DOE/PC/92111--T4

DEC 29 1993

Report No. FE-MIT-92111-4

# 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, 1993
DOE/PETC-MIT Contract No. DE-AC22-92PC92111

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## DISCLAIMER



Submitted to the United States Department of Energy
Pittsburgh Energy Technology Center
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Date Submitted: November 1993

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**Abstract**

The construction of the thermal plasma reactor is nearing completion. During the reporting period, work has concentrated on the design and construction of the plasma reactor and on procurement of related accessories for process monitoring and safety. With the plasma gun system mounted in the cooling chamber assembly inside the fragmentation containment room and with the cooling water system in place, a test-firing of the arc discharge with Argon was conducted in late September. This test, unfortunately, resulted in burn-out of some parts of the plasma gun apparently due to arcing outside of the inter-electrode region, setting back the projected date for completing apparatus construction. Options for a powder feeder investigated include scale-up of a home-made fluidized bed syringe feeder, used at MIT for delivering coal to a drop-tube furnace, and the employment of a mechanical wheel-type feeder sold by Miller Thermal, Inc., of Appleton, WI, which gave a promising demonstration run at MIT. The idea of using an Argon plasma as a heat source in carrying out mechanistic studies was also considered. Thus, the plasma reactor, once completed, might be useful for this purpose as well. Future plans are to rebuild the plasma gun, to assemble a sample collection system, and to continue installing safety and process monitoring equipment. The goals for the next period are to test-fire the gun successfully with Argon, to complete and test the sample collection system with an operating inert gas plasma, and then to perform a scoping run with methane and MgO/CaO powders delivered to the plasma.

## 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 (April 1 - June 30, 1993)

As of the end of the previous reporting period, we completed the construction of our fragmentation containment room in which our reactor and cooling chamber assembly would be housed. Mr. Modestino prepared the design for a water-cooled and gas-quenched sample collection probe. We finalized the design of the flange connection between the bottom section of the cooling chamber and the sample collection probe. The bottom part would consist of a steel flange 1A welded to the cooling chamber, a matching steel flange 1B which would rest on a 1/2" thick aluminum plate support 1C mounted inside the fragmentation containment room, a removable brass flange 1D for sample collection and a smaller brass flange 1E for supporting the probe 1F (see Figure 1). The removable brass flange was designed to contain two open inner channels: a top channel 1D-1 for pulling vacuum to divert the effluent gas from the reactor through two layers of sintered bronze filters 1G which form the top cover of the vacuum chamber and a bottom channel 1D-2 for water-cooling. Solid products that do not go into the probe would be deposited on these filters for later recovery and analysis. The channel would be aspirated with a mechanical vane vacuum pump. We were also working on the design of the flange connection between the top of the cooling chamber and the plasma gun. Finally, we were in the process of evaluating a commercial fluidized bed powder feeder made by METCO, a plasma gun system manufacturer based in Westbury, NY. Initial demonstration tests with MgO powder in the 10 to 44 μm range on METCO's powder feeder resulted in undesirable pulsating feeding.

### 1.2 Experimental Equipment Construction

In July, the major focus of our work was the fabrication of various parts of our plasma reactor set-up. Machining work on the bottom steel flange 1B and the aluminum plate 1C (Figure 1) had been completed. The design of the top steel flange was finalized (see Figure 2); it would have a water-cooling channel 2A and a counterbored hole to accept a round aluminum piece 2B to which the plasma gun is mounted by means of a threaded connection 2C. An O-ring seal 2D would be provided between the aluminum piece and the steel flange. We installed the bottom steel flange 1B and the aluminum plate 1C inside the fragmentation containment room and mounted the cooling chamber on the plate (Figure 1). All the parts of the sample collection probe had been fabricated; these parts still need to be brazed together. Some internal parts of the plasma gun were also fabricated. An anode nozzle 2E was machined out of graphite and a replacement insulation shield 2F made of alumina was fabricated with provision for a separate powder injection inlet (Figure 2).

The duct work from the top of the room to the exhaust chimney was completed. An air flow measurement, conducted by the MIT Safety Office at the bottom of the room with a hot wire anemometer, initially gave a low reading due to blockage of the upward flow by the aluminum mounting plate 1C (Figure 1) for the post-plasma chamber. We corrected this problem by boring large holes on the sides of the aluminum plate. Previous air flow measurement at the chimney was 1200 cfm. At the top of the room, the reading was 1000 cfm. Currently, the flow is about 800 cfm at the bottom. By further sealing our room, we expect to have an air flow of 1000 cfm at the bottom, which would be acceptable to the MIT Safety Office.

Commercial powder feeders we investigated are designed to operate at gas inlet pressures no more than a few psi above atmospheric. To meet this constraint while being able to accommodate the highest feed gas delivery rates desired in our experimental test matrix, we have provided for a separate powder injection inlet in our plasma gun. With this modification, we measured a pressure at the injection point of near-atmospheric with full gas delivery pressure (without firing the gun). We are thus confident that delivery pressure limitations of powder feeders would not present a problem. METCO performed two further test runs to assess the suitability of its powder feeder to the powder we would like to deliver to the plasma reactor. To see if the uneven feeding previously observed with MgO powder (>10 to <44 µm) was due to moisture, the same powder was dried prior to feeding. The same pulsating feeding pattern was observed. Next, we sent them larger size powder with narrower particle size ranges: a cut in the size range of 44 to 75 µm and a second cut in the 75 to 106 µm range. Only the latter cut (>75 to >106 µm) was fed satisfactorily. Because of the interest in studying small particle sizes especially under Task 2 (Mechanistic Foundations), we investigated other powder feeder options. As an alternative, we can try to scale up a home-made fluidized bed syringe feeder. For many years, this fluidized bed device has been used successfully at MIT to feed powdered coal to a drop tube furnace, but at mass delivery rates lower than those of current interest.

We also looked into other powder feeder manufacturers. On August 9, a representative from Miller Thermal, Inc., of Uxbridge, MA, a thermal spray gun manufacturer with headquarters in Appleton, WI, brought a demonstration powder feeder to our laboratory. This unit was equipped with a scale base for loss-in-weight measurement. Miller manufactures mechanical wheel-type powder feeders. Slots in a rotating wheel at the base of a powder canister fill with powder. When a slot lines up with an exit port, the powder is forced out of the slot into the port and is transported by a carrier gas through a powder hose to the plasma gun. The powder feed rate is predominantly a function of the wheel speed. We conducted a test run with MgO powder in the particle size range of >10 to <44 µm, the same powder which the fluidized bed powder feeder of METCO failed to deliver consistently. The Miller unit was able to feed the powder at rates down to as low as 5 g/min with minimal pulsation. Because the unit seemed promising, the Miller representative made an offer, which we are likely to accept, to loan the unit to us for a limited time when we are ready to run our experiments to allow us to further assess its suitability for our particular experimental needs.

When machining of the top and bottom flanges was completed, we ran into problems sealing the water cooling channels in the top steel flange 1H and bottom brass flange 1D (Figure 1) of our plasma reactor assembly and had to spend some time making the flanges leak-tight. We were, however, able to correct these problems during the period. Provisions were also made for fitting sintered bronze filters 1G onto the brass flange 1D.

A ceramic disk 2G (Macor®, a machinable high alumina ceramic insulation) relieved with a central orifice, was installed in the center opening in the top steel flange (Figure 2). This piece is needed to provide a well thermally insulated cylindrical channel 2H for confining the plasma jet. For the same reason, a smaller Macor® disk 2I was also cemented in the center hole in the round aluminum piece that holds the plasma gun onto the steel flange. With the cooling chamber set up on the aluminum plate inside the fragmentation containment room, the top steel flange installed and the plasma gun mounted, we proceeded to work on plumbing to provide interlock-protected flows of cooling water to remove heat from the plasma gun, cooling chamber, top steel flange, bottom brass flange and sample collection probe. It is important to be able to obtain a reliable heat balance for our plasma experiments, especially if routine measurements of plasma temperature prove too expensive or well-beyond the technical scope of our program. Thus, substantial care had to be given to the design, layout, and implementation of this plumbing system, e.g. to making provision for reliable measurements of inlet and outlet water flow rates and temperatures. Major water lines for this system were installed and completed during the period. Flowrate measurements were made on each line at appropriate overall water delivery rates to allow sizing of water flow switches to be used in a cooling water safety interlock system. Thermocouples were installed in the various outlet lines for temperature monitoring. The gas line from the control console was also laid out and completed.

With the cooling water system in place, the plasma gun was test-fired with Argon on September 23. The bottom flange was omitted since the probe was not yet ready and no sampling was to be done. This test, unfortunately, resulted in burn-out of some parts of the plasma gun. Arcing in certain sections of the gun other than the inter-electrode region seemed to have occurred. The arcing phenomenon was very localized, however, and affected only the insulator and the gas inlet. Fortunately, the major parts of the plasma gun were not damaged. In particular, both the water-cooled cathode assembly 2J and the water-cooled anode nozzle 2E (Figure 2) remained intact, even though there was evidence of arcing to an abnormal location on the cathode (i.e. not the thermionic emitter tip 2K). The damage was primarily to the insulator body, made mainly of nylon 2L and phenolic laminate 2M, and to a metallic gas inlet line 2N.

We have two hypotheses for the cause of the accident based on the location of indications of arcing. First, there is visual evidence that arcing occurred between the cathode assembly and the parallel gas inlet line (see Figure 2), resulting in melting of virtually the entire gas inlet line 2N (made of a brass fitting and stainless steel tubing) inside the plasma gun and the surrounding nylon 2L and phenolic laminate insulation 2M. When we tested the gun in February of this year with a temporary setup, we had insulated the gas line from ground by using a section of polyethylene tubing. We used metal tubing this time in compliance with safety regulations that all gas lines have to be made of metal. If arcing did indeed occur in this manner, then the insulation between the gas line and the cathode was insufficient. We will correct this situation by (1) redesigning the nylon insulator body so that the gas line does not enter the gun parallel to the cathode; instead, it will come in perpendicular to the cathode at the side (see Figure 2); and (2) insulating the gas line from ground with a short section of plastic tubing and nylon fittings. The second hypothesis is that arcing occurred between an exposed section of the cathode and water-cooled lines leading to the anode, as suggested by large carbonaceous deposits on one of the anode water lines. The cathode cooling water lines are insulated but the inlet to the cathode assembly is quite difficult to access, leaving a small uninsulated section (see Figure 2). This hypothesis seems less plausible because the distance between the exposed section of the cathode and the anode line is several orders of magnitude greater than the inter-electrode gap (design gap of 3/64"). However, to eliminate this as a possible arcing pathway, both the anode and the cathode lines will be completely insulated with plastic tubing.

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

There was little activity under Task 2 in this quarter, as we concentrated our efforts on the construction of our thermal plasma reactor. The idea of using an Argon plasma as a heat source in carrying out mechanistic studies was brought up in a meeting with some faculty members of the Chemical Engineering Department during Mr. Diaz's doctoral thesis proposal presentation. The thermal plasma reactor can be utilized in experiments where the plasma arc is used to generate high-temperature (2000 to 3000 K) argon flows for rapid contacting with initially cool $CH_4$-CaO mixtures. This will allow preselection of residence time and temperature at ~ 1 atm pressure, enable easier kinetics interpretation and generate greater product quantities for off-line characterization. Along these lines, we will explore the possibility of using our plasma reactor in Task 1 for mechanistic studies.

## 3. Other Accomplishments

In August, Mr. Diaz successfully presented his doctoral thesis proposal before members of his thesis committee, which includes faculty members of the Chemical Engineering Department. On September 27, Dr. Peters delivered a technical presentation on this project in the Gas-To-Liquids Session of the U.S. DOE Coal Liquefaction and Gas Conversion Contractors' Review Conference held in Pittsburgh, PA. We also submitted a paper (Diaz *et al.*, 1993) for inclusion in the Proceedings of this meeting. Furthermore, on September 21, the second U.S. patent (Peters and Howard, 1993) related to this work was issued, complementing the earlier patent of Peters and Howard (1990).

## 4. Future Plans

For the next period, we will focus on rebuilding our plasma gun, on assembling the sample collection system, and on installing improved safety (flow switches, alarm system, combustible gas monitors) and process monitoring (mass-flow controller, digital voltmeter and ammeter) accessories. We hope to be able to test-fire the gun successfully with Argon, to test our sample collection system with an operating inert gas plasma, and then, to perform a scoping run with methane and MgO/CaO delivered to the plasma.

## 5. Acknowledgements

We appreciate the professional hospitality of METCO, of Westbury, NY and of Miller Thermal, Inc., of Uxbridge, MA.

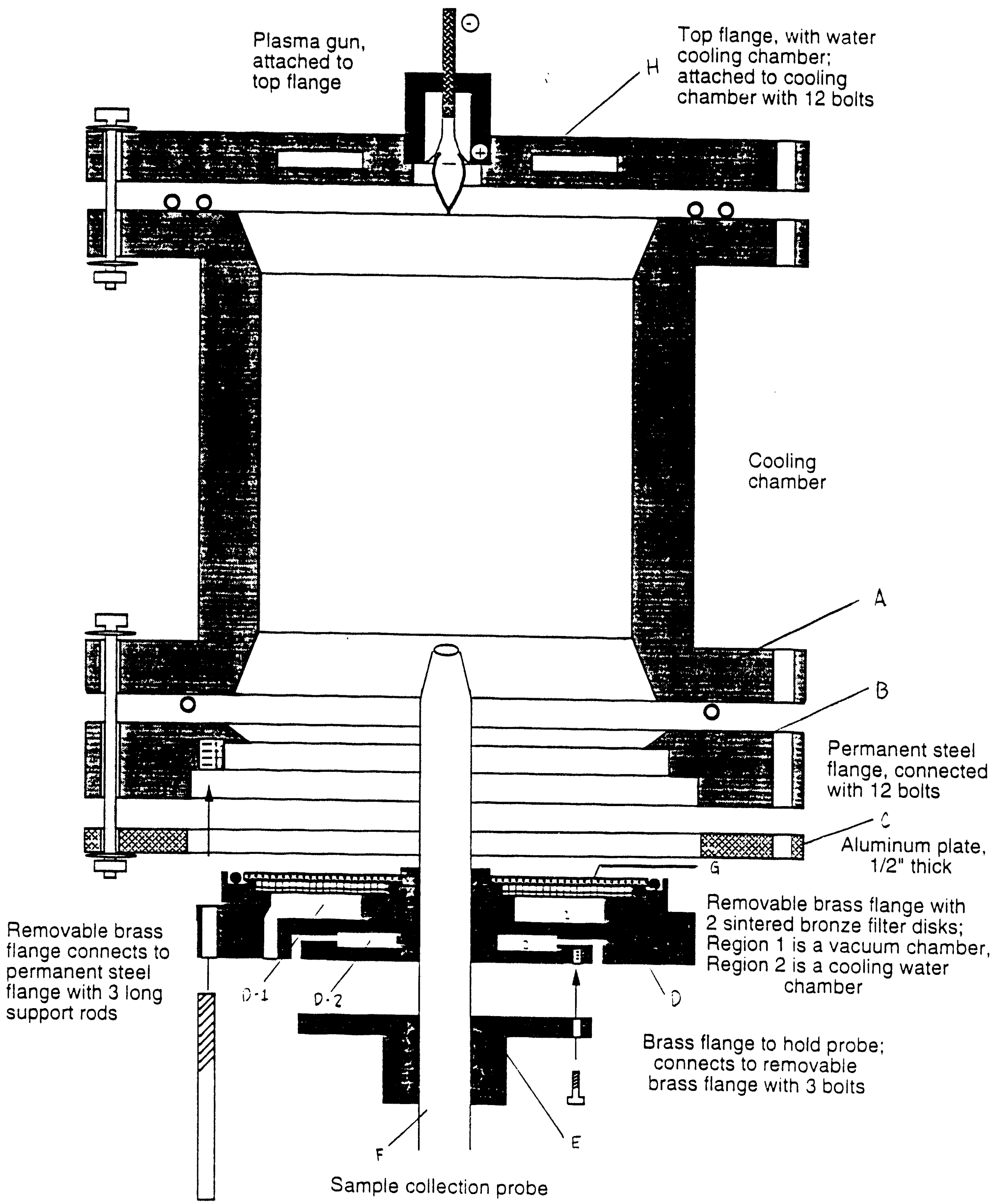
## 6. References

1. Diaz, A.F., A.J. Modestino, M.K. Chung, J.B. Howard, J.W. Tester, and W.A. Peters, "Conversion of Light Hydrocarbon Gases to Metal Carbides for Production of Liquid Fuels and Chemicals", *Proceedings of the US DOE Coal Liquefaction and Gas Conversion Contractors' Review Conference*, September 27-29, 1993. In press (c. 1994).

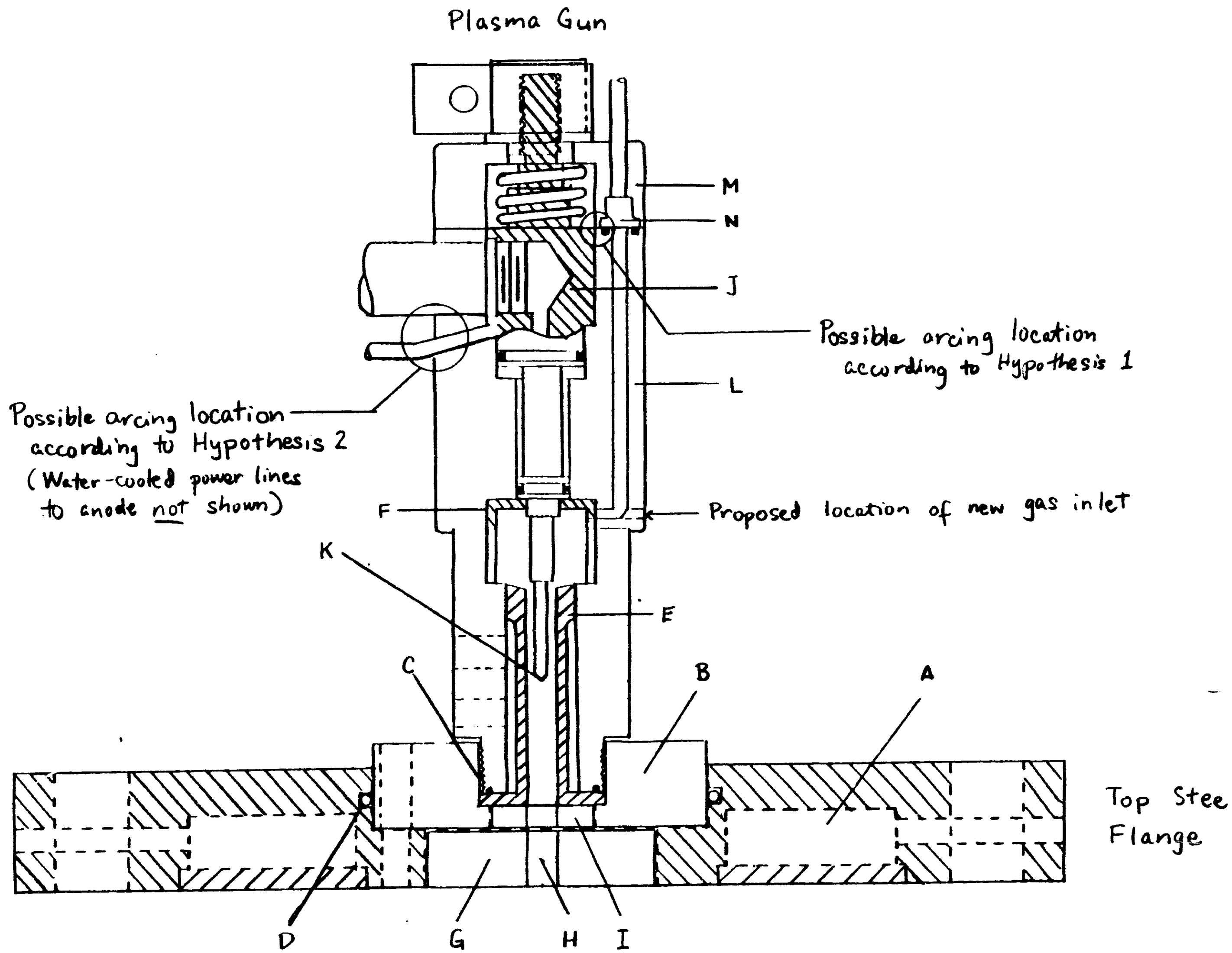
2. Peters, W.A. and J.B. Howard, "Method for Methane Conversion", 15 Claims. United States Patent No. 4,921,685, May 1 (1990); Assigned to the Massachusetts Institute of Technology.

3. Peters, W.A. and J.B. Howard, "Method for Methane Conversion", 10 Claims. United States Patent No. 5,246,550, September 21 (1993); Assigned to the Massachusetts Institute of Technology.

# Figure 1. Plasma Reactor Assembly



# Figure 2. Schematic Representation of Plasma Gun Internals and Mounting Connections



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