**METHANE PYROLYSIS AND DISPOSING OFF RESULTING CARBON.** P. K. Sharma[1], D. Rapp[2], and N. K. Rahotgi[3], [1]Mail Stop 183-401, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena CA 91109, USA (pramod.k.sharma@jpl.nasa.gov), [2]Mail Stop 157-205, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena CA 91109, USA (drapp@jpl.nasa.gov), [3]Mail Stop 125-224, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena CA 91109, USA (naresh.k.rohatgi@jpl.nasa.gov).

Introduction: Sabatier/Electrolysis (S/E) is a leading process for producing methane and oxygen for application to Mars ISPP. One significant problem with this process is that it produces an excess of methane for combustion with the amount of oxygen that is produced. Therefore, one must discard roughly half of the methane to obtain the proper stoichiometric methane/oxygen mixture for ascent from Mars. This is wasteful of hydrogen, which must be brought from Earth and is difficult to transport to Mars and store on Mars.

To reduce the problem of transporting hydrogen to Mars, the S/E process can be augmented by another process which reduces overall hydrogen requirement. Three conceptual approaches for doing this are (i) recover hydrogen from the excess methane produced by the S/E process, (ii) convert the methane to a higher hydrocarbon or other organic with a lower H/C ratio than methane, and (iii) use a separate process (such as zirconia or reverse water gas shift reaction) to produce additional oxygen, thus utilizing all the methane produced by the Sabatier process. We report our results here on recovering hydrogen from the excess methane using pyrolysis of methane. Pyrolysis has the advantage that it produces almost pure hydrogen, and any unreacted methane can pass through the S/E process reactor. It has the disadvantage that disposing of the carbon produced by pyrolysis presents difficulties.

Hydrogen may be obtained from methane by pyrolysis in the temperature range $1000°-1200°C$. The main reaction products are hydrogen and carbon, though very small amounts of higher hydrocarbons, including aromatic hydrocarbons are formed. The conversion efficiency is about 95% at $1200°C$. One needs to distinguish between thermodynamic equilibrium conversion and conversion limited by kinetics in a finite reactor.

The main reaction is

$$CH_4(g) \longrightarrow C(s) + 2H_2 \quad H = 74.9 \text{ kJ/mole} \quad [1]$$
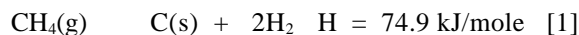
The solid carbon formed in the above reaction can be burned off with carbon dioxide at elevated temperatures (with an associated energy penalty) according to

$$C(s) + CO_2 \longrightarrow 2CO \quad H = 172.6 \text{ kJ/mole} \quad [2]$$

The energy requirement for reation [1] is moderate. Therefore, if a process can be devised where the carbon formed by pyrolysis is physically removed or stored without the burnoff reaction [2], pyrolysis could be a strong contender to augment the S/E process. If, however, the burnoff reaction is required, the energetics are less favorable. Nevertheless, despite the less favorable energetics, it is useful to know whether process (2) can be made viable.

The goals of a research program on recovery of hydrogen from methane are (in descending priority order):

1. Study the kinetics of pyrolysis to arrive at a pyrolysis reactor design that produces high yields in a confined volume at the lowest possible operating temperature.

2. Study the kinetics of carbon burnoff to determine whether high yields can be obtained in a confined volume at acceptable operating temperatures.

3. Investigate catalytic techniques for depositing carbon as a fine soot which can be physically separated from the reactor.

In the JPL program, we have made significant measurements in regard to goal 1, cursory measurements in regard to goal 2, and would plan to pursue goal 3 if additional resources are secured.

Measurements and Results: *Pyrolysis.* A tubular quartz reactor was used to study pyrolysis in the temperature range $1000°-1200°C$. The reactor was coupled to a mass spectrometer sampling system for analysis of gaseous products. The reactor could be opened up after one or several pyrolysis runs and total carbon deposited could be obtained. This experimental set up allowed the monitoring of both the solid carbon product as well as the reaction gas products.

The reactor was a 1.5" ID by 2-ft. long quartz tube which had a 6" long preheater zone and an 8" long quartz wool packed main reaction zone. A quartz wool trap was used to catch the small amounts of room temperature condensables formed and the reaction gas products were routed to the mass spectrometer sampling system. The pyrolysis was carried out in a series of 5 runs at flow rates of 50 to 200 ml/min of methane. For each run, a nearly constant temperature for the reaction zone was attempted. The gas phase product composition was monitored at 15 minute intervals. Thus, a near continuous monitoring of the reaction gas products was obtained for each run. At the end of the five pyrolysis runs, the reactor was opened and the quartz wool with deposited carbon was removed and weighed. Carbon deposited from the cumulative reaction in the five runs was obtained and compared with the theoretical value deduced from the product gas analysis and flow rate. The agreement was within 15%, and the error was expected due to certain simplifying assumptions made in the analysis. These results clearly show

Methane Pyrolysis: P.K. Sharma, D. Rapp and N.K. Rohatgi

that one can achieve >95% conversion of methane to hydrogen at 1200°C in a moderately sized reactor at appropriate flow rates. Further experiments are planned to refine the trade relationship between temperature and conversion at various flow rates.

Carbon burn off. To be able to test the burnoff of carbon from the pyrolysis reaction, the quartz wool with the deposited carbon was packed back into the reactor. The reactor was set up again and pure carbon dioxide was made to flow through it. The main reaction zone was maintained in the temperature range 1130° to 1150°C, though a part of the reaction zone cooled off to 850°C due to an electrical problem in the furnace. The flow rate of carbon dioxide was 200 ml/min. The reaction gas products (CO plus unreacted CO_2) were analyzed by the mass spectrometer at 15 min intervals. The regeneration run was continued for a total of 24 hrs. At the end of the run, the reactor was opened and examined visually. The quartz wool was taken out and weighed to determine the carbon that did not burn off. A major part of the quartz wool that was packed in the reaction zone that was at 1130°–1140°C was relatively close to the original color of the quartz wool, but the part of the zone that was at 850°C was quite black and did not appear to be well regenerated. The mass of the unburned carbon was compared to its predicted value based on the product gas analysis. The agreement was again within 15% error which can be explained due to some carbon lost in manual operations, as well as certain approximations that had to be made in making the calculations. In a limited set of runs, the reactor bed temperature was varied in the range 1000° to 1200°C and reaction product gas composition was determined. The kinetic rate constant can be obtained from this set of runs and used to carry out modeling in order to design and optimize a reactor which can achieve a high carbon burnoff with a high CO_2 utilization.

In order to examine the surface morphology on the quartz fibers before and after carbon burn off, small samples of quartz wool after pyrolysis (with deposited carbon) and after burn off with CO_2 were examined with Scanning Electron Microscopy (SEM). The SEM photographs illustrate that during pyrolysis, carbon builds up around the quartz fiber, apparently in a porous form. Subsequent reaction with carbon dioxide gradually removes the carbon deposit. In order to have a viable process, it may not be essential to remove the entire carbon deposit as long as the unreacted carbon does not continue to build up.

The work completed so far indicates that most of the carbon produced in pyrolysis can be burned off with CO_2 at a temperature of 1150°C. However, the energy penalty associated with the carbon burn off is substantial, and another problem is that excess CO_2 may have to go out the stack, requiring a larger compressor.

Pyrolysis without carbon burnoff.   To make the process of hydrogen recovery from methane energy effi-

cient, a process that mechanically removes the carbon (and does not need to burn it off) will be considerably more attractive.

Some recent advances in methane cracking over a Ni/silica catalyst have shown that carbon can be produced in filament form which create light hollow structures. This type of carbon can be elutriated out of the reactor bed and separated using a cyclone. In a scheme based on this concept, carbon burnoff is not essential and considerable energy could be saved, but questions of catalyst regeneration still have to be answered.

Summary: The JPL methane research program is one year old. At its completion, we will have measured the kinetics of pyrolysis and carbon burnoff. If future resources become available, we would like to pursue pyrolysis concepts that allow physical removal of the carbon, so that the energy intensive step (reaction [2]) can be avoided.

Detail of carbon wrapping on silica fiber
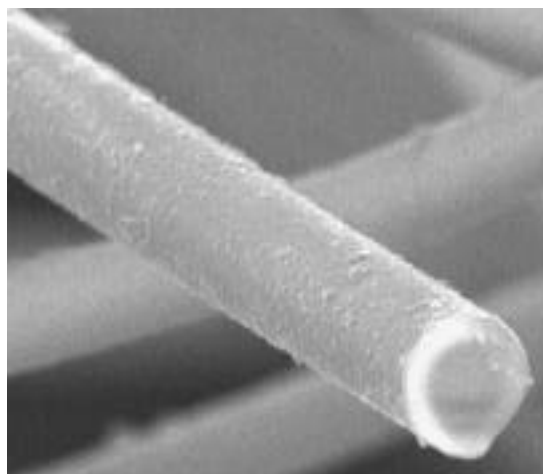
Silica fibers after carbon burnoff