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Plasma-Induced Conversion of Surface-Adsorbed Hydrocarbons

Authors:

Sackinger, W.M.

Contractor:

University of Alaska
Geophysical Institute
Fairbanks, Alaska 99775-0800

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ABSTRACT

Experimental results are reported for an electrical device for direct conversion of methane into higher hydrocarbons. A microchannel plate is excited with electrons from a photoemissive source, and electron impact ionization of methane on the inner surfaces of the microchannels creates an ion feedback process. The resulting low-density plasma creates higher hydrocarbons when charged particles impact the surfaces at grazing incidence. The production of C₂ to C₈-containing gases was noted, with a selectivity for C₂ of 39% in one case. The proportions of converted products and the conversion rates depend upon the electrical voltage, the microchannel geometry, and the operating pressure. Conversion rates increase with operating pressure.

I. Introduction.

Experiments have been conducted which make use of a partially-ionized, low density plasma, together with an electric field and an array of tubes, to convert methane into higher hydrocarbons and hydrogen. The device, described by Sackinger (1989; 1991), is based upon the microchannel plate (MCP), which has been used for electronic image intensification for three decades. The principles of the device operation are briefly described below, after which the experimental results are given in some detail.

II. Principles of Operation.

In Figure 1a, a single long tube is shown, on the inside surface of which methane molecules are absorbed from the ambient partial pressure of methane, in the range 0.4 Pa to 100 Pa or more. Electron flow is possible without a significant number of electron/neutral collisions in the volume above the surface. Electrons are generated from a suitable photoemissive or thermionic source outside of the tube, and are accelerated with a low voltage (10 v. to 150 v.) towards the end of the tube, where they strike the interior walls at grazing incidence and produce secondary electrons, ions, and other products. A charge balance is made possible by a semiconductor layer (typically with a resistivity of 10^{12} to 10^{14} Ω /square) on or just beneath the surface. An external voltage (e.g., 800 volts) is connected from the entry end to the exit end of the tube, causing a small current (e.g., 5.1×10^{-12} amperes) to flow in the semi-conductor layer. An operating power of $4. \times 10^{-9}$ to 4×10^{-11} watts/channel is typical. Secondary electrons cascade along the tube, acquiring energy from the electric field and striking the walls farther down the tube, where more electrons and ions are generated from their surface impact. The device functions as an electron multiplier at very low ambient gas pressures. More than 1 million such tubes, each about 12 micrometers in diameter, are fused together in a microchannel plate. The voltage connections are shown in Figure 1b.

The presence of adsorbed methane at the electron impact sites leads to the reduction of neutral methane, with some level of probability, and in a fraction of such cases, electron-stimulated desorption of hydrogen ions and methyl ions takes place. Positively-charged hydrogen ions thus generated have been known to provide an ionic feedback in channel multipliers (Sackinger and Gislason, 1972). Having acquired energy from the electric field, the ions strike the surface where they are quite effective in producing local dimerization of adsorbed gas species, as well as stimulating the emission of neutrals, ions, and electrons from their impact site. Thus, a cascading process ensues, which has been initiated by electrons, but which is dominated by ion flow, surface

Figure 1a. Electronic conversion of methane by electron-impact reduction, electron-stimulated desorption of ions, and ion-impact-stimulated chemical combination and desorption at inside surface of a single tubular microchannel.

(Sackinger 1989)

Figure 1b. Electrical circuit arrangement for methane conversion using microchannel plate (MCP) channel array.

impacts, and emission at impact sites. One of the effects is chemical conversion of methane to higher hydrocarbons at the impact sites.

Conversion of methane to higher hydrocarbons in the volume of r.f.-discharges has been described by Tachibana et al. (1984). However, the probability of collision of two methyl ions, or of a methyl ion and a methane neutral, is low. The production of C₁, C₂, and C₃ gases from the hydrogen ion bombardment of graphite is also widely known (Roth, 1983). The emission of hydrocarbons containing at least 12 carbon atoms has been reported by deVries et al., (1984) who bombarded frozen methane with hydrogen ions of 6 keV energy. Since the reduction of the methane to elemental carbon in the above device is a competing process, it is of interest to note that the yield of carbon-containing gaseous products per incident hydrogen ion is quite high (Yamada, 1987), and that a high flux of hydrogen ions should deplete carbon deposits rather than allow their buildup. Mixed carbon/hydrogen deposits have been noted in experiments attempting to deposit diamond thin films, and such deposits are also likely to yield gaseous products when bombarded with hydrogen ions.

The probability of ejection of surface-adsorbed molecules has been treated theoretically by Fenyö, Sundqvist, Karlsson and Johnson (1990) who regard the volume of ejected material as resulting from the conversion of incident ion energy into an expansion of the cluster of molecules at the impact site (Figure 2). They used molecular dynamic models to find yield, and angular and velocity distributions. Large organic molecules can be transferred to the gas phase in this way (Jonsson et al., 1989). Both charged and neutral species can be ejected from the surface. There is also a tendency for the energy of the ionic impacts to cause preferential formation of C-C bonds in some cases (Johnson and Sundqvist, 1992).

Our understanding of the process is still incomplete, and the role of methyl ions in promoting the formation of C-C bonds upon impact is not fully understood. Nevertheless, the essential principle of operation is the use of energetic ion impact to cause localized, instantaneous chemical changes and material ejection. The microchannel plate material, typically a SiO₂/Al₂O₃/PbO glass, will participate in the reaction if gas pressures are low, but has only a minor presence in the output product spectrum when gas pressures are higher, in the case where methane is the most common surface adsorbate and is quickly replenished on the surface, once used. At highest pressures, however, the volume interaction of the electrons and ions in the plasma above the surface is expected to impair their acquisition of energy from the electric field. Moreover, entry of methane into small microchannels is limited by channel size, and the optimum diameter for the microchannels remains to be determined.

Figure 2. Molecular dynamics model theoretical results (Fenyő et al., 1990) illustrating ejection of neutral molecules after ion impact upon a surface. The impact region is shown 0, 30, and 60 picoseconds after the expansion of the molecules in the ion track. Expanded and nonexpanded molecules are shown as solid and open circles, respectively.

III. Experimental Program.

Methane conversion experiments were conducted at The Blackett Laboratory, Imperial College, London, with a demountable, stainless steel, ultra high vacuum (UHV) system. The schematic diagram of the experimental apparatus is shown in Figure 3. It consisted of the following major components:

- 1) An image tube body containing a microchannel plate assembly (MCP), a gold photocathode, a phosphor screen, and electrical feedthroughs.
- 2) A high voltage power supply
- 3) An ammeter
- 4) A capacitance gauge
- 5) An ultraviolet light source
- 6) A large VacIon pump with UHV valve and ion gauge
- 7) A gas leak valve for gas injection
- 8) A small VacIon pump connected to mass spectrometer
- 9) A VacSorb pump
- 10) A mass spectrometer assembly.

An image tube body was used to hold the MCP assembly and a glass plate coated with a phosphor screen, within a large stainless steel tee-section. The quartz window with a graded seal was on one side of the flange of the tee-section. On the other flange, the image tube body was mounted. The flange consisted of four electrical feedthroughs and support rods. The MCP assembly was positioned between the phosphor screen and the gold photocathode. In the first sequence of experiments, at low pressure, the MCP assembly consisted of a single MCP. Higher-pressure experiments used 3 MCP's connected in series. Each MCP consisted of approximately 1.35 million channels, with 12 micrometer channel diameters and 40 diameters of channel length.

The initial system was designed to operate at ultra low pressures, between 1.4×10^{-7} (Pa) and 1.0×10^{-6} (Pa). The system was later modified to operate at higher pressures between 1.4×10^{-7} (Pa) to 100 (Pa) or more. For the high pressure experiments, the system was modified so that the mass spectrometer was separately pumped and was isolated from the test chamber by a low-conductance leak valve. A large VacIon pump with a pumping speed of 80 (litres/sec) was used to achieve ultra high vacuum in the MCP chamber when needed, between experiments. The pump could be isolated during each batch conversion experiment. A highly-accurate capacitance gauge with a range of 0.01 to 100 (Pa) was used to measure pressures during each high-pressure conversion experiment. A UV source was used to excite the thin-film gold cathode to produce electrons, which were then accelerated into the MCP by the electric field. A

Figure 3: Schematic Diagram of Ultra High Vacuum System Containing Microchannel Plate
Used for Methane Conversion

high voltage power supply capable of generating up to 3600 volts was connected to the electrical feedthroughs as shown in Figure 3. It was possible to apply three different separate voltages across the three different regions of the image tube body using this supply. A microammeter was used to measure input and output currents to and from the MCP.

The VacSorb pump was connected to the gas injection line and was used to pump down the system from ambient pressure to an intermediate vacuum level. A gas leak valve was used to inject gases from a gas cylinder into the system. A mass spectrometer assembly with a display screen, and a printer/plotter along with a data acquisition system was used for acquiring mass spectral data during the conversion process.

Prior to the start of conversion experiments, several precautionary and calibration steps were followed which included:

- 1) Bake out the system overnight at 250°C for wall outgassing
- 2) Helium leak tests to ensure that there were no leaks at flanges and joints
- 3) Electron scrubbing of the MCP to remove gas adsorbed from the atmosphere
- 4) Measurement of the resistance of the MCP (116×10^6 ohms)
- 5) Voltage-current relationship for the photocathode to MCP (Region I)
- 6) Calibration of UV filters for varying input current to MCP if needed
- 7) Measurement of electron gain of MCP at different voltages
- 8) Calibration of MS system
- 9) Measurement of conductance of leak valve.

Conversion experiments were conducted in both continuous and batch mode; while the continuous process is a more typical way of operating the device, the batch process provides more insight into kinetic aspects of conversion processes.

In a continuous process, the VacIon pump continuously pumped the system. After scanning and recording the background gas spectrum, methane was admitted continuously to the system by opening the leak valve. The position of the leak valve was adjusted to control the rate of methane injection and to set the desired pressure level in the system. The spectrum after pressure stabilization was recorded. The conversion experiments were then started by applying an electric field to all three regions (MCP, phosphor screen, and gold photo cathode) and turning the UV source on. The changes in the mass spectra with time were then recorded during the entire conversion experiment. After completion of the experiment, the gas leak valve was shut off and the gases were pumped back out of the system by the VacIon pump.

Initially, several continuous methane injection-conversion experiments were conducted to qualitatively identify the effect of process variables on methane conversion. The objectives of these experiments were as follows:

- 1) To identify the effect of pressure level on conversion;
- 2) To confirm that conversions were taking place in the MCP, by turning the UV light source on and off;
- 3) To identify the effect of the voltage on the MCP (V_2) on the conversion;
- 4) To identify the effect of changing voltages, and of retarding voltage, in the phosphor screen-MCP region (V_3);
- 5) To identify the effect of changing voltages in the cathode-MCP region (V_1).

In the batch experiments, the initial conditions were: a thoroughly pumped system at the ultra-high vacuum level (1.3×10^{-10} kPa) and no electric field applied to the MCP. The VacIon Pump was then isolated from the system and the residual gas background-spectrum recorded. Gas was injected into the main chamber through the leak valve and then that valve was closed after the desired pressure level was reached. The background methane spectrum was then recorded. The conversion process was then started by applying voltage to all these regions and turning the UV light source on. The mass spectra were recorded very frequently for accurate tracking of the kinetics of the conversion process. Many batch methane conversion experiments were conducted at various pressure levels (2.6×10^{-7} kPa - 1.3×10^{-1} kPa) and different MCP voltages (3 - 22.5 volts/diameter). In addition to methane (CH_4), higher hydrocarbons such as: deuterated methane (CD_4); isotopic methane ($^{13}\text{CH}_4$); deuterated ethane (C_2D_6); and deuterated propylene (C_3D_6) were also used for conversion in order to provide further insight into the conversion processes. Table 1 shows the summary of experimental settings for all conversion experiments.

DATA ANALYSIS AND RESULTS

For acquisition of mass spectral data, the bar charts of the mass spectra at various times during an experiment were stored into the hard disc of the computer. These bar charts were then converted to digital mass partial pressures, for 1-100 a.m.u., using special software. A separate computer program was then developed to convert the mass partial pressure data into gas component partial pressure data. The program uses mass partial pressure data and published fragmentation patterns for 127 different hydrocarbon gas species (Stenhagen et al., 1974; Cornu, 1975) as references, and determines the gas compositional analysis.

TABLE 1: Summary of Experimental Settings for Conversion Experiment

Experiment Number	Gas Used As Input	Process Type	Pressure (kPa)	Voltage (V ₁)	Voltage (V ₂)	Voltage (V ₃)	Duration (Hrs)	Remarks
1	¹² CH ₄	Continuous	2.60×10^{-9}	500	832	3500	short	Qualitative
2	¹² CH ₄	Continuous	6.00×10^{-9}	500	800	3500	short	Qualitative
3	¹² CH ₄	Continuous	6.65×10^{-9}	500	800	3500	short	Qualitative
4	¹² CH ₄	Continuous	2.00×10^{-9}	500	750 - 950	215	short	Qualitative
5	¹² CH ₄	Continuous	2.80×10^{-9}	0	0 - 1000	0	short	Qualitative
6	¹² CH ₄	Continuous	2.90×10^{-9}	0-500	1000	3500	short	Qualitative
7	¹² CH ₄	Continuous	2.90×10^{-9}	500	1000	0-3500	short	Qualitative
8	¹² CD ₄	Continuous	3.20×10^{-9}	500	800	0	short	Qualitative
9	¹² CD ₄	Continuous	3.20×10^{-9}	500	800	0 to -33	short	Qualitative
10	¹² CD ₄	Continuous	3.20×10^{-9}	500	800 - 950	4.80	short	Qualitative
11	¹² CD ₄	Continuous	2.40×10^{-8}	500	950	4.63	short	Qualitative
12	¹² CD ₄	Continuous	3.3×10^{-10} to 9.30×10^{-9}	500	950	28.3	short	Qualitative
13	¹² CD ₄	Continuous	4.00×10^{-10}	500	950	28.30	short	Qualitative
14	¹² CD ₄	Batch	9.30×10^{-8}	500	950	28.30	2.13	Quantitative
15	¹² CD ₄	Batch	2.86×10^{-6}	500	950	28.30	1.13	Quantitative
16	¹² CD ₄	Batch	2.86×10^{-6}	20	600	-6.30	1.40	Quantitative
17	¹² CD ₄	Batch	2.86×10^{-6}	500	800	22.90	1.55	Quantitative
18	¹² CD ₄	Batch	2.86×10^{-6}	20	500	-6.60	2.13	Quantitative
19	¹² CH ₄	Batch	2.60×10^{-7}	20	500	-6.60	1.30	Quantitative
20	¹² CD ₄	Batch	2.60×10^{-7}	20	500	-6.60	2.30	Quantitative
21	¹² CH ₄	Batch	1.74×10^{-3}	30	500 - 1150	0	7.50	Quantitative
22	¹² CH ₄	Batch	1.13×10^{-1}	30	variable	0	2.38	Quantitative
23	¹² C ₂ D ₆	Batch	1.30×10^{-1}	30	variable	0	2.58	Quantitative
24	¹² C ₃ D ₆	Batch	1.35×10^{-1}	30	variable	0	2.85	Quantitative
25	¹³ CH ₄	Batch	7.80×10^{-2}	30	variable	0	5.72	Quantitative
26	¹³ CH ₄	Batch	8.96×10^{-2}	30	variable	0	17.24	Quantitative
27	¹³ CH ₄	Batch	1.20×10^{-1}	30	480	0	2.62	Quantitative
28	¹³ CH ₄	Batch	3.88×10^{-3}	30	600	0	19.83	Quantitative
29	¹³ CH ₄	Batch	1.02×10^{-3}	30	1020	0	3.11	Quantitative
30	¹³ CH ₄	Batch	6.90×10^{-4}	30	1000	0	17.0	Quantitative
31	¹³ CH ₄	Batch	4.00×10^{-4}	30	1500	0	20.67	Quantitative
32	¹³ CH ₄	Batch	7.85×10^{-4}	30	0	0	0.12	Quantitative
33	¹³ CH ₄ + C ₆ D ₆	Batch	2.85×10^{-4}	30	1500	0	17.41	Quantitative
34	¹³ CH ₄	Batch	3.46×10^{-4}	30	1000	0	20.16	Quantitative
35	¹³ CH ₄	Batch	1.35×10^{-4}	30	1800	0	12.46	Quantitative
36	C ₃ D ₆	Batch	3.20×10^{-4}	30	840	0	25.00	Quantitative

In this paper, the results of the detailed analysis for three batch methane conversion experiments are presented.

Electron-Impact-Driven Methane Conversion at Ultra Low Pressure

In this experiment (Experiment A), which corresponds to Experiment 19 in Table 1, ultra pure methane (99.95% purity) was used for batch conversion to higher hydrocarbons. The average pressure during the experiment was at ultra low levels (2.6×10^{-7} kPa). At such low pressures, the conversion process is predominantly driven by the impact of electrons with the neutral methane molecules absorbed on the walls of the channel. The voltage across the MCP (V_2) was 500 volts (or 12.5 volts/diameter). The voltage between the photocathode and MCP (V_1) was maintained at 20 volts and the voltage from MCP to collector (V_3) was -6.56 volts. The strip current in the MCP was at 4.5×10^{-6} (amps) while the current to collector was at zero, in order to prevent the burial of generated ions into the phosphor screen. The power requirements were 2.25×10^{-3} (watts).

Since the walls outgas at a rate which can be significant at such low pressures, and which will affect the mass spectra, it was necessary to conduct a separate experiment to determine the rate of wall outgassing so that wall outgassing effects can be accounted for properly. In Table 2, the experimentally-determined rate of wall outgassing is given for the various gas species. The literature (Weston, 1985) suggests that moderately-baked stainless steel systems outgas at rates in the range of 2.7×10^{-11} to 2.7×10^{-13} (gmole/sec-cm²), whereas highly-baked systems outgas at a rate of about 2.7×10^{-19} (gmole/sec-cm²). In our system the measured outgassing rate was 4×10^{-20} (gmole/sec-cm²).

In Table 3, the calculated partial pressures of various hydrocarbon gases are provided, for the starting time of the conversion process ($t = 9$ minutes) and the ending time of the conversion process ($t = 78$ minutes). In this experiment the percentage conversion of methane in 69 minutes was about 78.6%, which was converted to deuterated methane (CD₃H), ethane (C₂H₆), deuterated ethane (C₂H₅D), and small quantities of propylene (C₃H₆). The selectivity values in Table 3 represent the percentage of methane converted to various hydrocarbons. In this particular experiment, there was also significant production of CO which might have resulted from the oxygen from the glass surface of the MCP. Because of the low pressure chosen, the rate of methane conversion was very low at 9.33×10^{-15} (gmole/sec.).

TABLE 2: Rate of wall Outgassing For Various Species in Ultra High Vacuum

Species	Partial Pressure at t = 0 (kPa)	Partial Pressure at t = 15 min (kPa)	Wall Outgassing Rate (Gmole/sec cm ²)
H ₂	3.38 x 10 ⁻¹⁰	3.60 x 10 ⁻⁹	2.18 x 10 ⁻²¹
HD	1.22 x 10 ⁻¹⁰	1.49 x 10 ⁻⁹	9.03 x 10 ⁻²²
D ₂	5.52 x 10 ⁻¹¹	2.69 x 10 ⁻¹⁰	1.41 x 10 ⁻²²
CH ₄	2.54 x 10 ⁻¹²	1.59 x 10 ⁻⁹	1.05 x 10 ⁻²¹
H ₂ O	7.80 x 10 ⁻¹³	1.87 x 10 ⁻¹⁰	1.23 x 10 ⁻²²
CD ₃ H	2.24 x 10 ⁻¹¹	2.84 x 10 ⁻¹⁰	1.72 x 10 ⁻²²
CD ₄	1.25 x 10 ⁻¹¹	2.00 x 10 ⁻¹⁰	1.24 x 10 ⁻²²
CO	1.14 x 10 ⁻¹¹	2.33 x 10 ⁻⁸	1.53 x 10 ⁻²⁰
N ₂	5.86 x 10 ⁻¹¹	2.74 x 10 ⁻⁸	1.80 x 10 ⁻²⁰
C ₂ H ₆	7.80 x 10 ⁻¹²	2.79 x 10 ⁻¹⁰	1.78 x 10 ⁻²²
C ₂ H ₅ D	8.60 x 10 ⁻¹²	1.07 x 10 ⁻⁹	7.01 x 10 ⁻²²
Ar	3.63 x 10 ⁻¹²	9.07 x 10 ⁻¹⁰	5.94 x 10 ⁻²²
CO ₂	1.60 x 10 ⁻¹¹	1.00 x 10 ⁻⁹	6.47 x 10 ⁻²²
O ₂	3.75 x 10 ⁻¹²	1.39 x 10 ⁻¹⁰	8.91 x 10 ⁻²³

**TABLE 3: Summary of Methane Conversion Experiment A
(Ultra-Low-Pressure Electron Impact Driven Conversion)
(P = 2.6 x 10⁻⁷ kPa)**

Component	Partial Pressure at Start (kPa)	Initial Mole% Species	Final Partial Pressure (kPa)	Final Mole% Species	Conversion Rate * (Gmole/sec)	Selectivity (%)
CH ₄	2.97 x 10 ⁻⁸	25.41	6.36 x 10 ⁻⁹	1.57	-9.33 x 10 ⁻¹⁵	-
CD ₃ H	4.54 x 10 ⁻⁹	3.88	1.14 x 10 ⁻⁸	2.82	2.74 x 10 ⁻¹⁵	23.54
C ₂ H ₂	0	0	0	0	-	-
C ₂ H ₄	0	0	0	0	-	-
C ₂ H ₆	1.95 x 10 ⁻⁹	1.67	1.22 x 10 ⁻⁸	3.02	4.09 x 10 ⁻¹⁵	70.27
C ₂ H ₅ D	3.23 x 10 ⁻⁹	2.76	4.13 x 10 ⁻⁹	1.02	3.60 x 10 ⁻¹⁶	6.18
C ₃ H ₆	8.97 x 10 ⁻¹¹	0.08	9.07 x 10 ⁻¹¹	0.02	4.00 x 10 ⁻¹⁹	-
C ₃ H ₈	2.21 x 10 ⁻⁹	1.89	2.21 x 10 ⁻⁹	0.55	0	-

* Minus Sign Indicates Consumption

Ion-Impact-Driven Methane Conversion at Intermediate Pressure

In this experiment (Experiment B), which corresponds to Experiment 31 in Table 1, ultra-pure isotopic methane ($^{13}\text{CH}_4$) was used for batch conversion to higher hydrocarbons. The system used 3 MCP's in cascade with each MCP having nominal 12 micrometer channel diameter and 40:1 length to diameter ratio. The average system pressure was in the intermediate range at 4×10^{-4} (kPa); this was below the pressure-voltage threshold for the initiation of a glow discharge. The applied voltage across the three MCP's (V_2) was 1500 volts (a normalized field strength of 12.5 volts/diameter), and from photocathode to the MCP the voltage (V_1) was 20 volts. The resistive strip current in the MCP was 5×10^{-6} amperes. In Table 4, the partial pressure of the several gas species is given at the start of the conversion experiment ($t = 91$ min) and at the end of the conversion experiment ($t = 1323$ min).

**TABLE 4: Partial Pressures of Various Gas Species
for Isotopic Methane ($^{13}\text{CH}_4$) Conversion Experiment B
(Ion-Impact-Driven Conversion)
($P = 4 \times 10^{-4}$ kPa)**

Component	Initial Partial Pressure (kPa)	Final Partial Pressure (kPa)	Component	Initial Partial Pressure (kPa)	Final Partial Pressure (kPa)
H ₂	7.35×10^{-10}	8.92×10^{-5}	CD ₄	1.31×10^{-7}	1.72×10^{-8}
HD	3.12×10^{-12}	1.09×10^{-6}	C ₂ H ₂	2.09×10^{-5}	3.45×10^{-5}
D ₂	4.45×10^{-12}	1.69×10^{-6}	C ₂ H ₄	3.04×10^{-6}	1.61×10^{-5}
H ₂ O	1.07×10^{-11}	1.41×10^{-11}	C ₂ H ₆ (*)	2.62×10^{-13}	1.28×10^{-5}
HDO	5.47×10^{-13}	2.84×10^{-13}	C ₂ D ₆	1.11×10^{-7}	5.95×10^{-7}
Ne	1.72×10^{-12}	1.76×10^{-12}	C ₃ H ₆ (*)	1.28×10^{-7}	1.69×10^{-6}
N ₂	3.85×10^{-12}	3.70×10^{-12}	C ₃ H ₈	8.29×10^{-14}	1.33×10^{-8}
O ₂	1.02×10^{-12}	9.83×10^{-13}	C ₄ H ₆	7.87×10^{-7}	9.18×10^{-7}
HCl	2.78×10^{-7}	2.11×10^{-6}	C ₄ H ₁₀	5.26×10^{-7}	8.16×10^{-7}
Ar	4.58×10^{-12}	4.97×10^{-12}	C ₅ H ₈	0	7.42×10^{-8}
CO	6.01×10^{-6}	1.24×10^{-5}	C ₆ H ₆ (*)	8.33×10^{-8}	4.33×10^{-7}
CO ₂ (*)	3.48×10^{-12}	3.48×10^{-12}	C ₇ H ₁₄	1.20×10^{-7}	1.23×10^{-7}
CH ₄ (*)	2.61×10^{-6}	8.08×10^{-8}	Total	3.6×10^{-4}	4.4×10^{-4}
CH ₄	3.24×10^{-4}	2.62×10^{-4}			

* Denotes ^{12}C Compounds

In Figure 4, the evolution of mass spectra with time is shown at $t = 91$ minutes (4a), $t = 311$ min (4b) and $t = 1323$ min (4c). The bar charts in Figure 4 represent mass partial pressures in Torr on a logarithmic scale, displayed versus mass number. The formation of higher hydrocarbons is very evident from the continuous growth of masses above 24. In this experiment the pressures were in an intermediate-range which was expected to convert methane into higher hydrocarbons by impact of ions with neutral methane molecules adsorbed on the surface of the channels. Types of hydrocarbons formed include acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), deuterated ethane (C_2D_6), propylene (C_3H_6), propane (C_3H_8), 1-butyne (C_4H_6), butane (C_4H_{10}), 2-3 pentadiene (C_5H_8), and 1-heptene (C_7H_{14}). The formation of ^{12}C -containing compounds is evidence of the residue of either ^{12}C or ^{12}C -hydrocarbons from previous experiments; similarly, the deuterated hydrocarbon formation arises from the residue of deuterated methane and deuterium from previous experiments. The rates of conversion and selectivity of the conversion of methane to the several higher hydrocarbons is given in Table 5. In Figure 5, a plot of ratios of mole fractions of various hydrocarbons to methane is shown as a function of time. The dominant products of the conversion process are C_2 and C_3 hydrocarbons whereas C_4 to C_7 hydrocarbons show relatively lower rates of formation. Since C_2 and C_3 creation involves a sequence of only 1 and 2 interactions, whereas C_4 requires 2 to 4 interactions and C_7 requires at least 5 interactions, this is to be expected.

Methane Conversion with Low-Density Plasma Glow Discharge at Moderate Pressure

In this experiment (Experiment C), which corresponds to Experiment 22 in Table 1, ultra-pure methane was used for batch conversion of methane to higher hydrocarbons. The system used 3 MCP's in cascade as in Experiment B. The pressure for this experiment was moderate, at 0.113 (kPa). At this pressure, a glow discharge was initiated between the fixture and the chamber walls for MCP voltages above 360 volts. The power supply was constructed so that the appearance of higher currents caused a rapid drop in voltage, which extinguished the glow discharge. The voltage then increased and the cycle repeated. Thus the voltage and current in this experiment varied with time. A separate experiment was conducted later, involving only a glow discharge between the fixture and the wall of the chamber, and negligible conversion of methane to higher hydrocarbons was observed. The main products were hydrogen and carbon deposits.

Figure 4: Evolution of Mass Spectra with Time for Isotopic Methane Conversion Experiment B (Plots Show Mass Partial Pressure Versus Mass Number) ($P = 4 \times 10^{-4} \text{ kPa}$).

**TABLE 5: Selectivity and Rates of Conversion of Methane
to Various Hydrocarbons for Experiment B
(P = 4×10^{-4} kPa)**

Hydrocarbon	Rate of Conversion* (Gmole/sec)	Selectivity (%)
C ₁	-1.65 x 10 ⁻¹²	-
C ₂	+5.67 x 10 ⁻¹³	85.62
C ₃	+3.30 x 10 ⁻¹⁴	7.48
C ₄	+8.80 x 10 ⁻¹⁵	2.66
C ₅	+1.55 x 10 ⁻¹⁵	0.59
C ₆	+7.32 x 10 ⁻¹⁵	3.32
C ₇	+6.32 x 10 ⁻¹⁶	0.33

* Minus sign indicates consumption

Figure 5: Ratio of Mole Fractions of Hydrocarbons for Experiment B
($P = 4 \times 10^{-4}$ kPa)

In Figure 6, the evolution of mass spectra with time for Experiment C is shown, indicating the significant continuous production of higher hydrocarbons. The production of C₂ to C₈ hydrocarbons occurred. Since the mass spectrometer measured mass partial pressures only up to 100 a.m.u., it was not possible to definitively detect hydrocarbons higher than carbon #8 (C₈) if they had formed during the conversion experiment. In Figure 6, the spectra at t = 0 min (background), t = 39 minute (methane injection point), t = 95, 130, 170, and 203 minutes are shown. The experiment was terminated at t = 203 min. In Table 6, the initial and final partial pressures are given of 32 different gaseous components. The rate of methane conversion was very high in this experiment, at 4.9×10^{-9} (gmole/sec), compared to experiments at lower pressures. The types of hydrocarbons produced from methane conversion included: acetylene (C₂H₂); ethylene (C₂H₄); ethane (C₂H₆); propyne (C₃H₄); propane (C₃H₈); diacetylene (C₄H₂); 1-butene-3-yne (C₄H₄); 2-butyne (C₄H₆); butane (C₄H₁₀); 2-methyl-1-butene-3-yne (C₅H₆); 2-3 pentadiene (C₅H₈); pentene (C₅H₁₀); 1-hexyne (C₆H₁₀); hexane (C₆H₁₄); 1-heptyne (C₇H₁₂); and octene (C₈H₁₆). Thus, mostly saturated (paraffins) and unsaturated (olefins) were formed, with the first aromatic (C₆H₆), benzene.

The selectivity and rates of conversion of methane to the various hydrocarbons are shown in Table 7. In that table, selectivity of methane to the hydrocarbons ranges from 39.4% for C₂ hydrocarbons, to 15.7% for C₈ hydrocarbons. In Figure 7, plots of the ratio of mole fractions of the various hydrocarbons to methane are shown as a function of time. It is very clear that all hydrocarbons show continuous growth with time although the rate of formation decreases with time, as would be expected in a batch experiment in which the available methane supply is decreasing with time..

In Table 8, the comparison is given of three methane conversion experiments from ultra low pressure (2.6×10^{-7} kPa) to moderate pressure (0.113 kPa). The results show significant enhancement in the rate of conversion with increase in pressure, as shown in Figure 8. This is attributed to the ion impact positive feedback which accelerates the conversion process as pressure increases.

The improvement in rate at this pressure (1.13×10^{-1} kPa) indicates that it may be possible to go to even higher pressures to increase conversion rate.

Figure 6: Evolution of Mass Spectra with Time During Batch Methane Conversion Experiment C (Plots Show Mass Partial pressure on Log Scale Versus Mass Number). ($P = 0.113$ kPa).

**TABLE 6: Partial Pressures of Various Gas Species
for Methane Conversion Experiment C
(Plasma-Induced Conversion with Intermittent Glow Discharge)
(P = 0.113 kPa)**

Component	Initial Partial Pressure (kPa)	Final Partial Pressure (kPa)	Component	Initial Partial Pressure (kPa)	Final Partial Pressure (kPa)
H ₂	1.6477×10^{-2}	2.7458×10^{-2}	C ₃ H ₄	0	2.8211×10^{-4}
HD	1.2346×10^{-5}	1.9330×10^{-5}	C ₃ H ₈	1.6025×10^{-4}	9.2152×10^{-4}
D ₂	8.3540×10^{-4}	1.1039×10^{-3}	C ₄ H ₂	9.0260×10^{-6}	6.3730×10^{-5}
N ₂	2.0532×10^{-10}	1.7199×10^{-10}	C ₄ H ₄	9.1730×10^{-6}	7.8530×10^{-5}
H ₂ O	8.3300×10^{-4}	5.3466×10^{-3}	C ₄ H ₆	1.2052×10^{-5}	7.6530×10^{-5}
HDO	2.9730×10^{-6}	3.0930×10^{-5}	C ₄ H ₁₀	0	8.7020×10^{-4}
Ne	1.7732×10^{-10}	1.8132×10^{-10}	C ₅ H ₆	0	3.1200×10^{-5}
O ₂	5.4529×10^{-11}	4.5863×10^{-11}	C ₅ H ₈	1.1430×10^{-6}	6.1190×10^{-5}
CO	5.4133×10^{-3}	6.1560×10^{-3}	C ₅ H ₁₀	5.0530×10^{-5}	3.1624×10^{-4}
CO ₂	3.5130×10^{-4}	7.1114×10^{-3}	C ₆ H ₆	5.7862×10^{-7}	1.2410×10^{-5}
Ar	1.5865×10^{-10}	1.9198×10^{-10}	C ₆ H ₈	1.2372×10^{-7}	2.9600×10^{-5}
CH ₄	8.4552×10^{-2}	5.9646×10^{-2}	C ₆ H ₁₀	5.1596×10^{-13}	9.2130×10^{-5}
HC ₁	1.9598×10^{-5}	4.4143×10^{-4}	C ₆ H ₁₄	1.2359×10^{-5}	3.6477×10^{-4}
C ₂ H ₂	0	1.3678×10^{-3}	C ₇ H ₈	0	1.1010×10^{-5}
C ₂ H ₄	4.0370×10^{-4}	1.6383×10^{-3}	C ₇ H ₁₂	0	2.3200×10^{-5}
C ₂ H ₆	5.5849×10^{-4}	3.3508×10^{-3}	C ₈ H ₁₆	9.773×10^{-6}	5.4875×10^{-4}
			Total	1.0971×10^{-1}	1.1800×10^{-1}

**TABLE 7: Selectivity and Rates of Conversion of Methane
to Various Hydrocarbons for Experiment C
(P = 0.113 kPa)**

Hydrocarbon	Rate of Conversion* (Gmole/sec)	Selectivity (%)
CH ₄	-4.902×10^{-9}	-
C ₂ (Lumped)	$+1.062 \times 10^{-9}$	39.4
C ₃ (Lumped)	$+2.054 \times 10^{-10}$	11.4
C ₄ (Lumped)	$+2.084 \times 10^{-10}$	15.5
C ₅ (Lumped)	$+7.026 \times 10^{-11}$	6.5
C ₆ (Lumped)	$+9.563 \times 10^{-11}$	10.6
C ₇ (Lumped)	$+6.733 \times 10^{-12}$	0.9
C ₈ (Lumped)	$+1.061 \times 10^{-10}$	15.7

* Minus sign means consumed

TABLE 8: Comparison of Methane Conversion Experiments

Experiment #	Conversion Mechanism	Gas Used	MCP Configuration	Voltage (Volts/Dia.)	Current (μ amp)	Pressure (kPa)	% Conversion	Conversion Rate (Gmole/sec)
A	Electron Impact	$^{12}\text{CH}_4$	1 MCP (12 μ Dia, 40:1)	12.5	4.5	2.6×10^{-7}	78.6	9.33×10^{-15}
B	Ion Impact	$^{13}\text{CH}_4$	3 MCP (12 μ Dia, 120:1)	12.5	5.0	4.0×10^{-4}	19.8	1.65×10^{-12}
C	Ion Impact	$^{12}\text{CH}_4$	3 MCP (12 μ Dia, 120:1)	Variable	Variable	1.13×10^{-1}	29.5	4.90×10^{-9}

Figure 7: Ratio of Mole Fractions of Hydrocarbons to Methane for Experiment C.
(P = 0.113 kPa)

Figure 8: Comparison of the Rate of Methane Conversion Versus Pressure for Experiments A through C.

IV. CONCLUSIONS

An electrical method for direct conversion of methane into higher hydrocarbons has been demonstrated over a wide range of pressures. Batch experiments have been used, with a microchannel plate, to produce C₂ to C₈ hydrocarbons, with C₂ selectivity at 39% in one case. The mixture of products and the conversion rates depend upon the electrical voltage used, the microchannel geometry, and the pressure. Greater ion feedback activity at higher pressure led to an increase in conversion. With the expected cost reductions for microchannel plate production in large quantities with relaxed specifications, the use of this method in large-scale commercial installations is quite possible. Continuous-flow experiments at higher pressures are needed, followed by construction of a bench-scale production device.

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