third body energy-transfer process. The presence of helium does not affect distributions of the product selectivities.

Next, ethane was added to the methane feed stream to determine its effect on the reaction. Initially, the feed stream consisted of ethane/methane with a 1:9 ratio and a flow rate of 20 mL/min. The applied voltages were again varied between 0 and 6.5 kV at a frequency of 50 Hz. The same experiments were also conducted using an ethane/methane ratio of 1:4. The effect of adding ethane to the feed on the conversion of methane is shown in Figure 5. The magnitude of the methane conversion for pure methane is also shown. From this figure, it can be seen that the presence of 10% or 20% ethane in the feed increases a methane conversion when compared to the case of pure methane. The single bond between the two carbon atoms in the ethane molecule is relatively weak compared to the carbon-hydrogen bond in methane. This suggests that the ethane molecules are activated by the electric discharge and these ethane-derived active species are able to activate methane more readily than those formed from methane itself. As the voltage increases, the methane conversion also increases in the presence of ethane. It is expected that ethane may also decompose to form methane using hydrogen from the dehydrogenation of ethane, thus limiting the obtainable increase in methane conversion.

The effect of the initial ethane concentration on the ethylene selectivity is plotted in Figure 6 along with the ethylene selectivity obtained from the case of pure methane. The coupling reactions forming C_2 – C_4 paraffins produce hydrogen. Due to the limitations of the analytical equipment, hydrogen was not measured at the time of these experiments, but later experiments verified substantial production of hydrogen. The production of hydrogen from coupling reactions is relatively small at low conversions and does not seem to affect the dehydrogenation rate of ethane. However, at high conversions the concentration of hydrogen becomes significant and may inhibit dehydrogenation. The trends shown in Figure 6 support this conclusion. The increase in ethylene selectivity with increasing initial ethane partial pressure points to a relation-

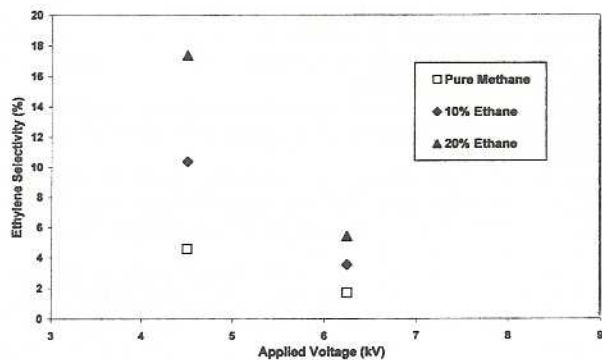


Figure 6. Effect of ethane concentration on the ethylene selectivity at two different applied voltages.

Flow rate = 20 mL/min. Frequency = 50 Hz.

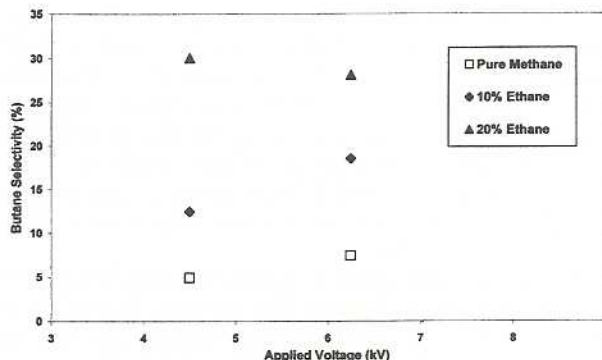


Figure 8. Effect of ethane concentration on the butane selectivity at two different applied voltages.

Flow rate = 20 mL/min. Frequency = 50 Hz.

ship between the dehydrogenation rate and the initial ethane concentration. Therefore, ethane dehydrogenation is favored over the cracking of ethane when the hydrogen partial pressure is low.

Figure 7 shows that an increase in the ethane concentration increases the selectivity for propane, probably by increasing the concentration of active C_1 and C_2 species available for coupling. Higher conversions of methane also increase the availability of active C_2 species. In this instance the propane selectivity decreases somewhat, possibly because of a greater probability for the production of C_4 species.

Figure 8 shows the butane selectivity plot at different levels of initial ethane concentration. The marked increase in butane selectivity observed can be explained with similar logic as that for propane selectivity. However, the probability of C_4 formation is lower than that for C_3 because it is generated primarily by the coupling of two C_2 species, which are present in much lower concentrations than the C_1 species. This means that the reactions to form C_2 and then C_3 species occur more frequently than those to form C_4 .

Another available pathway for the production of C_4 species is the coupling reaction between C_3 and C_1 molecules. Significant levels of C_4 paraffins are present in the product

stream, while propylene and higher olefins are not observed in any measurable quantity. The results suggest that both the combination of unsaturated C_2 species and the dehydrogenation of $C_3 +$ paraffins occur in small amounts.

Figure 9 shows the ethane concentration in the reactor outlet stream as a function of the applied voltage. This plot indicates a decrease in the ethane concentration as the voltage is increased, showing that net ethane consumption occurs in the reactor and is attributable to both cracking and carbon chain-building reactions.

Conclusions

In the present study, a dielectric-barrier discharge (DBD) reactor exhibited a feasible means of activating methane molecules for initiating conversion to higher hydrocarbons. Increasing the external voltage supplied to the reactor increased the density of the electrons. This in turn increased the rate of methane-molecule activation and coupling to higher hydrocarbons, primarily alkanes with hydrogen formation. Decreases in the reactor residence time reduce the probability of a methane molecule interacting with electrons that have sufficiently high energy for activation and result in a drop in methane conversion.

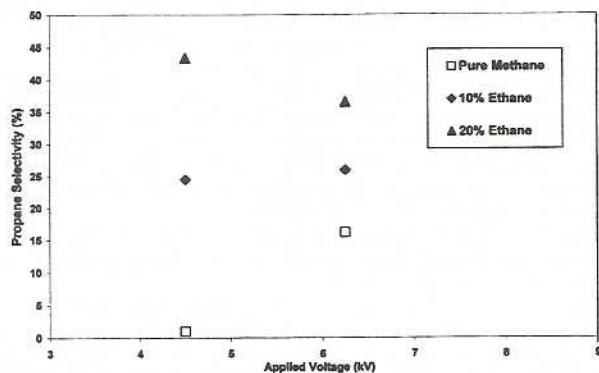


Figure 7. Effect of ethane concentration on the propane selectivity at two different applied voltages.

Flow rate = 20 mL/min. Frequency = 50 Hz.

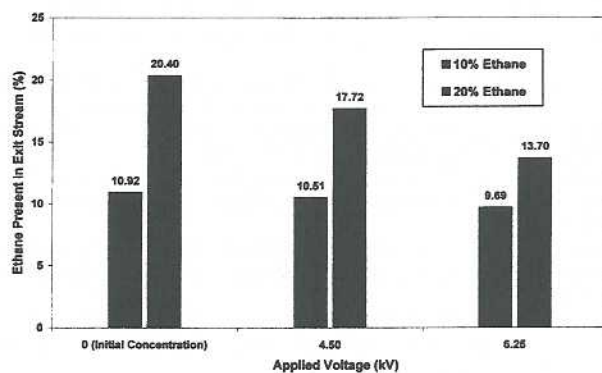


Figure 9. Variation in the ethane concentration as a function of the applied voltages.

Flow rate = 20 mL/min. Frequency = 50 Hz.

The products from this methane plasma reaction include ethane, propane, butane, ethylene, isobutane, and hydrogen (although H₂ was not quantified). Since the commercial value of these products is higher than methane, a process based on these phenomena could enhance methane upgrading without the production of carbon oxides. Although methane conversion was significantly affected by the applied voltage in this study, the selectivities of the products formed were nearly independent of voltage.

The formation of propane is thought to occur via the direct coupling of C₁ and C₂ species. The pathways leading to butane formation are believed to be the coupling of C₁ species with C₃ species and the coupling of C₂ species. The cracking reactions of the desired higher hydrocarbon products into smaller molecules were also possible under this discharge environment. The degree of decomposition increased with increasing voltage. Few olefins are produced because the presence of hydrogen generated by carbon chain building hinders dehydrogenation, but olefins are significant products when hydrogen is limited.

Helium has a synergistic effect and enhances the reaction of methane when present in significant quantities. The presence of ethane with methane in the feed also improved methane conversion. In this case, the selectivities of ethylene, propane, and butane also increased significantly.

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