

Hydrogen Recovery by Methane Decomposition in a Microwave Plasma Reactor

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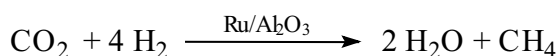
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ABSTRACT

In the Sabatier reactor, oxygen is recovered (as water) by hydrogenation of carbon dioxide. Half of the reacted hydrogen is contained within the product water, the other half forms methane (CH₄). To close the hydrogen loop, we are investigating methods for the efficient recovery of hydrogen from CH₄. This paper describes microwave plasma-based methods for the thermal decomposition (cracking) of methane to produce hydrogen, elemental carbon, and related carbonaceous substances. Two primary reactor configurations have been employed in this work: 1) a quartz tube vertically oriented within a section of rectangular waveguide, and 2) waveguide transmission through a quartz window into a cylindrical vacuum chamber based multimode cavity. Hydrogen recoveries of up to 98% have been obtained. Three primary mechanisms of methane decomposition have been identified: methane pyrolysis, methane oligomerization, and methane aromatization. In the multimode plasma chamber methane pyrolysis experiments, we have observed the formation of a highly dendritic form of elemental carbon which may be beneficial in the minimization of potential problems associated with carbon deposition. Alternatively, by optimization of the reactor to promote volatile oligomerization products, carbon formation is minimized.

INTRODUCTION

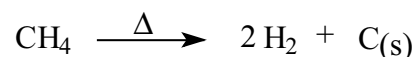
The Sabatier reaction has been studied extensively for the recovery of oxygen (as water) from carbon dioxide and is currently under advanced development for employment aboard manned spacecraft¹⁻¹³,



In the Sabatier reaction, half of the hydrogen is lost as methane. Currently, this methane is a waste product

because no equivalent amount of oxidant is produced, hence methane cannot be used as a fuel unless additional oxygen is provided. Another problem with methane is that in certain environments, such as the surface of Mars, venting may not be allowed due to planetary protection restrictions. Closure of the hydrogen loop, by recovery of the hydrogen which otherwise would be lost as methane, will significantly reduce the requirements for the resupply of hydrogen and will enhance the self-sustaining quality of Exploration Life Support (ELS) systems^{14,15}.

The use of microwave power has been investigated in various Life Support subsystem applications¹⁶⁻²⁴. Here, to achieve closure of the hydrogen loop, we are investigating the thermal decomposition of CH₄ to produce hydrogen via microwave plasma based methods. The classical methane pyrolysis reaction occurs via the thermally induced dissociation of methane to produce hydrogen gas and elemental carbon.



The solid elemental carbon product has proven very problematical with respect to the traditional catalytic methods employed to promote this reaction^{25,26}. Catalyst fouling (resulting in drastic losses in catalytic activity and hydrogen production efficiency), and bed plugging (resulting in decreased mass transfer efficiency) substantially decrease the duration of hydrogen production runs, and necessitate manpower intensive interventions to reactivate the catalyst, and to remove carbonaceous residues deposited within the reactor and associated piping. Using the microwave plasma based methods, which produce extremely high temperatures in a very small volume of space, the need for a catalyst is eliminated, as are the potential problems associated with catalyst fouling and plugging within fixed catalyst beds. To date, we have examined hydrogen production using two distinct plasma reactor configurations.

reaction tube vertically inserted through the center of a rectangular waveguide microwave transmission system, and 2) a vacuum chamber based multimode cavity.

WAVEGUIDE MOUNTED QUARTZ TUBE PLASMA REACTOR

A photograph of the basic waveguide mounted plasma reactor system is shown in Figure 1. The quartz tube is mounted vertically through the center of a section of rectangular waveguide. Feed gases enter the reactor from the bottom and exit from the top. A spark plug based plasma ignition system is mounted at the top of the reactor. The microwave plasma is confined to that section of the quartz tube which is confined within the waveguide. Microwave power is generated using a 0-2 kW variable microwave power source from Richardson

trigger the initial plasma. Influent gases are precisely metered using mass flow controllers. Gas phase reaction byproducts are sampled downstream and quantified by gas chromatography. Solid phase reaction products are separated by a down stream in-line filter element.

A variety of experiments were performed under varying conditions of inlet gas composition, system pressure, mass flow rate, and microwave power level. The microwave plasma system was initially operated using a pure argon feed stream. Once stable operation of the argon plasma was attained, methane-argon mixtures were fed to the system with progressively increasing methane concentrations, beginning with 10% CH₄ and culminating in a 100% CH₄ feed stream. With 100 W of microwave power, 98% conversion of an influent stream

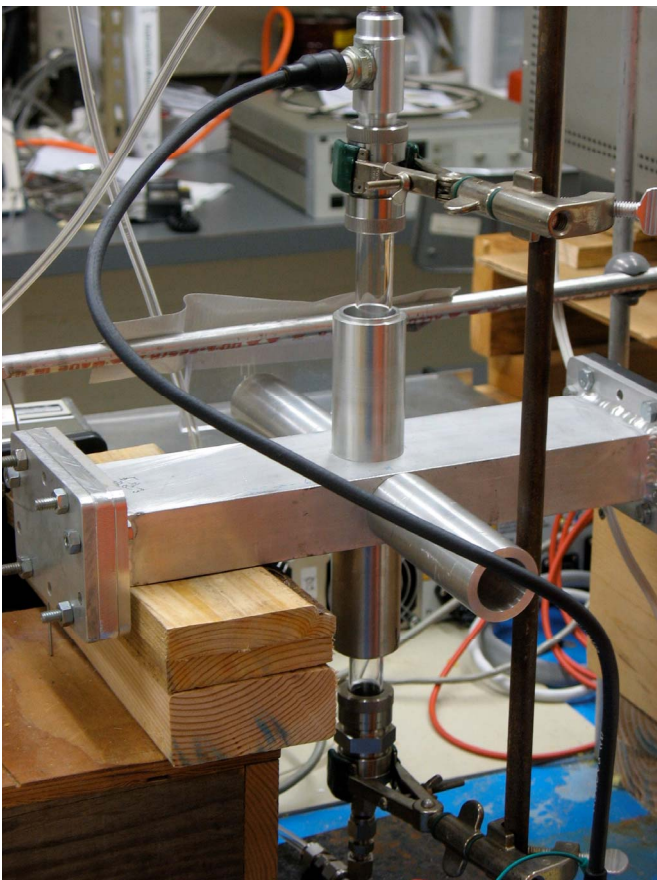


Figure 1. Photograph of Waveguide Mounted Quartz Tube Plasma Reactor.

Electronics. Any microwave energy which is not absorbed by the plasma is reflected by a shorting plate back toward the plasma. A viewing port is oriented horizontally through the waveguide section to facilitate visual inspection of the plasma formed within. A vacuum pump is used to maintain system pressure. At low pressure, the plasma ignites spontaneously under applied microwave power. At somewhat higher pressures the spark plug based gas igniter is used to

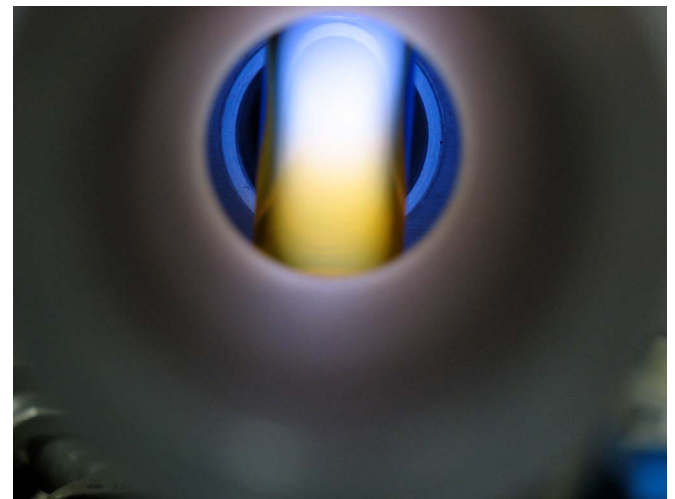
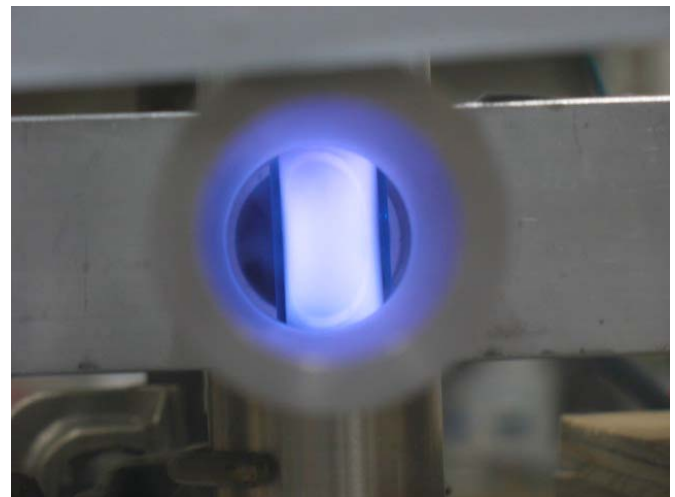


Figure 2. Photographs of Methane Plasma Taken Through Horizontal Viewport.
Top: Methane Plasma at 20 W, 50 cm³/min, 11 Torr.
Bottom: Discoloration of Quartz Tube due to Deposition of Carbonaceous Materials.

of pure CH_4 to hydrogen was achieved at a flow rate of $50 \text{ cm}^3/\text{min}$ (STP). At 200 W of incident power, this high level of H_2 production was sustained for flows up to $200 \text{ cm}^3/\text{min}$. However, deposition of carbonaceous material on the surface of the quartz reactor tube proved problematic with respect to the maintenance of high conversions over sustained periods of operation. The top photograph in Figure 2 illustrates a typical pure methane plasma as seen through the horizontal viewport. Here the system was operated at 20 W of microwave power, a methane flow of $50 \text{ cm}^3/\text{min}$, and a system pressure of 11 Torr. In the bottom photograph, a brownish discoloration is evident on the lower third (inlet side) of the quartz tube after a period of sustained operation. As shown in Figure 3, given sufficient power and exposure time, a significant build-up of

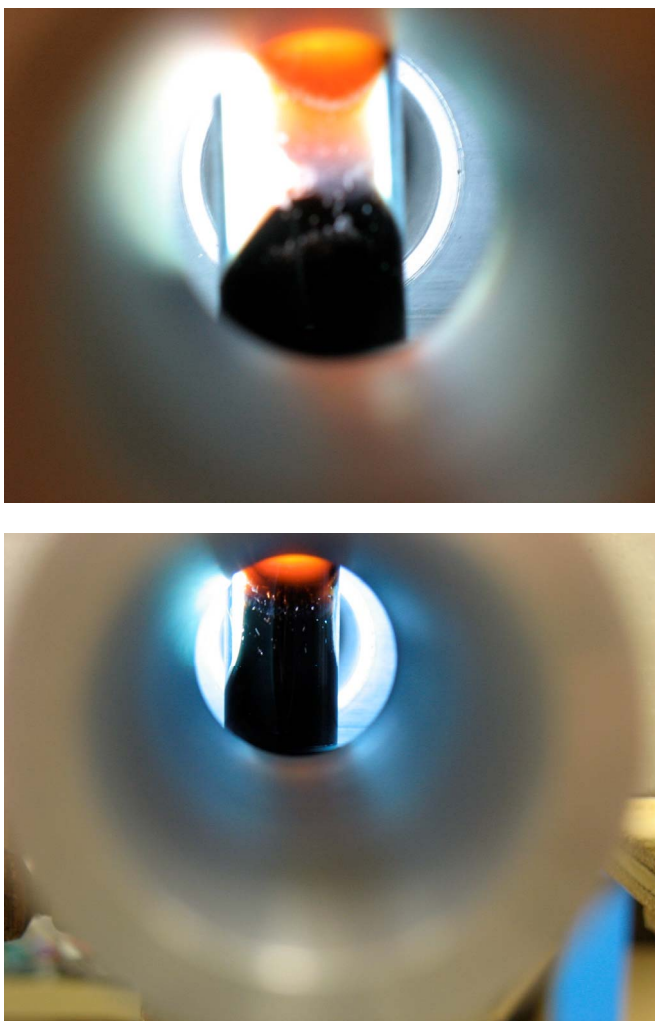


Figure 3. Carbon Deposition in Plasma Reactor.
Top: 100 W, $50 \text{ cm}^3/\text{min}$, after 20 Minutes;
Bottom: after 30 Minutes of H_2 Production.

carbonaceous materials occurs on the quartz reactor walls. Heterogeneous carbonaceous materials couple strongly with microwaves over a wide temperature range, leading to localized heating and softening of the quartz

tube²⁷⁻²⁹. These observations led us to consider alternative plasma reactor configurations.

CYLINDRICAL MULTIMODE CAVITY PLASMA REACTOR

The multimode cavity based plasma reactor was assembled via modification of a conventional cylindrical vacuum chamber. Two photographs of the system are presented in Figure 4. Microwaves enter the chamber via a quartz window which mates with the rectangular waveguide based microwave power generation and transmission system. Relative to Figure 4, feed gases enter the reactor from the right, and reaction byproducts

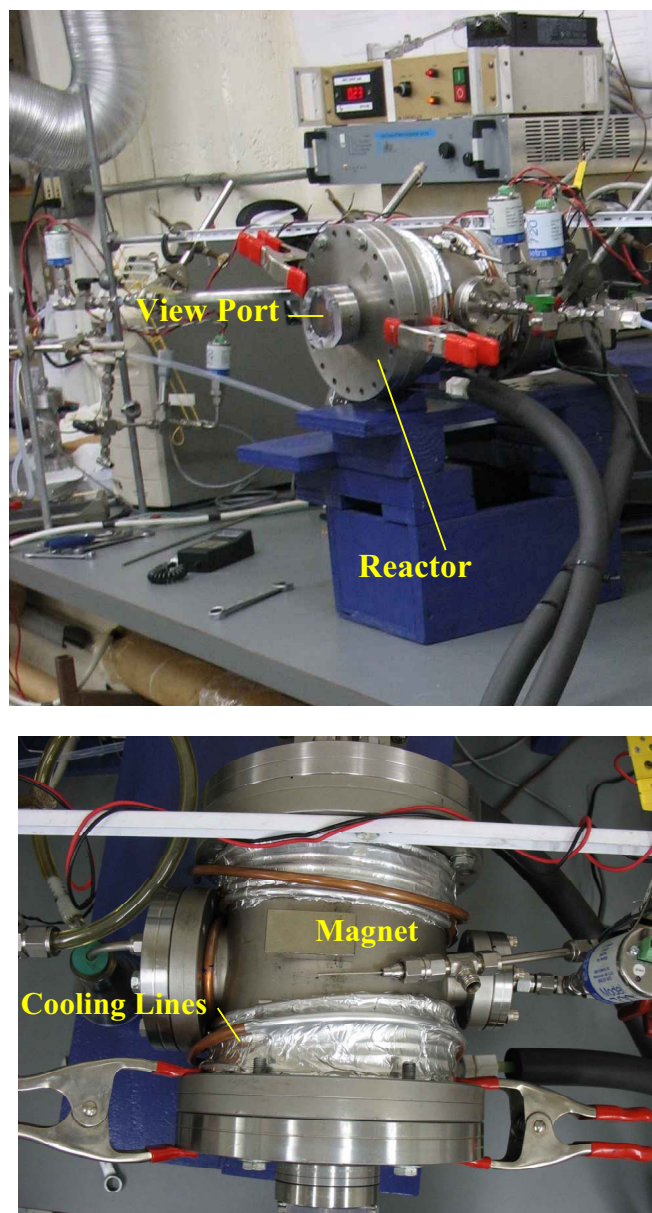


Figure 4. Multimode Cavity Microwave Plasma Reactor.

leave the reactor to the left. As with the previous configuration, a viewport was installed to allow observation of the plasma.