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

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Abstract

Scoping runs with up to 0.125 cfm methane in 1 cfm (ambient temperature) of argon and 12 g/min of MgO were performed in October using a graphite anode and tungsten cathode in the new plasma reactor. A GC analysis of the gas sample from the cooling chamber and of the head space gas above the hydrolyzed solid sample revealed the presence of C3H4 and C2H2, which suggests the formation of magnesium carbide. However, a similar run performed with MgO feeding into a pure argon plasma gave similar results, indicating possible reaction of the graphite electrode with the MgO to form carbides and/or direct formation of C3H4 and C2H2 in the arc. A GC analysis of the gas sample taken from the cooling chamber from a run in an argon plasma without MgO feeding did not yield any C3H4 and C2H2, suggesting that the MgO powder is hydrated and is a probable hydrogen source. Thus far, the main obstacle to performing a 100% methane/MgO scoping run is the instability of the methane plasma. Two approaches are being taken to address this issue: increasing the open circuit voltage of the power supply to permit operation of an arc at higher voltage levels and magnetically rotating the arc with a solenoid around the plasma reactor. The latter approach is currently being pursued.
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 (July 1 - September 30, 1994)

The first scoping run with methane and MgO in the plasma reactor was performed in August. After several attempts, a 1 cfm (ambient temperature) argon / 0.125 cfm (ambient temperature) methane plasma was sustained for about two minutes while feeding 12 g/min of MgO in the interelectrode region of the plasma reactor. The voltage was maintained at about 30 to 35 volts while the current fluctuated between 200 and 400 A. However, no solid product samples were available for analysis because, before the end of the run, the arc burned several small orifices through the wall of the water-cooled copper anode, resulting in water-flooding of the entire reactor system. This led to the adoption of a new design capitalizing heavily on features in the apparatus of Kim (1977) et al. (1979) utilizing graphite electrodes. The new plasma reactor was fabricated and underwent initial testing. A graphite cathode tip was found unsuitable because of its rapid consumption rate. Instead, a 2% thoriated tungsten tip was found to be more resistant to consumption and was selected for use in conjunction with a graphite anode in a scoping run with methane and MgO planned for the next quarter, i.e. Oct 1-Dec 31, 1994.

1.2 Progress during Current Reporting Period:

1.2.1 Scoping Run with Methane and Magnesium Oxide

A scoping run with methane and MgO was performed in October using a graphite anode and thoriated tungsten cathode in the new plasma reactor. The procedure was to initiate an argon plasma, then feed MgO powder into the interelectrode region, and then introduce methane a few seconds afterwards. Three attempts were made according to this procedure. In the first two, the arc extinguished within a few seconds after methane feeding commenced. In the third attempt, with simultaneous feeding of MgO and methane, the arc was sustained for 1.6 minutes.

In this third run, with 1 cfm (ambient temperature) of argon flowing into the reactor, a plasma was initiated and the arc current was raised to 400 - 500 Amp. MgO powder entrained in 9 cfh (ambient temperature) of argon carrier gas was fed at 12 g/min into the argon plasma. Methane was then slowly admitted into the reactor at a flowrate of 0.125 cfm at ambient temperature. With the current starting to fall as soon as the methane was introduced, current adjustments were made to raise the current to 400 Amp or higher. The arc voltage went up to as much as 40 volts. Solid samples were collected and hydrolyzed. A gas sample was then withdrawn from the head space above the hydrolyzed sample and analyzed in a gas chromatograph.
A GC analysis of this head space gas revealed the presence of $\text{C}_3\text{H}_4$ and $\text{C}_2\text{H}_2$, which suggests the formation of magnesium carbide. Realizing, however, the small amount of methane fed, it was necessary to investigate the possibility of having formed carbides from the graphite instead of, or as well as, from the methane. A similar run was then performed with MgO feeding into an argon plasma arc sustained between a tungsten cathode and a graphite anode but without the introduction of methane. During hydrolysis of a sample of solids collected from this run, bubble formation was observed, suggesting that some reaction was going on. A GC analysis of the head space above the hydrolyzed solid sample showed $\text{C}_3\text{H}_4$ and $\text{C}_2\text{H}_2$ peaks. Because no $\text{CH}_4$ was fed in this run, we hypothesized that carbides, e.g. $\text{Mg}_2\text{C}_3$ and $\text{MgC}_2$ were formed from carbon in the graphite anode, probably by the global reactions

$$3\text{C} + \text{MgO} \rightarrow \text{MgC}_2 + \text{CO}$$ (1)

$$5\text{C} + 2\text{MgO} \rightarrow \text{Mg}_2\text{C}_3 + 2\text{CO}$$ (2)

Thus, in the methane run just described, it seems probable that carbon from the anode was indeed contributing to carbide formation. This is very encouraging because, if $\text{Mg}_2\text{C}_3$ and $\text{MgC}_2$ can be formed from solid carbon, we expect that they could be formed from methane perhaps even more easily, provided a stable methane plasma can be sustained and effective $\text{CH}_4$-MgO contacting can be achieved.

The next question was whether methylacetylene/acetylene were being formed directly in the plasma reactor. A GC analysis of gas sampled from the cooling chamber would answer this question. To examine this possibility, another run with MgO feeding into an argon plasma was performed and a gas sample was withdrawn from the cooling chamber. This, too, revealed the presence of $\text{C}_3\text{H}_4$ and $\text{C}_2\text{H}_2$, but the source of hydrogen was a mystery. After checking for and not finding any water leaks in the reactor or water entrainment in the argon supply, these possible hydrogen sources were ruled out. The only remaining source was the MgO powder. MgO can exist in a hydrated form, $5\text{MgO}\cdot4\text{CO}_2\cdot\text{xH}_2\text{O}$ and it is plausible that water from this source reacted with the graphite to form $\text{C}_3\text{H}_4$ and $\text{C}_2\text{H}_2$. However, further study to assess this hypothesis was deemed appropriate.

Another run with an argon plasma but without MgO feeding was then carried out and a gas sample taken from the cooling chamber. A GC analysis of this gas sample did not detect any $\text{C}_3\text{H}_4$ and $\text{C}_2\text{H}_2$, which supports the theory that the MgO powder is the hydrogen source. A moisture determination on the MgO powder revealed a 1.2% weight loss on heating to 460°C. However, calcining at $>900^\circ\text{C}$ might be necessary to remove all impurities.

### 1.2.2 Methane Plasma Stabilization

Thus far, the main obstacle to performing a methane/MgO scoping run is the instability of the methane plasma. Two approaches were taken to address this issue. First, increasing the open
circuit voltage of the power supply was attempted. The electrical field strength required to ionize methane is higher than that for argon because additional energy is required for dissociation and excitation of rotational and vibrational levels. Thus, the voltage tends to increase upon introduction of methane into the system. Having a higher open circuit voltage will permit operation of an arc at higher voltage levels. A second approach is to magnetically rotate the arc by installing a solenoid around the plasma reactor. This is expected to stabilize the arc and may also promote better plasma-solid mixing.

The power supply's open circuit voltage was increased from 160 to 320 volts. Under this configuration, it should be possible to increase the load voltage from 80 volts up to 160 volts, which is considered desirable because the arc voltage presumably increases beyond 80 volts upon introduction of methane into the system.

Two initial trial runs with an argon plasma under the 320-volt OCV power supply configuration however revealed that the electrical feed lines to the power supply are rated only for operation under the 160-volt OCV configuration and thus resulted in the blow-out of a switchbox fuse or the tripping of the main circuit breaker. This can be fixed by upgrading the electrical feed lines but this has been postponed until after a solenoid has been installed around the plasma reactor to magnetically rotate the arc in hopes that the electrical modifications would be unnecessary. Kim (1977) et al. (1979) used a d.c. power supply with an OCV of 160 volts and employed magnetic rotation to stabilize the arc. Thus, it might not be necessary to upgrade the electrical lines if adding a magnetic coil can stabilize a methane plasma.

The magnetic coil was fabricated based on Kim's (1977) design. The solenoid placed concentrically around the plasma reactor works to rotate the arc column using an axial magnetic field. The axial magnetic field interacts with the radial arc column to produce a force perpendicular to the plane of the arc and the field. This force which induces rotation is given by:

\[ \vec{F} = \vec{I} \times \vec{B} \]

where \( \vec{I} \) is the arc current and \( \vec{B} \) is the axial magnetic field. Applying Newton's second law to equate the centrifugal force to the magnetically generated force, as given by Halliday and Resnick (1978):

\[ m_e \frac{v^2}{R} = q v B \]

where \( m_e \) is the electron mass in kg, \( v \) is the speed of electrons in m/sec, \( R \) is the interelectrode gap in meters, \( B \) is the required field strength in tesla, and \( q \) is the elementary charge in coulomb. Solving for \( B \) gives

\[ B = m_e v / q R \]

To determine the electron speed, \( v \), Blanchet (1963) used the following relation equating the potential existing between the anode and the cathode to the kinetic energy of the electrons:
The field strength $B$ for an infinite solenoid is given by

$$B = \mu_0 \cdot i_0 \cdot n$$

where $\mu_0$ is the permeability constant in Ampere's Law, $i_0$ is the solenoid current and $n$ is the number of turns per unit length. Kim (1977) used this to approximate a solenoid of finite length:

$$B = 1.26 \cdot i_0 \cdot N/l$$

where $N$ is the total number of turns, $l$ is the solenoid length in cm, $i_0$ is in amperes and $B$ is in gauss.

Based on these design considerations, Kim (1977) made a solenoid by winding two coils, one on top of the other, of No. 15 enameled copper wire over an 8" length of 12" O.D. by 11.5" I.D. plexiglass cylinder, with each coil consisting of two layers and a total of 126 turns. This resulted in a solenoid that produced a measured field of 120 gauss when a direct current of 13 amp was passed through the coils under an overall potential drop of 20 volts. In our present setup, a wider cylinder had to be used in order to clear the fittings and enclose the entire plasma reactor. The solenoid design consists of 4 layers of No. 15 enamel-coated copper wire windings over an 8" section of a 9" long bakelite tube 15.5" O.D. by 14.5" I.D. The number of turns per layer is approximately 130. The solenoid was fabricated and installed in December.

The solenoid was installed onto the reactor and connected to a 400 watt d.c. power supply. The resistance of the solenoid was measured to be 0.7 ohm. Thus, with a current of 13 amperes, the solenoid can theoretically have a maximum magnetic field of 420 gauss. However,
the presence of the steel cooling chamber can significantly alter the magnetic field strength at the center of the reactor. The solenoid will be tested in the next reporting period.

1.2.3 Other Refinements to the Apparatus

Another 17.7 cfm vacuum pump was installed in parallel with the existing vacuum pump used to aspirate the cooling chamber to increase the amount of dilution nitrogen that can be admitted in the pump intake to dilute potentially combustible gases from the chamber.

A pressure controller salvaged from dismantled equipment in the Department of Chemical Engineering was also installed in the reactor system December. This piece of equipment is critical to maintain the pressure inside the cooling chamber at atmospheric pressure. Upon initiation of the arc, the pressure inside the chamber always rises from 0 psig to about 3-6 psig. Thus, manual adjustments are always needed after starting the arc. The controller came with a small control valve so a larger valve (about 50 lpm) will have to be procured.

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

There was minimal activity under Task 2 during the reporting period as efforts were focused on scoping plasma runs with methane and MgO and stabilizing the methane plasma.

3. Future Plans

Methane/MgO scoping runs with the magnetic coil will be performed. If a stable methane plasma is not achieved, the electrical feed lines to the power supply will be altered to enable operation at the 320 volt open circuit voltage.

4. References


