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

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Abstract

Previous work at MIT indicates that essentially stoichiometric, rather than catalytic, reactions with alkaline earth metal oxides offer technical and economic promise as an innovative approach to upgrading natural gas to premium products such as liquid hydrocarbon fuels and chemicals. In this approach, methane would be reacted with relatively low cost and recyclable alkaline earth metal oxides, such as CaO and MgO, at high temperatures ($>1500^{\circ}\text{C}$) to achieve very high (i.e. approaching 100%) gas conversions to H_2 , CO and the corresponding alkaline earth metal carbides. These carbides exist stably in solid form at dry ambient conditions and show promise for energy storage and long distance transport. The overall objective of the proposed research is to develop new scientific and engineering knowledge bases for further assessment of the approach by performing laboratory-scale experiments and thermodynamic and thermochemical kinetics calculations. Work on this project will be performed according to two tasks. Under Task 1 (Industrial Chemistry), a laboratory-scale electric arc discharge plasma reactor is being constructed and will be used to assess the technical feasibility of producing Mg_2C_3 from MgO and methane, and to identify the operating conditions of interest for the commercial production of Mg_2C_3 and/or CaC_2 from MgO and/or CaO and methane. An old AVCO plasma gun system in the Department of Chemical Engineering consisting of a plasma gun, d.c. power supply, high frequency oscillator, and control console was revitalized and will be utilized as the plasma reactor for carrying out the reaction of methane with MgO and/or CaO. A 20-in long 6-in I.D. cylindrical steel pipe will be used as a post-plasma cooling chamber for quenching the reaction. During the reporting period, development of a sample collection system in the form of a probe was undertaken and detailed design of the flange connection between the bottom part of the cooling chamber and the probe was finalized. A 1.5 ft by 3 ft by 11 ft fragmentation containment chamber made of 1/8" thick aluminum plate was constructed to house the plasma reactor. Options for a commercial powder feeder unit are being explored. In particular, the performance of a powder feeder from METCO, a plasma gun system manufacturer based in Westbury, NY, is being assessed. The METCO unit has a microprocessor-based weight loss metering unit integrated with the fluidized bed system to provide continuous closed-loop monitoring and control of powder feed rates. Under Task 2 (Mechanistic Foundations), preliminary thermodynamic calculations were performed for the Ca-C-H-O and Mg-C-H-O systems using the Chemkin program. A scoping run with CaO in an electrical screen heater reactor under reduced methane pressure was also conducted. No appreciable quantity of acetylene was detected upon hydrolysis of the solid residue. This can be attributed to the very small quantity of methane at the very low pressure coupled with inadequate contacting of whatever methane was present with the CaO powder. Future work will focus on the completion of the experimental apparatus for Task 1 and on improving the contacting between methane and CaO and/or MgO both in the electrical screen heater set-up and possibly in another type of set-up under Task 2.

1. Background and Objectives

Previous work at MIT by Kim *et al.* [1,2] indicates that essentially stoichiometric, rather than catalytic, reactions with alkaline earth metal oxides offer technical and economic promise as an innovative approach to upgrading natural gas to premium products such as liquid hydrocarbon fuels and chemicals. In this approach, light hydrocarbon gases would be reacted with relatively low cost and recyclable alkaline earth metal oxides, such as CaO and MgO, at high temperatures ($>1500^{\circ}\text{C}$) to achieve very high (i.e. approaching 100%) gas conversions to H_2 , CO and the corresponding alkaline earth metal carbides. These carbides exist stably in solid form at dry ambient conditions and show promise for energy storage and long distance transport. They can subsequently be made to undergo simple upgrading, by hydrolysis, to acetylene or methylacetylene which would be useful as chemical feedstocks, as fuels, and as liquid fuel precursors.

Research is needed to provide key information for further technical and economic assessment of this approach. In particular, there is need:

- 1) To determine the technical feasibility of reacting MgO and methane under thermal plasma conditions to achieve high yields, selectivities and gas conversions to Mg_2C_3 , H_2 and CO, in analogy to the high methane conversion and selectivity to CaC_2 , H_2 , and CO, previously demonstrated at MIT by reacting methane with CaO in an electric arc discharge reactor[1,2];
- 2) To define preferred ranges of plasma operating conditions for methane reactions with CaO and/or MgO to provide desired yields, selectivities and conversions to CaC_2 and/or Mg_2C_3 , H_2 and CO, and which would be suitable for industrial practice;
- 3) To determine if, as implied by thermodynamic calculations, methane conversion to CaC_2 and/or Mg_2C_3 can be carried out under thermal conditions, without the need for an electrical arc discharge; and
- 4) To develop a better understanding of the underlying chemical and physical mechanisms by which this approach gives desired conversion/selectivity and kinetics behavior.

Work on this project will be performed according to two tasks:

Task 1: Industrial Chemistry and Applied Kinetics of Light Hydrocarbon Gas Conversion to Metal Carbides, H_2 and CO

We are building a laboratory-scale electric arc discharge reactor, in which to assess the technical feasibility of producing Mg_2C_3 , H_2 and CO from methane and MgO. We will also do experimental runs with CaO as well as mixtures of CaO and MgO and measure conversions of methane, CaO and/or MgO, and yields of Mg_2C_3 and/or CaC_2 , H_2 and CO to identify the operating conditions of interest for implementing these reactions on a commercial scale. Reaction conditions and parameters will be chosen based on the previous work at MIT with CaO and CH_4 and on results of thermodynamic and thermochemical kinetics calculations.

Task 2: Mechanistic Foundations For Converting Light Hydrocarbon Gases to Metal Carbides, H_2 and CO

We will evaluate the technical feasibility of carrying out methane reactions with CaO and MgO by thermal (e.g. 1500 - 2000°C) rather than under plasma conditions by performing experiments with the use of electrical screen heaters, heated tubular reactors, or other suitable apparatus. Extents and global rates of methane conversion, and yields as well as global production rates of CaC_2 , Mg_2C_3 , H_2 and CO will be measured upon subjecting mixtures of methane and CaO and/or MgO to high temperatures and controlled residence times. We will conduct hypothesis-testing of possible mechanistic pathways with selected experiments and perform reaction modeling to better understand the underlying chemical and physical processes that could influence process scale-up possibilities.

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

2.1 Status of Work on Task 1 as of the end of Previous Reporting Period (January 1 - March 31, 1993)

As of the end of the last reporting period, we had been successful in revitalizing the thirty-year-old AVCO plasma gun system at the Department of Chemical Engineering. We performed a system check-out and test-firing of the gun with Argon as the plasma-forming gas last February. All the components of the system were found to be in working order and would seem to be useable for our initial experimental set-up. With a working plasma gun, d.c. power supply, high frequency oscillator, control console for the plasma gun and remote

control console for the power supply, we still needed a post-plasma cooling chamber, powder feeder, sample collection system and vacuum pump. In addition, safety considerations require that we build a fragmentation containment chamber in which to house our reactor.

For a post-plasma cooling chamber, we planned on using one of three cylindrical sections of steel pipes with flanges welded onto them used as reactors in previous experiments in the Department. These chambers are about 20 inches long and 6 inches in diameter and are already equipped with cooling coils. We also managed to locate an old vacuum pump in the Department that is rated at up to 17.7 cfm, which we could use as a booster to exhaust the reactor effluent gases to a ventilation stack. For a powder feeder unit, we considered it worthwhile to still go in the direction of purchasing a commercially available unit rather than devoting significant development efforts to the design, construction and systematic testing of a "home-made" powder feeder. Finally, for a sample collection system, a design for a probe was being prepared by Mr. Modestino.

2.2 Investigation of Experimental Equipment Construction

In April, we completed the construction of our fragmentation containment chamber. An overall layout of the experimental set-up is given in Figure 1. The nominal dimensions of the room are 1.5 ft by 3 ft by 11 ft. The room was constructed with access from three sides. Both 3-ft wide sides have 8-ft high 1/8" thick aluminum doors that slide. A sliding door has the advantage over a swinging door of eliminating the need for optical alignment whenever the door is opened (in case we decide to have optical diagnostics). Access to the bottom part of the system, i.e. the probe and lower part of the cooling chamber, will be available from these two sides. The 1.5-ft wide front side of the room has dutch-style 1/8" thick aluminum swinging doors consisting of 7-ft and 3-ft high sections. The swinging doors allow additional access to the system, especially the upper part; the cooling chamber will be located 5 to 7 ft above the ground and the plasma gun and its connections at 7 to 9 ft. An opening with a 0.785 ft² area is provided at the bottom of the swinging door for flow of ventilation air. The upper 3-ft sections above the sliding doors have fixed aluminum panels. A fixed aluminum panel forms the back wall of the room against the plaster wall.

A design for a sample collection probe was prepared by Mr. Modestino.

We have finalized the detailed design of the flange connection between the bottom part of the cooling chamber and the probe and are doing the same for the connection between the top of the cooling chamber and the plasma gun. The bottom part will consist of a steel flange welded to the cooling chamber, a matching steel flange which will rest on a 1/2" aluminum plate support mounted inside our fragmentation containment chamber, a removable brass flange for sample collection and a smaller brass flange for supporting the probe (Figure 2). The removable brass flange will contain two open channels inside: one for water-cooling and another for pulling vacuum to divert the effluent gas from the reactor through two layers of sintered bronze filters which form the top cover of the vacuum chamber. Solid products that do not go into the probe will be deposited on these filters. The channel will be aspirated

with a mechanical vane vacuum pump. The small probe flange is readily available but the removable brass flange needs to be fabricated and the steel flange needs to be counterbored to match the removable brass flange.

We considered purchasing a fluidized bed powder feeder from METCO, a plasma gun system manufacturer based in Westbury, NY. We are particularly interested in a relatively new (one year on the market) model powder feeder, the 9MP, which has a microprocessor-based weight loss metering unit integrated with the fluidized bed system to provide continuous closed-loop monitoring and control of powder feed rates. Bay State Abrasives, Inc., in Westborough, MA sells fluidized bed powder feeders but without the weight loss metering system. We consider this feature an important advantage in making reliable determinations of material balances for our experiments. In June, Dr. Peters and Mr. Diaz visited a user of METCO powder feeders, Jet-Com Inc., in Wilmington, MA. Though this company has only the precursor to the 9MP, we considered a visit worthwhile to find out about Jet-Com's experience with METCO powder feeders. We then arranged for a demonstration and test run of the 9MP with METCO. On June 30, Mr. Diaz visited the METCO office in Westbury, NY. We supplied METCO with MgO powder (from Aldrich) in the particle size range of $>10\ \mu$ to <325 mesh ($44\ \mu$). The test run was set up to feed MgO powder to a container, not to a plasma gun. The demonstration revealed erratic feed rates, which were traced to packing of the powder. The powder would aggregate and the flow to the pick-up shaft of the feeder would slow down. At some point, the packed powder would collapse from the built-up pressure and the feed rates would increase momentarily, resulting in sudden spurts of powder. This problem is apparently not due to the type of powder feeder but rather to the nature of the powder. Even mechanical feeders would be expected to have the same performance if the powder packs upstream the pick-up point. METCO personnel pointed out that moisture (MgO and CaO are moisture-sensitive) and/or particle size and geometry could be playing a role. We agreed for them to try drying the powder first and performing another test run. Should there be no improvement, we will send them another type of powder, probably $>44\ \mu$ in size, for further testing.

One potential problem in using most fluidized bed feeders with our AVCO plasma gun is the maximum pressure at which the powder can be delivered. Our AVCO plasma gun does not have any provisions for a separate powder injection. We had originally intended to tee-in a connection to the gas inlet so that the powder comes in with the plasma gas. The plasma gas is delivered to the gun at about 30-40 psig. But the METCO feeder has a maximum delivery pressure of only 5 psig. The Bay State Abrasives feeder has a 7 psig delivery pressure. Clearly, we will not be able to feed the powder into the same inlet as the plasma gas. We are considering putting in a separate powder inlet in our plasma gun, sufficiently close to the arc zone that the required delivery pressure is only a few (i.e. ≤ 5) psig but far enough upstream of the arc zone so that gas-solid mixing occurs prior to gas ionization.

We intend to keep our feeder selection options open until we are satisfied that our performance criteria can be met.

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

We performed preliminary thermodynamic calculations using the Chemkin program for the Ca-C-H-O and Mg-C-H-O systems. Figures 3 and 4 show the equilibrium diagrams for the two systems at 1 atm pressure in the 1500-3500 K temperature range with 1:3 Ca:CH₄ and 2:5 Mg:CH₄ ratios, respectively. These are the stoichiometric ratios corresponding to the following reactions:

These plots give the predicted equilibrium mole fractions of major species containing these elements, including products of Reactions (1) and (2). Interestingly, when converted to percentage molar conversion of CaO to CaC₂, these preliminary calculations reveal a CaO molar conversion of 71% at 2900 K, which corresponds very well with the 70 ± 15% observed experimentally by Kim [1,2] using an arc discharge reactor. The molar conversion of MgO to Mg₂C₃ is calculated to be 50% at 2100 K.

We also conducted a scoping run with CaO in an electrical screen heater reactor under reduced methane pressure. One of the goals of the Task 2 work is to see if high conversions of CH₄ to CaC₂ and Mg₂C₃ can be achieved by thermal reactions with CaO and MgO, respectively. Prior work in our laboratory (H. Saito *et al.*, unpublished c. 1992) suggests that CH₄-CaO contacting in high temperature electrical screen heater test runs may have been inadequate so that CH₄ pyrolysis was dominant, with soot as a major product. Experiments at reduced total pressure elevate the mean free path of CH₄ and, while reducing the number of CH₄-CH₄ collisions per unit time, may increase the likelihood of CH₄-CaO collisions. With a thin layer of CaO powder sandwiched between two tungsten strips, methane was introduced into the reactor chamber. The pressure was brought down to as low as 0.29 mm Hg before firing the reactor to about 1900 K. The solids remaining on the tungsten strips after firing were placed in a bottle with a septum port and hydrolyzed. Samples of the gas evolved were analyzed in a gas chromatograph with a flame ionization detector. The analysis did not reveal any appreciable quantity of acetylene. This could be attributed to the very small quantity of methane at the very low pressure, coupled with inadequate contacting of whatever methane was present with the CaO powder. The CaO powder was exposed to the methane only through three punched holes on the top tungsten strip. In succeeding experiments, we will try to improve the CH₄-CaO contacting.

4. Future Plans

For the next reporting period, we will focus on the completion of our experimental apparatus for Task 1. Under Task 2, we will look into ways of improving the contacting between methane and CaO and/or MgO both in the electrical screen heater set-up and possibly in another type of set-up. For example: (1) forced contacting of a jet of CH₄ at low temperature with a solid CaO surface at high temperature; and (2) bubbling CH₄ gas through molten CaO are of interest.

5. Acknowledgements

We appreciate the professional hospitality of Jet-Com Inc., of Wilmington, MA and of METCO, of Westbury, NY.

6. References

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2. Kim, C.S., Baddour, R.F., Howard, J.B., Meissner, H.P., "CaC₂ Production from CaO and Coal or Hydrocarbons in a Rotating-Arc Reactor", Ind. Eng. Chem. Process Des. Dev. 18, 323-328, (1979).

FIGURE 1
LAYOUT OF EXPERIMENTAL SET UP

* VACUUM PUMP, POWDER FEEDER
& MASS SPEC NOT SHOWN

Figure 2. Cooling Chamber Assembly

Figure 3.

Figure 4.

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