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

**Quarterly Technical Status Report for the Period January 1 - March 31, 1994
DOE/PETC-MIT Contract No. DE-AC22-92PC92111**

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Abstract

The thermal plasma reactor system has undergone shakedown testing. The system flow capacity (cold reactor) was determined to be 3.35 cfm of argon at ambient temperature. A stable argon plasma is found to be obtainable up to 20 kW power input at a gas flowrate of 1 cfm. Further increases in power input level will be explored in the future as needed. Temperature profile measurements in the cooling chamber were performed at distances of 10.5 to 4.5 inches from the anode nozzle exit at power input levels of 5 to 20 kW and an argon gas flowrate of 1 cfm. The sample collection system was completed and will be tested simultaneously with a powder feeder that was acquired from Miller Thermal, Inc., of Appleton, WI, on a loan basis for trials on our system. Effectiveness of powder feeding will be investigated under argon cold flow (without firing) and hot flow (with firing) conditions. X-ray Photoelectron Spectroscopy was examined as a semi-quantitative technique for assessing the surface composition of carbides. Equilibrium diagrams for the Ca-C-H-O and Mg-C-H-O systems with the formation of C(s) suppressed at 1 atm pressure and over a temperature range of 1500 - 3500 K suggest that formation of CaC_2 can occur without C(s) but that the formation of significant quantities of either MgC_2 or Mg_2C_3 does not occur in the absence of C(s).

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

1.1 Status of Work as of the End of Previous Reporting Period (October 1 - December 30, 1993)

As of the end of the previous quarter, the plasma gun was redesigned, after an accidental burn-out in the previous period, to eliminate arcing pathways outside of the inter-electrode region. A stable argon arc discharge was obtained during the first test-firing of the completely rebuilt gun. The system flow capacity was determined to be about 3 cfm at ambient conditions. Procurement and installation of process and safety monitoring devices and of components of the sample collection system were in progress. The gas-quenched and water-cooled sample collection probe was fully assembled and was ready for installation. Shakedown-testing of the thermal plasma reactor had also commenced. Debottlenecking work on the gas and cooling water lines was performed to relieve excessive pressure drop through the gas and cooling water systems.

1.2 Progress during Current Reporting Period:

1.2.1 Experimental Equipment Construction

In preparation for shakedown testing of the plasma reactor system using argon in January, debottlenecking of the gas delivery line to the plasma gun and calibration runs on the gas rotameter on the control console were performed. We found that our system flow capacity (cold reactor) can go as high as 3.35 cfm of argon at ambient temperature, which is around 150% of the capacity of Kim's (1977) *et al.*(1979) thermal plasma system. In the previous month, we had discovered that the cooling water requirements of the plasma gun and the sample collection probe could not be supplied simultaneously by the same source because of its limited capacity. During January, we therefore had to tap into another cooling water supply header and connect a new supply line for the probe. With the newly configured cooling water system and an adequately-sized gas delivery line in place, we then proceeded with the shakedown testing of the plasma reactor.

In February, we focused on the assembly of the sample collection system. We installed additional instrument panels for controlling radial and axial flows of quench gas to the sample collection probe, for measuring the flow of sample gas, and for controlling the vacuum inside the cooling chamber as well as in various points along the sampling line. Assembly of the sample collection system was completed in March. The sample collection probe is aspirated with a direct-drive vacuum pump and vented to the exhaust duct of the fragmentation containment room housing the reactor. The probe is designed such that about 6 liters per minute of product gas at 2000°C is withdrawn and quenched with about 24 lpm of argon to below 500°C. A cascade impactor is connected downstream of the probe for particle collection and size classification of the solid products. A sample will be withdrawn from the gas collected through the probe via a gas sampling pump into a sampling bulb. During start-up of experiments, the oxygen content of the

gas withdrawn from the chamber will be measured with an oxygen meter prior to admitting methane into the system. By means of another vacuum pump, most of the gaseous products is aspirated from the cooling chamber through the sintered bronze filters at the bottom of the cooling chamber into the same exhaust stack.

Significant effort also went into sealing the fragmentation containment room to ensure adequate ventilation and dilution of exhaust gases, in preparation for firing the system with methane and CaO/MgO in the near future. The flow at the bottom of the room is now around 900 cfm, up from the previous reading of 800 cfm but still short of the target 1000 cfm. Rubber U-channel guides are being procured and will be installed along the perimeter of the doors of the room to further minimize air inflow through gaps along the length of the room.

1.2.2 Shakedown Testing of the Plasma Reactor System

In January, we first intended to determine the maximum power that can be delivered to our plasma reactor using Argon for each gas flowrate. We wanted a baseline to which we can compare future runs with methane. Our approach was to set the gas flowrate and increase the power input slowly and steadily up to the maximum power input for a preset current level. The power input was obtained as the product of the measured dc voltage and current. The firing was to be done with the bottom of the cooling chamber open (i.e. without the bottom flange and sample collection probe). The maximum acceptable power condition is the point at which some part of the system starts to overheat or the trigger point for a short circuit protection system built into the power supply. We installed a Type K thermocouple about four inches from the outlet of the cooling chamber to monitor the exit gas temperature. We began with a gas flowrate of 1 cfm at ambient conditions, which is roughly Kim's (1977) minimum flowrate. The open circuit voltage was 75 volts, prior to firing the gun. Once the arc is initiated, the operating voltage was stable at 25 volts. The gun was fired several times over a one-week period in an attempt to reach the maximum power condition. We were able to operate the arc with a current of up to 750 amperes for a power input of 18.75 kW and with an exit gas temperature of $\sim 600^{\circ}\text{C}$. However, this was not yet the maximum power condition. We did notice over the several times the gun was fired that the open circuit voltage eventually increased to 80 volts. This could be a sign of electrode erosion. The gun was taken apart and visually inspected but no signs of severe erosion were detected on the cathode. At this stage, we decided to exercise more caution in pushing our system to higher operating power levels. Kim's (1977, 1979) threshold power level for converting methane to CaC_2 was around 15 kW. Since we are confident that we can duplicate the conditions of Kim's (1977, 1979) experiments up to this power level, we have decided to proceed with completing our sample collection system and then with scoping runs with methane and CaO/MgO at the power levels already established as safe for our system. We will defer exploration of operability with argon at higher power levels and gas flowrates.

Preliminary temperature profile measurements in the cooling chamber using thermocouples were also performed in March to determine how close the sample collection probe can be placed to the plasma without fear of thermal damage. Temperature profiles of the cooling chamber under various power input levels for an argon plasma were measured using a Type K thermocouple probe. The sample collection probe was installed such that it penetrated about 4

inches into the 20 in. high cooling chamber, or about 16.5 inches from the anode nozzle exit of the plasma gun. The thermocouple probe was inserted into the sample collection probe and positioned such that the distance of its tip to the anode nozzle exit was varied in one-inch increments from 10.5 to 4.5 inches at current levels of 200 to 800 amperes, corresponding to input power levels of 5 to 20 kW. The voltage changed slightly but remained between 20 and 25 volts. Consequently, the power input at a lower current level may be the same as the power input at a higher current level but lower voltage. The flowrate of argon was 1 cfm at ambient temperature.

Figures 1 to 7 show the results of the temperature profile measurements. Above 700 amperes, corresponding to 15 kW or higher, a temperature decrease, rather than an increase, is observed. A plausible explanation is that the plasma power is determined by measuring the voltage and current at the outlet of the power supply, and that part of the power input measured is being dissipated as heat in the cables leading from the power supply to the high frequency oscillator and in the water-cooled power lines from the oscillator to the plasma gun. In fact, overheating of the cables was observed at currents ≥ 700 amp. Additional cables will be connected in parallel to lessen the resistance losses through the existing cables. In order to measure the power input into the plasma gun, a voltmeter and an ammeter will be installed as close to the gun as is practically feasible.

In the course of the temperature profile measurements, the cooling chamber pressure was found to fluctuate around 0 psig by 1 to 2 psi and thus affect the plasma conditions. During all runs, an attempt was made to maintain it at 0 psig. A pressure controller will be procured and installed to maintain a stable chamber pressure. In addition, after a series of start-ups and shut-downs of the plasma gun, the top layer of the sintered bronze filter at the bottom of the cooling chamber showed signs of discoloration, possibly due to overheating. Sintered stainless steel filters will be used as replacements in the future. Finally, cracks also started to develop in the Macor[®] piece that serves as thermal insulation for the walls of the top steel flange against the plasma. A small part of it had actually already shattered, presumably due to thermal stress. Should the steel flange become exposed to the plasma with more of the Macor[®] shattering, a porous thermal insulator will be used instead.

1.2.3 Examination of Analytical Techniques

We examined analytical techniques for carbide analysis. In particular, we looked at X-ray Photoelectron Spectroscopy (XPS) as a semi-quantitative technique for assessing the surface composition of our solid samples. We did XPS analyses of CaC_2 and CaO standards. In our analysis of CaC_2 standards, we however found significant quantities of O (37%) and N (4%), suggesting (1) surface adsorption by O and N, and/or (2) reaction of the CaC_2 with moisture in the air to form Ca(OH)_2 . We will therefore need to handle our CaC_2 products in an inert atmosphere, but it still remains to be established whether this technique can differentiate between CaO and CaC_2 .

We are also trying to obtain samples of Mg_2C_3 synthesized by a group in Norway (Fjellvag and Karen, 1992) for X-ray and neutron diffraction analysis of Mg_2C_3 structure. Our goal would be to use these Mg_2C_3 specimens as standards for calibrating various analytical methods.

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

Thermodynamic calculations using the Chemkin equilibrium program were performed for the Ca-C-H-O and Mg-C-H-O systems with the formation of C(s) suppressed at 1 atm pressure and over a temperature range of 1500 - 3500 K. The "carbon suppression" case is of interest because, under some conditions, Kim (1977) *et al.* (1979) were able to achieve high extents of conversion of methane carbon to CaC_2 , and thus almost eliminated solid carbon by-product formation. The results of these calculations are shown in Figure 8, for the Ca-C-H-O system, and in Figure 9, for the Mg-C-H-O system. These plots suggest that formation of CaC_2 can occur without C(s) but that the formation of significant quantities of either MgC_2 or Mg_2C_3 does not occur in the absence of C(s). However, high yields of C_2H_2 , H_2 , Mg, and CO are indicated.

3. Other Accomplishments

Dr. Peters gave a presentation on our work to Stone and Webster Engineering Corp. last January 28 in response to interest expressed by the firm. On February 28, Mr. Diaz presented our research efforts to Faculty from the MIT Department of Chemical Engineering as part of the requirements of his doctoral thesis.

4. Future Plans

At the end of March, we acquired a powder feeder from Miller Thermal, Inc. for a two-week trial period. A shakedown testing of the sample collection system will be undertaken in April simultaneously with testing of the powder feeder. Cold (no plasma) and hot (with plasma) flow powder feed tests will be performed. Parallel cables will also be installed from the power supply to the oscillator to lessen power line resistance losses. A voltmeter and an ammeter will be installed as close to the gun as is practically feasible. As a safety precaution, with the high compression ratio of the vacuum pump used to aspirate the cooling chamber, provisions will be made to add nitrogen gas to dilute the combustible mixture that will go into the intake of the pump.

5. References

1. Kim, C.S., "Formation of CaC_2 from CaO and 'Nascent' Carbon Species in a Rotating-Arc Reactor", Sc.D. Thesis, Department of Chemical Engineering, MIT, Cambridge, MA, (1977).
2. Kim, C.S., R.F. Baddour, J.B. Howard and H.P. Meissner, " CaC_2 Production from CaO and Coal or Hydrocarbons in a Rotating-Arc Reactor", *Ind. Eng. Chem. Process Des. Dev.* **18**, 323-328, (1979).
3. Fjellvag, F. and P. Karen, "Crystal Structure of Magnesium Sesquicarbide", *Inorg. Chem.* **31**, 3260-3263, (1992).

A maximum temperature of 1253°C was reached at 4.5 inches from the anode nozzle exit. Debottlenecking work and process improvements will be undertaken as necessary, such as upgrading of materials of construction, measurement of voltage and current as close to the plasma gun as possible, and installation of a pressure controller on the cooling chamber.

Fig 1. Temperature 10.5" from Anode vs Power Input

Fig 5. Temperature 6.5" from Anode vs Power Input

Fig 2. Temperature 9.5" from Anode vs Power Input

Fig 6. Temperature 5.5" from Anode vs Power Input

Fig 3. Temperature 8.5" from Anode vs Power Input

Fig 7. Temperature 4.5" from Anode vs Power Input

Fig 4. Temperature 7.5" from Anode vs Power Input

Figure 8. Equilibrium Diagram for Ca-C-H-O System with C(s) Suppressed (1 Atm and 1:3 Ca/CH₄ Ratio)

Figure 9. Equilibrium Diagram for Mg-C-H-O System with C(s) Suppressed (1 Atm and 2:5 Mg/CH₄ Ratio)

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