TITLE: PLASMA CONVERSION OF METHANE INTO HIGHER HYDROCARBONS AT SURFACES

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OBJECTIVE: PRODUCTION OF SYNTHETIC MISCIBLE GAS AND SYNTHETIC CRUDE OIL FROM METHANE FEEDSTOCKS

1. Introduction.

Natural gas is widely abundant, is easily withdrawn from reservoirs, is commonly produced as an associated gas along with crude oil production, and is found in many geologic settings as a resource separate from oil. A much larger fraction of the natural gas may be produced from a gas reservoir, as compared with a crude oil reservoir. However, natural gas is normally transported by pipeline, and the energy throughput of such a pipeline is perhaps only 20% to 30% of the throughput of an oil pipeline of the same size and cost. Gas is difficult to transport in moderate quantities at low cost, as it must either have a special pipeline or must be liquified into LNG, shipped in cryogenic LNG tankers, and regasified at the destination. It has been difficult to make use of methane as a fuel for transportation vehicles. The chemical stability of methane has made it difficult to convert it directly into conventional hydrocarbon fuel mixtures, and has also impeded its use as a feedstock for petrochemical production. Consequently, the economics of natural gas production and distribution have been rather different from the economics of oil. Nevertheless, the usage of natural gas for more than simple heating or electricity generation would be accelerated by development of technology which could convert natural gas into hydrocarbon liquids. Particularly with the growth of the "newly-developing economies" of the world, the need for liquid fuels is expected to grow very much more rapidly than in the recent past. Improvements in the standard of living in these emerging economies of the world are crucially dependent upon the availability of liquid fuels at modest prices. In this paper, we discuss the direct conversion of natural gas to higher hydrocarbon liquids by using energetic plasma interactions with surfaces.

2. Use Of Plasma Interactions With Surfaces

If neutral methane is ionized, and the ions are accelerated beyond the energy of about 15 eV, then when they collide with other methane neutrals, the C-H bonds are broken (Winters 1975) and chemical combinations take place. Historically, methane plasmas have been used to produce carbon, and to produce acetylene. Building higher hydrocarbons requires more than merely high ion energy; there must be a high probability of interaction, and the collision of three or more carbon-containing molecules and/or ions must be commonplace. A control of the recombination of the ions with neutrals is important.

A methane-based plasma initially contains methyl ions of several types, along with hydrogen ions, electrons, and methane and hydrogen neutrals. Electrons, ions, and neutrals will each be at different temperatures, generally, but at higher pressures with frequent interactions, the charged particles will deliver kinetic energy (below the threshold for ionization) to the neutrals, and much of this energy will be lost to the ambient and to the walls of the enclosure. Simultaneous multi-particle collisions in the volume of a plasma are extremely unlikely.

It has been shown that hydrogen ion bombardment of carbon-containing surfaces can produce all of the carbon-containing gases up to C_3 (deVries et al. 1984; Brown et al. 1982). We have extended this approach in our experiments. We have not made use of catalysts, high temperatures, or high pressures. Using low pressures, any kind of surface, and locally intense regions of high energy density associated with ionic impact, we have shown that in a time interval of a few picoseconds, methane ions and neutrals combine on the surface to form a wide spectrum of higher hydrocarbon molecules and ions. Some of these are ejected from the surface and can participate in additional reactions of the same type on adjacent surfaces. Kinetic energy is continually added to ions after they are created, and their energies quickly exceed the threshold values needed to ionize methane and thus allow the random creation of higher hydrocarbons. The technology is not highly selective; many output product gases and liquids should be expected. A traditional separation of them may be necessary for certain downstream chemical applications, but perhaps will be minimal for hydrocarbon fuel applications. The basic technology involves the use of an array of many small tubes, which are co-parallel and provide a large surface area for interactions. The direction defined by the axes of the tubes is co-parallel with a component of a superimposed electric field.

A pressure of gas is maintained at a low enough value so that an ion, once created, can acquire an energy greater than 15 eV, without a significant probability of an energy-transferring collision with a neutral gas molecule in the ambient. When such an ion strikes the inside wall of a tube, it will locally excite the neutral molecules on the surface, and a variety of chemical conversions will take place.

In our experiments, over 1.3 million tubes were used, arranged in a microchannel plate array, with each tube nominally 12 micrometers in diameter. The phenomenon can be explained most easily with reference to a single tube such as is shown in Figure 1a. Methane molecules are adsorbed on the walls of the tube from the ambient partial pressure of methane, which may be in the range of 0.4 Pa to 100 Pa or more. Electron and ion flow is possible without a significant number of collisions with neutrals in the volume above the surface. Ionization may initiated by using a suitable photoemissive, field emissive, radioactive or thermionic source outside of the tube, and the electrons from such a source are accelerated with a low voltage towards the end of the tube, where they strike the interior walls at grazing incidence and produce secondary electrons, ions, and other products. Secondary electrons cascade along the tube, acquiring energy from the electric field and striking the walls further down the tube, where more electrons and ions are generated. Positive ions are accelerated in the direction opposite that of the electrons, and strike the walls of the tube, producing electrons, ions, emitted neutrals, and chemical reactions. The ions produced at the walls of the tube are accelerated by the electric field, and acquire energy. Striking the neutrals which are adsorbed along the walls of the tube, the ions deliver most of their energy to the upper layers of atoms, allowing them to form new chemical combinations and to be released from the surface, either in ionic or in neutral form.

Some of the newly-formed neutrals are deposited upon the opposite wall of the tube, and are available for further ion-impact-stimulated chemical reactions. Newly-formed ions are accelerated by the electric field and then strike the walls of the tube further downstream (in the ionic flow direction), initiating another ion-impact-stimulated chemical reaction there. There is a statistical distribution of emission energies, emission angles, number of ions emitted, the number of neutrals emitted, and the ratios of chemical species produced, in each impact event. Therefore, there is a distribution of trajectory length, impact energy and angle of incidence for successive ion impact events. The energy delivered to the excited surface region will be a statistical process. One of the effects is the rapid chemical conversion of methane to higher hydrocarbons at the impact sites; There will also be a more gradual transfer of some of the residual ion energy into heat energy. Consideration of the energetics should be part of any development of a commercially feasible device.

Molecular dynamics models, developed by other researchers, (Johnson 1989; Johnson and Sundquist 1992) may be used to predict an excited region some 30 nanometers wide, 30 nanometers deep, and up to 1000 nanometers in length, for grazing incidence ions. Many ions and neutrals are emitted from a single event, as the energy required for separation of the product species from the surface (0.05eV to 0.2 eV)is small in comparison with the available ion impact energy (15eV to 200 eV). Rough surfaces

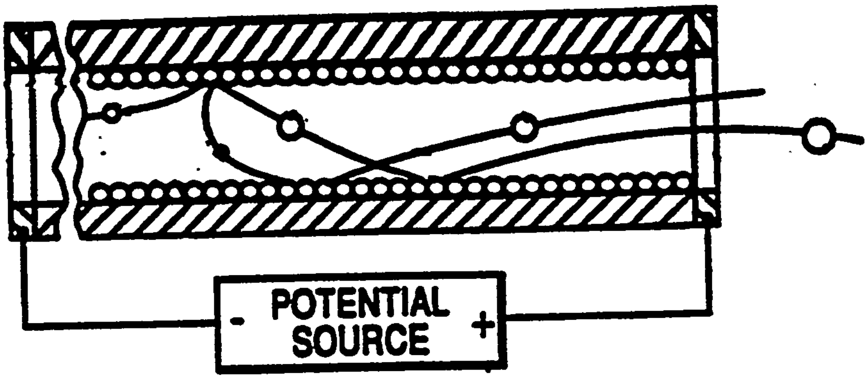


Figure 1a. Electronic conversion of methane by electron-impact reduction, electron-stimulated desorption of ions, and ion-impact-stimulated chemical combination and desorption at inside surface of a single tubular microchannel.

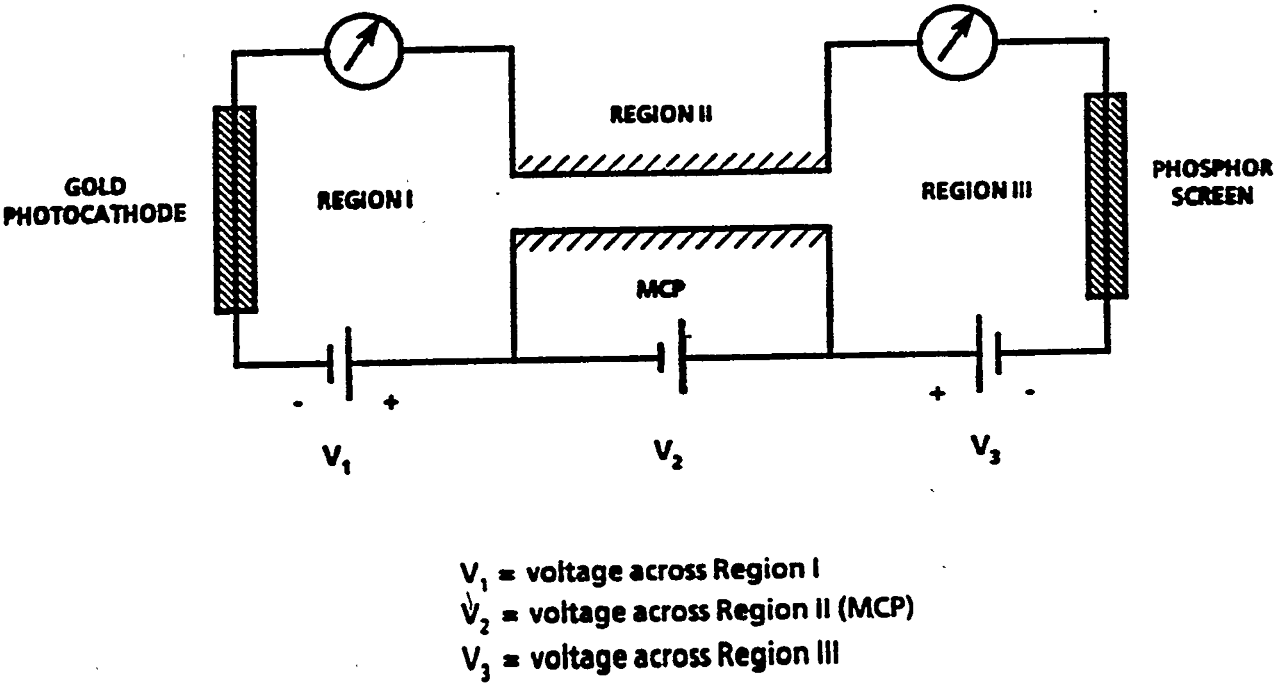


Figure 1b. Electrical circuit arrangement for methane conversion using microchannel plate (MCP) channel array.

are involved, and excited zones are irregular in shape. The time of emission is in the range of 5 picoseconds, and takes place long before thermalization of the residual amount of incident ion energy. The process is very fast, and chemical conversion and escape of products takes place long before a Maxwellian distribution of the residual energy is achieved. Thermal driving forces are not significantly involved in the chemical conversion. The fraction of incident ion energy which is slowly degraded into thermal energy, however, will be one factor determining the energy consumption of an operating device, and may place an upper limit on the specific conversion per unit area of surface. There are numerous choices for substrate materials, some of which can function at very high temperatures.

The electrical connections shown in Figure 1b were originally used in the first set of experiments, to check the electron gain of the microchannel plate. An additional invention of a related device in this family (Sackinger, Morgan, and Airey, 1992) makes use of an array of dynodes, rather than a microchannel plate. This second dynode-based device has not yet been experimentally investigated. It uses the same principles of plasma interaction with surfaces with an improved geometry involving construction from metal sheets. A higher electric field provides the required ion acceleration at a higher ambient gas pressure. The dynode-based device can be produced at a lower cost, is capable of a very high operating temperature, and will be included in future experimental programs.

3. Experimental Results

Conversion of methane into higher hydrocarbons was noted in <u>every</u> case when the electric field was above 4 volts/diameter (333 volts/millimeter). Thirty-two experiments were conducted, and have been reported elsewhere (Sackinger, Kamath, Morgan, and Airey, 1993). A summary of the most significant cases are discussed below, denoted as Cases 1,2,3,5,7, and 8 (see Table I).

Several batch and continuous methane conversion experiments were conducted at pressures ranging from 3.3×10^{-10} kPa to 0.113 kPa, using a demountable, stainless steel, ultra-high-vacuum (UHV) system. This consisted of the following major components: 1) an image tube sub-assembly containing a microchannel plate (MCP) assembly, a gold photocathode, a phosphor screen, and electrical feedthroughs; 2) a floating high-voltage supply, with three output voltages; 3) an ammeter; 4) an UV light source (mercury lamp); 5) a large VacIon pump with a UHV valve and ion gauge; 6) a gas leak valve for gas injection; 7) a mass spectrometer assembly; 8) a VacSorb pump with shutoff valve and down-to-air valve; 9) a capacitance gauge for pressure measurement.

Prior to the start of the conversion experiments, several precautionary and calibration steps were followed which included: a) Bake out the system overnight at 250°C for wall outgassing; b) Helium leak tests to ensure that there were no leaks at flanges and joints; c) Electron scrubbing of the MCP to remove gas adsorbed from the atmosphere; d) Measurement of the resistance of the MCP; e) Voltage-Current relationship for the photocathode-to-MCP region; f) Calibration of the UV filters for varying input current to the MCP; g) Measurement of the electron gain of MCP at different voltages; h) Calibration of the mass spectrometer system; i) Measurement of conductance of the gas leak valve.

In the batch experiments, the initial conditions were: 1) a thoroughly-pumped system at the ultra-high-vacuum level of 1.3×10^{-10} kPa; 2) no electric field applied to the MCP. The VacIon pump was then isolated from the system by closing the UHV valve, and the residual gas background spectrum was recorded. Gas was next injected into the main chamber through the leak valve, and that valve was closed after the desired pressure level was reached. The input methane background specrum was recorded. The conversion process was then started by applying voltage to all three regions as shown in Figure 1b and turning on the UV light source. The mass spectra were recorded very frequently, for accurate tracking of the kinetics of the conversion process. The mass spectra recorded at various times were then analyzed to compute composition of the gas in the main test chamber.

For the experiments reported in Table I, three MCP's were used in cascade, so that the effective length of each channel was 120 diameters or 1.44 millimeters. The pressures in the main chamber for the experiments ranged between 1.35×10^{-4} kPa to 1.13×10^{-1} kPa. The voltage in the Region 1 between the

TABLE I

Rate of Conversion, % Conversion and Selectivity of Methane to Various Hydrocarbons During Batch Methane Conversion Experiments

							% Selectivity to Various Hydrocarbons				
Case No.	Input Gas Used	Time (min)	Pressure (kPa)	MCP Voltage (Volt/dia)	Methane Conversion Rate (gmole/sec)	% Methane Conversion	C_2	C_3	C_4	C_5	C_6
1	$^{12}CH_4$	164	1.13×10^{-1}	Variable*	4.90×10^{-9}	29.5	47.2	13.7	18.5	7.8	12.8
2	$^{13}CH_4$	1446	8.96×10^{-2}	Variable*	1.13×10^{-9}	24.2	67.9	14.3	10.8	0.1	6.9
3	$^{13}CH_4$	1352	7.8×10^{-2}	Variable*	1.74×10^{-8}	24.5	67.2	19.3	8.6	0.3	4.6
5	$^{13}CH_4$	1125	3.88×10^{-3}	5	4.09×10^{-12}	22.7	88.0	3.2	8.8	0.0	0.0
7	$^{13}CH_4$	1232	4.00×10^{-4}	12.5	1.65×10^{-12}	19.8	85.6	7.5	2.7	0.6	3.3
8	$^{13}CH_4$	1125	3.46×10^{-4}	8.33	2.23×10^{-13}	11.4	81.6	6.8	7.2	1.0	3..4

*Low density plasma with glow discharge

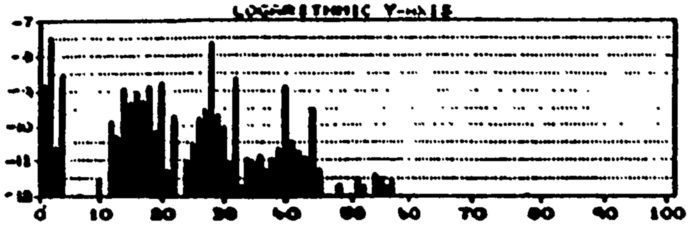
electron source and the MCP was set at 30 volts and in the Region 3 between the MCP and the phosphor screen was set at 0 volts in all experiments. The electric field across the set of MCP's was varied from 0 to 15 volts / diameter (or 0 to 1250 volts/millimeter). The mass spectrometer was separated from the main chamber by a low-conductance leak valve for the high pressure experiments.

Experiments at the highest pressures, which we shall discuss as cases 1, 2, and 3, were in the category in which a glow discharge was initiated between the fixture and the chamber walls, as well as within the MCP, for MCP voltages above 3 volts/diameter. These are discussed because they resulted in a substantial conversion of methane into higher hydrocarbons, and they illustrate the situation when a time-variable voltage may be beneficial.

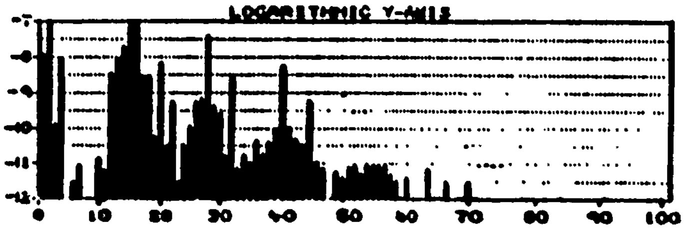
For case 1, operated at a pressure of 1.13×10^{-1} kPa, an evolution of the mass spectra is displayed as Figure 2, indicating the progressive production of higher hydrocarbons, at least as high as C_8. Since the mass spectrometer detected mass partial pressures only up to 100 a.m.u., the presence of hydrocarbons above C_8 was not definitively detected, but their presence cannot be ruled out, especially since the major (most probable) fragment of such large molecules is listed as appearing in the range of < 100 a.m.u.. We consider the presence of hydrocarbons up to C_{14} as being a possibility, but in quite small quantities. The statistics of ionic impacts seems to favor production of C_2, followed by C_3, C_4, C_5, C_6, C_8, and C_7, in that order. Consideration of case 2, which was conducted at a slightly lower pressure of 8.96×10^{-2} kPa, showed rapidly-varying conversion in the initial 100 minutes. (Most of it was an increase in higher hydrocarbons plus hydrogen). During the time used for the initial scanning of the mass spectrum after conversion had started, it is likely that the quantities of converted gases were increasing. Based on these rapidly-rising quantities, we have the qualitative impression that a continuous-flow conversion device would have an appreciable conversion in throughput times of the order of seconds or fractions of seconds. Over time intervals of the order of hours, in this batch experiment, there was a gradual conversion of methane and a diminishing level of ethylene. The relative proportions of ethane, ethylene, and acetylene are a function of time. At a pressure of 7.8×10^{-2} kPa, case 3 showed conversion into hydrogen and into roughly comparable levels of acetylene, ethylene, and ethane. A very long batch experiment, it showed continuous conversion over 1367 minutes, with about an order of magnitude difference in each of the product spectrum partial pressures of C_2, C_3, C_4, and C_6, respectively.

At lower pressures, the glow discharge between the fixture and the chamber wall was not initiated. Thus it was possible to have a series of different fixed voltage values on the MCP. These experiments may be discussed as cases 5, 7, and 8. The important summary parameters are presented in Table I. The two values of low electric field, which were 5 and 8.33 volts/diameter, in cases 5 and 8, were intended to explore the categories of products associated with near-threshold operations. In both cases, isotopic methane was used as the feedstock, but there was a mixed residual layer of ^{12}C, ^{13}C, H and D from earlier experiments. Thus, the presence of H_2 in both the initial and final stages of both experiments was very obvious. The formation of C_2 hydrocarbons is favored, after the very long time of this batch experiment, as compared with larger hydrocarbons.

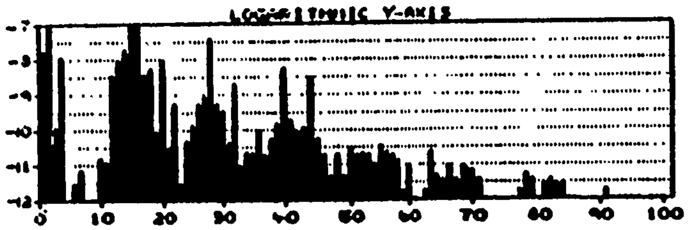
The relatively-high value of electric field of 12.5 volts/diameter was explored in case 7. A relatively low pressure, 4×10^{-4} kPa, was used. As reported in detail in our earlier work (Sackinger, Kamath, Morgan, and Airey, 1993), the C_4 production dominated over the C_3 production. The molecules containing a large and odd- number of carbon atoms, C_5 and C_7, were only produced at low levels. The reason for this may be that the ion impact energies available at such a value of electric field are only sufficient to commonly activate 1 or 2 or 3 carbon atoms which are bonded to the surface. An incoming hydrogen ion would thus contribute to the formation of C_1, C_2, or C_3 species, in order of decreasing probability; an incoming methyl ion would contribute to the formation of C_2, C_3, and C_4 species, in order of decreasing probability. This suggests that C_2 species would be most prominent, and if the C_4 category is the next most probable, it might be explained by a two-sequence process, which may take place during a fraction of those ion impact events. In this case and in most other cases, it was noticed that the residue from earlier experiments, in which ^{12}C was used, was converted during the ion impact experiments, into new methane, carbon dioxide, ethane, and ethylene made from this residual carbon. This more detailed



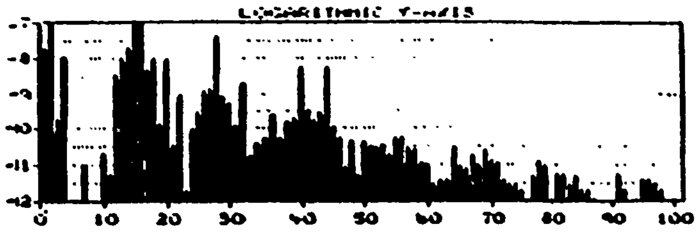
a) t = 0 min (Background Spectrum)



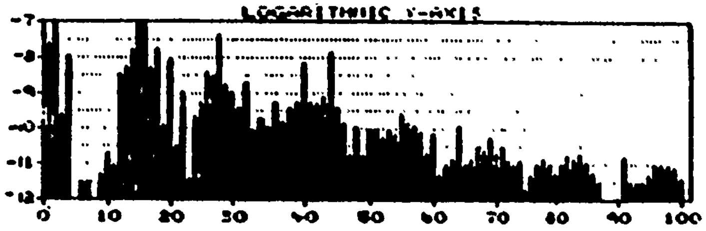
b) t = 39 min (CH_4 Injection)



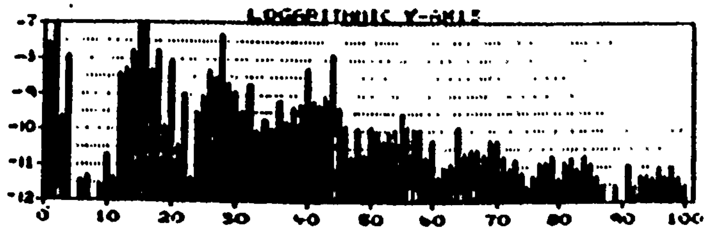
c) t = 95 min



d) t = 130 min



e) t = 170 min



f) t = 203 min (Final Spectrum)

Figure 2. Evolution of mass spectra as a function of time during case 1, at a pressure of 0.113 kPa, indicating progressive conversion of methane to higher hydrocarbons up to at least C_8.

data (Sackinger, Kamath, Morgan, and Airey, 1993) proved that hydrocarbons containing one, two, and even six residual carbon atoms can be produced and released from the surface by ionic impact.

Case 8 was conducted at a low pressure (3.46×10^{-4} kPa), and at an intermediate value of electric field strength, 8.33 volts/diameter. The decrease in methane and the increase in hydrogen were most obvious in the first part of the experiment, but continued throughout. A rapid growth in C_2H_2 and in C_2H_4 took place in the first 69 minutes, and the C_3 and C_4 gases also increased in that initial time interval. Oddly enough, the level of C_2H_6 remained near the background level throughout the 1200 minutes of the experiment. It was only after 250 minutes that increases were seen in the levels of C_5H_8 and C_3H_8, both of which contain an odd number of carbon atoms. Near the end of the experiment, there was a slow growth in most components, but a slow decrease in C_3H_6, C_6H_6, and C_5H_8. Such slowly-varying concentrations must be related to the presence of some of the initially-formed higher hydrocarbons at the ion impact sites later in the experiment, and the subtile details of how such larger hydrocarbons are transformed when impacts of hydrogen ions and methyl ions occur. In this experiment, the hydrogen neutrals and the methyl neutrals were over 1000 times more numerous than the higher hydrocarbons, so it is a reasonable assumption that the dominant ion impact events were with ions from these two species. One hypothesis may be presented for the production of molecules containing an odd number of carbon atoms, involving the impact of a methyl ion and one resident C_2 neutral, along the lines $[C + C_2] \longrightarrow C_3$. However, the presence of some unsaturated hydrocarbons of all carbon-numbers, early in the experiment, means that at this value of electric field intensity, multiple combinations of carbon ions and neutrals were taking place at each ion impact interaction event with the surface. Therefore, at this value of electric field strength, the presence of products such as C_2 on the surface is not a necessary condition for the full spectrum of higher hydrocarbons to be generated, but it may assist in the generation.

Examination of the summary of these cases, shown in Table I, shows the following summary facts. Percentage of methane conversion was remarkably in the 20%-30% range in cases 1, 2, 3, 5, and 7. Conversion clearly requires an electric field strength of 5 volts/diameter or more. Selectivities for C_2 are greatest for low electric fields, at 5 volts/diameter. Production of a rich spectrum including up to at least C_6 is the case for high electric field intensities, in the range 8 - 15 volts/diameter. Maximum mass throughput and conversion is at the highest pressures combined with higher voltages. The practical reason for using higher pressures is to reduce the transverse size of the plasma converter, for a given required mass throughput, and thus perhaps reduce the cost of the plasma converter as well. Subsequent compression stages would also involve less equipment cost.

In Figure 3, the trend of increase in mass conversion per second with increasing pressure is depicted. This is a plot on log-log coordinates of the methane conversion rate, in gram-moles/second, vs. the pressure, in kPa, for many of the cases. If there were only one mechanism responsible for the reaction, one would expect a straight line to be drawn through these points. The cluster of points in each pressure regime, in the vertical direction, expresses the fact that the choice of electric field strength affects the conversion rate. The obvious increase in the conversion trend from the 0.001 kPa region to the 0.1 kPa region may be explained by the viewpoint that the number of active ion impact events per unit length of the MCP, per second, is increasing nonlinearly. This may be because there are ions created by some of the collisions in the volume, as well as the fraction of ions created by the collisions at the surface. The implications are that higher operating pressures will lead to greater methane conversion rates, until the point is reached for which the ions created in the volume are unable to acquire sufficient energy from the electric field to cause the desired conversion when they strike the surface. Application of a higher electric field will cause this saturation of conversion to take place at still higher pressures. Therefore, higher pressures and higher electric fields should be one of the objectives of future experimental programs. Obviously, a glow discharge will be initiated within the MCP during such experiments. The extinction of the glow discharge within the MCP by the high gas pressure will be a sign of saturation of the conversion process. It may be noted that, at atmospheric pressure, one study has found that a corona discharge may be initiated in methane at an electric field strength of 2230 volts/millimeter. Since the electric field of 1250 volts/millimeter has already been demonstrated, and conversion has taken place, the possibility of carefully-designed fixtures, electric field intensities of 2200 volts/millimeter, and near-atmospheric pressures of methane, should be on the agenda for the future experimental program. Such an operating

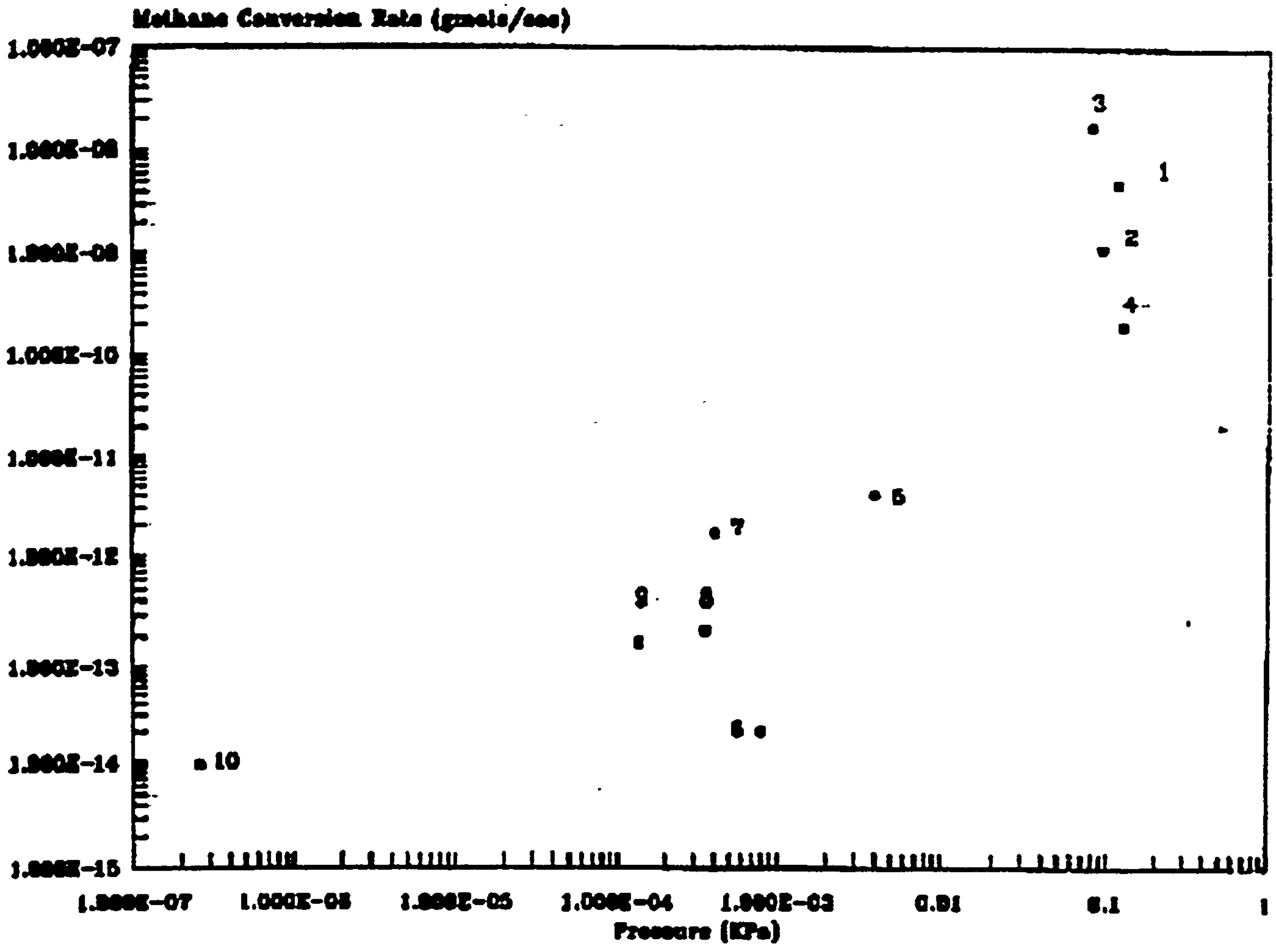


Figure 3. Log-log plot of methane conversion rate (gram-moles/second) vs. pressure, for ten experiments, showing a nonlinear increase in conversion rate as pressure increases, which is attributed to the increasing effect of ion interactions with the surface.

regime would be expected to produce a full spectrum of hydrocarbons, if one extrapolates the previous results, and would have the possibility of high throughput rates. Attention must be given to the diameter of the microchannels, as well, since that will affect the flow rate of the methane into and through the channels, and therefore the actual <u>in-situ</u> pressure within the microchannels.

4. Economic Aspects of Future Commercialization.

In order to determine the commercial applicability of this technology, the construction costs for units capable of producing much larger quantities, in the range 10 tonnes/day to 1000 tonnes/day, need to be estimated. Normally, such a task is done by first constructing one or several units of intermediate size, or "pilot-production- sized-units". Therefore, estimates of the cost and the conversion spectrum of large, continuous-flow units are necessarily based only upon parameters known at this time.

A practical alternative to MCP may be offered at large scale, by the metallic dynode structure for the conversion of methane into higher hydrocarbons, which is a related invention by Sackinger, Morgan, and Airey (1992). This provides for the conversion to take place when ions strike the metallic dynodes. The dynodes can be made in several geometrical formats, such as an array of tubes, or an array of slats as is found in a 'Venetian blind' structure, or an array of holes punched in a flat metal plate.

The costs of such metallic dynodes are little more than the costs of the metal from which they are made, and thus there is the prospect of large dynodes being fabricated at low cost. We estimate that the metal-dynode version of the device would contain many dynodes, but the main cost would be in the provision of the electrical feedthrough sub-assembly, and the labor involved in mounting the dynodes in a position in which they were hermetically-sealed to the wall of the enclosure. The operating life of such dynode-based devices is expected to be of the order of 10 years, as there is no need for electron emitters with limited life; field emitters or ß-emitters can provide the electrons needed for initiation of the plasma. It should also be noted that no dynode-based device has yet been tested, to establish its conversion efficiency.

Conversion of methane into higher hydrocarbons, plus hydrogen, requires the addition of energy, due to the different chemical bonding of the products. This may be calculated in kilowatt-hours, for each kilogram of product. However, the hydrogen is made available and can be burned, yielding energy which can help supply the energy for the reaction. This can be summarized as follows:

Product	**Energy Needed**	**Energy available From Burning Hydrogen**
C_2H_6	0.3735	-3.4468
C_2H_4	1.2997	-6.4351
C_2H_2	2.5885	-8.9648
C_3H_8	0.4872	-6.7431
C_3H_6	1.1002	-9.6561
C_3H_4	1.6495	-12.263
C_4H_{10}	0.5420	-9.9982
C_4H_8	1.0619	-12.874

The conversion of the hydrogen into electrical power, however, has an efficiency which may be in the range of 50%. The delivery of the electrical power to the electrical load representing the device also means that only 50% of the power from the generator may be made available for the reaction. In addition, there will be some energy lost to the subsurface materials, in the form of heat. The actual energy needed in each practical situation will depend upon the mix of output products, and is expected to be supplied primarily by the burning of the hydrogen produced, along with the burning of methane as required. As for the cost, the equipment cost is the most important, and can be estimated to be $0.01 per kilowatt-hour. The consumption of the electricity for the dynode-version is expected to be lower, as there is no continuous leakage current. The electrical power costs are expected to be in the range of $10 to $40 per tonne ($0.19 to $0.77 per MSCF) of methane converted depending on the product formed.

We note that the feedstock costs vary with the location, and are as low as $25 per tonne in the oilfield (or perhaps even less, if the gas is not marketable!). The natural gas costs in a consumer location vary with time, but can be as high as $200 per tonne if the pipeline costs are high, or if LNG is used as part of the transportation chain. It therefore appears that the most prominent low-cost location for the use of this technology is in the oilfield, where the gas may be today undeliverable, but where a higher hydrocarbon use (e.g. for miscible-gas injection into a reservoir) exists.

5. Some Possible Applications.

In one application, which is quite related to the Alaskan oil production effectiveness, the possibility is considered of converting the lean residue gas in the Prudhoe Bay gas handling facility into miscible gas injectant (C_2 to C_4) and TAPS compatible liquids (C_4 and higher). Miscible gas generated from this process can be used for improving oil recovery from Prudhoe Bay, Kuparuk River, West Sak and other smaller oil fields. The TAPS compatible liquids produced from this process can be transported through the existing oil pipeline (TAPS). Figure 4 shows projected annual production from the West Sak heavy oil reservoir by applying a miscible flooding process (Patil,1995). Thus, West Sak oil which is currently not being produced can help offset the decline in oil production from the Alaskan North Slope. Since natural gas is abundant on the Alaskan North Slope and is currently not marketable this seems to be one of the locations where the most favorable economics could be expected for this kind of technology.

For those oilfields in other parts of the world where there is presently no gas separation plant, the feedstock could be the natural mixture of CH_4, C_2H_6, C_3H_8, C_4H_{10}, with the C_5-and-higher hydrocarbons sent into the oil production stream. This feedstock would be enriched in C_2, C_3, and C_4 by the plasma device, and C_5, C_6, C_7, C_8 would also be produced. The presence of C_2H_4 and C_2H_2 in the output stream from the plasma device would open the possibilities for petrochemicals. This kind of conversion into petrochemical feedstocks could take place after pipelining, as well as before, as it may be most economic to position the petrochemical factories in locations where the petrochemical products can reach the consumers by normal overland transportation. The location of this completely-sealed type of ethylene production facility in regions of high population density, however, would not have the social disadvantages commonly associated with older ethylene units. However, it is also feasible to position the ethylene and propylene production units at the gas field. Tankers or pipelines may be used to carry the ethylene to downstream locations elsewhere.

A use which is simple in concept is to simply convert the natural gas of any gas field, or the produced gas of any oil field, into C_5 or larger molecules, with this kind of technology, and send it into the existing crude oil stream to be refined and utilized just as crude oil is today. Thus, the natural gas need not be reinjected, which has a cost. It need not be flared, which is done today in some offshore locations. This is essentially a method for the better use of the natural gas fossil energy resource. The negative value of wellhead natural gas which must today, by law, be reinjected, may be compared with the "API" value of the higher hydrocarbon liquids produced, which can be considerable. This offers an economic margin for the production of such liquids from natural gas, directly, using the plasma conversion process.

In relation to refining, the concept is to use this technology to try to upgrade the heavy residue oils coming from the refining of low-API crude oil. These oils, nominally selling for less than crude oil itself, are only sold into a very limited market, such as for power stations in locations near a refinery, or near a marine terminal, as they are difficult to move by pipeline. They fall outside the normal range of definition of transportation fuels, and are much thicker than lubricating oils. However, they will certainly vaporise at the temperatures and pressures used in the plasma-based units, and they may be combined with a methane or a natural gas feedstock to allow the plasma to produce a larger quantity of intermediate-range hydrocarbons than would be possible with a methane or natural gas feedstock alone. This category of processes can also be viewed as a cracking of the heavy oils using methyl ions and hydrogen ions in the plasma device. One would expect this to produce a very wide range of alkanes and olefins. The presence of petrochemical feedstocks in the output, for this category of experiments, should also be expected. The economics of this type of conversion would require that the margin available between the price of these heavy fuels, and the price of motor fuels, would be approximately the same as

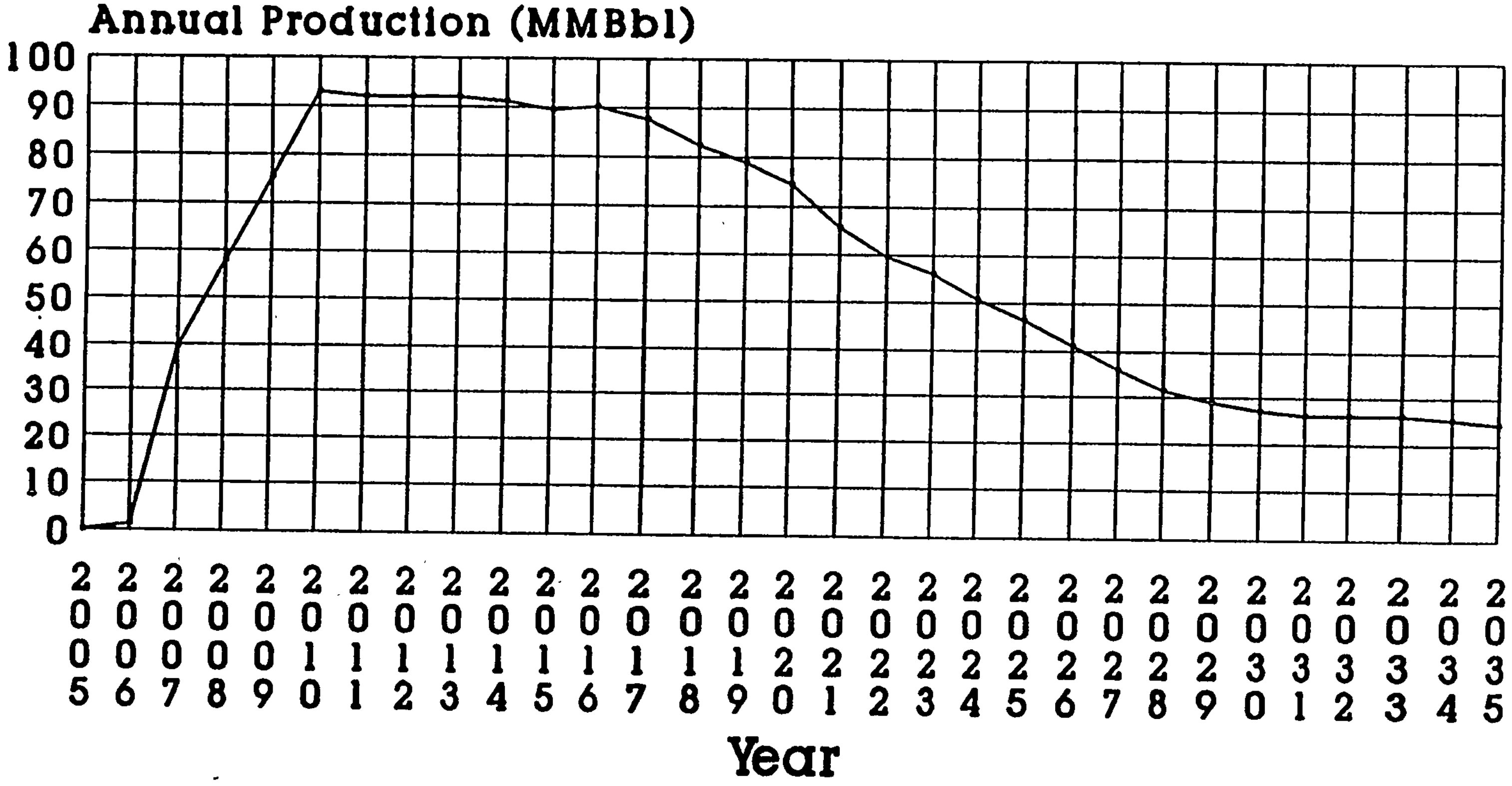


Figure 4. Projected annual heavy oil production from the West Sak heavy oil reservoir, Kuparuk River Unit, North Slope, Alaska by application of a miscible flooding process (after Patil 1995).

the marginal cost of operating the plasma conversion equipment. If this proves to be the case, then the use of plasma conversion in this segment of the petroleum industry would lead to a greater supply of gasoline and other transport fuels.

6. Conclusions

Experiments have been described in which a methane plasma is created, and the resulting methyl and hydrogen ions have been accelerated within a microchannel array so that they interact with neutral methane molecules on the inside surfaces of the microchannels. No catalysts are used, and the device operates at room temperature. Impact energies of the ions are in the range of 15 ev to greater than 100 ev, and the energy delivered in the interaction at the surfaces has caused the production of larger hydrocarbon molecules, such as C_2H_2, C_2H_4, and C_2H_6, along with C_3, C_4, C_5, C_6, C_7, and C_8 molecules. Conversion effectiveness is greater at higher pressure, due to the increased ionic activity. The yield of the higher hydrocarbons depends upon the external voltage used, and voltage can be used as a control parameter to adjust the output mixture proportions. In batch experiments, the selectivity for C2 has varied from 47% to 88%, and selectivity for C_6 was up to 12.8%. Other hydrocarbon selectivities also span a wide and useful range. The costs of production of the plasma conversion devices are projected to be quite low, and the technology appears to be commercially and economically feasible.

7. Recommendations For Future Development.

The feasibility of this category of conversion technology has been established. The economics, and the details of the implementation for high levels of throughput which would be needed in a production situation, remain to be established. Since Phase I, already completed, was a sequence of many batch experiments at sub-gram levels, it is appropriate to target Phase II at the level of 10 kilograms per day of throughput, and make experiments on a continuous-flow basis. Several types of experiments are planned, including those which vary the electrical voltage over all possible ranges, and which vary the pressure from the established values in Phase I, to higher pressures which would lead to a larger throughput for a given device cross-sectional area. The two fundamental parameters, pressure and electrical voltage settings, will be varied in every future experiment. Phase II is planned for 24 months duration. Phase III, set to build up to the level of 10 tonnes per day, is planned for 36 months duration.

Plasma conversion technology may be quite useful in those oilfields where there is presently no methane separation plant. The feedstock in such locations could be the natural mixture of CH_4, C_2H_6, C_3H_8, C_4H_{10}, with the higher hydrocarbons sent into the oil production stream. In such an application, this feedstock would be enriched in C_2, C_3, and C_4 by the plasma device, and C_5, C_6, C_7, C_8 would also be produced.

For experiments to examine these applications, in Phase II, we would expect to use feedstocks of CH_4, $^{13}CH_4$, C_2H_6, $^{13}C_2H_6$, various mixtures of $CH_4 + C_2H_6 + C_3H_8$, and natural gas (from Alaska and many other locations, to be supplied by cooperating industrial partners), natural gas without water, natural gas without water and without carbon dioxide. Output spectra would be monitored and recorded with the GC/MS equipment.

A second part of the Phase II program, a downstream application, is intended to consider some of the possible applications of this technology to refining and petrochemical feedstock production. As is evident from the Phase I results, production of ethylene, acetylene, and propylene is quite possible for certain ranges of voltage and pressure. Since this kind of technology is inherently statistical in nature, all possible product gases may be expected, but the more useful ones may be increased in quantity by proper choice of voltage, and can be separated out with low-temperature, low-pressure separation stages. The economics of the process will be connected with the costs for construction and operation of such separation equipment, as well as with the plasma-based stages themselves.

To use this technology to try to upgrade the heavy residue oils coming from the refining of low-API crude oil, we intend to combine them with a methane or a natural gas feedstock to allow the plasma to produce a larger quantity of intermediate-range hydrocarbons than would be possible with a methane or natural gas feedstock alone. This category of experiments can also be viewed as a cracking of the heavy oils using methyl ions and hydrogen ions in the plasma device. One would expect this to produce a very wide range of alkanes and olefins. Many possible mixtures are candidates for feedstocks, and certainly one should try some very precisely-known mixtures of two or three alkanes, as well as the practical mixtures which are representative of normal refinery residual outputs, which would be supplied by cooperating industrial partners. The presence of petrochemical feedstocks in the output, for this category of experiments, should also be expected.

In the plans described above, the several types of converter geometries using plasma would be tested, including the microchannel types, and the various configurations of the dynode types. Therefore, at least twenty such units would be constructed to span the most important variations in construction geometry.

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