**Conversion of Light Hydrocarbon Gases to Metal Carbides for
Production of Liquid Fuels and Chemicals**

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Abstract

Upgrading of the experimental apparatus was necessitated by problems encountered in the previous scoping runs with CH_4/MgO . To further improve plasma stability, a pressure controller was installed on the cooling chamber to maintain the chamber pressure constant at 1 atm and a mass flow controller was installed on the main plasma gas inlet line. With a fully functional data acquisition and control system, there is now the capability to record arc voltage, arc current, chamber pressure, feed gas mass flow, and cooling water and gas temperatures during the relatively short experimental runs. With this system, an improved sampling protocol can also be implemented whereby gas and solid sampling are initiated only when fully developed flowrates of methane and MgO are established in the plasma. Solid products from a scoping run under conditions of excess MgO above the stoichiometric requirement for 100% conversion of the methane exhibited intense reactivity in the open atmosphere, indicating high concentrations of magnesium carbide in the product. The hypothesis is that reaction begins with hydrolysis of the carbide by atmospheric moisture giving acetylene and/or methylacetylene which then, because of the intense local heating (possibly due to the fine particle sizes of the recently formed carbides), are ignited to produce flaming combustion.

1. Progress on Task 1: Industrial Chemistry and Applied Kinetics of Light Hydrocarbon Gas Conversion to Metal Carbides, Hydrogen and Carbon Monoxide

In this Section, the highlights of the progress on Task 1 are discussed. By way of introduction, a recap of the work in the previous quarter is first reported in Section 1.1. Section 1.2 presents a discussion of the work in the current quarter.

1.1 Summary of Work in Previous Reporting Period (January 1 - March 31, 1995)

The methane plasma stabilization problem was resolved with the reconfiguration of the DC power supply to give a higher open circuit voltage to enable operation of the arc at higher voltage levels and with the installation of a solenoid around the plasma reactor to magnetically rotate the arc. Cathode tip erosion problems were encountered with the 1/4-inch graphite and tungsten tips which necessitated a redesign of the plasma reactor. The new plasma reactor consists of an enlarged 3/4-inch O.D. graphite tip to reduce current density and a 1-inch I.D. graphite anode. Products from MgO/CH₄ scoping runs in the redesigned reactor gave strong indications that a breakthrough had finally been achieved i.e. that synthesis of magnesium carbides from MgO and methane in the arc discharge reactor had been demonstrated. Significant quantities of hydrocarbons, primarily C₃H₄ and C₂H₂, were detected in the headspace above hydrolyzed solid samples by GC analysis. In one run, solids glowed upon exposure to the atmosphere, strongly suggesting carbide reaction with moisture in the air, exothermically forming acetylenes which ignited instantaneously in the presence of oxygen and elevated temperatures arising from localized heat-up of the specimens.

1.2 Progress during Current Reporting Period

Following the success of the MgO/CH₄ scoping runs in the previous quarter, we proceeded to prepare for doing a more systematic study of alkaline earth metal carbide synthesis from methane and MgO/CaO. Section 1.2.1 describes the experimental apparatus upgrading needed in preparation for performing this study. Sections 1.2.2 and 1.2.3 discuss the results of the CH₄/MgO scoping runs made with the upgraded setup.

1.2.1 Upgrading of Experimental Equipment

The previous scoping runs made apparent certain features inherent in our proposed experiment that necessitated an upgrading of our apparatus. First, solid particles steadily clog up the sintered stainless steel filters at the bottom of the cooling chamber, leading to a rapid pressure build-up in the chamber. Second, the frequency of fluctuation of process variables such as current and voltage input to the plasma arc is such that no reliable reading could be made manually during the short run time. And third, due to the relatively short run time, which is on the order of only one to two minutes, there is not enough time to read all process variables, much less to open and close valves for solid and gas sampling. As a result, process conditions cannot be properly characterized and controlled, solid samples have to be taken throughout the entire run including the start-up period, and there is no time to obtain reliable gas samples during the run.

To address the pressure build-up problem, a 1.25" I.D. butterfly pressure control valve and a pressure controller were procured and installed on the main vacuum line connected to the cooling chamber. A pressure transducer and a digital pressure readout, which were obtained from the Department of Chemical Engineering, had previously been installed on the system. With the pressure control system, we now have the ability to maintain the chamber pressure constant at 1 atm. Although solid particles still steadily clog up the filters downstream of the cooling chamber, the pressure does not build up anymore as was previously experienced. A mass flow controller and a 50 slpm solenoid valve, also obtained from the Chemical Engineering Department, was installed on the main plasma gas inlet line to further improve plasma stability.

In order to make complete and accurate readings of all process variables, a data acquisition system was installed. The system consists of a 12-bit, 16-input channel, 32 digital I/O channel, Analog-to-Digital (A/D) board with a total sampling frequency of 100 kHz and is installed on a 100 MHz 486 PC, upgraded from a 20 MHz 386 PC (from the Chemical Engineering Department). In addition, a signal conditioner for converting the arc voltage (0 to 160 volt range) to a 0 to 10 volt signal (which can be accepted by the A/D board) was also installed. A 16-channel multiplexer with signal conditioning was obtained for recording thermocouple readings of gas and water temperatures. Furthermore, a windows-based data acquisition software package, LabTech Notebook, was acquired. With this system, we now have the capability to record arc voltage, arc current, chamber pressure, feed gas mass flow, and cooling water and gas temperatures during experimental runs. Arc power can be calculated and displayed during the run. Noise was previously observed in temperature readings but was minimized with the use of shielded thermocouple wires.

In the previous scoping runs, there was no attempt to quantify the carbide yield because the sampling was done cumulatively, i.e. sampling was done throughout the entire run before the desired reaction conditions were established. Thus, these samples disproportionately weighted unconverted CH_4 and/or MgO so that the experiments would have underestimated the true conversions attainable at steady-state operation. In what is envisioned to be a better-controlled experimental run, sampling is performed only when fully developed flows of methane and MgO are established in the plasma. This sampling protocol consists of a 45-second period of solid sampling and a 30-second period of gas sampling, both simultaneously initiated after establishing a 100% methane plasma with the desired MgO feedrate. This is accomplished with a timed triggering of solenoid valves that replace the manually-operated sampling valves used previously. Figure 1 shows the experimental layout and process flow scheme. Solenoid valve, S1, is installed downstream of the sample collection probe and connected to the intake of the vacuum pumps. Normally closed, it opens at the start of solid sampling. A three-way solenoid valve, S2, allows normal gas sample flow to the oxygen analyzer but diverts the flow to a gas sampling bulb upon commencement of gas sampling. Solenoid valve, S3, is installed downstream the gas sampling bulb and opens during sampling and closes at the end of sampling. Triggering of the solenoid valves is accomplished with solid state relays on an output board, actuated through the digital output channels of the A/D board. In addition, the powder feeder and power to the plasma arc are turned off by signals from the A/D board at the end of the run. Figure 2 shows the timing sequence to be used for each experimental run.

Figure 1. Process Flow Diagram

Figure 2. Timing Sequence of Reactor Operation

1.2.2 SR-M-3 Scoping Run with Partially Upgraded Apparatus

With the new pressure control system, a partially installed data acquisition system and the improved sampling protocol, we made another scoping run SR-M-3, with methane and MgO in May. Starting with a 1 cfm (ambient temperature) argon plasma, MgO feeding was established at 12g/min. The switchover to 100% methane was accomplished easily, within a few seconds. Then the data acquisition and control sequence were initiated. During the run, the arc voltage ranged between 65 and 110 v and the arc current fluctuated between 170 and 200 amperes. Temperature in the chamber rose to about 700°C. Because we did not yet have a fully functional data acquisition system at the time of this run, we were not able to record these variables. We did, however, observe that the plasma was more stable, as manifested by less voltage and current fluctuations and the sustainability of the methane plasma at relatively lower current levels. By comparison with previous scoping runs where current levels were in the range of 200 - 400 amperes, the plasma could now be maintained below 200 amperes. We attribute this to the constant chamber pressure.

The solid sampler was handled and opened inside a glove box which was continuously purged with argon. The amount of solid samples was greater than that under the previous sampling scheme. A few milligrams of the solid sample were placed inside a 50 ml flask, which was then covered with a septum. The headspace above the sample was analyzed by gas chromatography (GC). A significant amount of acetylene was still detected from this unhydrolyzed sample while relatively much lower quantities of the other hydrocarbons were detected. This suggests that the sample was reacting with moisture that had remained in the glove box and that, with adequate continuous purging of the glove box with argon, the release of the hydrocarbons can be minimized. The sample was then intentionally hydrolyzed by injecting distilled water through the septum from a syringe and the headspace gas was analyzed by GC.

This analysis revealed a significant amount of acetylene but relatively little methylacetylene, suggesting the presence of much more MgC_2 than Mg_2C_3 . It was observed that all the solids were wetted upon addition of water. In the previous scoping runs, there usually were some solids, probably soot particles, that did not go into solution and that floated on the water surface. The absence of wetted solids here may indicate that little soot was formed in these runs and thus that the converted methane carbon exists in other forms, i.e. carbides and CO.

The rest of the solid effluent from the reactor was collected on the 100 μm sintered disc at the cooling chamber bottom and in the filter train downstream of the chamber. The filter train consists of a 30 μm filter followed by a 5 μm filter. Upon disassembly of this filter train, we discovered that virtually all the solids were collected on the 30 μm filter and hardly any solids were deposited on the 5 μm cartridge.

In addition to GC analysis, the hydrolyzed sample was also analyzed for water-soluble and HNO_3 -soluble Mg content using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The water-soluble Mg represents magnesium carbide while the acid-soluble Mg represents unreacted MgO . Based on this analysis, conversion of the oxide to the carbide was calculated to be about 27%. Methane was in stoichiometric excess over MgO in the feed, so CH_4 conversion to magnesium carbide may have been lower.

With the new sampling scheme, a gas sample was obtained. This was analyzed by GC for hydrocarbons and fixed gases, separately. Acetylene was detected in significant amounts. Hydrogen and CO were also detected in a separate analysis. No quantification was done as we were still refining these analytical techniques.

1.2.3 SR-M-4 Scoping Run with Upgraded Apparatus

Another scoping run, SR-M-4, was performed with a feed of 30.4 slpm of CH_4 and 22 g/min of MgO to test the data acquisition and control system. In contrast to all previous scoping runs, the amount of MgO fed in this run was above (1.1 times) the stoichiometric requirement for 100% conversion of the CH_4 . Table 1 summarizes some of the important parameters measured during the run.

Table 1. SR-M-4 Data (Average Value Over 1 min Runtime $\pm$ 1 Standard Deviation)

Arc Current, amperes	391.2 $\pm$ 84.0
Arc Voltage, volts	70.0 $\pm$ 8.4
Arc Power, kW	27.0 $\pm$ 5.4
Chamber Pressure, mm Hg	759.6 $\pm$ 8.3
Chamber Temperature, $^{\circ}\text{C}$	764.2 $\pm$ 4.7

The solid effluent from the reactor was collected on the 100 μm sintered disc at the cooling chamber bottom and in the filter train downstream of the chamber. Upon disassembly of

this filter train in the open air, the solids which were mostly collected on the 30 μ m filter (hardly any solids were deposited on the 5 μ m cartridge), immediately began to spontaneously glow and ignited in the form of a luminous (apparently diffusion) flame. The same phenomena were observed when solid products were exposed to the atmosphere upon removal of the bottom flange of the cooling chamber. These observations suggest that, upon exposure to the open atmosphere, magnesium carbide(s) undergo rapid exothermic reaction(s). Our hypothesis is that reaction begins with hydrolysis of the carbide by atmospheric moisture giving acetylene and/or methylacetylene which then, because of the intense local heating (possibly due to the fine particle sizes of the recently formed carbides), are ignited to produce flaming combustion. From a safety point of view, we will be handling the filters in a glove box purged with N₂.

The solid sample collected on the filter cup through the probe was handled in a dry argon atmosphere and weighed 3.3878 g. This sample appeared gray compared to the rest of the solid effluent. To see how reactive this solid was, water was squirted on it in the open air. As with the samples described above, this sample rapidly ignited to give a luminous flame.

The filter cup on which the solid sample was collected had a layer of unreacted MgO. This presumably accumulated at start-up when MgO was being fed into the argon plasma. To eliminate this, a high-pressure argon probe purge before and after solid sampling will be installed.

We also tried using 98% ACS reagent grade MgO as feed instead of the +325 mesh to -150 mesh 95+ % MgO powder used in the scoping runs. This was done to test the hypothesis that the C₄'s and hydrocarbons other than acetylene and methylacetylene observed in the headspace gas above the hydrolyzed samples could be due to impurities in the 95+% pure MgO feed. However, the ACS reagent grade MgO consisted of very fine (presumably <10 μ m) particles and could not be handled by our powder feeder. For now, we will continue using the larger size 95+% purity MgO feed.

2. Progress on Task 2: Mechanistic Foundations for Converting Light Hydrocarbon Gases to Metal Carbides, Hydrogen and Carbon Monoxide

In view of the intense reactivity of our solid products in the open atmosphere, we are looking into ways to prevent or minimize unintentional exposure of these products to air or moisture during product recovery and sample preparation for further analysis. For example, we have had some success in improvising a way for sealing the solids in a sample holder for X-ray diffraction but preparing samples for electron microscopy without exposing them to the atmosphere does not seem feasible at the moment.

3. Conclusions

Based on the intense reactivity in the open atmosphere of the solid products from the scoping runs, there appears to be strong indications that we are producing magnesium carbides in

high concentrations from MgO and methane in the arc discharge reactor under better controlled conditions.

4. Future Plans

In the next reporting period, systematic study of magnesium carbide synthesis from MgO and CH₄ will be initiated. In the first set of runs, we will investigate the effect on carbide yields of variation of MgO feed from 1 to 2 times the stoichiometric requirement.