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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 July 1 - September 30, 1995
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Abstract

Two final scoping runs were conducted to test the experimental protocol for methane conversion to alkaline earth metal carbides in the thermal plasma reactor and to refine the techniques for carbide analysis. Having demonstrated the adequacy of the experimental protocol, the systematic study of metal carbide synthesis from methane and MgO commenced. Initial runs with MgO/CH₄ gave surprisingly low methane conversions (<2%) to magnesium carbides, despite high conversions (65-90%) to hydrogen. An X-ray diffraction analysis showed the presence of a significant amount of elemental magnesium, a finding supported by the observation of bright lights upon hydrolysis of the solid products in the open air. The high conversion to hydrogen and the presence of elemental Mg in the solid products suggest that the plasma effluent is not being quenched rapidly enough and any magnesium carbides formed may be decomposing into the elements. To test this hypothesis, attempts to increase quench rates were made including lowering the arc power level, decreasing the anode nozzle-to-probe distance and introducing more quench gas.

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 (April 1 - June 30, 1995)

Upgrading of the experimental apparatus was necessitated by problems encountered in 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. 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.

1.2 Progress during Current Reporting Period

Prior to doing a systematic study of alkaline earth metal carbide synthesis from methane and MgO/CaO, two final scoping runs were conducted to test the experimental protocol and to refine the techniques for carbide analysis. Section 1.2.1 describes these two scoping runs. Section 1.2.2 discusses the results of the first four runs of the systematic study of carbide synthesis from methane and MgO.

1.2.1 Final Scoping Runs

In July, two scoping runs were performed prior to starting the systematic studies of magnesium carbide synthesis from MgO and CH_4 . The first scoping run, SR-M-5, was performed as a trial run to test the experimental protocol, which already included the newly installed probe purge intended to keep solids from entering the probe and thus the sampler, before and after the sampling period. This run was performed with a feed of 30.4 slpm of CH_4 and 22 g/min of MgO. The data acquisition and control system functioned as intended and magnesium carbides were formed as suggested by the spontaneous ignition of the solids in the filter train upon disassembly of this filter train in

the open air. However, solids collection in the sampler turned out to be minimal due to excessive probe quench and radial gas flowrates. In the next runs, the argon gas flows to the probe were lowered sufficiently in order to enable solid collection through the probe. The spontaneous ignition of the solids in the filters also necessitated disassembly of the filters in a glove box purged with an inert gas in subsequent runs.

The second trial run, SR-M-6, was performed to identify which hydrocarbon detectable by a Flame Ionization Detector (FID) can be used as an internal standard to quantify the number of moles of C_2H_2/C_3H_4 released from hydrolysis of a known amount of solid sample. For this run, a new batch of MgO feed was prepared in an argon-purged glove box to avoid moisture and air exposure and then transferred to the powder feeder without exposure to the atmosphere. Of the C_1 to C_4 hydrocarbons, isobutane was not detected in the headspace above the solid sample. Thus, isobutane is used as a tracer in the headspace above the solid sample before hydrolysis in subsequent analyses.

The reactor solid effluent from SR-M-6, after having been left in the filter train overnight, was handled in a N_2 -purged glove box. Afterwards, the solids collected were hydrolyzed in the open air. Bright, sparkling lights and glowing ignition were observed, suggesting the presence of magnesium metal as well as magnesium carbides. The next day, all the solids remaining in the chamber, which we suspected had already reacted with moisture in the atmosphere, were collected in a pint-size tin can and hydrolyzed in the open air. After squirting distilled water into the can, a 7-foot-tall yellow-orange flame shot out of the can! This incident has made us more safety-conscious in terms of disposal of the solid effluents. In subsequent runs, small amounts of solids are to be added to an excess of water in the ventilated reactor room.

Aside from carbide yields, we also wanted to measure the yield of H_2 and CO from CH_4 . In order to do this, the gas flowrates through the probe and the main gas line from the chamber needed to be measured in addition to determining the composition of the sample gas by GC. Thus, high-capacity mass flowmeters (obtained from the MIT Department of Chemical Engineering) were installed on the main gas and probe gas lines. These were also connected to the data acquisition system for recording of the measurements.

1.2.2 Initial Runs of Systematic Study of Methane Conversion to Metal Carbides

Following Run M1 in August, which is the first in a series of runs to determine methane conversion to Mg_2C_3 , MgC_2 , H_2 , and CO, three runs were performed in September: Runs M2, M3 and M4. Table 1 summarizes the reactor conditions for all four runs:

Table 1. Reactor Conditions [Ave (± 1 s.d.)] for Runs M1, M2, M3 and M4

Run	M1	M2	M3	M4
CH ₄ Flowrate, slpm	30.0	30.0	30.0	30.0
MgO Feedrate, g/min	23.4	17.5	20.4	20.4
Inlet MgO/CH ₄ Molar Ratio	0.47	0.35	0.41	0.41
MgO Particle Size, μm	$44 < p < 104$	$44 < p < 104$	$44 < p < 104$	$44 < p < 104$
Chamber Pressure, mm Hg	751 ± 50	760 ± 15	762 ± 12	756 ± 15
Arc Power Input, kW	41.4 ± 7.6	44.0 ± 8.5	34.5 ± 6.8	32.8 ± 7.5
Nozzle exit-to-Probe Inlet, in	14	14	14	10

In each run, two samples of solid products collected in the solid sampler through the sample collection probe were weighed and were placed separately in two 50-ml flasks and covered with a septum stopper. The samples were prepared inside an argon-purged glovebox to avoid reactions with oxygen or moisture. GC analysis was then performed on the headspace gas above each sample before and after hydrolysis. A known quantity of iso-butane was injected into each flask prior to hydrolysis as an internal standard to enable determination of the total number of moles of C₃H₄ and C₂H₂ evolved upon hydrolysis and thus the number of moles Mg₂C₃ and MgC₂ produced. After GC analysis, dilute nitric acid was added to the solids remaining after hydrolysis to dissolve all the magnesium in preparation for total Mg analysis. Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) and - Atomic Emission Spectroscopy (ICP-AES) were used to determine the total Mg content of each sample. It is very reasonable to assume that all Mg in each sample entered the reactor as MgO feed. Thus, the number of moles of C₃H₄ plus C₂H₂ divided by the number of moles of Mg gives the fractional molar conversion of MgO in the feed to acetylenes in the product, α_{MgO} . Because the molar ratio of MgO to CH₄ in the feed, ϕ , was maintained at a known constant value, the corresponding fractional molar conversion of CH₄ to C₃H₄ plus C₂H₂, α_{CH_4} , can be directly calculated, i.e. $\alpha_{\text{CH}_4} = \phi \alpha_{\text{MgO}}$.

GC analysis of a gas sample from the reactor cooling chamber for each run yielded the following composition data (Table 2):

Table 2. Sample Gas Composition (Volume Percent)

Run	M1	M2	M3	M4
Hydrogen	70.5	76.2	75.5	74.99
Carbon Monoxide	19.9	15.5	16.1	16.8
Argon	9.1	7.4	7.8	7.2
Methane	0.1	0.2	0.2	0.4
Other Hydrocarbons	0.4	0.7	0.4	0.7

These composition data and the total gas flowrate measurements from the reactor allow the yields of H₂ and CO, and the amount of unconverted CH₄ to be readily calculated.

Table 3 gives the percentage of methane carbon and methane hydrogen converted to various products, calculated according to the procedures noted above.

Table 3. Percent Methane Conversion

Run	M1		M2		M3		M4	
Products	CH ₄ "C"	CH ₄ "H ₂ "	CH ₄ "C"	CH ₄ "H ₂ "	CH ₄ "C"	CH ₄ "H ₂ "	CH ₄ "C"	CH ₄ "H ₂ "
Mg ₂ C ₃	1.8		1.0		1.5		1.5	
MgC ₂	0.4		0.2		0.2		0.5	
CO	49.8		31.6		28.4		40.9	
Non-carbide C	a		a		a		a	
Unreacted CH ₄	0.3	0.3	0.4	0.4	0.3	0.3	0.9	0.9
H ₂		88.3		77.4		66.7		91.5

^a To be determined

In Table 3, "Non-carbide C" refers to carbon that may be present in the residue from hydrolysis of the solid products, i.e. it could also be designated "unhydrolyzable C". The composition of this material is at present not known, but it may consist of carbon-rich tar, and various forms of solid "carbons" such as soot. To determine the contributions of this "non-carbide C" to the overall carbon balance, samples of solid residues from hydrolysis will be sent to a commercial laboratory for elemental carbon assays.

Table 3 also shows very high hydrogen yields. Assuming a dry feed, the only source of hydrogen is the methane so these hydrogen yields also imply that 65-90% of the methane was converted. This is consistent with our finding, based on the product gas analysis, that unreacted methane accounted for less than 1% of the methane fed.

The apparently low Mg₂C₃ and MgC₂ yields are surprising in the light of the high hydrogen yield. X-ray diffraction analysis of a sample of the solid products was performed about a week after Run M-1. In agreement with our hydrolysis data, the X-ray diffraction analysis indicated only minimal MgC₂ in the sample, but interestingly showed the presence of a significant amount of elemental Mg.

In view of the low methane conversion to magnesium carbides in Run M1, the MgO feedrate was lowered below the stoichiometric requirement for Mg₂C₃ formation. Earlier thermodynamic equilibrium calculations showed that, with suppression of solid carbon, no Mg₂C₃ was formed but that the products were composed mostly of Mg and CO. Thus, Run M2 was performed under conditions that would give excess solid carbon to promote magnesium carbide formation. This run, however, still did not result in increasing the conversion of methane to the carbides.

The observation of bright lights upon hydrolysis of the solids in the open atmosphere suggests the presence of Mg metal, as was confirmed by X-ray diffraction of

a sample from Run M1. One hypothesis is that magnesium carbides are actually being formed in the region immediately downstream of the arc but are decomposing into elemental carbon and magnesium as they cool down in the chamber. This is supported by the known thermal decomposition of Mg_2C_3 into its elements at 740-760°C (Kosolopova, 1971). Temperature measurements halfway up the chamber made with a type K thermocouple indicate temperatures > 800°C. Thus, it appears that the plasma effluent is not being quenched rapidly enough to temperatures below 700°C and any magnesium carbides formed may be decomposing into the elements. To address this quenching issue, Run M3 was performed at a much reduced arc power level, 34.5 kW vs > 40 kW in the previous runs, and with a higher argon probe quench, 24 slpm vs 18 slpm. However, low conversions were still obtained in this run.

If elemental Mg is present in the solid samples, H_2 can be detected in the headspace gas upon hydrolysis according to the reaction:

For larger solid pieces of magnesium, Reaction (1) is arrested by the formation of a Mg(OH)_2 coating that inhibits H_2O from accessing yet unconverted Mg. However, for our specimens, it is believed that the Mg, if present, exists as very finely divided inclusions, e.g. a few μm diameter or less, so that Reaction (1) could proceed virtually to completion. If so, analysis of the headspace gas above the hydrolyzed samples of the solid products for H_2 could allow yields of elemental Mg to be quantified. We intend to get some Mg metal in powder form to use as a standard to test the accuracy of this method for Mg quantification.

In an attempt to quench the products more rapidly, a chamber quench line was installed that would allow argon to be injected into the upper portion of the chamber to quench the reaction faster. A thermocouple was also installed with its tip right at the nozzle exit. A run was attempted whereby 20 slpm Ar was introduced as chamber quench. This, however, overloaded the system and caused the circuit breaker of the power supply to trip. A temperature of about 1600°C was read during the run. In the next attempt to achieve better quenching, the copper sample collection probe was moved 4 inches higher up into the chamber to give an anode nozzle exit-to-probe tip distance of 10 inches in Run M4. A probe tip radiation shield made of low-density alumina was also installed to keep the probe tip cool. Despite this, the solder at the probe cap melted and a small water leak developed, which was not detected until after the run. The effect of water or steam seemed encouraging because, although the conversions were still low, no bright lights were observed upon hydrolysis of the solids in open air, indicating less Mg metal present. The probe can still be repaired but, in the next runs, the stainless steel spare probe will be utilized, whose cap is welded, not soldered.

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

An SEM analysis was conducted on some solids recovered from the bottom of the cooling chamber in SR-M-5. Taking SEMs of the solids proved to be challenging as the solids were found to be electrically charging. Figure 1 shows an SEM of the solid particles which are about 0.1 μm in size.

We attempted to do an FTIR analysis of our samples for magnesium carbide detection but, as with other analytical methods, we encountered difficulties from atmospheric exposure during sample preparation. With some analytical instruments, which have very demanding sample preparation requirements (e.g. size, mass, shape, ease of access, etc.), it is very difficult, even with glove box techniques, to completely eliminate all atmospheric contact.

3. Conclusions

Initial runs with MgO/CH_4 gave low methane conversions (<2%) to magnesium carbides, despite high conversions (65-90%) to hydrogen. An X-ray diffraction analysis showed the presence of a significant amount of elemental magnesium, which is supported by the observation of bright lights upon hydrolysis of the solid products in the open air. The high conversion to hydrogen and the presence of elemental Mg in the solid products suggest that the plasma effluent is not being quenched rapidly enough and any magnesium carbides formed may be decomposing into the elements.

4. Future Plans

Our systematic study of magnesium carbide synthesis from MgO and CH_4 will continue in the next period, with a focus on achieving higher methane conversions to metal carbides by increasing quench rates, either by decreasing the nozzle exit-to-probe tip distance or introducing a chamber quench of argon.

5. References

Kosolapova, T. Ya., translated from Russian by N.B. Vaughan, *Carbides: Properties, Production, and Applications*, Plenum Press, New York-London, (1971).

Figure 1. SEM of Solid Particles from Chamber Bottom, SR-M-5