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

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Quarterly Technical Status Report for the Period January 1-March 31, 1993
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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.

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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, H₂ and CO

We are building a laboratory-scale electric arc discharge reactor, in which to assess the technical feasibility of producing Mg₂C₃, H₂ 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 Mg₂C₃ and/or CaC₂, H₂ 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 CH₄ and on results of thermodynamic and thermochemical kinetics calculations.

Task 2: Mechanistic Foundations For Converting Light Hydrocarbon Gases to Metal Carbides, H₂ 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 CaC₂, Mg₂C₃, H₂ 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 (Oct 1 - Dec 31, 1992)

As of the end of the last reporting period, we had decided to revitalize an old AVCO plasma gun system at the Department of Chemical Engineering. This was after consultations with a number of commercial plasma gun vendors indicated that the manufacturers would not guarantee stable operation of their gun with methane. We had initially planned on purchasing

a commercial plasma gun system, rather than devoting significant efforts to the design, construction, and systematic testing of a "home-made" unit, which would provide the equivalent of Kim's arc generator assembly. We expected significant time savings in procuring a turn-key unit complete with vendor's guarantee. Without this guarantee, however, there did not seem to be any distinct advantage in purchasing a commercial unit. Reviving our old plasma gun system presented the option which would enable us to attain our experimental needs at the least cost.

We came up with a preliminary design basis for our experimental apparatus, covering a wider range of parameter values than what Kim had examined. We considered various issues in the design and operation of our reactor in the light of this basis. In addition to the plasma gun system which consisted of a power supply unit, a control console, a high frequency oscillator and a plasma gun, there is need for a powder feeder and a product quenching and collection system, which would consist of a movable, cooled cylindrical sampling probe mounted in a separate post-plasma cooling chamber. We had intended to initially proceed with a 7-in. ID, 18-in. long chamber made of carbon steel.

We have chosen a location for our reactor, which is in the Fuels Research Laboratory on the First Floor of the Chemical Engineering Building. Our decision for this choice was influenced mainly by (a) the presence of appropriate electrical utility connections for the power supply unit, the absence of which would entail significant costs to the project, and (b) the availability of a high ceiling that addresses the concern of heat dissipation from the power supply.

Finally, we conducted literature reviews, particularly, on analytical methods for identification and quantification of samples to be collected in our experiments.

2.2 Re-evaluation of Design Basis

We had planned to design our experimental apparatus for a maximum methane gas flowrate of 8 cfm (200 liters per min). Kim had used up to 2 cfm (48 liters per min) and had a maximum power of 27 kW. In our attempt to cover a wider range of conditions in our experiments, and with our power supply rated at up to 83 kW, we estimated a maximum flowrate of 8 cfm of methane at maximum power input. This would then entail a hydrogen emission rate of 16 cfm (the carbide synthesis reactions forming 2 moles of hydrogen per mole of methane). The Industrial Hygiene Office at MIT has recommended dilution to 25% of the Lower Explosive Limit (LEL) of any flammable gases to be vented. For hydrogen, the LEL is 4%, so our effluents would have to be diluted to 1%. This would mean that a total exhaust rate of 1600 cfm would be required for safe emission. We explored various options for venting this amount of exhaust gases. Among them was to use a PVC exhaust duct that runs through the chase in the Chemical Engineering Building. This would be turn out to be very costly because the MIT Safety Office would require corrosion-proof sprinklers to be installed every 15 vertical feet inside the PVC duct. The most feasible option is to vent the

gases through one of two ceramic-lined steel chimneys of the Fuels Research Lab, in the vicinity of the proposed location of our reactor. We intend to use the second chimney, Chimney B, since access to it is available by the removal of a flange. We first had to have diverted to the first chimney, Chimney A, other effluents exhausting into Chimney B so that we would have a dedicated chimney for our experiments. Flowrate measurements taken at Chimney B indicated that it can handle only up to 1250 cfm. This rate is limited by a combination of an ejector system and a fan, one of which is at its maximum capacity and would require costly modifications to increase its capacity. We anticipate slightly higher flowrates would be possible by removing a weather cap at the top of the stack but not sufficiently higher to accommodate 1600 cfm. Thus, we had to compromise by lowering our maximum methane gas flowrate to 6 cfm for a hydrogen production rate of 12 cfm. We do not consider this a major drawback as there might be other bottlenecks in our system. For example, we do not yet know if the power supply can go up to the full 83 kW rating.

2.3 Revitalization of AVCO Plasma Gun System

We have been successful in revitalizing the thirty-year-old AVCO plasma gun system at the Department of Chemical Engineering in February. We were able to perform a system check-out and test-firing of the gun with Argon as the plasma-forming gas last February 18. 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. These include a plasma gun, an AIRCO power supply unit, rated by the manufacturer at up to 83 kW, a high frequency oscillator, a control console for the plasma gun and a remote control console for the power supply unit.

2.4 Investigation of Experimental Equipment Construction

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 need a post-plasma cooling chamber, powder feeder, sample collection system and vacuum pump. The vacuum pump would be used as a booster to exhaust the reactor effluent gases to a ventilation stack. In addition, safety considerations require that we build a fragmentation containment chamber in which to house our reactor.

Before we proceeded with the original plan of having a cooling chamber fabricated, we located three cylindrical sections of steel pipes with flanges welded onto them used as reactors in previous experiments in the Department, which may be of use to us as a post-plasma cooling chamber. Kim had used a 24-in. long cooling chamber with an inside diameter of 7 in. We have a 20-in. long section and two other sections that are about two inches shorter, all of which are 6-in. ID, complete with cooling coils, making them potentially useful in our experiments. These sections, though, are not equipped with optical access ports. However, since there are three of them, we can set up our experiment with one and, should the need for optical access arise in the future, experiments can still be conducted while one of

the two spares are re-machined. We anticipate significant time savings with this development

Our sample collection probe is currently being designed by Mr. Anthony Modestino. The spare probe in the lab, also designed by Mr. Modestino and which we had also planned on using, had to be installed in another reactor, whose probe burned out due to a cooling water system failure. The sample probe being designed will be adapted more closely to the specific needs of our experiment.

We have also contacted various manufacturers of powder feeding devices. We will be evaluating both screw-type and fluidized-bed feeders in terms of their accuracy, uniformity of powder delivery, turndown ratio and cost.

We intended to purchase a vacuum pump that will be used as a booster to exhaust reactor effluent gases to a ventilation stack. We were, however, able to locate an old pump in the Department that is rated at up to 17.7 cfm. We tested the pump, flushed it and changed its oil, and found it to be in working order. Its capacity may be on the low end, as pumps with a rating at up to 4 to 6 times the volume to be handled are normally used; otherwise, the relatively large volume of gases going through the pump causes oil carry-over. We will still try using it initially until such a time that it becomes a bottleneck to smooth operations.

The fragmentation containment chamber for our reactor will require ventilation. The required rate, however, will be significantly less than 1200 cfm. Since the reactor effluent and the room will be vented together into Chimney B, the air flow through the room will actually have to be increased in order to dilute the 12 cfm of hydrogen to 1200 cfm. Thus, the size of the room is not that critical. Our major consideration in sizing the room is accessibility to the equipment it will house, i.e. the plasma gun, cooling chamber and sample collection system. The most difficult equipment to access is the sample collection probe which will be held in place by two o-rings for vertical alignment and has to be pulled down from the cooling chamber. We consider 3 ft to be sufficient for the purpose of pulling down this probe. One need not enter the room physically to gain access so the room does not have to be big enough for a person to enter it. Furthermore, only one side is needed to gain access to the equipment. Although we had proposed to build a 3 ft by 3 ft by 8 ft fragmentation containment chamber from 1/8" aluminum sheets, we thought it better to go with half the size, 1.5 ft by 3 ft by 8 ft, to economize on laboratory space. A 3 ft sliding door would be installed as opposed to a swinging door to eliminate the need for optical realignment (in case we decide to employ optical diagnostics) every time the door is opened. We also need to put a 0.785 sq. ft. hole at the bottom of the room through which ventilation air will be drawn. We have firmed up the design and layout of our room and have begun its construction.

The power supply unit has two large cooling fans that blow air horizontally. With limited space in the lab, the power supply is inconveniently located in close proximity to the control console. To address potential air flow interference problems for the operator, a duct for diverting the exhaust of the power supply unit's cooling fans upwards has been installed.

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

We have given very preliminary consideration to options for a category of apparatus for carrying out a purely "thermal" reaction, among them, a low-pressure thermal reaction chamber and shock tube. Preliminary calculations indicate that a pressure as low as 5 μ may be needed to increase the mean free path of methane sufficiently to make the methane reactions with CaO and MgO proceed preferentially over competing pyrolysis reactions.

The use of chemical tracers, i.e. introducing a chemical reaction of known kinetics through the plasma, has been brought up in a meeting with members of the Faculty of the Chemical Engineering Department, as part of Mr. Diaz's doctoral thesis requirements. We intend to look into this more closely in our mechanistic studies.

Finally, we have searched the literature for thermodynamic data on the reactants and products of the reactions we are investigating. We found that data for CaC_2 and Mg_2C_3 are not commonly reported in literature. We were, however, able to locate data from different sources but consistency among these data needs to be ascertained. For our thermodynamic calculations, we are considering using a software package such as Aspen PlusTM, which has a built-in combustion database based on JANAF tables, and supplementing it with data on CaC_2 and Mg_2C_3 .

4. Future Plans

By the end of the next reporting period, we expect to have a working experimental apparatus for Task 1 and to have performed thermodynamic calculations under Task 2.

5. References

1. Kim, C.S., "Formation of CaC_2 from CaO and 'Nascent' Carbon Species in a Rotating-Arc Reactor", Sc.D. Thesis, Dept. of Chemical Engineering, MIT, Cambridge, MA (1977).
2. Kim, C.S., Baddour, R.F., Howard, J.B., Meissner, H.P., " CaC_2 Production from CaO and Coal or Hydrocarbons in a Rotating-Arc Reactor", Ind. Eng. Chem. Process Des. Dev. 18, 323-328, (1979).

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