Magnesium Carbide Synthesis From Methane and Magnesium Oxide - A Potential Methodology for Natural Gas Conversion to Premium Fuels and Chemicals

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1. Executive Summary

Pseudo-stoichiometric (i.e. non-catalytic) reactions of methane with low-cost, recyclable, alkaline earth metal oxides at temperatures above 2100 K

$$3\ CH_4 + CaO \rightarrow CaC_2 + 6\ H_2 + CO \tag{1}$$

$$5\ CH_4 + 2\ MgO \rightarrow Mg_2C_3 + 10\ H_2 + 2\ CO \tag{2}$$

indicate technical and economic promise for upgrading natural gas to solid metal carbides that can be stored, transported, and hydrolyzed to acetylenes:

$$CaC_2 + 2\ H_2O \rightarrow Ca(OH)_2 + C_2H_2 \text{ (acetylene)} \tag{3}$$

$$Mg_2C_3 + 4\ H_2O \rightarrow 2\ Mg(OH)_2 + C_3H_4 \text{ (MAPD, i.e. methylacetylene/propadiene)} \tag{4}$$

The acetylenes can subsequently be converted to premium liquid fuels and petrochemicals. The overall goal of the present project is to develop new scientific and engineering knowledge for improved technical and economic assessment of Reactions (1) and (2) as bases for gas-to-liquids upgrading. One specific objective is to assess the technical feasibility of achieving high conversions of CH_4 to Mg_2C_3 via Reaction (2) in a thermal plasma.

A series of scoping runs was conducted wherein MgO was reacted with CH_4 in a magnetically rotated d.c. arc discharge plasma reactor, yielding solid products which evolved C_2H_2 and C_3H_4 upon hydrolysis. The results of these runs strongly indicate that a breakthrough has finally been achieved in that synthesis of magnesium carbides from MgO and CH_4 in the arc discharge reactor has been demonstrated.

2. Introduction

Diversification of the raw materials base for manufacturing premium fuels and chemicals offers U.S. and international consumers economic and strategic benefits (Longwell, 1993). Extensive reserves of natural gas in the world provide a valuable source of clean gaseous fuel and chemical feedstock. Assuming the availability of suitable conversion processes, natural gas offers the prospect of improving flexibility in liquid fuels and chemicals manufacture, and thus, the opportunity to complement, supplement, or displace petroleum-based production as economic and strategic considerations require. Many attractive deposits of natural gas are remotely located from key market sites. In order to utilize this remote resource commercially, natural gas must be transported to the market from the production site either via extensive pipeline distribution networks under pressure or in specially designed ocean-going tankers as liquefied natural gas at low temperatures. Due to the state in which it exists at normal conditions, natural gas has a low energy content per unit volume compared to petroleum or coal. This relatively low energy density contributes to elevated transportation costs which exclude significant quantities of gas from commercial exploitation. Thus, there is considerable interest in developing new approaches to the volumetric energy densification of natural gas to enhance its marketability.

The composition of natural gas varies from reservoir to reservoir but the principal hydrocarbon constituent is always methane (CH_4). With its high hydrogen-to-carbon ratio, methane has the potential to produce hydrogen or hydrogen-rich products. However, methane is a very chemically stable molecule and, thus, is not readily transformed to other molecules or easily reformed to its elements (H_2 and carbon). With the interest in upgrading natural gas to "value-added" products, several technologies for methane conversion to liquid fuel and chemical precursors currently exist at various stages of scientific and technological development. In many cases, further research is needed to augment selectivity to desired product(s), increase single-pass conversions, or improve economics (e.g. there have been estimates of $50/bbl or more for liquid products) before the full potential of these methodologies can be realized on a commercial scale. With the trade-off between gas conversion and product selectivity, a major challenge common to many of these technologies is to simultaneously achieve high methane single-pass conversions and high selectivity to desired products.

2.1 Motivation for Present Study

Prior work at MIT (Kim, 1977; Kim *et al.*, 1979) has demonstrated that, by reacting methane with calcium oxide (CaO) in a laboratory-scale rotating direct current (d.c.) arc reactor, high (>95%) methane single-pass conversions to molecular hydrogen (H_2) and calcium carbide (CaC_2) can be obtained, according to the reaction:

$$3\,CH_4 + CaO \rightarrow CaC_2 + 6\,H_2 + CO \qquad (1)$$

Hydrogen can be used as a fuel in thermal processes and in fuel cells to generate electricity at efficiencies which may approach 60%. It finds wide applications in petroleum refining (and could be used extensively in coal liquefaction) to improve fuel quality, e.g. by increasing hydrogen-to-carbon ratio and lowering the fuel content of pollutant precursors such as sulfur, nitrogen, and heavy metals. Mixtures of H_2 and carbon monoxide (CO) in various proportions are known as synthesis gas which is valuable as a fuel. By various catalytic processes, synthesis gas can be upgraded to a wide range of premium products, e.g. liquid fuels, methanol, and waxes, many of which are manufactured from petroleum. Calcium carbide, which exists as a solid at dry ambient conditions, is a particularly attractive product with significant commercial benefits in the present context: (a) being a solid, it can be separated from the gaseous products of Reaction (1) relatively easily; (b) it has an equivalent heating value (based on acetylene - see Reaction (3)) of about 8700 BTU/lb and thus, like low-rank coal, can be stored and transported over long distances at reasonable cost; and (c) by well-established hydrolysis processes, it can be converted to acetylene (C_2H_2) by the reaction:

$$CaC_2 + 2\ H_2O \rightarrow Ca(OH)_2 + C_2H_2 \qquad (3)$$

Acetylene is a reactive raw material that can be converted to a diverse array of organic chemicals and to high-grade liquid fuels.

In the light of the success of the previous work by Kim (1977) *et al.* (1979), there is incentive to investigate comparable reactions of methane with other alkaline earth metal oxides. In particular, magnesium oxide (MgO) undergoes analogous reactions to produce hydrogen, carbon monoxide and magnesium sesquicarbide (Mg_2C_3) and/or magnesium dicarbide (MgC_2). Thermodynamic calculations imply that the sesquicarbide is strongly favored over the dicarbide above 2000 K. Of interest is the fact that magnesium is the only alkaline earth metal known to form a sesquicarbide, which, upon hydrolysis, yields methylacetylene (C_3H_4), providing a route for C_1-to-C_3 conversion. Furthermore, methylacetylene offers a potential route to benzene by condensation/dehydrocyclization. Concepts for synthesizing magnesium sesquicarbide from magnesium oxide and methane, with further upgrading of the sesquicarbide to C_3 hydrocarbons by hydrolysis, are described by Peters and Howard (1990; 1993). Earlier experimental work by Kim (1977) *et al.* (1979), together with preliminary cost estimates (Peters and Howard, 1989), indicate that the metal carbide route for methane upgrading offers sufficient potential for good thermal efficiency and favorable economics to warrant further systematic study.

2.2 Description of Proposed Methane Upgrading Approach

In the proposed approach, methane would be reacted, essentially stoichiometrically (rather than catalytically), with relatively low cost and recyclable alkaline earth metal oxides such as calcium oxide (quicklime), magnesium oxide (magnesia) or mixtures of the two (calcined dolomite) to achieve very high (approaching 100%) conversion to hydrogen, carbon monoxide and the corresponding alkaline earth metal carbide, according to the reactions:

$$3\ CH_4 + CaO \rightarrow CaC_2 + 6\ H_2 + CO \qquad (1)$$

$$5\ CH_4 + 2\ MgO \rightarrow Mg_2C_3 + 10\ H_2 + 2\ CO \qquad (2)$$

In order to carry out Reactions (1) and (2), the high chemical stability of methane would be overcome under high severity conditions, i.e. high temperature (>2000 K), in an electrical arc discharge (thermal plasma) reactor or in a purely thermal (i.e. non-plasma) reactor.

The carbides produced are solids at dry ambient conditions. Thus, they could be more readily separated during processing and would be more attractive for storage and transport. Their value as fuel precursors and chemical intermediates is further enhanced when, upon reaction with water, they yield the valuable hydrocarbon gases acetylene and methylacetylene:

$$CaC_2 + 2\ H_2O \rightarrow Ca(OH)_2 + C_2H_2 \text{ (acetylene)} \tag{3}$$

$$Mg_2C_3 + 4\ H_2O \rightarrow 2\ Mg(OH)_2 + C_3H_4 \text{ (MAPD, i.e. methylacetylene/propadiene)} \tag{4}$$

Reactions (3) and (4) are expected to produce acetylene and methylacetylene in high purity. Thus, the carbide approach may exhibit simpler and lower cost separation and purification steps than those needed in alternative processes for acetylene manufacture. Acetylenes can be upgraded to a wide range of chemicals or to premium-value liquid hydrocarbon fuels.

CaO and MgO for reuse in Reactions (1) and (2) can be regenerated by heating $Ca(OH)_2$ and $Mg(OH)_2$, respectively, and subsequently recycled back to the process, according to:

$$Ca(OH)_2 \rightarrow CaO + H_2O \tag{5}$$

$$Mg(OH)_2 \rightarrow MgO + H_2O \tag{6}$$

A conceptual process wherein Reaction (1) [or (2)] is carried out under thermal plasma conditions followed by low temperature Reaction (3) [or (4)] to produce CO, H_2 and C_2H_2 (or C_3H_4) is estimated to have a reasonably high thermal efficiency. In the ideal case of perfect heat integration where the plasma provides only the endothermicity of Reaction (1) or (2) and where CH_4 is used to generate electricity for driving the plasma reactor at 33% efficiency, Table 1 shows that the process thermal efficiencies are about 60%, which compare well with the 60% thermal efficiency of commercial H_2 production by steam reforming of CH_4 (Gary and Handwerk, 1984).

Table 1. Estimated Process Thermal Efficiency of Methane Conversion in a Thermal Plasma[(a)]

Product LHV as a Percentage of Total Input CH_4, i.e. CH_4 Converted to Products or Used to Manufacture Electricity to Run Plasma[(b)]

Reaction[(c)]	H_2	CO	C_2H_2	C_3H_4	Total
(1) and (3)	32	6	28		66
(2) and (4)	29	7		22	58

[(a)] Assumes perfect heat integration so the plasma supplies only endothermicity of Rxns (1) or (2).
[(b)] Methane is assumed to be converted to electricity at 33% efficiency.
[(c)] All chemical reactions are assumed to proceed to 100% completion.

2.3 Objective of Research Supported by U.S. DOE/PETC

The major goal of this research is to develop new scientific and engineering knowledge bases for assessing the technical and economic promise of converting methane to alkaline earth metal carbides for subsequent production of acetylenes, chemicals and premium-value liquid hydrocarbon fuels. A specific objective is to determine the technical feasibility of converting CH_4 and MgO to Mg_2C_3, H_2 and CO, according to Reaction (2), under thermal plasma conditions to achieve high single-pass CH_4 conversions and strong selectivity to these three products.

3. Experimental Section

A laboratory-scale electrical arc discharge (thermal plasma) reactor is used to carry out Reaction (2) and will be utilized to systematically investigate the effects of variations in thermal plasma operating conditions on the conversion of methane to metal carbides.

3.1 Description of Experimental Apparatus and Procedure

The experimental apparatus, shown in Figure 1, consists of a plasma generator system, a mechanical powder feeder, a post-plasma cooling chamber for thermally quenching the plasma effluent, and a sample collection system. The plasma generator system is composed of an arc discharge d.c. plasma torch as the reactor, a high frequency oscillator (for initiating the arc), a control console and an AIRCO d.c. power supply unit rated by the manufacturer at up to 83 kW and capable of providing open circuit output voltages of 80, 160 and 320 volts.

The heart of the plasma reactor, shown schematically in Figure 2, consists of a cylindrical graphite cathode (¾ in. O.D. by 1½ in. long) and a cylindrical graphite anode (1 in. I.D. by 2½ in. O.D. by 4 in. long). The top of the anode is counterbored to a depth of 2 in. to accommodate: (a) an annular boron nitride shield (1 in. I.D. by 1½ in. O.D. by ½ in. long) to electrically insulate the upper end of the anode from the cathode; and (b) a replaceable annular graphite insert (1 in. I.D. by 1½ in. O.D. by 1½ in. long). The insert (b) allows for convenient replacement of that section of the anode most subjected to arc impingement. The top 2½ in. of the outside wall of the anode are threaded so that the anode can be mounted by screwing it into a water-cooled brass support piece. This anode holder is held between the top flange of the cooling chamber and a nylon cap by three screws that secure the cap to the flange (Figure 2). The nylon cap is thermally insulated from the anode by a flat disk of low density alumina, and from arc radiation by an annular insert of high density alumina. This cap supports a water-cooled copper cathode extension piece, indented and threaed at its lower end to mount the graphite cathode tip. Gas, or a mixture of gas and entrained powdered solids (e.g. MgO), is introduced axially to the plasma arc via a 1/8 in. thick by ¾ in. I.D. annular space between the cathode and the anode (Figure 2).

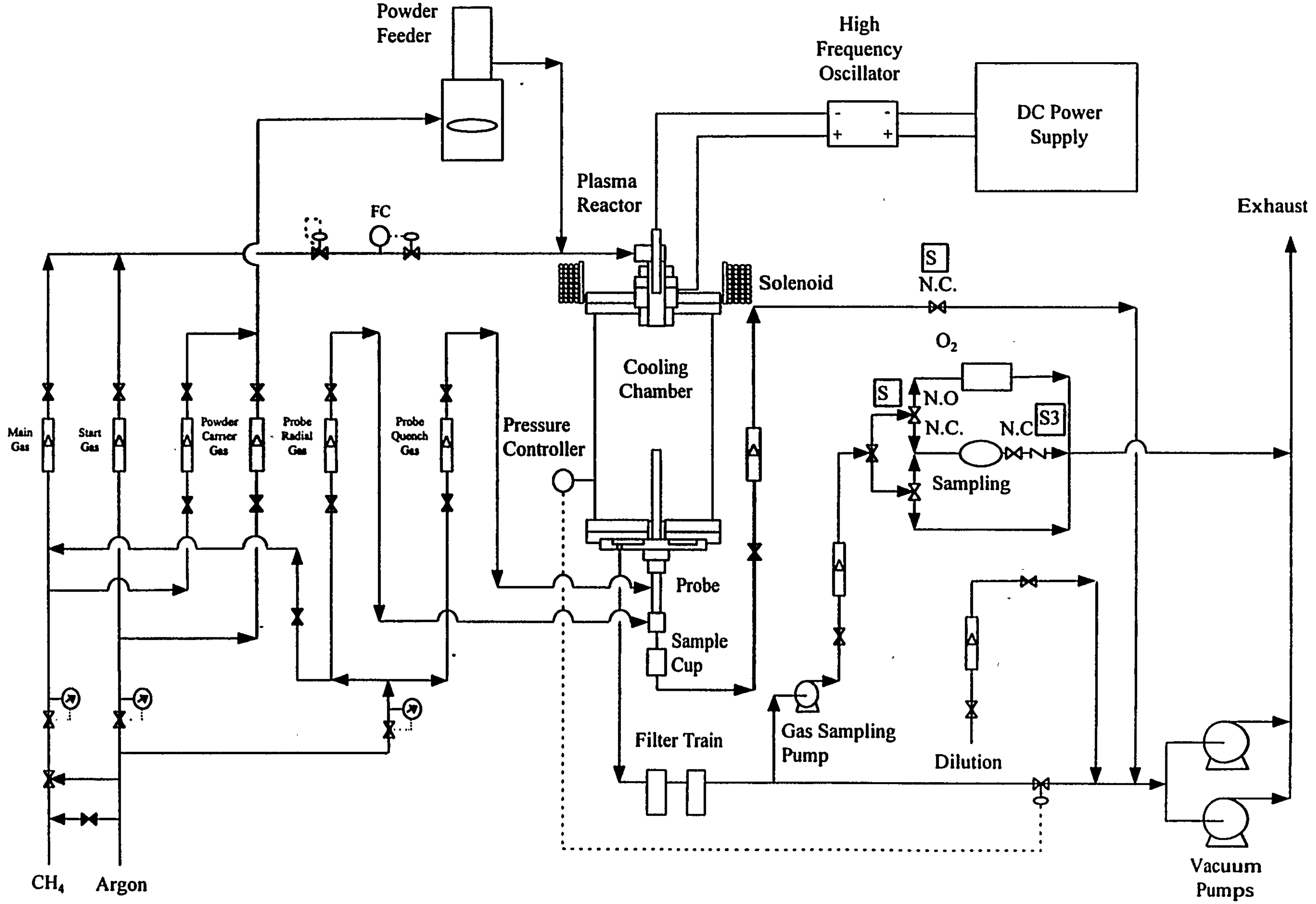


Figure 1. Process Flow Diagram

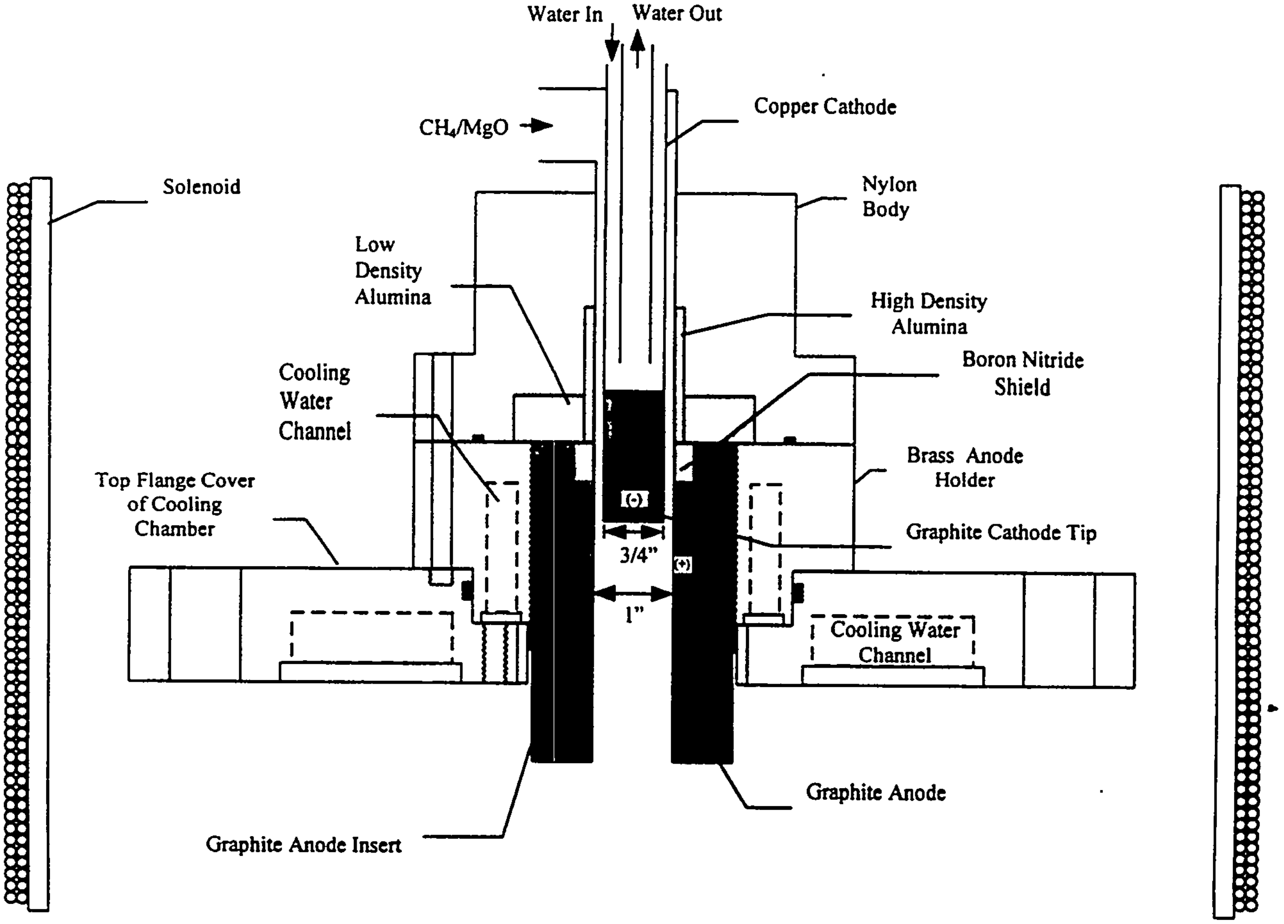


Figure 2. Schematic Representation of Plasma Reactor

Using a solenoid, a magnetic field is applied perpendicular to the arc current, inducing in the charged particles a velocity component perpendicular to their original direction of travel. Consequently, the path of charged particles moving in a plane perpendicular to the magnetic field will curve. However, the mean free path of the particles remains practically unaltered. One effect is that the electric conductivity of the plasma becomes more anisotropic under these conditions (Gross *et al.*, 1969), resulting in a better confined plasma.

Powder is delivered with argon as carrier gas to the reactor gas inlet using a Miller Thermal, Inc. Model 1270 mechanical wheel-type powder feeder. The plasma reactor is mounted on top of a steel, cylindrical, post-plasma cooling chamber, with a water-cooled wall. This chamber helps cool the plasma effluent and facilitates rapid quenching and recovery of solid and gaseous reaction products. Using two vacuum pumps, the gaseous products are aspirated from this chamber through a sintered disc at the chamber bottom and a filter train downstream of the chamber. The pumps exhaust to a ventilation stack.

The product quenching and collection system consists of a movable, water-cooled and gas-quenched cylindrical collection probe mounted at the bottom of the cooling chamber. This probe is designed so that the distance of separation between the end tip of the plasma "flame" and the entrance to the probe can be adjusted. Solid samples are collected on a sintered stainless steel filter cup located downstream of the probe. The rest of the solid effluent from the reactor is collected on the sintered disc at the chamber bottom and on the filters downstream of the chamber (Figure 1). Gas samples from the chamber are collected with a sampling pump in a sample bulb.

In scoping runs performed to investigate the viability of Mg_2C_3 synthesis, an argon plasma was first established at a flowrate of 1 cfm (ambient temperature). Powder feeding was then initiated 30 seconds later. MgO powder entrained in 9 cfh (ambient temperature) of argon was introduced at a feed rate of 12 g/min into the plasma. After a few seconds of establishing powder feeding, the argon feed gas to the plasma was gradually switched to methane until the feed gas was 100% methane. On average, this switchover to methane was complete within three minutes of initiation of the argon plasma and an operating (100% methane) plasma could be sustained long enough to carry out the desired experiments.

3.2 Analysis of Solid Products

A small fraction of the solids was collected in the sampler downstream of the probe while most of them were deposited on the sintered stainless steel disc at the bottom of the cooling chamber. These solid were analyzed for the presence of carbides indirectly by measuring the acetylene/methylacetylene evolved upon hydrolysis, using a Hewlett-Packard 5830A gas chromatograph (GC) with a flame ionization detector and a helium carrier gas. A few milligrams of the solid product were placed inside a vial which was then fitted with a septum. Distilled water was injected into the vial to hydrolyze the solid. A 0.5 ml aliquot of the headspace gas above the hydrolyzed sample was injected into the GC. The analysis consisted of aliquot injection onto a Graphpak column at 10°C, followed by a 6.5 minute wait. After this time had elapsed, the C_2 species eluted, and the remainder of the aliquot was switched onto a Porapak-T column. At this point, the GC oven temperature was increased at a rate of 30°C/min to 50°C and there held to a final time of 28 minutes to complete the analysis.

4. Results of CH_4/MgO Scoping Runs

The results of two scoping runs are presented. In the first run, the arc voltage and current ranged from 125 to 135 volts and between 200 and 400 A, respectively. The voltage and current were fluctuating so greatly that taking a reading proved to be very difficult. The pressure in the cooling chamber, which was to be maintained at 760 mm Hg, rose above 1000 mm Hg upon initiation of the argon plasma. Manual attempts to control it at below 760 mm Hg proved futile. In the second run, the arc voltage ranged from 80 to 100 volts and the current from 250 to 450 A. The pressure build-up problem in the cooling chamber was addressed with the installation of a filter cartridge with a larger surface area downstream of the chamber. Thus, chamber pressure was successfully maintained below 760 mm Hg.

4.1 Scoping Run No. SR-M-1: "Breakthrough" Run

GC analysis of the headspace above both unhydrolyzed and hydrolyzed solid samples collected from this run revealed the presence of significant quantities of C_3H_4 and C_2H_2, i.e. in percentage, not ppm, levels. In addition to C_3H_4 and C_2H_2, which together, comprised more than 90% of the gas sample, various other hydrocarbons such as CH_4, C_2H_4, C_2H_6, C_3H_8, C_3H_6, and C_4's were detected. Significant bubble formation accompanied by a distinct smell was observed upon hydrolysis of the solid samples in an open atmosphere. To test the hypotheses that other hydrocarbons are methane pyrolysis products and that they were carried out of the reactor adsorbed onto the carbides or soot particles, the solid samples were subjected to various kinds of treatment including heating, vacuum degassing and combinations thereof. Table 2 summarizes the results of the GC analyses of the headspace above these samples.

Table 2. Summary of GC Analyses of Headspace above Solid Samples

Source of Sample	Treatment of Solids Before Hydrolysis[a]	Hydrolysis[b]	Amount of HC[c]	% C_3H_4 + C_2H_2[d]	C_3H_4: C_2H_2 Ratio
Downstream Probe	None	Yes	+	96	1:2
Cooling Chamber Bottom	Heated to 100°C for 5 min	No	+	95	1:2
Cooling Chamber Bottom	Heated to 100°C for 5 min; Vacuum degassed @ ambient T	No	-	78	1.5:1
Cooling Chamber Bottom	Heated to 100°C for 5 min; Vacuum degassed @ ambient T	Yes	+	87	1.5:1
Cooling Chamber Bottom	Vacuum degassed @ ambient T	No	-	89	1:1
Cooling Chamber Bottom	Vacuum degassed @ ambient T	Yes	+	e	1:1
Cooling Chamber Bottom	Vacuum degassed @ 120°C overnight	No	-	e	e
Cooling Chamber Bottom	Vacuum degassed @ 120°C overnight; heated to 100°C for 10 min	No	-	77	1:3
Cooling Chamber Bottom	Vacuum degassed @ 120°C overnight; heated to 100°C for 10 min	Yes	+	74	3:1

[a] Treatment was intended to allow any adsorbed gases to escape from the solids prior to withdrawing samples of the headspace gas for GC analysis.

[b] Bubbling was visible in all hydrolysis cases.

[c] Amount of Hydrocarbons detected: (+) significant; (-) minimal.

[d] Corresponds to uncorrected area count. GC calibration to be performed in future runs.

[e] Data not available.

No quantification of the carbide yield was done in this study because the sampling was done cumulatively, i.e. sampling was done throughout the entire run. In what is envisioned to be a better-controlled experimental run, sampling will be performed only when fully developed flows of methane and MgO are established. Nevertheless, the study provided several insights. First, the observation of bubble formation on hydrolysis is a strong indication of the formation of magnesium carbides. Figures 3 and 4, which are the GC analyses of the headspace above pre- and post-hydrolysis solid samples, respectively, show strong increases in hydrocarbon formation after hydrolysis. Second, heat treatment of the solid samples seems to increase the yield of C_3H_4 relative to C_2H_2, which suggests that MgC_2 (which hydrolyzes to C_2H_2) is being converted to Mg_2C_3 (which hydrolyzes to C_3H_4) upon heating. Third, although C_3H_4 and C_2H_2 are the major gaseous products of hydrolysis, the detection of other hydrocarbons upon hydrolysis may be indicative of other hydrolysis reactions taking place or of desorption of hydrocarbons generated earlier by methane pyrolysis. The latter could arise by displacement of hydrocarbons sorbed on soot or carbide surfaces, or by release of trapped hydrocarbons due to disintegration of the carbides during chemical reaction.

Because detection of acetylenes from hydrolysis of the solid products is an indirect method of carbide identification, X-ray diffraction analysis was performed as a direct identification technique. Figure 5 shows the X-ray diffraction pattern of the solid sample from the bottom of the cooling chamber. Peaks represent actual data while vertical lines represent the carbide spectral pattern. The diffraction pattern reveals three peaks matching MgC_2 and two peaks matching Mg_2C_3. Although the complete diffraction patterns for MgC_2 and Mg_2C_3 show several other lines, the absence of peaks coresponding to these lines in the present specimens may reflect the small size of the crystals in the sample.

4.2 Scoping Run No. SR-M-2: Run with Lower Chamber Pressure Build-up

The difficulty of controlling the chamber pressure in the MgO/CH_4 run described above was due to clogging of the sintered stainless steel disc at the bottom of the chamber. A 5μ filter cartridge with a larger area was therefore installed downstream of the cooling chamber. With this configuration, another scoping run with MgO/CH_4 was performed.

Upon withdrawal of the probe from the chamber, some solid particles dislodged from the probe glowed instantaneously upon exposure to the ambient atmosphere. When the cartridge filter was removed, the solids in the cartridge likewise glowed once exposed to the atmosphere. This strongly suggests that the solid products are carbides that reacted with moisture in the air, exothermically forming acetylenes which, because of the elevated temperatures arising from localized heating of the specimens, were able to ignite instantaneously in the presence of oxygen. Samples of the reactor solids that had exhibited this instantaneous glowing behavior were hydolyzed. GC analysis of the headspace above these hydrolyzed samples revealed very little CH_4, C_3H_4 and C_2H_2 (and no other hydrocarbon). This would suggest that the hypothesized hydrolysis of reactor solids (i.e. magnesium carbides) upon exposure to the moist atmosphere proceeded virtually to completion leaving little or no carbides to generate acetylenes upon controlled hydrolysis in the septum vial. It should also be noted that the rapid and instantaneous reaction may be attributed to the small particle size of the carbides. The solids in the filter cartridge are presumably between 5 and 100 μ, and even smaller particles may be sorbed on these. In future experiments, particle sizes will be determined more quantitatively by electron microscopy.

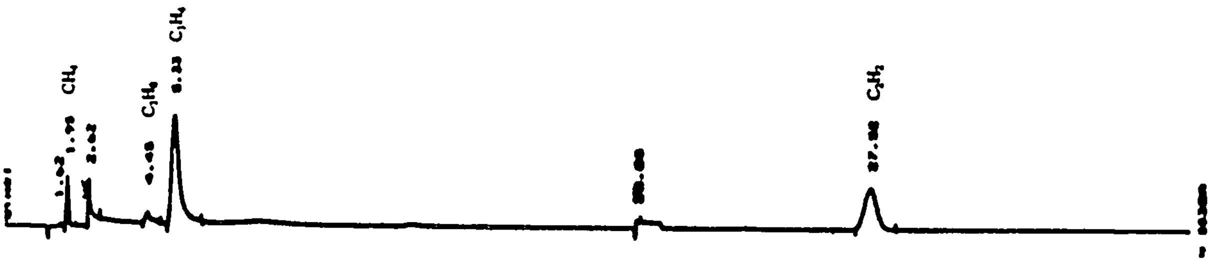


Figure 3. GC Analysis of Headspace Gas Above Unhydrolyzed Solid Sample Heated to 100°C for 5 minutes; Vacuum Degassed at Ambient T 0.5 ml Sample Gas Injection

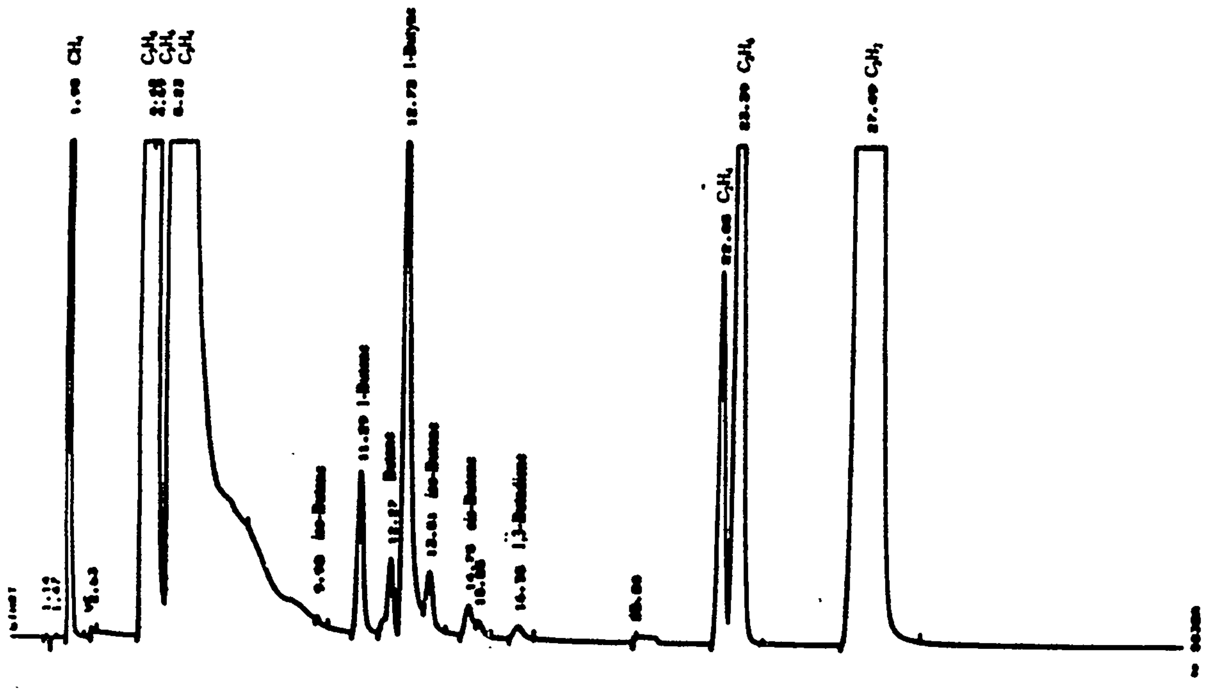
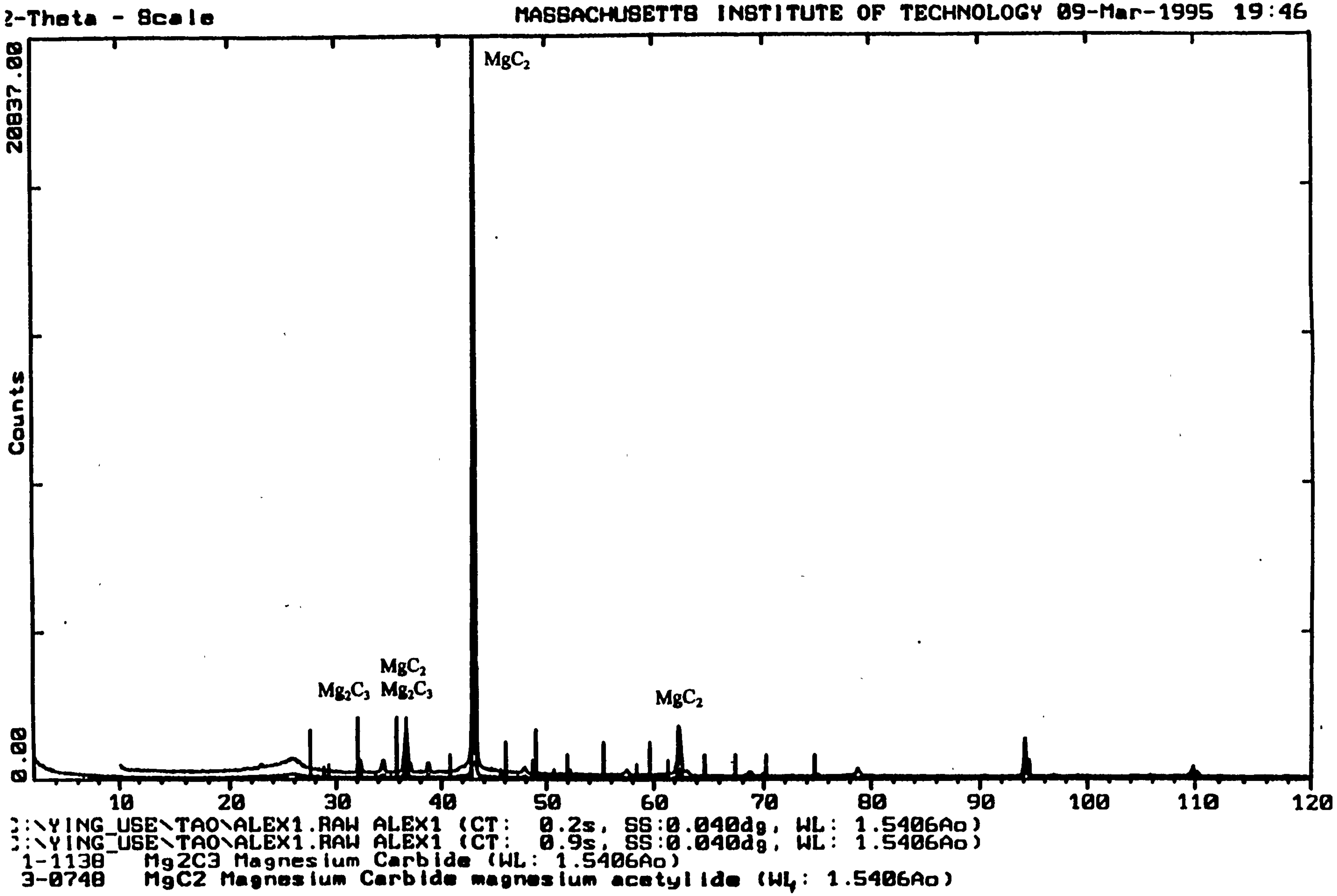


Figure 4. GC Analysis of Headspace Gas Above Hydrolyzed Solid Sample Heated to 100°C for 5 minutes; Vacuum Degassed at Ambient T 0.5 ml Sample Gas Injection

Figure 5. X-ray Diffraction Pattern of Solid Sample From Chamber Bottom



5. Conclusions

Based on the results of the scoping runs, there appears to be strong indications that a breakthrough has finally been achieved in that synthesis of magnesium carbides from MgO and methane in the arc discharge reactor has been demonstrated.

6. Future Plans

In preparation for a systematic study of carbide formation in the rotating arc reactor, the experimental apparatus had to be upgraded to allow for improved characterization of the process conditions. A sampling scheme that allows solid and gas sampling only during a period of the run time when the flows of methane and MgO are fully established was implemented using solenoid valves actuated according to a prescribed time sequence by an automatic control system. An automatic pressure controller was installed to maintain the chamber pressure at 760 mm Hg and a data acquisition system was installed so that arc voltage and current can be recorded on a computer. In addition, analytical techniques are being explored for quantifying carbide yields and for more detailed chemical and physical characterization of the solid products.

In the planned study, methane conversion, product yields and, to the extent feasible, products global formation rates will be measured in the plasma reactor as affected by independent variations in operating conditions of practical interest such as average temperature, power input, apparent average residence time, quench time, CaO/CH_4 and MgO/CH_4 ratios, initial particle size of CaO and MgO, methane partial pressure and partial pressure of a diluent such as hydrogen.

7. Acknowledgements

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