**Natural Gas Conversion to Higher Hydrocarbons
Using Plasma Interactions with Surfaces**

Final Report

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EXECUTIVE SUMMARY

EXPERIMENTS ARE REPORTED IN WHICH A METHANE PLASMA IS CREATED, AND THE METHYL IONS AND HYDROGEN IONS ARE 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 10 eV TO GREATER THAN 100 eV, AND THE ENERGY DELIVERED IN THE INTERACTION AT THE SURFACES CAUSES 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. THERE IS A DECREASING PERCENTAGE OF LARGER MOLECULES PRODUCED, IN COMPARISON WITH THE C_2 AND C_3 TYPES. 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. A CONVERSION ENERGY OF 2.59 KILOWATT HOURS/KILOGRAM OF OUTPUT HAS BEEN DEMONSTRATED, AND A REDUCTION OF THIS BY A FACTOR OF 10 IS POSSIBLE USING KNOWN TECHNIQUES. IN BATCH EXPERIMENTS, THE SELECTIVITY FOR C_2 HAS VARIED FROM 47% TO 88%, AND SELECTIVITY FOR C_6 HAS RANGED FROM 0% TO 12.8%. OTHER HYDROCARBON SELECTIVITIES ALSO SPAN A WIDE AND USEFUL RANGE. THE ESTIMATED COSTS FOR HYDROCARBONS PRODUCED WITH THIS TECHNOLOGY ARE IN THE RANGE OF \$200 TO \$250 PER TONNE, IN PRODUCTION QUANTITIES, DEPENDING UPON NATURAL GAS COSTS. PILOT PRODUCTION EXPERIMENTS ARE RECOMMENDED TO MAKE THESE ESTIMATES MORE PRECISE, AND TO ADDRESS STRATEGIES FOR SCALING THE TECHNOLOGY UP TO PRODUCTION LEVELS. APPLICATIONS ARE DISCUSSED.

I. INTRODUCTION.

The most prominent use for crude oil is in the production of liquid motor- fuels and heating fuels, which can represent over half of the output of a modern refinery. A major investment has been made in transportation equipment, such as automobiles, trucks, locomotives, and aircraft, which are driven by liquid hydrocarbon fuels. The evolution of the technology and economics of the petroleum industry for the past century has been in support of such applications, and the synergism between the transportation infrastructure of the world and the petroleum production and refining infrastructure of the world has contributed significantly to the advance of civilization in the past century.

However, as oil fields are gradually depleted, new resources must be found if this synergism is to continue. The petroleum industry has been successful in the discovery of new oilfields, in locations which are technically more difficult to produce, such as the deep offshore and the Arctic regions. The production cost of oil from these areas is higher, and these increased costs have been passed along to the consumer. At the same time, the petroleum industry has discovered reserves of natural gas, a fuel which can be substituted for oil in the industrial and residential heating sectors. Natural gas has also been used to supply feedstocks for petrochemical production, in those cases where a significant quantity of ethane and propane are contained in the natural gas. It has been difficult, however, to make use of the major component of the natural gas, that is, methane, as a source for transportation vehicles or as a feedstock for petrochemical production. This is due to the chemical stability of methane. Consequently, the economics of natural gas production and distribution have been rather different from the economics of oil. On one hand, the natural gas is easily withdrawn from reservoirs, and a much larger fraction of the natural gas is produced from a reservoir, as compared with crude oil, (for which more than half of the oil in the reservoir is normally left in place). 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. Furthermore, it is difficult to transport small quantities of natural gas associated with oil production from remote offshore oil platforms, because of the cost of an undersea gas pipeline. It is also difficult to transport natural gas at low cost in tankers, because of the cost of liquifying the gas to make LNG, shipping it in cryogenic LNG tankers, and regasifying it at the destination terminal. These factors have limited the speed of conversion of the

petroleum industry from crude oil to natural gas. Nevertheless, the usage of natural gas, as a percentage of the total energy usage, has grown rapidly in the past four decades, whereas the growth in usage of crude oil, expressed as a percentage of the total energy usage, has grown very slowly and is now stagnating. These trends have been recognized in the petroleum research plans of both government and industry, where there has been a concerted effort for the past three decades to develop technology which could convert natural gas into hydrocarbon liquids, usable as both petrochemical feedstocks and as fuels, as a means of accomodating some of the demands of society for an increasing amount of energy. 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. The supply of such fuels from indigenous reserves of natural gas, through application of an inexpensive technological process, would contribute to political stability and economic growth in these regions. The search for an inexpensive technological process has therefore been launched, and the success of traditional chemical processes has so far been at the margin, in terms of the costs of production. While synthetic liquids produced from natural gas can be made, they are expected to be priced in the range of \$30 to \$40 per barrel. A fullsize production installation in New Zealand, constructed in 1982-85, has demonstrated these economics. The search continues, and the more novel and non-traditional methods are being considered.

The research described in this report is certainly beyond the traditional, in chemical engineering terms, as it does not make use of catalysts, or of high temperatures, or of high pressures. Rather, it makes use of low pressures, of any kind of surface, and of locally intense regions of high energy density associated with ionic impact. In a time interval of 5 picoseconds, methane ions and neutrals combine to form a wide spectrum of higher hydrocarbon molecules and ions, which 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 destroy methane and thus allow the random creation of higher hydrocarbons. The approach is called the DIRECT CONVERSION OF METHANE INTO HIGHER HYDROCARBONS, USING LOW-DENSITY PLASMA INTERACTION WITH SURFACES. In this report, the first experimental results are given which show the performance of this type of device. This

conversion was observed in over 24 experiments, and was present in all experiments. In principle, the conversion method can be applied to any chemical reformation process desired, beyond its current application to hydrocarbons. Any gaseous feedstock mixture can be used, and a new gaseous or liquid mixture will be the product. The technology is not highly selective; many output product gases and liquids should be expected, and a separation of them may be necessary for downstream chemical applications, but perhaps will be minimal for hydrocarbon fuel applications. Preliminary estimates of the cost of production using this technology suggest that the product will be at the \$200 to \$250 per tonne level, in 1993 dollars. While not less expensive than transport fuels, the product is likely to be competitively priced with them, and will depend upon the natural gas feedstock cost as well as the local electricity cost.

In the following sections of this report, emphasis will be placed upon the technology, upon the experimental results, upon the theory which has recently been developed by others, and upon the plans for future phases of development of this technology.

II. TECHNOLOGY FOR METHANE CONVERSION TO HIGHER HYDROCARBONS USING PLASMA INTERACTIONS WITH SURFACES.

The basic technology of the process is in the use of an array of many tubes, which are co-parallel and provide a large surface area for interactions. Coupled with this concept of a direction defined by the axes of the tubes is that of a direction defined by a superimposed electric field, which has a component in the direction defined by the axes of the tubes. A pressure of gas is maintained which is low enough so that an ion, once created, can acquire an energy greater than at least 12 eV, without a significant probability of 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.

Although in the experiments to be reported, 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. In the single long tube of Figure 1a, methane molecules are adsorbed from the ambient partial pressure of methane, which may be in the range of 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. Ionization is initiated by using a suitable photoemissive, field emissive, 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. Some ions emerge from the end of the tube and strike the electron source, producing electrons upon impact and making the process of electron emission self-sustaining if the flux of ions is high enough.

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

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)

V_1 = voltage across Region I
 V_2 = voltage across Region II (MCP)
 V_3 = voltage across Region III

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

to form new chemical combinations and to be released from the surface, either in ionic or in neutral form. The newly-formed neutrals are deposited upon the opposite wall of the tube, and are available for further ion-impact-stimulated chemical reactions. The 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, and emission angles, for the ions, and there is a statistical distribution in the number of ions emitted, the number of neutrals emitted, and the ratios of chemical species produced, in each of the impact events. Therefore, there will be a distribution in trajectory length, and thus a distribution in impact energy and in angle of incidence for the successive ion impact events. One must also expect that the energy delivered to the excited surface region will be statistically described. Development of a theory to describe this process will be a long-term objective of researchers in this field. However, one can see that a cascading process, including feedback of ions and forward multiplication of electrons, is active. It is dominated by ion flow, surface impacts, and emission at impact sites. One of the effects is the rapid chemical conversion of methane to higher hydrocarbons at the impact sites. Another effect is the more gradual transfer of some of the ion energy into heat energy. Therefore, a consideration of the energetics should be part of any discussion of a commercially feasible device.

Our understanding of the energy partitioning of the incident ion energy is still incomplete. However, generally speaking, if the ionization energy has been invested to create the ion, then that energy is available at the instant of ion impact. If an ion is emitted as an output particle after the impact event, then one may conceive of an approximate "exchange" of ionization energy, at least insofar as the quantity of energy is concerned, between the incoming ion and the outgoing ion. The ionic state of some of the particles may be regarded, then, as a kind of intermediate condition and not necessarily as a "sink" of electrical energy. Since the incoming ion and the outgoing ion are different, in the general case, the quantities of energy associated with the ionization of each will be slightly different, and this difference will appear in another form. One can also discuss the creation of an ion 'ab initio', as a "sink" of electrical energy, but one must also recognize the recombination of an ion and an electron as a "source" of energy. The recombination energy may be available in a form which can cause, or assist in, further ionization or chemical reactions of adjacent neutrals. The

probability of this is always less than unity, however, and some of the energy available from recombination will gradually change into heat. Some of that recombination energy, however, may assist in the emission of ions or neutrals from the surface, in the excited zone of the surface, via processes which are presently incompletely understood. Certainly, the kinetic energy of impact of ions on a surface has only recently been studied intensively, and the molecular dynamics models, which will be discussed in detail in a later section, 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 is small in comparison with the available ion impact energy. In the practical cases, rough surfaces are involved, and the excited zones are irregular in shape. The time of emission is in the range of 5 to 60 picoseconds, and takes place long before thermalization of the residual amount of incident ion energy. Thus, this is a process which is very fast, thermally speaking, and it is not meaningful to think of temperature, of a Maxwellian distribution, or of thermal driving forces in making a theory for chemical conversion for this device. Nevertheless, the energy which is residual after the ion impact event, the chemical changes, the emission of ions, electrons, and neutrals, and the surface rearrangement of atomic layers, all take place, will be available to excite phonons in the substrate, and by this process will eventually degrade into random thermal energy. One unanswered question is to determine the fraction of incident ion energy which is thus degraded into thermal energy. This will be one factor in determining the energy consumption of an operating device, and may place an upper limit on the specific conversion per unit area of surface, depending upon the integrity of the substrate material as its temperature increases. As will be shown below, however, there are numerous choices for substrate materials, some of which can function at 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. The microchannel plate has been used for electronic image intensification for three decades (Lampton 1981), and is presently commercially available as a standard component of both second-generation and third-generation image intensifiers. It is also used in astronomical applications. The charged particles emerging from the microchannel plate and entering Region III in Figure 1b are either electrons or negatively-charged ions. If they strike the anode, they may produce positively-charged

ions which would be accelerated by the electric field in Region III, would enter the microchannel plate (MCP), Region II, and would participate in the chemical reaction process. Some chemical reactions should also be expected when electrons and ions strike the anode, however.

For a more detailed explanation of the operation principles of this kind of device, the reader is referred to the first published documentation (Sackinger, 1989; Sackinger, 1991). 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 been experimentally investigated in the program of applied research reported here. Nevertheless, it uses the same principles of plasma interaction with surfaces to accomplish the same objectives of methane conversion into higher hydrocarbons, albeit with an improved geometry. The dynode-based device lends itself to construction from rugged metal sheets, and offers the possibility of a higher electric field, with the required ion acceleration before surface impact being achieved at a higher ambient gas pressure. The dynode-based device is expected to be produced at a lower cost, is capable of a much higher operating temperature if necessary, and should be included in future experimental programs, such as the Phase II, Phase III, and Phase IV programs which are recommended later in this report.

In the microchannel plate version of this device, there is a continual small current flowing just beneath the surface of each tube, due to the manufacturing process which created a semiconducting layer beneath the surface, typically with a resistivity of 10^{12} to 10^{14} Ω /square. This is introduced for the purpose of creating a supply of secondary electrons, when the device is used in ultra-high vacuum conditions as an electron multiplier. The need for this semiconducting layer is diminished if the device is operated at a higher pressure, as is the case with methane conversion, because each ionization event can produce at least one...and perhaps more...electrons, at the time that the ion is created, and the net charge drawn from a subsurface semiconducting layer will be very low. For the single microchannel, a small current (e.g. 5.1×10^{-12} amperes) will flow in the subsurface layer. However, this can be reduced by a factor of 10 to 100 by a simple change in the processing schedule of the microchannel plate. The power consumed by this resistive current therefore is in the range of 4×10^{-9} to 4×10^{-11} watts/channel, typically. The treatment which produces this resistive layer is a high-temperature exposure to hydrogen gas,

which reduces the PbO of the glass to form a region of reduced Pb islands. The semiconduction is thought to occur by electron transfer across the short spaces between lead islands. Since the glass used to make microchannel plates is saturated with hydrogen from this treatment, there is a continual diffusion of hydrogen to the surface and a supply of hydrogen ions (Sackinger and Gislason, 1972) which produce ion feedback in the manner described. However, each ion impact event upon a methane neutral can be expected to have a high probability of creation of a hydrogen ion and a methyl ion. The ionization processes at a surface have not been studied in detail for such a case, but it is believed at this time that the most probable ions are H^+ , CH_3^+ , CH_2^+ , and CH^+ . Double and triple charged ions are also possible. Negative methyl ions are also a possibility. Once higher hydrocarbons are created, a wide variety of ions containing C-C bonds, C=C bonds, and $C\equiv C$ bonds are possible. As will be shown in the experimental results section, the availability of oxygen atoms from the glass itself, in the case of low pressure operation, makes possible the production of CO, CO_2 , and H_2O , all of which may become ionized and may participate in the conversion process. In the case of higher-pressure operation, an amorphous mixed layer of carbon and hydrogen forms on the surface and effectively forms the reaction layer available for activation by ion impact. This surface layer, rich in carbon and hydrogen, essentially prevents the participation of the underlying oxygen atoms in the chemical transformations, and thus the relative production of oxygen-containing gases is minimal.

Entry of the neutral methane into the microchannel tubes, in a continuous-flow production device, would depend in part upon the diameter of the tubes and the pressure chosen for operation. The single value of tube diameter, 12 micrometers, is not necessarily near optimum. Channels are formed by the drawing of glass tubes, the stacking of the tubes together, and the redrawing to finer diameter. Thus, there is a capability in the industry to make whatever channel tube size is deemed to be optimum, down to a diameter of 33 nanometers (0.033 micrometers) which is the smallest channel diameter demonstrated to date. Larger channel diameters improve the flow of neutral gas molecules into channels, to replenish those reacted, and furthermore allow the escape of the reaction product molecules more easily. On the other hand, the smaller-channel-diameter array has more surface area than the larger-channel-diameter array, thus improving conversion. Further experiments will help to define not only channel diameter choices, but also channel length choices. Generally, a longer channel will offer more conversions in a continuous-flow mode, and will

produce larger hydrocarbon molecules. In future phases of pilot production experiments, the effects of these geometric parameters upon device and system optimization should be more precisely defined.

Because of the complexity of the device operation, this section has been rather descriptive rather than quantitative. The theory for this kind of device is in its earliest stages of development. In the course of discussion with industry representatives and others, many questions have been asked about this family of devices. These have been collected together, 128 in all, and their answers have been given in similiarly descriptive terms. These Questions and Answers have been included in this report as Appendix A.

III. EXPERIMENTAL PROGRAM.

Methane conversion experiments were conducted at The Blackett Laboratory, Imperial College of Science, Technology, and Medicine, London, United Kingdom, with Principal Collaborators Dr. Brian W. Morgan and Dr. Robert W. Airey, who acted as Consultants and who took a very significant role in the experimental program, as well as kindly providing the equipment and the technical support which was absolutely indispensable for the success of the experiments. Two experimental intervals were executed; the first, in January of 1991, concentrated upon the proof of the principle of methane conversion, starting at high-vacuum conditions; having successfully proven this, the second set of experiments, in October of 1991, were designed to extend the operating pressure of the conversion processes to values which were 5 orders of magnitude higher than the previous experiments. These were also successful, and the apparatus functioned in an improved manner in the second set of experiments, since the experimental trials of the first sequence of tests revealed possible areas of improvement, which were implemented successfully in the second set of tests.

The apparatus used in both sets of experiments was a demountable, stainless steel, ultra-high-vacuum (UHV) system. The first set of tests were done with the arrangement shown in Figure 2. 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 ultraviolet 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.

(This configuration was modified for the second set of experiments, as will be reported in a later section of this chapter).

An image tube body sub-assembly was used to hold the MCP assembly, and also the 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 sub-assembly was mounted. The flange consisted of four electrical feedthroughs and several 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 with approximately 1.35 million tubular channels, each channel being of 12 micrometers diameter, and of length equal to 40 diameters. (In the second set of experiments, three MCP's were used, to be described below).

The initial system was designed to operate at ultra-low pressures, between 1.4×10^{-7} Pa and 1.0×10^{-6} Pa. A large VacIon pump with a nominal pumping speed of 80 liters/second 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, by means of the UHV valve between that pump and the rest of the system. An ultraviolet source was used to excite the thin-film gold photocathode to produce electrons, which were then accelerated into the MCP by the electric field. The high-voltage power supply, capable of generating 3600 volts, was connected to the feedthroughs. It was possible to apply three different separate voltages across the three different regions of the image tube body sub-assembly 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 external gas injection line and was used to pump down the system from ambient pressure to an intermediate vacuum level. The 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, was used for acquiring mass spectral data during the conversion process. (For the second sequence of experiments, this mass spectrometer system was replaced with a new one which had digital data acquisition features as well).

Prior to the start of the 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 ($116 \times 10^6 \Omega$);
5. Voltage-current relationship for the photocathode-to-MCP region;
6. Calibration of the ultraviolet filters for varying input current to the MCP if needed;
7. Measurement of electron gain of MCP at different voltages;
8. Calibration of the mass spectrometer system;
9. Measurement of conductance of the leak valve.

Conversion experiments were conducted initially in a continuous mode, and subsequently in a batch mode. In the initial continuous-mode experiments, however, it was possible for a large amount of methane introduced into the chamber to bypass the converter MCP section altogether, flowing into the VacIon pump. The qualitative features of the experiment were observable in either mode, however. It should be emphasized that the mounting of the MCP converter in the vacuum system was in no way a hermetic arrangement which would force all input methane to flow through the MCP converter. Rather, the MCP converter must be viewed as always connected between its output and its input by a gas chamber of very large volume. Therefore, a considerable amount of methane never made its way through the converter in a given experiment. With this in mind, one can distinguish the continuous experiment from the

batch experiment. In the continuous experiment, the Vaclon 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 setting 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 was recorded after pressure stabilization took place. The conversion experiments were then started by applying an electric field to all three regions shown in Figure 1, and by turning on the ultraviolet light source. 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 Vaclon pump.

Initially, several continuous methane-injection 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 ultraviolet light source on and off;
3. To identify the effect of the MCP voltage on the conversion;
4. To determine the effect of changing magnitude and polarity of the voltage in Region 3, upon the conversion;
5. To find out the effect of changing voltage in Region 1, upon the conversion.

Many continuous experiments were carried out, with pressures ranging from 3.3×10^{-10} kPa to 2.4×10^{-8} kPa.

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 Vaclon 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 background methane spectrum was then recorded. The conversion process was then started by applying voltage to all three regions and turning on the ultraviolet light source. 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 ranging from 9.3×10^{-8} kPa to 2.86×10^{-6} kPa during the first set of experiments. The electric field strength in these experiments spanned the range from 0 to 25 volts/diameter. The expression of the electric field strength in normalized terms of volts/diameter is convenient for scaling to other channel diameter sizes, as the trajectory calculations can be normalized in terms of the diameter as well. However, the actual field strength was over the range from 0 to 2083 volts/millimeter.

In addition to normal methane, $^{12}\text{CH}_4$, other feedstocks in some of the experiments included deuterated methane, $^{12}\text{CD}_4$, isotopic methane, $^{13}\text{CH}_4$, deuterated ethane, $^{12}\text{C}_2\text{D}_6$, deuterated propylene, $^{12}\text{C}_3\text{D}_6$, and a mixture of isotopic methane, $^{13}\text{CH}_4$, with deuterated benzene, $^{12}\text{C}_6\text{D}_6$. These experiments using isotopes of hydrogen and of carbon were conducted after experiments with normal methane, in an attempt to separate out the produced mass fractions of hydrocarbons from the peaks at mass number 28 which are contributed by nitrogen, N_2 , and by carbon monoxide, $^{12}\text{C}^{16}\text{O}$. The initial continuous experiments first used normal methane, and then later used deuterated methane. The batch experiments also used these two feedstock gases. It was in the second experimental program, described below, in which all of the different feedstocks were tried.

Before discussing all of the experimental results, we may describe the apparatus and feedstock conditions for the second experimental program, which took place in October of 1991. The objective of the second experimental program was to extend the range of conversion to much higher pressures. The limitation of the system as shown in Figure 2 was that the mass spectrometer was directly connected to the reaction chamber pressure. The mass spectrometer operates by creating a plasma with electron ionization, and by passing the resulting ions through an r.f.-excited quadrupole system which is followed by either a Faraday cage collector or a single channel electron multiplier which delivers current to an anode. The electron ionization for the mass spectrometer depends upon thermionic emission from a heated filament. In the first experiments, the normal tungsten filament was used, but it was limited at higher pressures by the possibility of oxidation of the tungsten, followed by filament

Figure 2: Schematic Diagram of Ultra High Vacuum System Containing Microchannel Plate Used for Methane Conversion

burnout. There was a safety relay circuit to interrupt filament current when the pressure was too high. Thus, an alternate method was devised to sense higher pressures. The use of an iridium filament is a normal remedy, and such a filament was acquired. However, it was also possible to rearrange the system configuration as shown in Figure 3, so that the mass spectrometer was separated from the chamber pressure by the intervening leak valve. This resulted in a vast extension of the range of experiments, by a factor of the order of 10^5 . In the second set of experiments, however, it became necessary to measure the chamber pressure accurately, and so a capacitance pressure gauge was installed which had a range of 0.01 to 100 Pa. It was also necessary to attach a small VacIon pump and back-to-air valve on the mass spectrometer line, as shown in Figure 3, to provide for continuous pumping of the gas which was escaping through the leak valve, and also to facilitate the initial evacuation of the system, which otherwise would have been only through the gas leak valve.

In the higher-pressure experiments, three MCP's were used in cascade, so that the effective length of each channel was 120 diameters, or 1.44 millimeters. No attempt was made to mount the microchannel plates in registration, so it must be assumed that there was a slight offset between channels at the junctions of the plates. This did not produce any detectable effect. The procedures prior to the experiment were the same as mentioned above. Pressures in the main chamber for testing of conversion were in the range 1.35×10^{-4} kPa to 1.13×10^{-1} kPa. The voltage in the Region 1 between the electron source and the MCP was set at 30 volts in all experiments at higher pressures. Also, the voltage in the Region 3 between the MCP and the phosphor screen was set at 0 volts in all higher-pressure experiments. These values were those found previously, by qualitative experiments, to be near the optimum for conversion, and easy to implement.

The electric field across the set of MCP's was varied from 0 to 15 volts/diameter, or, in dimensional terms, from 0 to 1250 volts/millimeter. Several experiments were accomplished using the isotopic feedstocks mentioned above. A comprehensive listing of the experiments in both the first and second sets are given in Table I.

One factor which became apparent in the experiments at highest pressure was the onset of a glow discharge in the chamber, in the region between the test assembly and the chamber wall. This was probably due to the specific electrode arrangements and clearances in that region. It does not necessarily set a limitation on the operating

Figure 3. Schematic diagram of ultra-high-vacuum system containing microchannel plate adapted for methane conversion at higher pressures.

pressure of the system, as we had no evidence of the glow discharge in the channels of the MCP. The power supply used in the system was constructed with a safety circuit which reduced the voltage very abruptly when the higher current of the glow discharge was sensed, and then slowly raised the voltage to the formerly preset level. The entries in Table I in which the voltage V_2 is noted as "variable" correspond to this situation. Conversion was appreciable during such situations. However, a test situation in which the voltage from the sub-assemblies to the chamber was still high enough to initiate the glow discharge, but the voltage across the MCP's was set to zero, led to the result of much less conversion, and the generation of large quantities of hydrogen and carbon deposits, as would be expected.

Data analysis was based upon the mass spectral data collected by the Spectrametrics Mass Spectrometer system. The bar charts of the mass spectra at various times during each particular experiment were stored into the hard disc of the computer which was a part of the MS system. These bar charts were then converted to digital mass partial pressures, for 1 to 100 a.m.u., using special software. During each experiment, there were printouts also made in real time of some of the mass spectral data. Thus, two types of data sets were available for interpretation. Because of the vast quantity of data, major emphasis was given to the computerized data as the method for understanding details of the results. A separate computer program was developed to convert the mass partial pressure data into gas component partial pressure data. The conversion program uses the published fragmentation patterns found in the reference works by Stenhagen et.al. (1974), and also in the book by Cornu and Massot (1975). These give the 10 most prominent mass fragments for each gas, from experimental data published over many years. This information was entered into the computer program for 127 different gas species; thus, the reference table contained 1270 entries.

In searching for a solution it was found that no unique solution could be guaranteed, as some of the experimental data could be satisfied by several different mixtures of the highest hydrocarbons. The strategy was adopted to retain all C_1 , C_2 , and C_3 product gases, as well as all of the non-hydrocarbon-containing gases, but only retain some of the more probable gases in the C_4 to C_8 range. In tests of the sensitivity of these assumptions, it was found that the outcome of the computations was affected only to a slight (~ 1% of C_2 concentration) extent by the assumptions made as to the choice of which C_4 - C_8 gases were to be retained.

IV. EXPERIMENTAL RESULTS.

Conversion of methane into higher hydrocarbons was noted in every case when the MCP electric field was above 4 volts/diameter (333 volts/millimeter).

Experiments at the highest pressures, which we shall discuss as cases 1, 2, and 3 here (corresponding to entries 22, 26, and 25, respectively, in Table I), were in the category already mentioned, in which an arc discharge was initiated between the fixture and the chamber walls for MCP voltages above 3 volts/diameter. These are discussed because they resulted in a substantial conversion of the methane into the higher hydrocarbons, and they illustrate the situation when a time-variable voltage may be beneficial. As mentioned above, a control experiment was conducted, case 6 here (corresponding to entry 32 in Table I), in which over 99% of the methane was decomposed, primarily into hydrogen and into carbon deposits on the chamber walls.

In cases 1, 2, and 3, substantial conversion of methane took place in the MCP as a function of time. For case 1, operated at a pressure of 1.13×10^{-1} kPa, an evolution of the mass spectra is displayed as Figure 4, 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. In Figure 5, plots of the ratio of mole fractions of the various hydrocarbons to the fraction of methane present are plotted as a function of time. Conversion continues with time, but at a reduced rate, as less methane is available in that batch experiment, due to earlier conversion events. 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 (entry 26 in Table I), which was conducted at a slightly lower pressure of 8.96×10^{-2} kPa, showed rapidly-varying conversion in the initial 100 minutes (Figure 6). (Most of it was an increase in higher hydrocarbons plus hydrogen). During the time used for the initial scanning of the mass spectrum after

TABLE I 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 x 10 ⁻⁹	500	832	3500	short	Qualitative
2	¹² CH ₄	Continuous	6.00 x 10 ⁻⁹	500	800	3500	short	Qualitative
3	¹² CH ₄	Continuous	6.65 x 10 ⁻⁹	500	800	3500	short	Qualitative
4	¹² CH ₄	Continuous	2.00 x 10 ⁻⁹	500	750 - 950	215	short	Qualitative
5	¹² CH ₄	Continuous	2.80 x 10 ⁻⁹	0	0 - 1000	0	short	Qualitative
6	¹² CH ₄	Continuous	2.90 x 10 ⁻⁹	0-500	1000	3500	short	Qualitative
7	¹² CH ₄	Continuous	2.90 x 10 ⁻⁹	500	1000	0-3500	short	Qualitative
8	¹² CD ₄	Continuous	3.20 x 10 ⁻⁹	500	800	0	short	Qualitative
9	¹² CD ₄	Continuous	3.20 x 10 ⁻⁹	500	800	0 to - 38	short	Qualitative
10	¹² CD ₄	Continuous	3.20 x 10 ⁻⁹	500	800 - 950	4.80	short	Qualitative
11	¹² CD ₄	Continuous	2.40 x 10 ⁻⁸	500	950	4.63	short	Qualitative
12	¹² CD ₄	Continuous	3.3 x 10 ⁻¹⁰ to 9.30 x 10 ⁻⁹	500	950	28.3	short	Qualitative
13	¹² CD ₄	Continuous	4.00 x 10 ⁻¹⁰	500	950	28.30	short	Qualitative
14	¹² CD ₄	Batch	9.30 x 10 ⁻⁸	500	950	28.30	2.13	Quantitative
15	¹² CD ₄	Batch	2.86 x 10 ⁻⁶	500	950	28.30	1.13	Quantitative
16	¹² CD ₄	Batch	2.86 x 10 ⁻⁶	20	600	-6.30	1.40	Quantitative
17	¹² CD ₄	Batch	2.86 x 10 ⁻⁶	500	800	22.90	1.55	Quantitative
18	¹² CD ₄	Batch	2.86 x 10 ⁻⁶	20	500	-6.60	2.13	Quantitative
19	¹² CH ₄	Batch	2.60 x 10 ⁻⁷	20	500	-6.60	1.30	Quantitative
20	¹² CD ₄	Batch	2.60 x 10 ⁻⁷	20	500	-6.60	2.30	Quantitative
21	¹² CH ₄	Batch	1.74 x 10 ⁻³	30	500 - 1150	0	7.50	Quantitative
22	¹² CH ₄	Batch	1.13 x 10 ⁻¹	30	variable	0	2.38	Quantitative
23	¹² C ₂ D ₆	Batch	1.30 x 10 ⁻¹	30	variable	0	2.58	Quantitative
24	¹² C ₃ D ₆	Batch	1.35 x 10 ⁻¹	30	variable	0	2.85	Quantitative
25	¹³ CH ₄	Batch	7.80 x 10 ⁻²	30	variable	0	5.72	Quantitative
26	¹³ CH ₄	Batch	8.96 x 10 ⁻²	30	variable	0	17.24	Quantitative
27	¹³ CH ₄	Batch	1.20 x 10 ⁻¹	30	480	0	2.62	Quantitative
28	¹³ CH ₄	Batch	3.88 x 10 ⁻³	30	600	0	19.83	Quantitative
29	¹³ CH ₄	Batch	1.02 x 10 ⁻³	30	1020	0	3.11	Quantitative
30	¹³ CH ₄	Batch	6.90 x 10 ⁻⁴	30	1000	0	17.0	Quantitative
31	¹³ CH ₄	Batch	4.00 x 10 ⁻⁴	30	1500	0	20.67	Quantitative
32	¹³ CH ₄	Batch	7.85 x 10 ⁻⁴	30	0	0	0.12	Quantitative
33	¹³ CH ₄ + C ₆ D ₆	Batch	2.85 x 10 ⁻⁴	30	1500	0	17.41	Quantitative
34	¹³ CH ₄	Batch	3.46 x 10 ⁻⁴	30	1000	0	20.16	Quantitative
35	¹³ CH ₄	Batch	1.35 x 10 ⁻⁴	30	1800	0	12.46	Quantitative
36	C ₃ D ₆	Batch	3.20 x 10 ⁻⁴	30	840	0	25.00	Quantitative

Figure 4. Evolution of mass spectra as a function of time during case 1 (experiment 22), at a pressure of 0.113 kPa, indicating progressive conversion of methane to higher hydrocarbons up to at least C_8 .

Figure 5. Ratio of mole fractions of hydrocarbons to methane as a function of time (minutes), for case 1 (experiment 22), at a pressure of 0.113 kPa.

Figure 6. Progressive conversion of methane into higher hydrocarbons, as a function of time (minutes), for case 2 (experiment 26), at a pressure of 8.96×10^{-2} kPa.

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 (C_2H_4), as shown in Figure 6. The relative proportions of ethane, ethylene, and acetylene are shown to be a function of time. Formation of polyethylene on the walls of the chamber might be making some contribution to the ethylene decrease, but the conversion of ethylene into acetylene and/or ethane is undoubtedly taking place to some extent as well, under these particular pressure and voltage conditions. In the initial, brief time intervals between mass spectral scans, and possibly during the time intervals between mass spectral samples later in the experiment, complicated interchanges between species take place so that individual species concentrations do vary. Judged by the indicators of methane and hydrogen, however, most conversion to higher hydrocarbons took place in the first 300 minutes. The C_5 formation was least probable.

At a pressure of 7.8×10^{-2} kPa, case 3 (entry 25 in Table I) showed conversion into hydrogen and into roughly comparable levels of acetylene, ethylene, and ethane, as illustrated in Figure 7. 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, and thus it was possible to have a series of different fixed voltage values on the MCP. These experiments may be discussed as cases 4,5,7,8, and 9 (corresponding to entries 27, 28, 31, 34, and 35, respectively). The important summary parameters of cases 1 through 9 are presented in Table II. The onset of conversion was at an electric field strength of 4 volts/diameter, as shown in case 4. The three values of low electric field, which were 4, 5, and 8.33 volts/diameter, in cases 4, 5, and 8, respectively, were intended to explore the categories of products associated with near-threshold operations.

Plots of the produced gases are not presented as a function of time in these cases, because of the relatively few times of recorded digital data points. Graphical records were taken at intermediate times, however. The initial and final partial

Figure 7. Conversion of methane into higher hydrocarbons, as a function of time (minutes), for case 3 (experiment 25), at a pressure of 7.8×10^{-2} kPa.

TABLE II

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

Case No.	Input Gas Used	Time (min)	Pressure (kPa)	MCP Voltage (volt/dia.)	Methane Conversion Rate (gmole/sec)	% Methane Conversion	% Selectivity to Various Hydrocarbons				
							C ₂	C ₃	C ₄	C ₅	C ₆
1	¹² CH ₄	164	1.13x10 ⁻¹	Variable*	4.90x10 ⁻⁹	29.5	47.2	13.7	18.5	7.8	12.8
2	¹³ CH ₄	1446	8.96x10 ⁻²	Variable*	1.13x10 ⁻⁹	24.2	67.9	14.3	10.8	0.1	6.9
3	¹³ CH ₄	1352	7.80x10 ⁻²	Variable*	1.74x10 ⁻⁸	24.5	67.2	19.3	8.6	0.3	4.6
4	¹³ CH ₄	45	1.20x10 ⁻¹	4	1.91x10 ⁻¹⁰	0.35	78.9	13.4	3.6	0.9	3.2
5	¹³ CH ₄	1125	3.88x10 ⁻³	5	4.09x10 ⁻¹²	22.7	88.0	3.2	8.8	0.0	0.0
6	¹³ CH ₄	89	7.85x10 ⁻⁴	0†	1.99x10 ⁻¹⁴	99.4	2.54	1.54	13.82	0.0	0.0
7	¹³ CH ₄	1232	4.00x10 ⁻⁴	12.5	1.65x10 ⁻¹²	19.8	85.6	7.5	2.7	0.6	3.3
8	¹³ CH ₄	1125	3.46x10 ⁻⁴	8.33	2.23x10 ⁻¹³	11.4	81.6	6.8	7.2	1.0	3.4
9	¹³ CH ₄	767	1.35x10 ⁻⁴	15.0	1.74x10 ⁻¹³	6.8	66.0	11.3	10.4	0.0	12.2

*Low density plasma with glow discharge.

†Glow discharge present outside MCP (methane cracking to H₂ and C).

pressures of the system component gases are presented in Table III, for cases 4 and 5. 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. Relatively little decomposition of methane took place in case 4, but it was sufficient to cause production of acetylene and ethane, along with a slight drop in ethylene. Both propylene and propane were produced in case 4. A slight decrease of C_4H_{10} in case 4 was accompanied by an increase in C_4H_6 , in C_5H_8 , and in C_6H_{12} . Very few ^{12}C -containing products appeared at the threshold voltage of case 4, however, suggesting that the substrate carbon residue is bonded with energies greater than those energies statistically to be expected at the ion impact events. The fact that ^{13}C -containing oxides appear with quantities which are over 6 orders of magnitude greater than those of the ^{12}C -containing oxides may be explained by the concept that active, ^{13}C -containing ions arriving at the top surface of the overlayer are the primary agent for chemical reactions. The partial pressures of ^{13}CO and $^{13}\text{CO}_2$ decreased only slightly during the time of case 4, which is consistent with the view that the oxygen from the glass substrate is required for these to form and to be ejected from the surface overlayer. The oxygen available at the top of the surface overlayer is probably depleted during the experiment, and is not replaced by diffusion from beneath, at a rapid rate, during the experiment. The thickness of the overlayer is thus probably greater than the thickness of the zone activated by ion impact, for this threshold experiment, case 4.

It is instructive to compare case 4 with case 5; in case 5, an electric field was used which was 25% greater, but the ambient pressure was reduced by a factor of 40. Thus, case 5 should be considered as possibly instructive, but farther away from a desirably-high operating pressure. The percentage changes in the various partial pressures are of the most interest. There certainly was a decrease in methane, by 22.7%. Hydrogen increased, of course. As Table III indicates, there was in case 5 an increase in acetylene of 60%, and an increase in ethylene of 206%, while ethane decreased by 20%. One may also point, in the same case 5, to an increase in propylene of 96% and a decrease in propane of 41%. This suggests that the ion impact energy spectrum extends to higher energies, and that this leads to the preferential formation of $\text{C}=\text{C}$ bonds such as are found in the olefins, rather than the single $\text{C}-\text{C}$ bonds found in the saturated hydrocarbons. The availability of ions such as CH_3^+ , and CH_2^+ , which combine with neutral methane and neutral ethane, would

TABLE III

Partial Pressures of Various Gas Species for Cases 4 and 5

Component	Case 4		Case 5	
	Initial Partial Pressure (kPa)	Final Partial Pressure (kPa)	Initial Partial Pressure (kPa)	Final Partial Pressure (kPa)
H ₂	2.186x10 ⁻²	2.222x10 ⁻²	2.758x10 ⁻³	2.839x10 ⁻³
HD	1.891x10 ⁻⁴	1.885x10 ⁻⁴	1.329x10 ⁻⁵	3.461x10 ⁻⁵
D ₂	3.980x10 ⁻⁴	4.881x10 ⁻⁴	2.758x10 ⁻⁵	2.584x10 ⁻⁵
¹³ CH ₄	9.685x10 ⁻²	9.651x10 ⁻²	7.854x10 ⁻⁴	6.068x10 ⁻⁴
H ₂ O	3.100x10 ⁻¹¹	2.921x10 ⁻¹¹	2.065x10 ⁻¹¹	1.547x10 ⁻¹¹
HDO	1.909x10 ⁻¹²	2.257x10 ⁻¹²	1.424x10 ⁻¹²	1.163x10 ⁻¹²
Ne	5.385x10 ⁻¹¹	5.477x10 ⁻¹¹	8.489x10 ⁻¹²	3.573x10 ⁻¹²
¹³ C ₂ H ₂	1.577x10 ⁻⁴	2.493x10 ⁻⁴	1.097x10 ⁻⁴	1.758x10 ⁻⁴
¹³ C ₂ H ₄	1.836x10 ⁻⁴	1.660x10 ⁻⁴	1.231x10 ⁻⁵	3.772x10 ⁻⁵
¹³ C ₂ H ₆	1.427x10 ⁻⁴	2.332x10 ⁻⁴	1.165x10 ⁻⁴	9.326x10 ⁻⁵
N ₂	4.761x10 ⁻¹¹	4.288x10 ⁻¹¹	2.252x10 ⁻¹¹	2.221x10 ⁻¹¹
¹³ CO	1.794x10 ⁻⁴	1.666x10 ⁻⁴	2.128x10 ⁻⁵	3.285x10 ⁻⁵
O ₂	4.960x10 ⁻¹²	4.214x10 ⁻¹²	3.320x10 ⁻¹²	3.188x10 ⁻¹²
HCl	9.239x10 ⁻⁶	6.703x10 ⁻⁶	4.820x10 ⁻⁷	1.487x10 ⁻⁶
Ar	1.836x10 ⁻¹⁰	2.296x10 ⁻¹⁰	3.195x10 ⁻¹¹	9.211x10 ⁻¹²
¹³ C ₃ H ₄	2.382x10 ⁻¹³	2.382x10 ⁻¹³	6.275x10 ⁻⁶	4.293x10 ⁻⁶
¹³ C ₃ H ₆	1.362x10 ⁻⁴	1.507x10 ⁻⁴	1.118x10 ⁻⁵	2.191x10 ⁻⁵
¹³ C ₃ H ₈	4.368x10 ⁻⁵	4.783x10 ⁻⁵	1.746x10 ⁻⁵	1.034x10 ⁻⁵
¹² CO ₂	4.105x10 ⁻¹²	4.818x10 ⁻¹³	5.490x10 ⁻¹²	2.588x10 ⁻¹²
¹³ CO ₂	8.557x10 ⁻⁶	6.701x10 ⁻⁶	1.549x10 ⁻⁶	6.090x10 ⁻⁷
¹³ C ₄ H ₆	1.812x10 ⁻⁶	2.580x10 ⁻⁶	8.820x10 ⁻⁷	1.177x10 ⁻⁶
¹³ C ₄ H ₁₀	8.687x10 ⁻⁵	7.111x10 ⁻⁵	1.819x10 ⁻⁶	4.944x10 ⁻⁶
¹³ C ₅ H ₈	2.816x10 ⁻¹⁴	7.620x10 ⁻⁷	2.630x10 ⁻⁷	0
¹³ C ₆ H ₁₂	1.301x10 ⁻⁵	1.526x10 ⁻⁵	3.734x10 ⁻⁶	2.111x10 ⁻⁶
¹² C ₆ H ₆	3.290x10 ⁻⁷	1.640x10 ⁻⁷	1.000x10 ⁻⁷	0

explain this trend. At any rate, one may notice from Table II that the formation of C_2 hydrocarbons is favored, after the very long time of this batch experiment, as compared with larger hydrocarbons.

The results from cases 6 and 9 are given in Table IV. As was mentioned above, case 6 had only a glow discharge between the fixture and the chamber wall, with no voltage applied to the MCP. Conversion of most of the methane (99.4%) took place quickly in that experiment. A carbon deposit was the result, plus the production of hydrogen. A decrease in the residual ethane in the chamber, by six orders of magnitude, and an increase of the residual ethylene and acetylene, also occurred. Reaction at chamber walls and at fixture surfaces, which were stimulated by available ions, must be the cause. Ionic activity does produce effects, both in the plasma volume and on the chamber walls, but the character of the output spectrum is distinctly different for case 6 as compared to all of the other cases.

The case 9 was another distinctly lower-pressure experiment, designed to assist in the understanding of the behavior of the MCP converter at the larger values of electric field. This was the largest value of electric field used in the second experimental sequence. Because of the low pressure, the conversion rate of methane in absolute terms was lower than in the other experiments. However, it should be noted that, with proper attention given to fixture design, the operation at this value of electric field, and at a pressure over 1000 times higher, should be practical. The decrease in methane was accompanied by the expected increase in hydrogen. There was a 219% increase in ethane, over five orders of magnitude increase in ethylene, and a 2330% increase in acetylene. The diacetylene (C_3H_4) increased by over six orders of magnitude, but the propylene diminished by 34% and the propane remained at trace levels. Increases of seven orders of magnitude in C_4H_6 were noticed, as was a 4137% increase in C_4H_{10} . Even C_6H_{12} showed an increase of more than seven orders of magnitude. The distribution of these higher hydrocarbons is shown in the entry for case 9 in Table II. Clearly, the effects of the high electric field are to produce a wide distribution of ion impact energies, a creation of larger hydrocarbon molecules during each ion impact event, and a trend towards unsaturated hydrocarbons. Ethane, however, was (after acetylene) the second most prominent C_2 produced, which suggests that in these energetic ion impact events, there are appreciable probabilities of single, double, and triple carbon-carbon bonds. The absolute quantity of C_6H_{12} which was produced was surprisingly high, and since this is hexene, a liquid at room

TABLE IV

Partial Pressures of Various Gas Species for Cases 6 and 9

Component	Case 6		Case 9	
	Initial Partial Pressure (kPa)	Final Partial Pressure (kPa)	Initial Partial Pressure (kPa)	Final Partial Pressure (kPa)
H ₂	3.854x10 ⁻⁴	8.382x10 ⁻⁴	5.396x10 ⁻⁵	6.285x10 ⁻⁵
HD	2.290x10 ⁻⁶	3.900x10 ⁻⁵	3.750x10 ⁻⁷	2.857x10 ⁻⁶
D ₂	1.685x10 ⁻⁶	1.726x10 ⁻⁶	4.305x10 ⁻⁷	1.854x10 ⁻⁶
¹³ CH ₄	2.662x10 ⁻⁴	1.578x10 ⁻⁶	7.570x10 ⁻⁵	7.053x10 ⁻⁵
H ₂ O	1.723x10 ⁻¹²	4.313x10 ⁻¹²	1.189x10 ⁻¹²	4.838x10 ⁻¹²
HDO	1.042x10 ⁻¹³	2.082x10 ⁻¹³	6.770x10 ⁻¹⁴	1.719x10 ⁻¹³
Ne	4.889x10 ⁻¹³	4.204x10 ⁻¹³	2.142x10 ⁻¹³	3.090x10 ⁻¹³
¹³ C ₂ H ₂	1.855x10 ⁻⁶	6.770x10 ⁻⁶	4.144x10 ⁻⁷	1.007x10 ⁻⁵
¹³ C ₂ H ₄	1.695x10 ⁻¹³	2.340x10 ⁻⁷	1.143x10 ⁻¹²	4.520x10 ⁻⁷
¹³ C ₂ H ₆	1.640x10 ⁻⁶	1.355x10 ⁻¹³	1.236x10 ⁻⁶	3.947x10 ⁻⁶
N ₂	3.353x10 ⁻¹²	3.032x10 ⁻¹²	2.664x10 ⁻¹²	2.120x10 ⁻¹²
¹³ CO	3.481x10 ⁻⁶	4.553x10 ⁻⁶	1.348x10 ⁻¹²	1.816x10 ⁻⁶
O ₂	3.009x10 ⁻¹³	3.578x10 ⁻¹³	2.956x10 ⁻¹³	3.061x10 ⁻¹³
HCl	1.731x10 ⁻⁶	7.600x10 ⁻⁷	1.747x10 ⁻⁷	9.802x10 ⁻⁷
Ar	2.293x10 ⁻¹²	1.523x10 ⁻¹²	1.100x10 ⁻¹²	1.369x10 ⁻¹²
¹³ C ₃ H ₄	6.460x10 ⁻⁷	1.276x10 ⁻⁶	2.490x10 ⁻¹³	1.823x10 ⁻⁶
¹³ C ₃ H ₆	2.629x10 ⁻¹⁴	1.997x10 ⁻¹⁴	1.041x10 ⁻⁶	6.831x10 ⁻⁷
¹³ C ₃ H ₈	4.980x10 ⁻⁷	1.287x10 ⁻⁶	6.910x10 ⁻¹⁴	1.520x10 ⁻¹³
¹² CO ₂	6.747x10 ⁻¹³	1.018x10 ⁻¹¹	2.204x10 ⁻¹³	1.996x10 ⁻¹²
¹³ CO ₂	4.800x10 ⁻⁷	9.12x10 ⁻⁷	1.472x10 ⁻¹³	2.922x10 ⁻⁷
¹³ C ₄ H ₆	3.430x10 ⁻⁷	9.721x10 ⁻⁶	2.496x10 ⁻¹⁴	8.391x10 ⁻⁷
¹³ C ₄ H ₁₀	1.139x10 ⁻¹⁴	1.490x10 ⁻⁷	4.133x10 ⁻⁹	1.751x10 ⁻⁷
¹³ C ₅ H ₈	4.800x10 ⁻⁸	3.700x10 ⁻⁸	0	0
¹³ C ₆ H ₁₂	2.530x10 ⁻⁷	1.940x10 ⁻⁷	2.664x10 ⁻¹⁴	7.927x10 ⁻⁷
¹² C ₆ H ₆	6.000x10 ⁻⁹	1.610x10 ⁻⁷	1.915x10 ⁻¹⁵	1.367x10 ⁻¹⁵

temperature and pressure, it may indicate that single-stage production of liquids is practical. The higher hydrocarbons produced in this energetic case 9 can be placed in their order of abundance, as follows: C_2H_2 , C_2H_6 , C_3H_4 , C_4H_6 , C_6H_{12} , C_3H_6 , C_2H_4 , C_4H_{10} . If the most abundant product in this list is given a relative abundance value of 100, then the relative abundances are: 100, 39, 18, 8, 8, 7, 5, 2, in integer terms. Since each ion impact event is separate in time and space, even at very much higher pressures than used in case 9, this distribution may be expected to be approximately fulfilled at this electric field strength at other pressures. Further experiments are needed to confirm this viewpoint. It is also our opinion, based upon our understanding of the kinetics of an ion impact event and the high energies involved, that the presence of an available higher hydrocarbon such as C_2H_2 in the pathway of the impacting ion is not a prerequisite for the formation of the hydrocarbons containing more than two carbon atoms. The reasoning which leads us to this conclusion is the simple observation that the relative abundances of methane and of hydrogen are, on this same scale, 705 and 628, respectively. Therefore, the basic reactant molecules are over 1000 times more numerous in the volume, and presumably on the surfaces, than are any or all of the product molecules. Therefore, this order of relative abundances of the products may also be obtained when one is conducting continuous-flow experiments in which the flow of the input methane gas is allowed to enter the MCP only, and the output products are allowed to exit from the MCP only, and are then pumped out of the system, provided only that the electric field strength remains the same as in case 9. The number of conversions will, of course, be greater in a single-pass MCP reactor if the length-to-diameter ratio of the reactor is greater than the 120 diameters used in these experiments.

The relatively-high value of electric field of 12.5 volts/diameter was explored in case 7. Again, a relatively low pressure, 4×10^{-4} kPa, was used. In Figure 8, the mass spectrometer actual spectrum is presented for initial, intermediate, and final times. A semilog plot of the ratio of mole fractions, as a function of time, normalized against the methane fraction, is shown in Figure 9. The actual table of the components at initial and final times for this case 7 is given as Table V. The C_4 production dominated over the C_3 production, if one considers only the ^{13}C products, and 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

Figure 8. Evolution of mass spectra showing conversion of methane into higher hydrocarbons, as a function of time (minutes), for case 7, at higher electric field and relatively lower pressure of 4×10^{-4} kPa.

Figure 9. Semilog plot of the ratio of mole fractions, normalized against the methane fraction, as a function of time (minutes) for case 7.

Table V. Partial pressures of various gas species for isotopic methane ($^{13}\text{CH}_4$) conversion, case 7, pressure of 4×10^{-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_2H_2	2.09×10^{-5}	3.45×10^{-5}
D_2	4.45×10^{-12}	1.69×10^{-6}	C_2H_4	3.04×10^{-6}	1.61×10^{-5}
H_2O	1.07×10^{-11}	1.41×10^{-11}	C_2H_6 (*)	2.62×10^{-13}	1.28×10^{-5}
HDO	5.47×10^{-13}	2.84×10^{-13}	C_2D_6	1.11×10^{-7}	5.95×10^{-7}
Ne	1.72×10^{-12}	1.76×10^{-12}	C_3H_6 (*)	1.28×10^{-7}	1.69×10^{-6}
N_2	3.85×10^{-12}	3.70×10^{-12}	C_3H_8	8.29×10^{-14}	1.33×10^{-8}
O_2	1.02×10^{-12}	9.83×10^{-13}	C_4H_6	7.87×10^{-7}	9.18×10^{-7}
HC1	2.78×10^{-7}	2.11×10^{-6}	C_4H_{10}	5.26×10^{-7}	8.16×10^{-7}
Ar	4.58×10^{-12}	4.97×10^{-12}	C_5H_8	0	2.82×10^{-15}
CO	6.01×10^{-6}	1.24×10^{-5}	C_6H_6 (*)	8.33×10^{-8}	4.33×10^{-7}
CO_2 (*)	3.48×10^{-12}	3.48×10^{-12}	C_7H_{14}	1.20×10^{-6}	1.23×10^{-6}
CH_4 (*)	2.61×10^{-6}	3.08×10^{-8}		3.6×10^{-4}	4.4×10^{-4}
CH_4	3.24×10^{-4}	2.62×10^{-4}	Total		

* Denotes ^{12}C Compounds

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. This would be along the lines, conceptually, of $[C + C] + [C + C] \rightarrow C_4$. On the basis of the existing evidence, however, this must be regarded as a tentative hypothesis, to be verified by future experiments. Certainly, another obvious inference from the data in Table V is 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, ethylene, and benzene, made from this residue carbon. This proves that hydrocarbons containing one, two, and even six residual carbon atoms can be produced and released from the surface by ionic impact. Additional experiments are needed to determine the conditions for release of hydrocarbons from the residue layer, as a function of ion impact energy.

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. Results are shown in Figure 10. The decrease in methane and the increase in hydrogen are 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 subtle 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 $[C + C_2] \rightarrow C_3$. However, the presence of some unsaturated hydrocarbons of all carbon-numbers,

Figure 10. Plot of methane, hydrogen, and higher hydrocarbon levels as a function of time (minutes) for case 8, at an intermediate electric field strength and a pressure of 3.46×10^{-4} kPa.

early in the experiment, means that at this value of electric field intensity, multiple combinations of carbon ions and neutrals are 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 II, shows the following summary facts. Percentage of methane conversion was remarkably in the 20%-30% range in cases 1,2,3,5,and 7. Threshold for conversion is clearly at an electric field strength of 4 volts/diameter. 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.

In Figure 11, 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. 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

Figure 11. 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 surfaces.

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 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 in-situ pressure within the microchannels.

Early in the experimental program, the principles of conversion were demonstrated in a number of experiments at ultra-low pressure, one of which may be designated case 10 (corresponding to experiment 19 in Table I). The results of case 10 are plotted in Figure 11. The pressure used was 2.6×10^{-7} kPa. This case 10 used only one MCP, of length equal to 40 diameters. The electric field strength was 12.5 volts/diameter. The wall outgassing rate was of significance, in comparison to the production rate, for case 10, and a procedure for measurement of that effect was devised. The results of the measurements of wall outgassing have been reported in an earlier publication (Sackinger et.al. 1992). In Table VI, the results of case 10 are presented, after the effects of wall outgassing were fully taken into account. It is clear from Table VI that methane consumption took place, and that production of partially-deuterated methane, ethane, partially-deuterated ethane, and propylene took place. This shows that the ion-impact collisions at the surfaces can in fact produce molecules with three carbon atoms, as well as with two carbon atoms, and also that one of the products of the collisions is newly-created methane. In the experiments operated at such low pressures, it was common to observe the creation of carbon monoxide, carbon dioxide, and water, from the interaction of the hydrogen ions and the methyl ions with the oxygen available at the surface of the relatively clean glass wall of the MCP. In practical devices, the presence of a mixed carbon/hydrogen amorphous layer at the surface must be viewed as a beneficial condition, which prevents the erosion of the oxygen and other elements of the glass surface.

The mass spectra of Figure 4 may be examined in the interval from mass numbers 5 to 12, for possible further evidence of trace impurities from the glass substrate. The presence of lines at mass 6 and 7 may be due to the two naturally-

**Table VI. Summary of methane conversion experiment at
ultra-low pressure of 2.6×10^{-7} kPa, case 10.**

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

* Minus Sign Indicates Consumption

occurring isotopes of lithium, ^6Li and ^7Li , since it is known that lithium is a component of the Corning Code 8161 glass used in manufacturing the MCP. Similarly, the lines at mass 10 and 11 may be explained by the naturally-occurring isotopes of boron, ^{10}B and ^{11}B , since it is known that in the manufacture of the MCP, a core glass is put inside of the starting tube of Code 8161 glass, in order to insure its dimensional stability during drawing and fusing processes, and that core glass (which is subsequently dissolved out with acid) contains boron, as well as other elements. The appearance of these rather unique mass spectral lines suggests that there can be some ion-impact-driven chemical reactions which somehow react with trace levels of these elements which are present in the surface, or in the overlayer. The gases which carry the lithium and the boron to the mass spectrometer may be hydrides, or organometallic species, or other types of molecules or clusters of molecules. The presence of HHH or HHD or HDD or DDD, which are metastable molecules, of masses 3, 4, 5, and 6, respectively, may also be possible and could bring about the mass spectral line at 6. (However, a mass spectral line at mass 5 was not observed). An explanation at this time for the mass spectral line at mass 9 is very difficult, since beryllium, ^9Be , is not known to be part of the composition of either of the two starting glasses in MCP production, nor a part of any of the manufacturing processes. The possibility of the compound ^7LiD , a lithium deuteride at mass 9, may be mentioned, and the corresponding compound ^7LiH , lithium hydride, should also be present at mass 8. Data at mass 8 was observed in case 7, illustrated in Figure 8, at the time 1323 minutes (the final spectrum).

Experiments using higher hydrocarbons as feedstocks also took place, which have been mentioned as experiments 23 (case 11), 24 (case 12), 33 (case 13), and 36 (case 14) in Table I.

In case 11, deuterated ethane, $^{12}\text{C}_2\text{D}_6$, was used as the input gas. This conversion experiment was characterized by a high pressure (0.13 kPa) batch operation, with sequential step increases in the electric field strength in the MCP region from 3 volts/diameter to 17 volts/diameter, a value at which the onset of a glow discharge took place. The objective of this experiment was to determine if the deuterated ethane feedstock cracks to C_1 , or converts to higher hydrocarbons, or if both processes take place simultaneously. Again, while no conversion was evident for an electric field strength of 3 volts/diameter, conversions did take place at higher field strengths and during glow discharge. A quantitative analysis of this experiment,

however, unfortunately could not be done since ion fragmentation data in the mass spectrometer for the higher deuterated compounds are not reported in the literature; if they were, it would be possible to use them to identify the main products. However, the examination of the mass spectra at the start of the experiment (Figure 12a) and the mass spectra at the end of the experiment (Figure 12b) reveals some important clues. First, the partial pressures of masses 34 and 36 drop by about 10% from the beginning to the termination of the experiment, indicating about 10% net conversion level. Secondly, the masses 14 through 20 remain at a stable level, indicating an approximate balance between cracking and creation of deuterated or partially-deuterated methane. Thirdly, an order-of-magnitude increase in partial pressures occurs for masses 47, 48, and 52, which indicates that the prominent products of conversion are deuterated propylene ($^{12}\text{C}_3\text{D}_6$), partially-deuterated propylene ($^{12}\text{C}_3\text{D}_5\text{H}$), and deuterated propane ($^{12}\text{C}_3\text{D}_8$). In addition, approximately half-order-of-magnitude increases in partial pressures occur for masses 46, 49, 50, 51, 54, 56, 58, and 64, which may relate to the possibility of other higher hydrocarbon products such as $^{12}\text{C}_3\text{D}_4\text{H}_2$, $^{12}\text{C}_3\text{D}_5\text{H}$, $^{12}\text{C}_4\text{H}_6$, $^{12}\text{C}_4\text{H}_4\text{D}_2$, $^{12}\text{C}_4\text{H}_3\text{D}_3$, $^{12}\text{C}_4\text{D}_4\text{H}_2$, and $^{12}\text{C}_4\text{D}_8$. Since the spectra of the highest of these is not known, the relative amounts of these cannot be estimated. In summary, case 11 shows that some deuterated ethane, $^{12}\text{C}_2\text{D}_6$, converts into partially- or fully-deuterated methane, and also converts into higher hydrocarbons in the C_3 and C_4 range.

In case 12, with similar experimental conditions as were used in case 11 (e.g. pressure of 0.135 kPa., batch operation, sequential field strength step increases from 3 volts/diameter to 17 volts/diameter, with an onset of glow discharge), deuterated propylene, $^{12}\text{C}_3\text{D}_6$, was used as the input gas. Once again quantitative analysis of this experiment was not possible for the reasons mentioned above. Figures 13a and 13b show mass spectra at the beginning and at the end of this conversion experiment. Clearly, significant levels of conversion took place in this particular experiment. Table VII gives the actual partial pressures of masses 2 through 100, initially and finally. Noting that $^{12}\text{C}_3\text{D}_6$ was the input gas, whose fragmentation pattern definitely includes mass 48, Table VII shows that the drop in partial pressure of mass 48 from 2.7×10^{-8} kPa to 1.8×10^{-8} kPa indicates a conversion of $^{12}\text{C}_3\text{D}_6$ to be about 33 percent. Similarly, mass 46, which also corresponds to one of the fragments of $^{12}\text{C}_3\text{D}_6$, decreased by 31 percent. The major increases occur for masses 49 through 52, indicating formation of deuterated and partially-deuterated propanes, followed by masses 53 through 68, indicating formation of deuterated and partially-deuterated

Figure 12a. Mass spectrum at the beginning of case 11, using deuterated ethane as feedstock at a pressure of 0.13 kPa.

Figure 12b. Mass spectrum at the end of case 11, using deuterated ethane as feedstock at a pressure of 0.13 kPa, showing production of deuterated and partially-deuterated propylene, deuterated propane, and a balance between creation and conversion of methane.

Figure 13a. Initial mass spectrum for case 12, with deuterated propylene as feedstock at a pressure of 0.135 kPa.

Figure 13b. Final mass spectrum for case 12, with deuterated propylene as feedstock at a pressure of 0.135 kPa, showing conversion to deuterated and partially-deuterated propane, butynes, butenes, butanes, and higher hydrocarbons.

TABLE VII

	Case 12	
Mass #	Initial Partial Pressure (kPa)	Final Partial Pressure (kPa)
2	4.8×10^{-8}	4.5×10^{-8}
3	2.4×10^{-8}	4.2×10^{-8}
4	4.2×10^{-8}	7.5×10^{-8}
12	9.2×10^{-10}	1.8×10^{-9}
13	1.0×10^{-10}	1.7×10^{-10}
15	3.6×10^{-10}	5×10^{-10}
16	7.1×10^{-9}	7.2×10^{-9}
17	2.1×10^{-9}	3.7×10^{-9}
18	7.9×10^{-9}	1.2×10^{-8}
19	1.5×10^{-9}	5×10^{-9}
20	1.0×10^{-8}	1.5×10^{-8}
21	6.5×10^{-10}	6×10^{-10}
22	1.2×10^{-9}	1.3×10^{-9}
23	1.8×10^{-10}	1.2×10^{-10}
24	2.6×10^{-10}	7.7×10^{-10}
25	3.8×10^{-11}	1×10^{-10}
26	1.2×10^{-9}	3.3×10^{-9}
27	9.0×10^{-10}	2.6×10^{-9}
28	3.6×10^{-7}	3.9×10^{-7}
29	3.3×10^{-9}	6.2×10^{-9}
30	1.8×10^{-8}	2.1×10^{-8}
31	6.3×10^{-10}	9.1×10^{-10}
32	4.8×10^{-8}	4.5×10^{-8}
33	1.2×10^{-10}	8.5×10^{-10}
34	3.2×10^{-10}	1.3×10^{-9}
35	1.1×10^{-11}	3.6×10^{-10}

TABLE VII (Cont'd)

36	6.6×10^{-10}	9×10^{-10}
37	4.0×10^{-11}	6×10^{-11}
38	3.6×10^{-9}	2.8×10^{-9}
39	2.6×10^{-10}	2.6×10^{-10}
40	2.7×10^{-8}	3.3×10^{-8}
41	5.0×10^{-10}	4.3×10^{-10}
42	2.1×10^{-8}	1.5×10^{-8}
43	8.2×10^{-10}	7.5×10^{-10}
44	9.5×10^{-9}	9.5×10^{-9}
45	1×10^{-9}	9.3×10^{-10}
46	3.9×10^{-8}	2.7×10^{-8}
47	1.7×10^{-9}	1.3×10^{-9}
48	2.7×10^{-8}	1.8×10^{-8}
49	9.3×10^{-10}	1.2×10^{-9}
50	2.6×10^{-11}	8.2×10^{-10}
51	1×10^{-11}	7.2×10^{-11}
52	2.5×10^{-11}	7.4×10^{-10}
53	4.0×10^{-12}	3×10^{-11}
54	6.0×10^{-12}	1.8×10^{-10}
55	9.5×10^{-12}	2.2×10^{-11}
56	6×10^{-12}	2.2×10^{-10}
57	6×10^{-12}	1.5×10^{-11}
58	6×10^{-12}	1.2×10^{-10}
59	-	6×10^{-12}
60	-	1.6×10^{-10}
61	-	1.6×10^{-11}
62	9.5×10^{-12}	5.3×10^{-11}
63	1×10^{-12}	2.4×10^{-11}
64	4×10^{-11}	2.4×10^{-10}
65	-	2.2×10^{-11}
66	-	2.6×10^{-11}
67	1×10^{-12}	5×10^{-12}
68	-	2.4×10^{-11}

TABLE VI (Cont'd)

69	1×10^{-12}	2.0×10^{-12}
70	-	1.4×10^{-11}
71	-	2.0×10^{-12}
72	-	2.8×10^{-11}
73	-	-
74	-	9×10^{-12}
75	-	-
76	-	7×10^{-12}
77	-	1×10^{-12}
78	1×10^{-12}	1.2×10^{-11}
79	-	1×10^{-12}
80	-	7×10^{-12}
81	-	-
82	-	3×10^{-12}
83	-	-
84	-	7×10^{-12}
85	-	-
86	-	1×10^{-12}
87	-	-
88	-	-
89	-	-
90	-	-
91	-	-
92	-	-
93	-	-
94	-	-
95	-	-
96	-	-
97	-	-
98	-	-
99	-	-
100	-	-

butynes, butenes, and butanes. There are also increases in masses 69 through 86 indicating formation of deuterated and partially-deuterated C_5 - olefins, C_5 - paraffins, C_6 - olefins, and deuterated and partially-deuterated benzene. Higher hydrocarbons can also be a possibility if their fragmentation pattern occurs in the same range. In addition, in this experiment there is also some possibility of cracking of $^{12}C_3D_6$ into deuterated and partially-deuterated methanes, as seen from increases in masses 13 through 20 in Table VIII. Further evidence of cracking is the presence of C_2 products as seen from increases in masses 25 through 36. A concurrent process is formation of C_1 and C_2 products from the residual carbon and hydrogen mixed deposits on the walls of the MCP.

In case 14, with deuterated propylene as the input gas at a lower pressure of 3.2×10^{-4} kPa and electric field strength of 7 volts/diameter, similar behavior was observed as in case 12, except that the amount of conversion was much smaller, mostly because of reduced numbers of ion impact events (as was observed for other experiments with methane as feedstock at lower pressure).

Finally, in case 13, isotopic methane ($^{13}CH_4$) was added to deuterated benzene ($^{12}C_6D_6$) as the input gas. This experiment is characterized by a low pressure (2.85×10^{-4} kPa), an electric field strength of 12.5 volts/diameter, and 17.41 hours duration. Figures 14a and 14b show the mass spectra at the beginning and at the end of the conversion experiment. The partial pressure of mass 17, which corresponds to the major fragment of $^{13}CH_4$, fluctuated slightly around a relatively metastable value of 2.7×10^{-10} kPa throughout the experiment. The partial pressures of masses 14, 15, and 16, which also represent fragments of $^{13}CH_4$, also fluctuated slightly around average values at the beginning and at the end of the experiment. However, during the experiment itself, it was observed that there were some time variations in the conversions taking place, which may be described by formation and decomposition of many different compounds. For example, increases in masses 29, 30, 32, 52, 54, and 56 were noted in the first few scans, but later these mass lines returned to their original levels. Similar time variations in the partial pressures of masses 82 and 84 and other higher masses were also observed. The masses at 99 and 100 may be caused by the formation of deuterated toluene, for example. It may be possible to explain this in terms of molecular dynamics in the future. At this point, these phenomena are not clearly understood and further experiments at higher

pressures and voltages, with these feedstocks, are recommended to resolve this type of behavior.

Figure 14a. Mass spectra for the start of case 13, in which a mixture of isotopic methane and deuterated benzene were used as feedstock, at a pressure of 2.85×10^{-4} kPa.

Figure 14b. Mass spectra at the end of case 13.

V. THEORETICAL MODELS...A DISCUSSION.

The first approach to an explanation of the theory applicable in this device was directed towards electron impact ionization, both in the gas phase and also on surfaces. This approach was taken prior to the experiments, and was based upon the excellent book by Mark and Dunn (1985), and upon several other standard reference sources (Meek and Craggs 1978; Hirsh and Oskam, 1978; McGowan, 1980). Experimental cross-sections for the dissociation of methane by electron impact have been given by Winters (1975). The peak for dissociation was at about 70 eV, and the dissociation cross-section was about $4 \times 10^{-16} \text{ cm}^2$ at that peak. He also reported that the dissociation into neutral fragments has about the same probability as the dissociation into ionic fragments for electron energies above 50 eV. The ionization began to be observed for electron energies of about 14 eV, but dissociation began at about 10 eV. It was nonlinear near threshold.

However, when the chemical conversion was accomplished in our first experiments at pressures which were very low, it was clear that interactions of ions with neutrals in the volume space were not responsible for the observations, but rather, ion interactions with "inertially-confined" neutrals on the surfaces of the tubes were responsible. Therefore, a search was made of the literature dealing with ion interactions with surfaces. There has been a rich literature, with many recent scientific advancements in this field.

Several of the contemporary theories of ion-impact-induced chemical reactions at the surface of a solid have been reviewed by Johnson (1987). At that time, he divided models according to two aspects, one relating to the principal energizing mechanism, and the second to the description of the "expansion" process. A first category of models requires the incident ion to excite the solid to a relatively long-lived intermediate state, followed by the statistical distribution of energy among the available final exothermic states of the system. Times greater than 10^{-11} sec. are required. One category of such models, the "Coulomb explosion" model, uses the energy of charge separation in the track core to heat the solid and then calculates the yield as a thermally-activated desorption (Seiberling et.al. 1980). Somewhat modified models along these lines have been presented by Ritchie and Claussen (1982), by Watson and Tombrello (1985), and by Kissel and Kreuger (1987). Variations on this approach may be found in the "thermal spike" models, which use a "thermal" diffusivity

of the material to describe the radial cooling of the track energy (Vineyard 1976; Sigmund and Claussen 1981; Lucchese, 1986). There is considerable confusion in the literature on the use of the word 'temperature' in these models. Expansion models have also been proposed (Derrick 1986; Williams and Sundqvist 1987). Hydrodynamic 'shock' models have also been proposed (Carter 1979; Yarmanura 1982).

Considerable progress was, however, made with the molecular dynamics model by Fenyő, Sundqvist, Karlsson, and Johnson (1990) which was developed after the earlier models showed some inconsistencies with the experimental data. In the molecular-dynamics technique, Newton's law of motion for the system of a large number of classical particles is approximated using a difference equation which gives the motion of each particle as a function of time. This was introduced by Alder and Wainwright (1957). It has been applied to many different problems, such as nuclear sputtering (Anderson 1987), radiation damage (Gibson et.al. 1960), and laser-induced ablation of organic solids (Garrison and Srinivasan 1985). In their work, they did not address the cause of the expansion of the molecules in the track, but assumed that at time $t = 0$ the molecules expanded by approximately 10% in the radial direction, within a cylinder with its axis aligned with the track. They discuss the creation of an activated region, a region of atoms about 30 nm wide, up to 1000 nm long (depending upon incidence angle), and 30 nm deep, which is excited in times of the order of 5×10^{-12} sec. Their assumptions also included the case of a fast ion, for which the penetration distance was very long and the energy deposition along the ion track was constant, in the region of interest near the surface. The random path direction which might be expected from a slow ion was not included in their theory, nor was the roughness of a typical surface. Nevertheless, their results give dramatic insight into the processes of ion emission and neutral emission. Typically, a crater is formed at the point of ion impact. For normal incidence angle, the yield of nonexpanded (i.e. non-ionized) molecules was proportional to the third power of the energy deposition. If one includes the expanded (i.e. ionized) molecules, the dependence stays cubic for high-excitation densities. The yield was found to be independent of the cohesive energy of the material. The yield also increases with angle of incidence, at a faster rate than found for models based on a cylindrical thermal spike process (Johnson 1989). The ejected molecules could be divided into different groups. One group consists of those which have collided several times before leaving the sample, or which have been ejected in the form of a cluster. There is another group, which is in the majority, which

are simply pushed out of the sample in a direction roughly perpendicular to the direction of the incident ion. The ratio of ion ejection to neutral ejection depends upon the sample surface roughness. A discussion of some of the experimental data which led to the development of this theory is given by Johnson and Sundqvist (1992), from which Figure 15 is reproduced.

When a fission fragment from a ^{252}Cf source has been used as the excitation particle, the energy deposited per unit path length has been of the order of 10 KeV/nm, forming a highly-excited track region (Johnson and Sundqvist 1992). Many chemical reactions take place, and both neutrals and ions are emitted. The yield (molecules per incident ion) has been presented by Johnson and Sundqvist (1992) and is reproduced here as Figure 16. A hydrogen ion produces less than one molecule per ion, but ions of greater mass, in the range of mass 12 to 20, produce 10 molecules per ion when the ion energy is in the range 20 to 1000 eV/u. Methyl ions therefore should be expected to cause such emission.

The possibility of reactions under these circumstances has been inferred from similar discussions of astrophysical situations (Johnson 1990), in which energetic hydrogen ions from the sun strike surface atoms on interplanetary bodies (such as asteroids) which are not protected with atmospheres, causing chemical reactions (Hoyle and Wickramasinghe, 1991). The role of grain surfaces in interstellar space in assisting molecule formation has been discussed by several early authors (van de Hulst, 1949; McCrea and McNally, 1960; Gould and Salpeter, 1963; Knaap et.al. 1966; Solomon and Wickramasinghe, 1969). Reproduced in Figure 17 is a table showing the interstellar molecules which have been discovered by radio and millimeter wavelength spectroscopy measurements up to 1990 (Hoyle and Wickramasinghe 1991). Most of the atomic building blocks are hydrogen, carbon, nitrogen, silicon, oxygen, and sulfur. Theories of formation of organic grains in space include the polymerization of formaldehyde (Wickramasinghe 1974; 1975), and this has been experimentally verified by detection in the gas coma of Comet Halley (Huebner 1987; Mitchel et.al. 1987). However, laboratory experiments have also been conducted in attempts to verify such ion-impact-driven chemical effects upon surfaces.

For example, bombardment of D_2O ice yielded typically 8 molecules per ion; in explaining these laboratory results of Brown et.al. (1982), Johnson (1990) pointed out that D_2 is attached to ice with an energy of the order of 0.02 eV, that O_2 is attached with

Please consult an original printed document for color reference.

Figure 15. Computer simulation of ion impact on a surface, showing molecular dynamics and the activated region; escape of neutral molecules, and also ions, from the activated region is shown (after Johnson and Sundqvist (1992)).

Figure 16. Yield of molecules per incident ion (after Johnson and Sundqvist (1992)).

INTERSTELLAR MOLECULES LISTED ACCORDING TO NUMBER OF ATOMS

2	3	4	5	6	7	8	9	10	11	13
H ₂	H ₂ O	H ₂ CO	H ₂ C ₂ O	HCONH ₂	HC ₃ N	HCOOCH ₃	HC ₇ N	CH ₂ C ₄ N	HC ₉ N	HC ₁₁ N
CH	H ₂	H ₂ CS	H ₂ CNH	CH ₃ CN	HCOCH ₃	CH ₂ C ₃ N	(CH ₃) ₂ O	CH ₂ COCH ₃		
CH ⁺	HCN	HCNH ⁺	H ₂ NCN	CH ₃ NC	CH ₃ C ₂ H		CH ₃ CH ₂ CN			
C ₂	HNC	HNCO	HC ₃ N	CH ₃ OH	CH ₃ CHCN		CH ₃ CH ₂ OH			
CN	HCO	HNCS	HCOOH	CH ₃ SH	NH ₂ CH ₃		CH ₃ C ₄ H			
CO	HCO ⁺	HOCO ⁺	CH ₂ CN	C ₄ H	C ₆ H					
CS	HOC ⁺	C ₃ H	C ₃ H ₂							
NO	HCS ⁺	C ₃ N	C ₄ H							
NS	HNO	C ₃ O	SiH ₄							
OH	N ₂ H ⁺	C ₃ S	CH ₄							
SiO	C ₂ H	NH ₃								
SiS	OCS	H ₂ O ⁺								
SO	SO ₂	C ₂ H ₂								
SO ⁺	SiC ₂	C ₂ H ₄								
HCl	C ₂ S									

Figure 17. Interstellar molecules which have been discovered by radio and millimeter wavelength spectroscopy methods, showing that hydrocarbon synthesis by ion impact upon the surfaces of interstellar bodies and grains takes place (after Hoyle and Wickramasinghe (1991)).

an energy of the order of 0.10 eV, and that H₂O requires 0.52 eV for removal. Measurements of the product species in such fundamental experiments is complicated, but Johnson et.al. (1993) have reported that for incident ions of ¹⁶O⁺, striking a cold target of ice at an ion energy of 35 KeV, a mass equivalent of 35 water molecules is emitted for each incident ion. In other results, in which large ions bombarded a polymer (C₂H₂F₂)_n, the emission of fullerenes (C₆₀) was noted (Johnson and Sundqvist 1992). Early experiments by deVries et.al. (1984) in which solid CH₄ was bombarded with H⁺ ions at 6 KeV of energy showed the production of neutral large hydrocarbon species with mass numbers up to 170, and with at least 12 carbon atoms in some of the molecules. The production of C₁, C₂, and C₃-containing gases as a result of the hydrogen ion bombardment of a graphite surface is also known (Behrisch, 1983; Yamada, 1987).

These results serve to indicate that the interaction of charged ions at medium energy with surfaces produces a very efficient transfer of energy to the surface atoms, and allows the possibility of energy transfer among them, in times of the order of a few picoseconds. Release of the newly-formed atoms is also favored, and some of the released species will be ionic, whereas others will be uncharged (Johnson and Sundqvist 1992). The surface of a solid thus offers the opportunity to take advantage of medium-energy interactions, with the certainty of numerous collisions of hydrogen and methyl ions with the relatively stationary methane neutrals resident in place upon the surface. [This may be considered as "inertial confinement" of the target methane neutrals.] The further advantage is that the products of the reactions are easily and quickly released into the low ambient pressure environment of the test chamber, for diagnosis by GC/MS instrumentation. Conversion of residual energy from the interaction into random thermal energy in the substrate takes place after release from the surface, and after chemical conversions, with a much longer time-constant. Higher-hydrocarbon neutrals, methane neutrals, and hydrogen neutrals which participate in chemical reactions and leave the surface, due to such ion-impact-events, will be replenished (in times of the order of microseconds) by normal deposition of neutrals from the ambient neutrals available in the plasma, or by other more complex surface transfer processes.

Theoretical explanations are far from complete, however. More attention should be given to the details of interaction of an incident ion of medium energy during the first brief (~10⁻¹⁴sec) time interval of its interaction with the first few atoms of the

surface. The question of whether the bond of the surface atom with its surface-atom neighbors is severed first, and then an excitation into a higher state (perhaps including ionization) takes place, is worthy of discussion. Furthermore, the random path taken by an incident ion of grazing incidence, as it interacts with the final numbers of surface atoms, is also of interest. The dependence of the interaction of the ion upon the mass of the incident ion is important when one is considering the possibility of larger hydrocarbon ions. Finally, the difference in conversion performance, if any, between surfaces of insulators with methane overlayers, and surfaces of metals with methane overlayers, should be considered both experimentally and theoretically.

VI. POTENTIAL FOR LARGE-SCALE PRODUCTION AND COMMERCIAL USE.

The interactions of energetic hydrogen and methyl ions with surfaces at grazing incidence have been shown to lead to chemical transformations into higher hydrocarbons, which can be used as petrochemical feedstocks and as useful fuels. This has been accomplished in a microchannel plate, a structure with over 1.35 million small co-parallel tubes, aligned with an applied electric field which adds energy to ions after they are created, and moves them into parabolic pathways which intersect the inside surfaces of the tubes at grazing incidence. Experiments have been at sub-gram levels. 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, at this time, estimates of the cost and the conversion spectrum of large, continuous-flow units are necessarily based only upon parameters known at this time.

One development pathway to consider is to simply fabricate microchannel plates in large diameters, and to allow them to operate in parallel, in a large array. The standard production diameters of microchannel plates are 18 mm, 25 mm, 40mm, and 80 mm. Larger ones are occasionally made but the fixtures, furnaces, and other production facilities are not easily amenable to extend the present technology to vastly larger sizes. There is a possible approach, in which hexagonal shaped MCP's are made in the 40 mm size, and then many such hexagonally-shaped MCP's, without rim glass, are fused together on their edges, during a pass through a furnace. This approach has been used successfully in the fabrication of large telescope mirror blanks, and sizes of the order of several meters across are conceivable. The handling of such a large piece of glass would be difficult but not impossible, especially insofar as it would be made thicker, of the order of 1 cm. The cost would, as ever, depend upon the number of such units which were ordered.

Another approach is to mount several hundred of the smaller MCP's in a single 'sandwich' fixture. This makes use of the low cost and economies-of-scale of existing production facilities. This approach is viewed as quite practical for intermediate production levels, of 1 kg/day to 10 kg/day. In order to extend this method to larger

units, the limit on transverse size will come into consideration. Practical production units which are 3 meters to 5 meters in diameter can be planned, and possibly larger. However, it will be more practical to construct many such units and connect them in parallel for very large factories.

Another alternative is offered by the metallic dynode structure for the conversion of methane into higher hydrocarbons, which is a related invention by Sackinger, Morgan, and Airey, described in Appendix B. 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 for much less than \$1.00 each. The structure described in Appendix B is therefore used as the basis for our present cost-competitive estimates.

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 connection of the dynodes to the electrical feedthrough terminals would require clever engineering so that the parts cost and labor costs were minimized. Techniques for doing this have been developed in the vacuum tube production industry over the past 50 years, and therefore improvements on such basic designs should result in costs of these converters which are similar to those of multiple-gridded vacuum tubes, in the range of \$40 to \$200, depending upon the costs of labor at the production location. 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 β -emitters can provide the electrons needed for initiation of the plasma. With full control of the voltages, and of the gases entering the chamber, electrode erosion can be controlled to ensure long life. The cost of ancillary equipment which is needed to separate the output spectrum into its various components remains to be estimated for each particular application. No estimate will be given at this time. However, the amortization of the dynode-based converters over a 10-year period, and assuming that each can produce 10 kg/day, or 36.5 tonnes over its lifetime, means that one must allocate approximately \$2 to \$10 per tonne produced, to pay for the device cost.

Added to that cost will be plant operation and control costs, amortization of associated equipment for product separation, interest on investment, royalties, electrical costs, feedstock costs, overhead, contingency, and profit. At this time, an electrical energy of 2.59 kilowatt hours per kilogram has been demonstrated, based upon the conversion rate of the highest-pressure device during its first few minutes of operation, and extrapolating this value to a continuous-flow device (which has yet to be tested). It should also be noted that no dynode-based device has yet been tested, to establish its conversion efficiency. However, the microchannel-based device can have its electrical power usage decreased by a factor of 10, by changing the resistivity of the semiconducting layer which is formed during fabrication. We have background knowledge which includes the process changes required to bring about this x10 reduction in electrical power consumption. Assuming that a factor of x10 is used, the electrical energy required to produce 1 tonne of product will be 259 kilowatt hours, and the cost of this will vary from approximately \$2.59 at an oilfield location near the wellhead, to \$25.90 in a consumer location remote from a generation facility. The cost of the electricity for the dynode-version is expected to be lower, as there is no continuous leakage current. However, this remains to be established as such a device has not yet been built and tested. 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 methane supplied. 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:

HIGHER HYDROCARBON FORMED	ENERGY NEEDED	ENERGY AVAILABLE FROM BURNING HYDROGEN
C_2H_6	0.3985	-3.6772
C_2H_4	1.4854	-7.3544
C_2H_2	3.1852	-11.0316
C_3H_8	0.5314	-7.3544
C_3H_6	1.9784	-14.7088
C_4H_{10}	0.5979	-11.0316
C_4H_8	1.2132	-14.7088

The trend is for the burning of the hydrogen to provide more than enough energy for the reaction. 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. Thus, the required values of energy will be 2 times higher, and the electrical energy from hydrogen burning will be 1/2 times the values shown. A factor of 4 must be used to relate the energy from burning of hydrogen to the energy (in delivered electrical form) used for the formation of the new compounds. In addition, there will be some energy lost to the subsurface materials, in the form of heat. Nevertheless, the excess power available from hydrogen burning ranges from -1.0586 (when an alkane likethane is produced) to -0.7064 (when an olefin like ethylene is produced) to +0.8546 (when acetylene is produced). Thus, the additional burning of extra methane to supply electrical energy is necessary when acetylene is the only desired product. 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 cost for each component of the product stream will be different, according to the above table. A tonne of butane, for example, will have a minimum electricity cost of \$5.98, whereas a tonne of ethylene will have a minimum electricity cost of \$14.85. To this must be added the costs of the conversion of a fraction of the ion impact energy into heat, if the heat is not recovered; if a microchannel plate is used, and heat is generated in the semiconductor layer, an additional cost of \$2.59 per tonne would be added, assuming that the resistivity of the microchannel plate were increased by a factor of 10 using known technology. The cost of the electricity for the dynode-version is expected to be lower, as there is no continuous leakage current. However, this remains to be established as such a device has not yet been built and tested. We can summarize these considerations by estimating that electrical power costs will be in the range of \$10 to \$40 per tonne of methane feedstock.

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, and even negative 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. It would be well if a pipeline, or a tanker linkage for hydrocarbon liquids, does exist, so that marketable liquids can be thus transported. Costs of the other parts of the production installation, as mentioned above, are likely to dominate the total cost of the facility. Since these are size specific, and regionally-specific, and applications-specific, no attempt is made at this time to estimate those factors. However, the conclusion is drawn that the potential for low-cost production using this technology certainly does exist. The further phases of testing which will verify this are outlined in the chapter which follows.

VII. SOME POSSIBLE APPLICATIONS.

In one application, which is quite related to the Alaskan oil production effectiveness, the possibility is considered of converting the methane which is produced with the oil, into C₂, C₃, C₄, C₅, C₆, C₇, C₈, etc. The C₂ and C₃ can conveniently be used in the miscible-gas injection program at the Prudhoe Bay reservoir. At Prudhoe Bay, the principle has already been proven of additional recovery of the oil in place, by alternating the seawater injection with the miscible gas injection in 70 of the total of 130 waterflood patterns (Cockin 1992). Currently, an area of 8,742 hectares is under miscible gas flooding, which originally contained 3.5 billion barrels of oil. The expansion of this successful approach to a total 22,258 hectares and an original oil-in-place volume of 6.3 billion barrels is planned. The total incremental oil recovery due to miscible gas injection is estimated to be 410 to 480 million barrels of oil. The success of this project and of any miscible gas project depends upon the availability and separation of ethane, propane, and carbon dioxide from the produced natural gas stream. Reservoir management includes the use of methane injection, waterflood, miscible gas injection, and selective drilling and completion choices. The original estimated recoverable oil reserves at Prudhoe Bay, 9.6 billion barrels, have been increased to more than 12 billion barrels, using these tools (Szabo and Meyers 1993). However, at the end of the field life, approximately 12 billion barrels will be still in place, using today's technology as the limiting factor. The availability of larger quantities of miscible injectant, manufactured directly from methane using the plasma-based process, may offer an opportunity for recovery of more this oil, as well as oil in other nearby reservoirs. Rather than producing only some 30%-40% of the oil in place, it is possible in some parts of the reservoir to produce as much as 60%-62% of the oil in place, by miscible-gas injection of C₂ and C₃. The C₄, C₅, C₆, C₇, C₈, etc. also made by the plasma converter can be sent through the existing oil pipeline. Since electrical power and natural gas are abundant and available at a very low cost at the oilfield, 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 CH₄, C₂H₆, C₃H₈, C₄H₁₀, with the C₅-and-higher hydrocarbons sent into the oil production stream. This feedstock would be enriched in C₂, C₃, and C₄ by the plasma device, and C₅, C₆, C₇, C₈ would also be produced. The presence of C₂H₄ and C₂H₂ 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 which has been brought to our attention 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. Many possible mixtures are candidates for feedstocks, and certainly it would be appropriate to

experiment with some very precisely-known mixtures of two or three alkanes, as well as the practical mixtures which are representative of normal refinery residual outputs. 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 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.

VIII. 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 10 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 C3, C4, C5, C6, C7, and C8 molecules. There is a decreasing percentage of larger molecules produced, in comparison with the C2 and C3 types. 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. A conversion energy of 2.59 kilowatt hours/kilogram of output has been demonstrated, and a reduction of this by a factor of $\times 10$ is possible using known techniques. In batch experiments, the selectivity for C2 has varied from 47% to 88%, and selectivity for C6 has ranged from 0% to 12.8%. Other hydrocarbon selectivities also span a wide and useful range. The estimated costs for hydrocarbons produced with this technology will be in the range of \$200 to \$250 per tonne, in production quantities, depending upon natural gas costs and many other plant costs. 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. Pilot production experiments are recommended to make these estimates more precise, and to address strategies for scaling the technology up to production levels. These are addressed in the next section.

IX. 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 would be appropriate to target Phase II at the level of 1 to 3 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 16 months duration. Phase III, set at the level of 100 kilograms per day, is planned for 18 months duration, and Phase IV, to be at 10 tonnes per day, is also for 18 months.

As discussed above, the 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 C2, C3, and C4 by the plasma device, and C5, C6, C7, C8 would also be produced.

For experiments to examine these applications, in Phase II, we would expect to use feedstocks of CH_4 , $^{13}\text{CH}_4$, C_2H_6 , $^{13}\text{C}_2\text{H}_6$, various mixtures of $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$, 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 of our Petroleum Development Laboratory, for future analysis.

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 experiments 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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Questions and Answers

❖ 1. What is the electrical method for converting molecular weights?

It involves ionizing gases at a reduced pressure, accelerating the ions to an energy larger than the chemical bonding energies, and impacting the ions at grazing incidence upon surfaces where neutral gas molecules are adsorbed. The energetics of impact creates new gas species; both neutrals and ions of the new species are released from the surfaces by the energy of the impact events. A microchannel plate has been used, with high available surface area, and ion flow produced by the electric field. In the diagram, positively-charged ion movements are shown in a single tubular channel. (Initial ionization is produced by an electron source, and it's

cascade of electrons, when they strike the neutral atoms on the surfaces of the channel). Over one million such small tubular channels are in a single microchannel plate.

❖ 2. What materials can it be used upon?

Any single gas or combination of gases, or any liquids which can be in vapor form at the reduced pressure inside of the device, can be used as feedstock. The gas molecules will be broken into fragments, perhaps down as far as the single-atom level, and these energetic ions will recombine with available neutrals and ions to form a spectrum of new gaseous compounds.

❖ 3. Why is a plasma used?

A plasma is a convenient way to add energy to the molecules, to give enough kinetic energy to them to break chemical bonds upon surface impact, and to provide enough energy to release the new species from the surface. The ions are accelerated by an electric field, produced by an external voltage supply.¹³

❖ 4. How does the plasma interact at the surfaces?

When an ion strikes a surface at grazing incidence, many effects are possible. Some of the energy of impact can be transferred to neutral gas species adsorbed on the surface. Chemical bonds can be broken, as the available ion energy is several times larger than the ionization energy of the neutrals. Over an area of about 300 square nanometers, in a time of 60 picoseconds, new chemical bonds are formed, neutrals and ions are released from the surface and undoubtedly light is emitted. The incident ion participates in the chemical reaction. Some small amount of energy is transmitted into the bulk material. Details remain to be discovered.

❖ 5. Don't the surfaces get hot when ions strike them?

A small amount of the incident ion energy must be changed into thermal motion of the substrate atoms, but most

of the energy is used to drive chemical reactions at the surface and to allow release of adsorbed molecules from the surface.

❖ **6. What kind of surface materials can be used?**

If the neutral gaseous materials are continually being deposited on the surface, then there is a balance which is possible between ion-impact-driven removal processes, and normal deposition of gas molecules from the low-pressure ambient. The kind of material used for the substrate is chemically unimportant since it is covered with the multiple-layers of reactant molecules. If the net effect of operation is to remove surface material, then the substrate atoms will begin to participate in the reaction and will appear as part of the output products. In the microchannel plate, a lead oxide/silica glass is used, and a semiconducting layer of reduced lead within the glass is present to help ensure a stable charge and voltage profile.

❖ **7. What is the surface temperature during operation?**

The surface temperature is not meaningfully defined, as the impact velocity of an ion is in one direction, at an energy of 10 eV to 50 eV. Most of this is used in chemical changes and in ion or neutral emission processes. The average temperature of the substrate material is slightly above room temperature.

❖ **8. Can this kind of approach be used in a continuous-flow system?**

Yes, this can be used in continuous-flow operation as all positively-charged ions move from the gas inlet side of the microchannel plate to the gas outlet side. Some negatively-charged gas ions

may flow against this dominant direction but their effect is not presently believed to be significant, according to recent data.

❖ **9. What is the operating pressure in the device?**

The operating pressure has been varied from very low values, to as high as 0.1 kPa, in the first experiments. Future experiments should show that an operating pressure in the range 0.5 kPa to 1 kPa is feasible. Nevertheless, this device is expected to operate below atmospheric pressure.

❖ **10. Can the amount of flow of material through the device be increased, by increasing the pressure?**

The flow of material through the device is a linear function of pressure, and it is believed that an increase in throughput of from 5 to 10 times the demonstrated rate should be feasible.

❖ **11. What happens when the internal operating pressure is too high?**

When the internal operating pressure is too high, the ions and electrons will strike neutrals in the gas phase, before the ions and electrons have acquired enough energy to cause the desired chemical reactions and desorption of new species at the surfaces. Although some ions and electrons produced in this way from gas-phase collisions may be useful, the ions must still have a sufficiently long path to acquire the necessary energy for the surface reactions.

❖ **12. What voltages are used in the device?**

The choice of voltage depends upon the length of the tubular channels. It has

been found that 4 volts per diameter is a threshold field strength for the reactions to begin. In recent experiments with channel length of 120 diameters, a minimum voltage of 480 volts was used for conversion. Higher voltages, up to 15 volts per diameter, have been used successfully. With higher resistance microchannel plates, even higher voltages may be used.

❖ **13. How much electrical current flow is needed?**

There is a small electrical current flow in the semiconducting layer within the glass, of the order of 5 picoamperes per channel, in the microchannel plates used. This depends upon the activation process in microchannel plate manufacture, and can be controlled to be lower by a factor of 100. An operating power of 4×10^{-9} to 4×10^{-11} watts/channel is typical.

❖ **14. What is the electrical energy used to convert a kilogram of input methane?**

Conversion of methane into higher hydrocarbons, plus hydrogen, requires the addition of energy, due to the different chemical bonding of the products. The energy needed will depend on the product mixture. On the basis of a kilogram of methane input, 0.4 kilowatt-hours is needed to produce ethane, 1.5 kilowatt-hours for ethylene, 3.2 kilowatt-hours for acetylene; 0.5 kilowatt-hours for propane, 1.3 kilowatt-hours for propylene, 1.97 kilowatt-hours for diacetylene, 0.6 kilowatt-hours for butane, and 1.2 kilowatt-hours for butene. Similar values can be calculated for higher hydrocarbons. Added to this will be 2.59 kilowatt-hours for electrical leakage current in the microchannel plate; if the resistivity of the microchannel plate is increased by a factor of 10 using known technology, this power will become about 0.2

kilowatt-hours. A total power of about 0.6 to 1.7 kilowatt-hours is expected.

❖ **15. What is the electrical energy cost for a kilogram of input material?**

Hydrogen is also produced, and can be burned in an electric generator to provide nearly all of the power required, for most product mixtures. The fuel cost for electricity is negligible. The electric generator depreciation will result in an electricity cost of about \$.01/kilowatt-hour, and a kilogram of input material can be expected to be converted for \$.006 to \$.017 (i.e., \$6-\$17/tonne) of electrical cost. To this must be added the local cost of the feedstocks to be converted, for a full economic analysis.

❖ **16. What is the output spectrum of materials when the input is methane?**

Methane input gives outputs of hydrogen; methane; ethane, ethylene, acetylene; propane, propylene, diacetylene; C₄, C₅, C₆, C₇, and C₈-containing hydrocarbons; carbon monoxide; and trace gases. Some methyl ions and hydrogen ions are recombined back into methane, so net conversion is less than 100%. The main products are in the C₂ and C₃-containing hydrocarbons. These are further upgraded to larger hydrocarbon molecules as operation time is increased.

❖ **17. Isn't there any way you can make the output material more selective?**

The inherent statistics of this process means that all hydrocarbons might be made. It has been found that hydrocarbons with fewer hydrogen atoms (e.g., olefins) are produced at higher electrical voltages, so that the output spectrum mix is voltage-dependent and pressure-dependent.

❖ **18. What is the effect of changes in operating voltage?**

Changes in operating voltage affect the conversion rate and also the output spectrum.

❖ **19. Don't the surfaces get clogged with carbon deposits as the device operates? Is there any way around such a problem?**

There is a mode of operation in which the surfaces are net accumulators of both carbon and hydrogen. However, these can be removed by the action of hydrogen ions. We have used isotopes of hydrogen, and isotopes of carbon, to explore this phenomenon to some extent. It is certainly practical to limit the buildup of deposits by removing them with an appropriately high level of hydrogen in the system, at a proper microchannel voltage, and for a limited time. However, the operating conditions can be chosen to provide a near-balance at the surface, with accumulation being a very slow process.

❖ **20. Can the sizes of the channel diameters be made larger or smaller? What are the limitations on size of channel diameter?**

The channel diameters may be made larger, thus admitting neutral gas molecules more readily. The disadvantage is that a smaller surface area is available, for a given device volume, and the interaction and conversion processes are at a reduced rate. On the other hand, the channels, which are made by glass fiber drawing technology, can be made smaller than the 12-micron size used in past experiments. A channel diameter of 33 nanometers (.033 microns) has been demonstrated. Although such a microchannel plate has greater surface area, the entry of the feedstock gases into the small channels may be rather

slow, limiting the reaction rates. The optimum choices of channel diameter will depend on input pressure, channel length, gases chosen for conversion, and on operating voltage.

❖ **21. What technology is used to make a microchannel plate?**

In the manufacture of microchannel plates, the usual process is to use a core glass rod and a different cladding glass tube as a starting assembly. These are heated and drawn to small fibers. The fibers are packed together, and the resulting "multi-fiber" bundle is redrawn to a smaller size. The drawn "multi-fiber" bundles are then packed together and fused to make a "boule." The boule is sliced to make individual plates. After polishing the plates, an acid etch removes the core glass, leaving a microchannel plate with 1.3 million holes, each of about 12-micron diameter. This plate is fired in hydrogen to produce the semiconducting layer, inside the channels. The final step is to evaporate metallic contacts on both faces. A hollow-draw technology has been developed which avoids the etching step, in the case where dimensional control of channel hole size is not critical.

❖ **22. How long can the channels be made?**

The microchannel lengths are, for the solid-core-approach, limited by the etch ratio of core glass-to-cladding glass, to a length of the order of 500 diameters. Present construction is at about 40/1 ratio of length to diameter. Several microchannel plates can be stacked together, if longer lengths are needed. Alternatively, the hollow-draw technology can be used and there is no practical limit on the available length-to-diameter ratio in that case.

- ❖ **23. How large can these microchannel plates be made?**

Microchannel plates for electronic high-speed devices have been up to 120 millimeters in diameter.

- ❖ **24. Can one conceive of microchannel plates several meters in diameter and several millimeters thick? How might they be made?**

The technology for making many hexagonal or square microchannel plates, placing them adjacent to and touching each other, and fusing them in a furnace, is a possibility. This approach has been successful in making low-expansion glass plates for astronomical mirrors.

- ❖ **25. Do the channels have to be circular in cross-section?**

The channels have started with circular cross-section in the first draw because round glass rods and tubing are commonly available. However, custom glass fabricators have started draws with square cross-section, and with many other shapes. Shape is preserved in the drawing process, and the cross-section shape can be chosen to allow minimum quantity of glass, for example, or can be based on other criteria. All shapes will give conversion on the interior surfaces.

- ❖ **26. Do the faces of the microchannel plate have to be polished flat?**

The microchannel plate faces are polished flat to reduce undesirable electron emission noise in electron devices. In this device, extra electrons enhance the ionization probability and a rough microchannel plate surface could be advantageous.

- ❖ **27. How are the electrodes applied to the faces of the microchannel plates?**

Electrodes are applied by vacuum evaporation of a metal film, such as aluminum, onto the faces.

- ❖ **28. I produce ethylene now for petrochemical feedstock. My factory uses naphtha crackers. Why should I consider this new technology for a future factory?**

This method uses natural gas directly, with feedstock prices in the range of zero to about \$52 per tonne, depending upon distance from the natural gas wellhead. Development of this technology should produce ethylene for \$250 to \$300 per tonne, a cost saving over present equipment. The spectrum of output products can be varied in this device to adapt to production requirements, by changing pressure and voltage. This type of device, using abundant natural gas feedstock, avoids the fluctuations in naphtha prices which are linked to crude oil prices. In the long time perspective, world oil stocks are being depleted while natural gas reserves are abundant.

- ❖ **29. If natural gas is to be used as a feedstock for a major part of the industry, won't this cause an increase in natural gas prices?**

The manufacturers who first embrace this technology will lock in options or ownership of large natural gas reserves at today's low prices. This technology can be applied readily to regions where natural gas reserves are not yet deliverable by pipeline, and are presently valued at low prices. As the technology becomes widespread to the point where natural gas for plasma-based conversion reaches 10%–20% of the pipelined natural gas used as fuel, there would probably be an increase in natural gas prices related to the use of

natural gas for the higher-value-added products produced by this process.

- ❖ **30. I am buying crude oil and refining it to make transportation fuels and heating oil. Can natural gas be my basic input material, and can I get this kind of device to produce transportation fuels?**

The technological performance of this device does include production of transportation fuels and heating oils. Favorable economics, in relation to products based on crude oil, will require several years of device development with attention given to reduction of device manufacturing costs. Once this is done, transportation fuels are expected to be directly produced from natural gas feedstock using these plasma-based surface conversion principles. This would provide a way to utilize excess natural gas produced with oil, in both offshore and onshore locations.

- ❖ **31. How large a device is needed to produce 1 kilogram of output per day?**

Based on demonstrated conversion rates and pressures already used, a device 400 millimeters (15.7 inches) in diameter and 100 millimeters (3.9 inches) in height would produce 1 kilogram of output per day. If, as expected, higher operating pressures are possible, this size would be reduced. A first prototype device at this level of throughput would probably have somewhat greater height, for fabrication simplicity.

- ❖ **32. How much will it cost to build 1000 devices, each of which will produce 1 kilogram of output per day?**

It is not possible to give close estimates, but certainly the cost of production

would decrease as more devices are built. Production costs in the range \$500 to \$800 per device should be possible, depending mainly upon the cost of assembly labor.

- ❖ **33. Are there any discharges into the environment associated with the use of this device? What are they?**

This device is a totally-sealed system and there are no discharges into the environment. It may be found that trace quantities of water and carbon dioxide are produced in large production units, and these would be selectively removed in the cryogenic distillation unit which follows this device. These could be considered for possible discharge, if necessary. However, since oxygen is not fed into the device when it is used as a methane converter, these oxygen-containing output gases would be at very low (trace) levels. The hydrocarbon inputs imply hydrocarbon and hydrogen outputs only.

- ❖ **34. Can this device be used to produce liquid hydrocarbons which will have a lesser impact on the environment than those burned today?**

Yes. The ion impact process produces single, double, and triple carbon-carbon bonds. However, the production of aromatics such as C_6H_6 (benzene) and larger aromatic compounds seems to be absent for most electrical voltages, and at very low trace levels for some special conditions of voltage and pressure. Aromatics, which are carcinogenic, would be at only trace levels in fuels made by this process. The cryogenic distillation of the output spectrum of this device would automatically isolate butane, pentane, hexane, heptane, octane, nonane, decane, etc.—all of which have the maximum number of bonded hydrogen atoms for their carbon-number. These could be

blended for fuel use and the resulting release of combustion products would maximize the ratio of water to carbon dioxide, for a given amount of energy produced. This would minimize the carbon dioxide release, as compared with combustion of aromatics in fuels derived from crude oil, and is viewed as environmentally desirable.

❖ **35. What can one do with the excess hydrogen produced by this device?**

The hydrogen produced from the device could be used for local industrial purposes, such as the hydrogenation of various recycled plastic materials. It can be recycled into the plasma conversion device, together with acetylene, to increase production of ethylene and ethane, if desired. It can also be burned as fuel, or to generate electricity, while releasing no carbon dioxide. If the hydrogen is produced near an oil reservoir, it may be useful in tertiary oil recovery technology, in which the hydrogen is injected into the reservoir. If coal is locally available, the use of hydrogen in coal gasification or coal liquefaction could be considered. Hydrogen can also be used in advanced-technology mineral smelting and refining processes.

❖ **36. Can this conversion be used to produce only small quantities of liquids, instead of large quantities?**

It is possible that conversion units could be made which would produce tens, hundreds, or thousands of kilograms per day, in consumer locations. The full utilization of all of the product spectrum derived from such a unit is unlikely, however, in such a scenario, so provision for recirculating unneeded output fractions back into the unit would have to be made to ensure full use of all of the input material and no waste output product.

❖ **37. Can it be a consumer-level product, making liquid transportation fuels in each homeowner's garage for use the next day?**

Possibly, with clever engineering, such a small unit would be as easy to manufacture in large quantities as large multi-tonne units. Units sized to meet the daily throughput needs of gasoline filling stations are another possibility.

❖ **38. Can it be used to upgrade gasoline or liquid fuels presently produced, to make them more environmentally acceptable when they are burned?**

The methane can be combined with gasoline or liquid fuels in this device. The experiments remain to be done, but the expected effect would be to convert aromatics into olefins or paraffins, adding hydrogen to them, and leading to a higher ratio of water-to-carbon dioxide when these molecules are burned. This minimization of carbon dioxide release is viewed as environmentally desirable.

❖ **39. If natural gas is the preferred fuel to use as oil is depleted, will this device make it easier to use gas for many other purposes, more than those in use today?**

Yes. This technology can provide the linkage between natural gas, the most likely fuel for the twenty-first century, and the portable, concentrated liquid hydrocarbon fuels which drive today's and tomorrow's equipment. Re-engineering of the world fleet of hydrocarbon-burning equipment is therefore not necessary. The use of more environmentally-suitable fuels, in today's equipment, would be the consequence of this technology.

- ❖ **40. Can this be used to convert natural gas, near the well-head, into easily-transportable liquid fuels?**

Yes. Natural gas could be converted, near the wellhead, into ethylene and propylene, which is shipped routinely in cooled tanker ships to petrochemical factories at other locations in the world. Higher hydrocarbons could be shipped as liquids in tankers, or blended into a crude oil or refined product pipeline if available. The liquid fuels could also be used to operate equipment, such as transport vehicles, in the gas field development.

- ❖ **41. If liquid fuels such as pentane and hexane are produced using this device, and are transported by ship, what would be the impact upon the environment of a shipping accident, as compared to a ship filled with crude oil?**

Pentane and hexane are lightweight hydrocarbons that evaporate readily when exposed to ambient air. They leave no residue, such as one would have in the case of a crude oil spill. Their possible carcinogenicity is not well-known but is expected to be lower than that of aromatic hydrocarbons such as benzene, found in crude oil.

- ❖ **42. Can the output hydrocarbons from this device be used for aircraft fuels?**

Yes. Both jet fuels and aircraft gasolines may be blended products produced from the spectrum of hydrocarbons produced by this technology.

- ❖ **43. Can methane from biomass be used as an input to this device, to produce useful fuels?**

Methane from any source, including biomass, can be used as input to this device. Liquid fuels can thus be provided from the outputs of methane—generating anaerobic bacteria.

- ❖ **44. Can this device produce methyl alcohol, or ethyl alcohol, or MTBE?**

The production of partially-oxygenated hydrocarbons, such as alcohols and MTBE, is possible in principle in this device but has not been demonstrated as yet. The addition of small quantities of water to the input methane feedstock stream would be one possible approach. Ionization of water would occur, with production of carbon monoxide, water, carbon dioxide, and alcohols within the sealed system. After cryogenic distillation of the alcohols, the other oxygen-containing gases could be recirculated into the system.

- ❖ **45. Can this device be used to crack large molecules, containing 12 to 20 carbon atoms, to change heavy fuels into lighter fuels?**

Yes. When operated at high voltage values, this device seems to be able to disrupt carbon-carbon bonding and change heavy hydrocarbons into lighter ones. However, more experiments are needed to determine whether this is economic.

- ❖ **46. What happens if this device is fed with trace impurities in the natural gas, such as hydrogen sulfide, sulphur dioxide, and carbon dioxide? Do these interfere with the performance of the device? What output products would be expected?**

Trace impurities in the feedstock stream will certainly be ionized, as the methane is ionized, and will recombine with the carbon and hydrogen present to form new trace compounds, as well as the original starting compound. The

performance of the device would not be impaired, and the cryogenic distillation of the output would enable the separation of the various trace impurities present. They would have to somehow be disposed of, as recirculating them into the device would only lead to unwanted buildup. They could be combined with oxygen, nitrogen, or other gases in a separate plasma-induced conversion device, to put them into a benign chemical form prior to discharge.

❖ **47. Are there any other devices using these principles, which might be competitive with this device?**

Two devices are patented in the USA, and pending in other countries. One, described above, uses the microchannel plate. The other uses an array of metal dynodes. Both are assigned to the University of Alaska and are available as a package for licensing.

❖ **48. Why not use existing technology involving catalysts for molecular conversion?**

Catalysts require periodic regeneration or replacement. They are expensive to produce. They often require the use of a high temperature to supply energy for breaking the carbon-hydrogen bond in methane. Some catalyst-supported chemical pathways are complicated with chlorine reactions, for example, and by-products may be difficult to recycle.

❖ **49. Can this be used to treat the exhaust gases from automobiles or power plants? Can it change the CO₂, NO_x, SO_x emissions?**

Generally, any molecule can be ionized, and combined with others, in this device. A mixture of CO₂, NO_x, and SO_x could be combined with methane or ammonia to change the output mixture. Adding a hydrogen-containing gas to the device

should give a larger amount of the output oxygen in the form of water. Experiments have yet to be done in this direction, but the possibilities do exist for treating power plant or auto emissions with the throughput of the device increased.

❖ **50. Is there any possibility of using this device to dispose of used, reclaimed chlorofluorocarbon gases?**

Yes, the chlorofluorocarbon gases would be ionized and could be combined with other elements such as hydrogen, carbon, or oxygen. The most benign family of output gases would have to be sought, and experiments would be required.

❖ **51. Both carbon dioxide and methane are recognized greenhouse gases which relate to global warming. Is there any way that this type of device can help reduce release of carbon dioxide and methane into the air?**

Use of this device would mean a greater use of methane for man's needs. Hydrogen would be available as one of the outputs and could be used as a fuel to generate electricity, either by combustion or in fuel cells. Carbon dioxide production would be less, for a given amount of energy produced, as compared with the combustion of oil or coal.

❖ **52. How much glass is used to make this device? What is the energy cost of making the glass, and what are the components of the glass?**

In recent tests, the three microchannel plates together had a mass of about 0.9 grams. The glass used was a mixture of silicon dioxide, lead oxide, aluminum oxide, and the oxides of sodium, potassium, lithium, cesium, and rubidium in smaller quantities. Many variations on this glass composition are

known to work. The energy needed to melt these oxides and form this glass is small and depends upon furnace design efficiency.

❖ **53. Where in the world does the technology exist to make microchannel plates?**

Technology to make microchannel plates to the moderate specifications needed for this device exists in the U.S.A., The Netherlands, France, Germany, Czech Republic, Russian Federation, Japan, and probably elsewhere.

❖ **54. In what countries are there patents issued or pending on this device and it's dynode counterpart device?**

Patents are issued or pending in USA, Canada, Europe, Norway, Finland, Russian Federation, Latvia, Hungary, Japan, South Korea, and Australia.

❖ **55. Is it difficult to make this device?**

No, the microchannel plate is described in the Scientific American of May 1981, pp. 62-71. It is made by the glass redrawing techniques, known for over 30 years.

❖ **56. What is the production yield expected?**

Production yields of over 95% are expected because of the moderate, relaxed specifications on the device when used for gas conversion purposes.

❖ **57. What is the expected operating life of the device? What is the limiting factor on operating life?**

Since the device has not yet been subjected to life testing, only an initial estimate is available. An expected

operating life of 10 years appears reasonable. Deposits of carbon in the device are removed continuously by hydrogen ion impact reactions; Hydrogen diffusion into dynode substrate metals has been suggested as one factor to quantify; other factors limiting life have not been identified.

❖ **58. What are the next logical steps in the development process for this device?**

Three development requirements have been identified. First, several devices capable of throughput of 1 to 10 kilograms per day need to be built and tested. Secondly, a set of dynode-based units operating at 1.10 kilograms/day should be built and tested. Thirdly, experiments with devices at the 100-1000 kg/day need to be built.

❖ **59. How can these development tasks best be accomplished?**

Construction of the 1-10 kilogram/day devices in the University of Alaska Fairbanks, and construction of the second device types in other laboratories, are under consideration. Testing can take place at either the University of Alaska, or in other laboratories.

❖ **60. What time frame is needed to finish development?**

A time frame of 16 months for the first task, and three years for the second and concurrent third task, is envisioned.

❖ **61. What costs are needed to finish development?**

Estimates are that US\$0.5 million is needed to completely finish development of the 1-10 kilogram/day device.

- ❖ **62. What applied research is to be directed towards making the production costs of the output products to be as low as possible?**

Cost-reduced mounting and assembly methods, and trials of the simple multiple-metal-dynode version of the device, are part of the development process.

- ❖ **63. How can I get an exclusive license to make, sell, or use this kind of device? Who owns the rights to the device?**

The University of Alaska owns the device rights and is aggressively pursuing license opportunities.

- ❖ **64. Is there any special know-how in making or using this device? If so, how can I get access to it?**

Experiments, and theoretical research, have built up a body of trade secrets which are available as part of licensing agreements. In countries where patents are not being applied for, these are the basis for the licensing process.

- ❖ **65. Can this device be used to prepare other industrial or agricultural chemicals or fertilizers?**

The plasma reaction process, where energetic ions react with neutrals at surfaces, can combine any starting gases to give a mix of possible output compound gases. An example is nitrogen and hydrogen combining to make ammonia. Any substance with an appreciable vapor pressure (e.g., 0.1 kPa) at room temperature can be part of the reaction.

- ❖ **66. If this device is used near the well heads of an oilfield, to convert the methane associated with oil**

production, can some of the products be injected into an oil pipeline and sent through the existing oil refinery chain?

Yes, the gas liquids produced in this device (C₃-C₆) can be put into an oil pipeline in limited quantities. Higher hydrocarbons may be injected in unlimited quantities.

- ❖ **67. Does this device produce gas liquids from methane, that could be reinjected into an oil reservoir to increase net oil recovery?**

Yes, this device produces C₂, C₃, C₄, C₅ and higher hydrocarbons. One use is to inject them into an oil reservoir to increase oil recovery.

- ❖ **68. Can this device be used to molecularly combine methane with gas liquids to give hydrocarbon fuels or pipeline-transportable liquids?**

Yes, C₂ and C₃ hydrocarbons will combine with methane within this device to give C₄, C₅, C₆, C₇ and higher hydrocarbons which are simple to use as fuels or to move by pipeline.

- ❖ **69. What is a typical cost of electricity in an oilfield where abundant natural gas is available and is being reinjected?**

Electricity costs depend upon gas turbine/generator set maintenance and amortization schedules, but are rather low... in the range \$0.01 per kilowatt-hour.

- ❖ **70. Can natural gas found in remote Arctic regions be converted to fuel liquids with this device, and then shipped by tanker to world markets directly, bypassing the refinery?**

In principle, natural gas in any remote tidewater location—Arctic or tropic—can be converted, blended, and shipped directly to world spot markets using this device to create the usable product spectrum.

❖ **71. Does the U.S. government have any rights, title, or interest in this device?**

The U.S. Department of Energy has supported the experiments proving the commercial feasibility of the device, but the invention took place prior to the government support so the U.S. government has no intellectual property rights.

❖ **72. Can licensing terms to a company be linked to a shared equity interest in the company, and/or to a royalty interest in the output products of the device?**

Yes, a license can include an equity share in the licensee company to be transferred, initially or Technology Development Corporation, to the University of Alaska Foundation. A license can also provide for an initial cash payment and/or a cash royalty based upon device throughput when production takes place.

❖ **73. Is there any historical evolution of microchannel plates which has led to this device?**

Microchannel plates have been known to have hydrogen ion feedback for over twenty-five years, as the ions have caused degradation of the photocathodes of image intensifiers using microchannel plates. However, the chemical reaction concept is new.

❖ **74. How are microchannel plates used today?**

They are the electron gain element in Generation II and III image intensifiers and television cameras, for low-light-level applications. They also have uses in space instrumentation.

❖ **75. Are there any examples in nature where the physical process of ion interaction with solid surfaces, at low pressures, have been studied?**

For many years, cosmologists and astrophysicists have studied the flow of energetic hydrogen ions away from the sun (the "solar wind") and what effects these have when they strike surfaces of planets and moons which do not have a protective atmosphere. The chemical conversions on such interplanetary surfaces have been the subject of several laboratory studies; several books and many journal articles have been written on this subject.

❖ **76. Can this device be used with inputs of methane and hydrogen chloride or other chlorine-containing feedstock to produce vinyl chloride or other more complex petrochemicals?**

Yes, complex chlorinated petrochemicals should be produced in this device. Future experiments will include this possibility.

❖ **77. What is the velocity of an ion which has been accelerated through a one-volt potential difference?**

An ion accelerated through a one-volt potential has a velocity which depends on its mass. The reactions which take place depend primarily upon the ion energy (eV) which should exceed the chemical bonding energy of the neutrals on the surface.

❖ **78. What are some ranges for the value of the input gas (methane) and**

the output gases (hydrogen, ethylene, acetylene, ethane, etc)?

The economic value of methane ranges from less than \$20/tonne at a remote oilfield, to \$100/tonne at a consumer pipeline, to \$200/tonne at a LNG regasification facility. The economic value of hydrogen is \$500 to \$800/tonne, ethylene is \$300-\$500/tonne, and other gases are similarly variable, depending on location.

❖ **79. How do you separate the mixture of output gases into individual gas streams?**

The output gas may be separated by cryogenic liquifaction/distillation.

❖ **80. Can this device be used for making rare or corrosive gases?**

In principle, most gases can be made.

❖ **81. Can this device be used to convert coal-bed methane into useful liquid fuels?**

Yes, once coal-bed methane is extracted, this device can convert it into useful liquid fuels.

❖ **82. Can this device be used to decompose water into hydrogen and oxygen?**

Yes, this device will decompose water but it will also recreate water. An input of water vapor will give an output of oxygen, hydrogen, and water vapor. This is of doubtful commercial use.

❖ **83. Can this device be used to decompose NO_x into nitrogen and oxygen?**

Yes, NO_x would be decomposed and could be combined with hydrogen to make water and ammonia.

❖ **84. What role does the University of Alaska want to take in the technical development of this device?**

The University wishes its scientists to be available to participate in the development of production devices, which, however, may be primarily accomplished in industrial development laboratories. Research questions may be addressed in either University laboratories, industrial laboratories, or government laboratories with the contributions of University scientists and others.

❖ **85. Who have been the scientists principally responsible for this device?**

The four scientists are W.M. Sackinger, V.A. Kamath, B.L. Morgan, and R.L. Airey.

❖ **86. Who has funded development of this device so far?**

The U.S. Department of Energy, Morgantown Energy Technology Center, has provided funding.

❖ **87. Is it possible for industrial laboratories to continue device development, in a collaboration with the University of Alaska and the inventors?**

Yes, this would be an ideal arrangement.

❖ **88. Is the University of Alaska seeking government funding to further develop this device?**

Yes, the DOE is being asked for some next-stage funding, as is the Alaska Science and Technology Foundation.

❖ **89. Is this device technically and commercially feasible?**

Yes, the attached manuscript proves technical feasibility and the cost estimates show commercial feasibility.

❖ **90. What opportunities are available for small companies and/or venture capital to participate in this device development and exploitation?**

Licenses may be signed with small companies, in exchange for equity shares.

❖ **91. Is the State of Alaska involved? If so, how?**

The State of Alaska has assisted in arranging for some licensing discussions with Pacific Rim companies.

❖ **92. What is a realistic target date for devices of this type to be developed, produced, and sold or leased at an incremental profit?**

Development of the pilot-scale device will take two years. A full-scale production unit would take an additional 2-4 years, with first commercial production in 1997-1999.

❖ **93. How much capital would be required for a small company to do this?**

A small company would probably invest \$1 million in the next stage, and the bank financing of the production unit stage would depend on the size chosen, but would be at least at the \$20 million level. This would be paid by the product value added over the unit operating life.

❖ **94. What strategic alliances with gas owners would be useful for a company developing and exploiting this technology?**

A gas delivery contract, at a favorable price, would help lock in profits from the value-added contribution of this device.

❖ **95. Are there any other related technologies which are not yet proven, but which could provide additional broader markets for devices in this general family?**

A device to use methane plasma in combination with coal, to gasify and liquify coal, has been invented. The use of methane plasma to reduce mineral ores is also being planned.

❖ **96. Can custom fuels be made for engines using this device, which may have more complete combustion and/or lower undesirable emissions when used in conventional engines?**

Fuels made in this way would be low in aromatics, having a clean-burning character like one experiences with propane and butane.

❖ **97. How can a moderately-sized independent oil or gas producing company exploit this device?**

An independent company can contract to buy methane in a low-priced location where it is undeliverable; convert it to a liquid hydrocarbon mixture; and deliver it to market.

❖ **98. How can a major oil or gas company exploit this technology?**

A major oil and gas company can acquire significant holdings of natural gas in tidewater/undeliverable locations around the world; then convert the gas to liquid hydrocarbons, and market it in normal channels. They can also use this technology to convert natural gas produced with the oil in the oil field, thus

avoiding reinjection costs or flaring of the gas.

❖ **99. How can a petrochemical producer exploit and profit from this technology?**

A petrochemical producer can acquire holdings of natural gas, or delivery contracts, at favorable prices; then convert the methane to ethylene, acetylene, propylene, and vinyl chloride near the well-head; and ship the products to feed the existing or newly-constructed petrochemical facilities. Old steam-crackers can be retired.

❖ **100. How can the owner of large natural gas reserves utilize this device to increase the value of his resources and move them to market?**

The owner of natural gas can invest in the development of the device, as it will increase the value of methane resources in the ground. He can reap eventual profits wherever the device is used.

❖ **101. How can internal combustion engine manufacturers make profits from this technology?**

The production of clean-burning fuels from cheap natural gas means less expense in pollution control equipment on combustion engines. The possible use of this technology on vehicles to reduce pollution, as a replacement for catalytic converters, is also worthy of investigation.

❖ **102. How can government agencies advance the public interest by moving this technology into the production phase?**

Government missions, such as increasing the use of abundant domestic supplies of natural gas, reducing

greenhouse gas emissions, reducing pollution, and increasing coal usage by using this family of devices to liquify coal, would all be advanced by government investment.

❖ **103. How can a government agency improve the environment with this family of technical approaches?**

Greenhouse gas emissions would be less, and aromatics in fuels would be lessened.

❖ **104. How can a financial specialist benefit from the transition of this technology from the laboratory to full global use?**

The value added by this technology can be partially captured by investors who provide venture capital and financial services to move this to production.

❖ **105. Which countries in the world are best poised to use this new technology?**

All of the countries in the developed and emerging sectors can use this technology. They can also apply this technology in less-developed countries where methane reserves exist.

❖ **106. How might this device benefit the living standards of those living in lesser-developed countries?**

The local production of transport fuels, from indigenous methane resources, will give an improvement in the balance of payments.

❖ **107. Can this device be made and/or utilized in lesser-developed countries?**

It requires a full knowledge of the manufacturing techniques to make it in

the lowest-labor-cost countries of the world.

- ❖ **108. How much ethylene is produced each year as petrochemical feedstock?**

About \$27 billion to \$30 billion worth of ethylene is produced each year.

- ❖ **109. Is ethylene shipped in cryogenic tanker ships regularly?**

Yes, over a million tonnes of ethylene is shipped in bulk carriers each year.

- ❖ **110. What price range has ethylene had for the past several years?**

Ethylene prices have fluctuated in the \$400-\$500/tonne range, following a known cyclical behavior related to facilities over expansion in the petrochemical business.

- ❖ **111. Is the existing ethylene business profitable?**

Recently, there has been an oversupply.

- ❖ **112. What is the growth rate, and the replacement rate, for ethylene production plants?**

An industry growth rate of 5%/year, and a retirement rate for steam crackers of 5%/year, has been mentioned. Thus, new ethylene plants are... over the long term....justified.

- ❖ **113. What is the use of industrial hydrogen at a petrochemical factory; at a remotely-located oil and gas field?**

Hydrogenation can be used to recycle plastics. Hydrogen can be used as fuel. It can upgrade heavy oil fractions in crude oil in remote locations.

- ❖ **114. Has there been some theoretical analysis of ion impact effects on surfaces?**

Yes; these are computer analyses by Sundqvist and colleagues.

- ❖ **115. I am a new manufacturer of glass and special products based on glass. How can I profit from the exploitation of this device?**

The clever, low-cost construction of large-area glass microchannel plates would be a good initiative.

- ❖ **116. Do you plan to make computer simulations of these ion-driven surface chemistry conversion processes, to further study the basic operations of this device?**

We will collaborate with others to do such basic studies.

- ❖ **117. What are the similarities, if any, between the physics of this device and the physics of the aurora?**

The plasma physics in this device relies upon methane plasma striking surfaces. The aurora is a plasma in the upper atmosphere, where few particle surfaces are present. The creation of ions by energetic hydrogen and by electrons, and some of the basic physics, are similar.

- ❖ **118. What are the competing processes today to change natural gas into liquid fuels?**

The usual process is the Fischer-Tropsch method, the production of synthesis gas at high temperature, the partial oxidation of methane to methanol, and the use of catalysts and high temperatures.

- ❖ **119. At what value of crude oil, approximately, does this new technology become an economical alternative to the use of crude oil for liquid fuels?**

The essential factor is the well-head price of natural gas (\$??\$/tonne), added to the projected cost of this device's use (\$200/tonne), in relation to the crude oil + refinery costs (\$??\$/tonne). This technology and any methane-source technology will put a ceiling on the crude oil price, and provide an "insurance policy" for the consumer against extremely high oil prices.

- ❖ **120. At what value of naphtha, approximately, does this new technology become an economical alternative to the naphtha cracking for production of ethylene?**

The similar equations may be applied, with the amortization of the naphtha cracker included in the ethylene cost.

- ❖ **121. How can a chemical engineering equipment contractor exploit this technology?**

The front-running equipment manufacturer will lead in the installation of the next generation of ethylene plants using this technology.

- ❖ **122. Isn't there energy needed to produce the ionizations? Is it recovered?**

Energy for ionization is recovered at recombination, and may be used for escape of neutrals and ions from the surface. Optical photon emission and absorption is present as well; most energy is recaptured.

- ❖ **123. When an ion recombines with the methane neutrals and an electron to make a larger neutral molecule, the**

electron may have come from a region of lower potential, and energy will have been used to move it to the recombination site. Does this energy, supplied presumably from the exterior power supply, get converted into thermal energy?

A fraction of impact energy and of photon energy will be converted gradually to thermal energy. Most impact energy will cause chemical reactions and escape from the surface, due to the grazing incidence angle of the impacting ions and the short (10^{-12} sec.) time required for these favorable processes. The electron resistive heating takes place in the glass microchannel device but not in the dynode device.

- ❖ **124. Depending upon the efficiency of the natural-gas-fired electric power generator, it may require approximately 265 grams of fuel to produce one kilowatt-hour of electrical energy. Using the demonstrated value of 2.59 Kwh/kg, for the electrical energy needed to produce one kilogram of output, it seems that a total of 1.686 kg of input natural gas would be needed to produce 1.00 kg of output; this is a conversion efficiency of about 59%. How can this be improved, and what are the economic consequences?**

The level of efficiency may be improved by using a microchannel device with a factor of ten larger resistivity, as noted above, for which the expected energy requirement would be .26 Kwh/kg. The produced hydrogen can be used as fuel, and will meet nearly all of the electrical requirements. Alternatively, the dynode device approach could be used, with energy requirements expected to be lower as well. In economic terms, this efficiency will influence the permissible range of feedstock costs, for a given device capital cost and a break-even

scenario. By moving the location of operation of these units closer to the gas wellhead, or by using waste gases with zero value as feedstocks, the efficiency becomes of less economic importance.

- ❖ **125. Petrochemical installations have joints in their pipe connections, a small fraction of which will have leaks. Operating at a pressure above atmospheric, this leads to a minor discharge into the atmosphere, but if the system were to be operated below atmospheric pressure, oxygen and nitrogen from the air would be leaking into such a system mixing with the methane, and possibly leading to an explosive mixture within the system. Is there any way to prevent this?**

The chamber in which plasma-based conversion is accomplished will very likely be below atmospheric pressure and must be free of leaks. Adjacent connections must also be free of leaks, up to the input side of the vacuum pump. Welding technology for standard underwater submersibles or for natural gas pipelines should be adequate.

- ❖ **126. Can the electric field be increased in the dynode device, so that ions can gain more energy per unit distance traveled? This may permit either a multiple number of ionization events as a single electron or ion interacts with several neutrals, in sequence, in the gas volume above the surface, or it may permit operation of the dynode device at a higher gas pressure and therefore at a greater throughput.**

In principle, the operating pressure is limited by the phenomenon of extinguishment of the ionization by a sequence of charged-particle/neutral collisions which do not produce more ions and electrons. High electric fields do produce ionization and breakdown, at

high pressures. The photons and electrons present do influence the onset of breakdown. At atmospheric pressure, one study reported the onset of corona (i.e. electrons) in methane at an electric field of 2.23 kV/mm. Clearly, experiments in this direction would be worthwhile, and operation at atmospheric pressure could be a possibility.

- ❖ **127. Have you taken into consideration the capital costs of the low-temperature, low-pressure gas separation unit which would follow this device? Have you considered the capital costs and operating costs of the large vacuum pumps which would be needed in a production system?**

We are aware that this equipment, which is generic to any conversion plant with low-carbon-number output gases, is a substantial fraction of total plant cost and operating expense. We are also aware that the principle of economy of scale is present for this equipment as presently used, favoring large plant capacity choices. We are expanding our team of consulting engineers to include specialists who are familiar with these considerations, so that preliminary values for total plant capital costs and operating costs can be produced. We are also considering novel methods for efficient cryogenic separation of output gases at medium scales of throughput.

- ❖ **128. Is there any way that particles of waste plastics can be recycled using some modification of this process?**

A related invention in this family of devices involves the electrostatic projection of particles into a methane plasma region, where the large fraction of hydrogen ions can impact the particle surfaces. It is expected that high-carbon-number molecules would be hydrogenated, and that low-and-medium

carbon-number molecules would be produced. These could be recycled back into the petrochemical feedstock chain or into the fuels chain. A U.S. patent has recently been granted on this device.

US005141715A

United States Patent [19]

[11] Patent Number: 5,141,715

Sackinger et al.

[45] Date of Patent: Aug. 25, 1992

- [54] ELECTRICAL DEVICE FOR CONVERSION OF MOLECULAR WEIGHTS USING DYNODES
- [75] Inventors: William M. Sackinger, College, Ak.; Brian L. Morgan, Croyden; Robert W. Airey, London, both of England
- [73] Assignee: University of Alaska, Fairbanks, Ak.
- [21] Appl. No.: 682,386
- [22] Filed: Apr. 9, 1991
- [51] Int. Cl.⁵ B01J 19/08; B01J 19/12
- [52] U.S. Cl. 422/186.04; 422/186
- [58] Field of Search 422/186, 186.01, 186.03, 422/186.4, 186.07, 186.18, 186.21, 186.29, 204/172

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[57] ABSTRACT

An electrical device is provided for the conversion of molecules of one molecular weight into molecules of another molecular weight. A reaction chamber comprises an array of dynodes, each of which possesses a plurality of apertures. External voltages are available which are applied between dynodes, producing an electric field. During operation, electrons and ions strike the interior surfaces of the dynode apertures, ionizing neutral molecules absorbed on the surfaces, which are desorbed by the energy of the impact, and which are accelerated by the electric field to a new dynode surface location, where they combine with absorbed molecules there to form a variety of new, larger molecules, or different, smaller molecules. Certain ones of the ions created are repetitively moved to one end of the device, where they may be pumped away separately. The controlled electron and ion impact ionization in the device can also produce reactions among several molecular species which would be unlikely or impossible under normal chemical equilibrium conditions, or with normal catalysts.

18 Claims, 3 Drawing Sheets

FIG. 2 **FIG. 4** **FIG. 5**

B3

FIG. 6

ELECTRICAL DEVICE FOR CONVERSION OF MOLECULAR WEIGHTS USING DYNODES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the conversion of the size of molecules in a process stream, using an electrical method, and can be used either to combine small molecules into larger molecules or to separate larger molecules into smaller molecules.

2. Discussion of the Related Art

Electrical conversion of molecules of one molecular weight into molecules of another molecular weight has been described in the patent application published as PCT/US88/03228 in WO 89/02868 (Sackinger), corresponding to U.S. patent application Ser. No. 07/485,856, filed Feb. 22, 1990, which is a continuation application of Ser. No. 07/102,361, filed Sep. 28, 1987. In that application, an array of tubular elements with a semiconducting layer beneath their interior surfaces is used as a converter. Electron and ion impact upon the interior surfaces of the tubes is used to fragment neutral molecules absorbed there. Energy for electron and ion impact is provided by an electric field, produced by the voltage applied from one side of the array to the opposite side of the array. Ion impact, fragmentation and ion emission take place on the interior surfaces of the tubes and also ion recombination into new gas species takes place. It can be said that the device operates using electron and ion impact, an electric field, and a very large interior surface area. This can have applications in the petrochemical process industries.

In the petroleum process industries, for many decades a thermal separation process has been applied to crude oil, which is a mixture of hydrocarbons, to separate out various fractions which are subsequently used for specific purposes. For example, diesel fuel, gasoline, naphtha, lubricating oils, and asphalts are separated by vaporization and subsequent condensation at appropriate different temperatures and heights in a tower. The resulting yields of refined products are dependent upon the characteristics of the crude oil supplied, which will be different for each petroleum reservoir. The market demand for each category of refined products is variable in time, and therefore the adjustment of the petroleum refining process to changes in input composition and output demand can be difficult and challenging.

One remedy which has been recognized for many years is to convert larger molecules into smaller ones, a process called cracking, which has been normally accomplished by catalytic action on special surfaces at high temperatures. In this way, for example, an extra quantity of heavy oils can be converted into gasoline, which may be more marketable. Moreover, light naphtha, which is a mixture of pentanes and hexanes, may be catalytically cracked to produce ethylene, C_2H_4 , a building block molecule for many petrochemicals. Limitations of this approach include the cost of catalysts, the range of input molecules for which they are effective, and the thermal energy required for the process, which is difficult to recover. In addition, the world supply of liquid hydrocarbons is also being consumed, leading to higher prices for liquid feedstocks. Obvious alternatives include the utilization of other natural sources of hydrocarbons which are in more abundant supply: natural gas, and heavy oil. It is clear that an important advantage would be derived from methods to

convert natural gas (methane in particular) into higher hydrocarbons such as ethylene, propylene, and larger molecules. Most processes rely on the high-temperature combination of methane and steam to produce hydrogen and carbon monoxide. For example, a Davy-McKee reformer furnace in New Zealand operates at 880° C. and 30 bar pressure with a nickel catalyst. After cooling to 35° C. at 17 barg pressure, and removal of excess steam, the reformed gas is compressed to 100 barg and passed over a $ZnO/CuO/Al_2O_3$ catalyst at 210°-240° C. The output product is crude methanol containing 17% water. An alumina catalyst is then used (at 310°-320° C. and 26 barg pressure) to create dimethyl ether. Clearly, high operating temperatures, high pressures, and costly equipment are necessary. An approach which involves a single-stage direct conversion, and in which the energy which is to be supplied to a reaction is specifically used to accomplish the molecular conversion, with a minimum waste as heat, would represent an improvement.

The electrical method briefly described above offers significant improvements in that low pressures (such as 0.001 to 0.1 bar) and room temperatures are involved. The use of oxygen is not essential, and water need not be part of the reaction unless specified output products containing oxygen are desired.

A limitation on the electrical device, however, is that a lower throughput of molecules is inherent at lower pressures, so that an equipment designer will naturally attempt to choose the operation pressure of the electrical device to be as high as possible, consistent with a specific conversion reaction. Each impact of ion and electron on the tubular reaction surfaces will result in a portion of the impact energy being converted into thermal energy in the material beneath the surface. A large value of pressure implies more ion impacts and more conversion reactions per second, and more heat (random thermal energy) generated in the material. The semiconducting material on the inside surfaces of the tubular elements may, in certain cases, have a negative temperature coefficient of resistance, so that high pressure operation would lead to heating, lower resistance, and higher leakage currents through the semiconductor layers. This may lead to self-heating and thermal runaway of the semiconductor layer, followed by destruction of electrical continuity through the layer. Proper choice of materials can prevent this effect, but it is the object of this invention to provide an alternative array of electrodes so that the semiconducting layer is not needed. Thus, higher pressure and higher throughput operation is facilitated.

It is also possible that in the aforementioned electrical device, operating at high pressures, that the high density of ions in the high-pressure ends of the tubular elements could give rise to an electric field distribution which would depend upon space charge density, which in turn could lead to plasma instabilities and the onset of arc discharge phenomena. In an ideal device, the intensity of the electric field strength would be controlled by external means, and would be time-variable and spatially-variable according to an adaptive and progressively more optimal pattern of applied external voltages. With the tubular elements and their semiconductor layer, this is difficult to accomplish inasmuch as only one voltage is imposed across the ends of the tubes. With this invention hereinafter described, this limitation is removed.

Although the foregoing discussion of molecular conversion is oriented towards hydrocarbon gaseous conversion, it is obvious that compound gases containing other elements, such as oxygen, chlorine, fluorine, bromine, nitrogen, sulfur, hydrogen, silicon, and other elements could be changed in composition in order to accomplish certain benefits, such as the diminution of toxicity prior to release into the natural environment, or the alteration of composition so as to render harmful gases into harmless liquids or gases prior to release into the environment. Accordingly, it is an object of this invention to provide an electrical device which will accomplish the function of combining molecules of low molecular weight into molecules of higher molecular weight. A further object of the invention is to provide an electrical device for separating molecules of higher molecular weight into other molecules of lower molecular weight. Moreover, an additional object of the invention is to provide an electrical device for combining two or more different molecular species into new molecular species.

SUMMARY OF THE INVENTION

Briefly the present invention comprises an array of dynodes, made of metal, or of glass or ceramic with metal coatings. The term "dynode" is intended to mean any type of electrode which, upon being struck at by a single electron, yields several electrons. By applying a voltage between one dynode and an adjacent dynode, an electric field is established between dynode surfaces. A source of electrons is located at or just outside of the negatively-connected side of the dynode array, and these electrons are accelerated towards the first dynode, striking its surface with energies which may range from several electron volts to more than a hundred electron volts. For electron flow, gas pressures of less than 1 Torr are usually used, although operation at pressures several orders of magnitude higher is possible if volume electron/ion interaction effects are to be used for a supplemental improvement in operation. A gas which is to be converted is admitted into the chamber on the side of the dynode array which is opposite the electron source. Diffusion of the source gas into the dynode array takes place, with absorption of the gas molecules on the surfaces of the dynodes. Upon impact of the electrons upon the surfaces of the dynodes, several processes take place, the most obvious of which is the disruption of molecular bonding of the absorbed gas. In the case of methane source gas, a hydrogen ion is created, H^{30} , which immediately is separated from its parent molecule by the action of the electric field. Hydrogen ions thus created are accelerated away from the dynode upon which they were created, moving towards the adjacent, more negative dynode. Upon impact at the adjacent dynode, the hydrogen ion disrupts the bonding of the methane molecules there, and serves as an additional electron source via ion-induced secondary electron emission. The impact of electrons also creates secondary electron emission, with a net gain in electron flux along the dynode array. Furthermore, once methane molecules are stripped of one or more hydrogen atoms, and have been released from the dynode surface by the energy associated with electron or ion impact, they are accelerated towards the positive end of the dynode array. In such a state of ionization, they will bond readily to other similar species, and to neutrals, upon collision with them, and the formation of carbon-carbon bonds is probable. By the repeated appli-

cation of this process in a methane source gas, formation of higher-order mixtures of paraffins, aromatics, olefins, and polyenes takes place. A physical separation of the available hydrogen from the newly-formed higher-order hydrocarbon products is made possible by the electric field. Charge exchange is possible because of the flow of electrons through space, and the flow of electrical current through the metallic surfaces of the dynodes. Energy for the dissociation is provided by the electric fields between dynodes, which accelerates electrons, hydrogen ions, and complex hydrocarbon ions. Energy transfer is by direct impact at the surfaces of the dynodes. Volume interaction effects also take place at higher pressures, with similar results. Both chemi-absorbed molecules and physically absorbed molecules at the dynode surfaces are affected and transformed by the electron impact process. The higher-order molecules are electrically moved to the region of higher inlet gas pressure, where they are carried by the inlet gas pressure gradient laterally to an outlet stream. A condensation stage then removes the higher-order species and the residual methane may be recirculated through the device. The same device, if operated in a high electron flux mode, could decompose high-order hydrocarbon molecules deposited on the surfaces of the dynodes and a separate collecting electrode held at a slightly positive voltage would attract such fragments. In this mode, lower molecular weight species could be produced from large molecules. It is clear that the admission of gaseous mixtures into this apparatus would result in a variety of output compounds, with a very large number of possibilities which could be considered. It is also clear that the hydrogen ions emerging from the region of the most negative dynode could be either pumped away or could be used to fragment large-molecular-weight hydrocarbon molecules via either a surface interaction or a volume interaction.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a section view of a simplified reaction chamber of a first embodiment of the present invention;

FIG. 2 is an end section view of part of the parallel array of tubes comprising one dynode of the first embodiment; and

FIG. 3 is a section view of one such tube with an angle between dynode face and tube axis of the first embodiment;

FIG. 4 illustrates examples of nine dynodes of a third embodiment of the present invention;

FIG. 5 illustrates an example of a dynode of a fourth embodiment of the present invention; and

FIG. 6 illustrates examples of four dynodes of a fifth embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to the drawings and, in particular, to FIG. 1, there is shown an electrical device 10 for conversion of hydrocarbon molecular weights using dynodes, comprising a chamber 12 with walls constructed of glass, ceramic, or metal, with an inlet gas source 27, an outlet gas port 28, and a hydrogen outlet gas port 29. Disposed upon or near the inside wall of chamber 12 is an electrode 26 constructed of metal, and on the opposite side of chamber 12 is another electrode 22 constructed of metal or a suitable semiconducting material, which can serve as an electron source. Within the central part of chamber 12 is mounted a plurality of tubular

dynode elements 30. Each dynode element comprises metallic tubes 33 which are joined together along their outer boundaries in an array so that the axes of the tubes 33 are co-parallel. The tubular elements 32 comprise metal, such as nickel or tantalum, and are bound together by brazing at their boundaries 36, as shown in FIG. 2. The interior of the tubes 32 are open cylinders 34 with interior surfaces 35 which have secondary-electron-emitting properties. High secondary electron emission yields may be obtained, for example, from layers of a silver-magnesium alloy or a copper-beryllium alloy. There is an angle between the tubes' axes 33 and the face 40 of the dynode array which is at least as large as the arc cosine of d/l , where d is the individual tube diameter and l is the individual tube length.

Each dynode 30 is separated from the adjacent dynodes by a suitable spacing, and each dynode is separately connected electrically to a metallic connection which penetrates the insulating part of the enclosure. For each pair of dynodes 30 a potential source 41 is required. Each pair of adjacent dynodes 30 has a separate potential source 41 connected between them. Also, source 44 is connected from the final dynode 30 to electrode 26, and source 43 is connected from electrode 22 to first dynode 30. Connection of these sources through a glass or ceramic chamber 12 is shown, whereas if a metallic chamber wall is used, separate insulative feed-through connections through the chamber wall would be required.

Briefly describing the operation of the device in the mode which increases hydrocarbon molecular weights, the input gas such as methane CH_4 is admitted through port 27 into the chamber 10, with an ambient pressure of 10^{-6} to 1 Torr, for example. Diffusion of the gas into tubes 32 of each dynode occurs, with some of the gas absorbing on the interior walls 35. Electrons originating either from the electron source 22, or from field emission from the metallic coating on face 22, or from cosmic rays, photoemission, or other natural sources, are accelerated along the length of the region from source 22 to first dynode 30, striking the interior walls 35 with substantial energies such as 10 to 100 electron volts. The range of energy values is adjustable with potential source 43. A sequence of cascading impacts takes place, which will be described below in detail, which removes hydrogen ions from the absorbed molecules, and allows hydrogen ions to move in the open cylinders 34 towards source 22, while at the same time allows negatively-charged hydrocarbon ions to move in the open cylinders 34 towards the next adjacent dynode 30. Subsequent impact of these hydrocarbon ions with other similar charged or neutral species on adjacent dynode 30 causes combination into larger hydrocarbon molecules, which emerge from the face 40 of final dynode 30 and are pumped away into outlet 28. Concurrently, the extracted hydrogen ions are carried by the electric field due to potential source 43 towards source 22 where they combine with others of the same species and are pumped away into outlet 29. A partition 37 of the chamber 10 prevents mixing of hydrogen with hydrocarbons. Some of the inlet methane will pass, by diffusion, directly into outlet port 28 and will be separated in subsequent condensation stages from the heavier hydrocarbon molecules formed by the device operation, after which the methane may be recirculated back into the inlet stream which feeds port 27.

To further elaborate upon the details of the separation and recombination mechanism, with reference to

FIG. 3, the methane molecules 55 may be considered to be absorbed upon the interior walls 34 in a strong, chemisorbed bond, which pertains to a surface monolayer, and also in a weaker, multi-molecular-layer bond for additional molecules. When interior surfaces 35 are struck by an incident electron 51 with energy in the range 10 to 100 electron volts, a variety of processes are initiated. Some of the incident electron 51 energy goes to create secondary electrons 57 which are emitted from the wall 35 and which are accelerated in complex trajectories 58 to perpetuate the process at the next impact on the next dynode 30 with wall 35a. In order to extract the secondary electrons thus created in dynode 30, the distorted electric field associated with the presence of the open aperture at the end of the tubes 33 must extend nearly to the region of secondary electron creation, which in turn is within about one to two diameters of the electron-input side of the dynode 32. Thus, the length l of the tubular elements 33 will be only 2 to perhaps 5 times the diameter d of a tubular ion 52 from an absorbed gas molecule 55, also creating a negatively-charged hydrocarbon ion 53, for example CH_3 or CH_2 . Some of the incident electron 51 energy imparts sufficient kinetic energy to these ions 52 and 53 so that they depart from their surface creation site and are accelerated along the electric field direction, in complex curved paths. The hydrogen ion 52 will subsequently strike an adjacent dynode tube wall 35 with sufficient energy to create secondary electrons which will contribute to the electron cascade required for the process; this is a positive ion feedback effect. The same impact of hydrogen ion 52 on wall 35 will also provide sufficient energy to disrupt the bonding of one or several gas molecules 55 absorbed at that site, thus creating more positive hydrogen ions and negative hydrocarbon ions which are released from that site and which are accelerated in opposite directions, thus contributing to the process. The hydrocarbon ion 53, acquiring kinetic energy along its path, strikes an adjacent dynode tube wall 35 with energy sufficient to disrupt bonds of molecules 55 at the site of impact, permitting the formation of a carbon-carbon bond at that site, and thus the creation of a higher weight hydrocarbon molecule. At the site of formation of the carbon-carbon bond, other processes such as secondary electron production, and hydrogen ion production also may be expected to take place. In some cases, the higher-weight hydrocarbon may not leave the wall 35 immediately upon creation but will be dislodged by a subsequent electron or ion impact. The net trend of these processes may be summarized by noting that (a) electron and ion kinetic energy is applied to the surface zone where the hydrocarbon molecules are absorbed; (b) rupture of at least one of the hydrocarbon bonds leads to a species separation by means of the electric field; (c) the arrival of an energetic hydrocarbon ion at the surface zone further disrupts absorbed molecules and causes them to form carbon-carbon bonds; and (d) higher weight molecules are moved, as ions, in a direction opposite that of the excess hydrogen, to the end of the device where they are pumped out.

Replenishment of methane molecules 55 on the surface will take place rapidly by diffusion and deposition from the gas phase present in the tube. Some degree of interaction between charged particles and neutral molecules in the volume space of the tube will also take place, with charge-separation and species separation

trends as described for the walls 35, further enhancing the process.

The proper amount of charge required for electron current conservation at each impact site is provided by the metal dynodes 32.

The paths of the electrons and of the ions, as described above, have a length which depends upon the dynode-to-dynode electric field strength, upon the initial kinetic energy of the particles, and their direction of emission from the surface. Inasmuch as the impact-creation of these charged particles involves the combination of many random processes within the wall 35, the direction and initial kinetic energy of the particles will follow a statistical distribution function. The alternate orientation of the axes of the tubes in adjacent dynodes is chosen so that ion impact is assured on each dynode, and therefore electrons and ions are not passing through a dynode cylinder without impacting the interior surface 35 of a tubular element 32.

Other dynode shapes are possible. For example as shown in FIG. 4, a dynode may be constructed of an array of flat strips of metal, with the faces co-parallel and inclined at an angle, resembling the well-known "Venetian-blind." Each such "Venetian-blind" dynode would have the main length direction of the strips oriented orthogonal to the length direction in the adjacent dynodes. Other possible dynode shapes include, for example, an array of intersecting strips which form squares (FIG. 5), or plates with an array of conical holes drilled or punched into their surface (FIG. 6).

Inasmuch as the present invention is subject to many variations, modifications, and changes in detail, it is intended that all subject matter discussed above or shown in the accompanying drawings be interpreted as illustrative and not in a limiting sense. Such modifications and variations are included within the scope of this invention as defined by the following claims.

We claim:

1. An apparatus for converting a first substance having a first molecular weight into a second substance having a second molecular weight, the apparatus comprising:

a first dynode having a first end and a second end, said first dynode including an electrically-conductive material, or either glass or ceramic with an electrically-conductive coating;

a second dynode having a first and second end, the first end of said second dynode being separated from the second end of said first dynode, said second dynode including an electrically-conductive material, or either glass or ceramic with an electrically-conductive coating;

means for supplying the first substance to said first and second dynodes; and

means, connected to said first and second dynodes, for establishing a first potential throughout the electrically-conductive material or electrically-conductive coating of said first dynode and a second potential, different from said first potential, throughout the electrically-conductive material or electrically-conductive coating of said second dynode to establish an electric field across the separation between the second end of said first dynode and the first end of said second dynode and to convert the first substance into the second substance.

2. The apparatus of claim 1, wherein each of said first and second dynodes comprises at least one tubular element.

3. The apparatus of claim 2, wherein said tubular elements have a length and a diameter, said length being 2-5 times larger than said diameter.

4. The apparatus of claim 2, wherein each of said tubular elements has a central axis, and wherein said first and second dynodes are arranged such that their respective central axes are at different orientations.

5. The apparatus of claim 2, wherein said electric field extends into at least a portion of each of said tubular elements.

6. The apparatus of claim 1, wherein each of said first and second dynodes comprises flat strips arranged mutually co-parallel in both a main length direction and in a width direction.

7. The apparatus of claim 1, wherein each of said first and second dynodes comprises flat strips arranged to form at least one tubular element having a polygonal cross-section.

8. The apparatus of claim 1, wherein each of said first and second dynodes comprises a plate having at least one conical opening formed therethrough.

9. The apparatus of claim 1, further comprising:

a third dynode having a first end and a second end, the first end of said third dynode being separated from the second end of said second dynode, said third dynode including an electrically-conductive material, or either glass or ceramic with an electrically-conductive coating;

a fourth dynode having a first end and a second end, the first end of said fourth dynode being separated from the second end of said third dynode, said fourth dynode including an electrically-conductive material, or either glass or ceramic with an electrically-conductive coating;

means, connected to said second and third dynodes, for establishing a third potential, different from said second potential, throughout the electrically-conductive material or electrically-conductive coating of said third dynode to establish an electric field across the separation between the second end of said second dynode and the first end of said third dynode and convert the first substance into the second substance; and

means, connected to said third and fourth dynodes, for establishing a fourth potential, different from said third potential, throughout the electrically-conductive material or electrically-conductive coating of said fourth dynode to establish an electric field across the separation between the second end of said third dynode and the first end of said fourth dynode and to convert the first substance into the second substance.

10. The apparatus of claim 9, wherein each of said first, second, third and fourth dynodes comprises a tubular element, each of said tubular elements having a central axis, and wherein said tubular elements are arranged such that their respective axes have selected orientations.

11. The apparatus of claim 9, wherein each of said first and fourth dynodes comprises flat strips arranged mutually coparallel in both a main length direction and a width direction.

12. The apparatus of claim 9, wherein each of said first, second, third and fourth dynodes comprises flat

strips arranged to form at least one tubular element having a polygonal cross-section.

13. The apparatus of claim 9, wherein each of said first, second, third and fourth dynodes comprises a plate having at least one conical opening formed there-through.

14. The apparatus of claim 1, wherein said means for establishing an electric field includes means for time-varying and/or spatially-varying said electric field.

15. An apparatus for converting a first substance having a first molecular weight into a second substance having a second molecular weight, the apparatus comprising:

a first array, said first array including a plurality of dynodes each having a first end and a second end, said dynodes of said first array including an electrically-conductive material, or either glass or ceramic with an electrically-conductive coating;

a second array, said second array including a plurality of dynodes each having a first end and a second end, the first ends of said dynodes of said second array being separated from the second ends of said dynodes of said first array, said dynodes of said second array including an electrically-conductive material, or either glass or ceramic with an electrically-conductive coating;

means for supplying the first substance to said first and second arrays; and

means, connected to said first and second arrays, for establishing a first potential throughout the electrically-conductive materials or electrically-conductive coatings of said plurality of dynodes of said first array and a second potential, different from said first potential, throughout the electrically-conductive materials or electrically-conductive coatings of said plurality of dynodes of said second array to establish an electric field across the separation between the second ends of said dynodes of said first array and the first ends of said dynodes of said second array and to convert the first substance into the second substance.

16. The apparatus of claim 15, further comprising:

a third array, said third array including a plurality of dynodes each having a first end and a second end, the first ends of said dynodes of said third array being separated from the second ends of said dynodes of said second array, said dynodes of said third array including an electrically-conductive material, or either glass or ceramic with an electrically-conductive coating;

a fourth array, said fourth array including a plurality of dynodes each having a first end and a second end, the first ends of said dynodes of said fourth array being separated from the second ends of said dynodes of said third array, said dynodes of said fourth array including an electrically-conductive material, or either glass or ceramic with an electrically-conductive coating;

means, connected to said second and third arrays, for establishing a third potential, different from said second potential, throughout the electrically-conductive materials or electrically-conductive coatings of said plurality of dynodes of said third array to establish an electric field across the separation between the second ends of said dynodes of said

second array and the first ends of said dynodes of said third array and to convert the first substance into the second substance; and

means, connected to said third and fourth arrays, for establishing a fourth potential, different from said third potential, throughout the electrically-conductive materials or electrically-conductive coatings of said plurality of dynodes of said fourth array to establish an electric field across the separation between the second ends of said dynodes of said third array and the first ends of said dynodes of said fourth array and to convert the first substance into the second substance.

17. In an apparatus including a first dynode having a first end and a second end and a second dynode having a first end and a second end, the first end of the second dynode being separated from the second end of the first dynode, and each of the first and second dynodes including an electrically-conductive material, or either glass or ceramic with an electrically-conductive coating, a method, performed by the apparatus, for converting a first substance having a first molecular weight into a second substance having a second molecular weight, the method comprising the steps of:

supplying the first substance to the first and second dynodes; and

establishing a first potential throughout the electrically-conductive material or electrically-conductive coating of said first dynode and a second potential, different from said first potential, throughout the electrically-conductive material or electrically-conductive coating of said second dynode to establish an electrical field across the separation between the second end of the first dynode and the first end of the second dynode and to convert the first substance into the second substance.

18. In an apparatus including a first array having a plurality of dynodes each having a first end and a second end, and a second array including a plurality of dynodes each having a first end and a second end, the first ends of the plurality of dynodes of the second array being separated from the second ends of the plurality of dynodes of the first array, and the plurality of dynodes of the first and second arrays including an electrically-conductive material, or either glass or ceramic with an electrically-conductive coating, a method, performed by the apparatus, for converting a first substance having a first molecular weight into a second substance having a second molecular weight, the method comprising the steps of:

supplying the first substance to the first and second arrays; and

establishing a first potential throughout the electrically-conductive materials or electrically-conductive coatings of said plurality of dynodes of said first array and a second potential, different from said first potential, throughout the electrically-conductive materials or electrically-conductive coatings of said plurality of dynodes of said second array to establish an electric field across the separation between the second ends of the plurality of dynodes of the first array and the first ends of the plurality of dynodes of the second array and to convert the first substance into the second substance.

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