2002 NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

JOHN F. KENNEDY SPACE CENTER
UNIVERSITY OF CENTRAL FLORIDA

AN INVESTIGATION OF THE REVERSE WATER GAS SHIFT PROCESS AND OPERATING ALTERNATIVES

Dr. Jonathan E. Whitlow
Associate Professor
Department of Chemical Engineering
Florida Institute of Technology
NASA COLLEAGUE: Clyde Parrish

ABSTRACT

The Reverse Water Gas Shift (RWGS) process can produce water and ultimately oxygen through electrolysis. This technology is being investigated for possible use in the exploration of Mars as well as a potential process to aid in the regeneration of oxygen from carbon dioxide. The initial part of this report summarizes the results obtained from operation of the RWGS process at Kennedy Space Center during May and June of this year. It has been demonstrated that close to complete conversion can be achieved with the RWGS process under certain operating conditions. The report also presents results obtained through simulation for an alternative staged configuration for RWGS which eliminates the recycle compressor. This configuration looks promising and hence seems worthy of experimental investigation.

1. INTRODUCTION

The human exploration of Mars will require the utilization of resources present in the Martian environment in order to minimize the payload mass imported from Earth. Reverse Water Gas Shift (RWGS), which reacts carbon dioxide and hydrogen to form water and carbon monoxide, when coupled with water electrolysis is a candidate technology for oxygen production on Mars. The use of the RWGS process for In-Situ Resource Utilization, (ISRU) was originally studied by Pioneer Astronautics, who determined the RWGS process to be a viable candidate for oxygen production. [1-2]

An RWGS system has been operated at Kennedy Space Center (KSC) on an intermittent basis over the past 15 months. Although the operating time has been limited, several conclusions on the RWGS operation have been made and problem areas identified as discussed in this report. An overview of the process components for RWGS is given below followed by a discussion of the results obtained from operation of the system. This report also includes a description of an alterative RWGS configuration, which is being presented in this report for the first time. An evaluation of this new configuration is also included along with a discussion of the modeling equations used to simulate the system.

2. AN OVERVIEW OF THE EXISTING REVERSE WATER GAS SHIFT PROCESS

RWGS uses carbon dioxide and hydrogen as reactants to produce oxygen and carbon monoxide with a copper on alumina catalyst. Prior to operating the RWGS system the copper catalyst, which s produced from copper oxide reduction, must be conditioned to insure no oxygen is present in the system. Operating temperatures for processes on Mars are constrained and in general designs are not being considered which exceed 500 Celsius. At such temperatures, the RWGS reaction equilibrium is limited and does not favor the production of water. Thus in order to improve the overall conversion a separation step is required to allow the non reacted hydrogen and n dioxide to be recycled. This is achieved by passing the exit gases to a condenser to remove most of the water and then to a hollow fiber polymeric membrane, which preferentially permeates hydrogen and carbon dioxide. From the membrane, the reactants can be recycled while the byproduct carbon monoxide can be vented. The water produced is stored in a vessel and used as feed to an electrolysis unit, which produces oxygen as product and hydrogen, which can also be recycled to the reaction process. A simple RWGS process flow schematic is presented in Figure 1 below.

As stated above the RWGS process has been operated on an intermittent basis over the last 15 months. One of the largest problems in performing an analysis of the process has been associated with the composition analysis using the gas chromatograph (GC). The GC used for the process also is used in other laboratory projects and hence scheduling conflicts exist. In addition, the column has required frequent recalibration and in some cases changes in the methods used to perform the analysis (eg retention time and temperature ramp slope). As a result many days the system has been operated in which a lack of composition data exists.

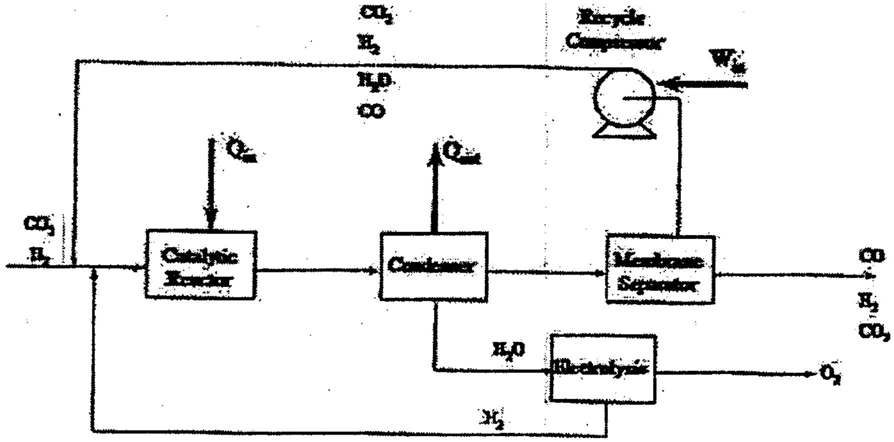

Figure 1 Current RWGS Process Flow Diagram

A summary of the operational data which has included an analysis of the discharge from the process is shown below in Tables 1 and 2. Table 1 is a summary of single pass operations while Table 2 gives the results from operating with the use of a recycle compressor. Both tables include data taken from the first few weeks of the summer but also some taken in February of this year. It can be observed from Table 1 that in February the single pass data showed in general an approach to theoretical equilibrium (calculated from equations 1 & 2) of greater than 90%. The data taken in May did not show the same approach to equilibrium and hence additional data is needed. Due to the operational problems associated with the GC as discussed above, it is likely that the May data is invalid. The data in Table 2 shows that under conditions of low feed rate (0.5 slpm H_2 & CO_2) and the recycle valve being 0% closed (ie 100% open) that essentially complete conversion can be achieved. More operating data is needed and will be collected with subsequent operation of the RWGS system over the next several months.

3. STAGED RWGS PROCESS MODELING

In the current RWGS configuration, the recycle compressor is used to push the equilibrium constrained reaction toward completion by recycling the un-reacted H_2 and CO_2 multiple times with the aid of the separation membrane. The compressor is a component in the system which is costly in terms of both mass and energy. In addition, the mechanical nature of the component brings in to question reliability and the need for redundancy for actual flight. If this component could be eliminated without sacrificing the goal of the system which includes conversion of hydrogen with minimal loss in the reject, it would be a substantial process improvement. Figure 2 shows a staged configuration with no recycle stream that has been evaluated with simulation as a part of this work. Each stage of the alternative RWGS Process consists of a series of three components namely a reactor, condenser and membrane. The idea is to take the reaction products and with the condenser remove most of the water and then with the membrane reject the CO thus leaving reactant CO_2 and H_2 permeate to serve as feed to the next reactor stage.

Table 1 Analysis of Single Pass RWGS Operation

Date	H2 Flow slpm	CO2 Flow slpm	Temp Celsius	Pressure psia	Actual CO2 Conversion	Theoretical Conversion	Equilibrium Approach
2/22/2002	0.5	0.5	400	45	20.82	22.71	0.917
2/15/2002	0.5	0.5	400	45	20.30	22.71	0.894
2/22/2002	1.0	1.0	400	45	22.05	22.71	0.971
2/22/2002	3.0	3.0	400	45	19.98	22.71	0.880
2/15/2002	3.0	3.0	400	45	19.54	22.71	0.861
2/20/2002	1.0	2.0	400	45	15.00	15.77	0.951
2/22/2002	2.0	1.0	400	45	30.21	31.55	0.958
2/20/2002	1.0	1.0	350	45	16.94	18.24	0.929
2/20/2002	1.0	1.0	375	45	19.82	20.47	0.968
2/25/2002	1.0	1.0	425	45	23.68	24.91	0.951
2/25/2002	1.0	1.0	450	45	24.71	27.08	0.913
2/26/2002	1.0	1.0	400	19	22.16	22.71	0.976
2/26/2002	1.0	1.0	400	30	22.33	22.71	0.984
5/28/2002	3.0	1.0	400	45	29.03	37.59	0.772
5/29/2002	1.0	1.0	400	45	17.84	22.71	0.786
5/29/2002	2.0	2.0	400	45	16.89	22.71	0.744
5/30/2002	0.5	0.5	400	45	17.272	22.71	0.761
5/30/2002	1.2	1.2	400	45	17.52	22.71	0.772

Table 2 Analysis of RWGS Recycle Operation

Date	H2 Flow slpm	CO2 Flow slpm	Temp Celsius	Pressure psia	CO2 Conversion	Recycle Valve
2/21/2002	1.0	1.0	400	45	52.52	(100% closed)
2/21/2002	1.0	1.0	400	45	63.31	(66% closed)
2/21/2002	1.0	1.0	400	45	95.81	(33% closed)
2/21/2002	1.0	1.0	400	45	99.05	(0% closed)
2/27/2002	0.5	0.5	400	45	66.63	(100% closed)
2/27/2002	0.5	0.5	400	45	99.98	(0% closed)
6/3/2002	1.0	1.0	400	45	45.87	(100% closed)
6/4/2002	1.0	1.0	400	45	98.48	(0% closed)
6/5/2002	0.5	0.5	400	45	99.37	(0% closed)
6/7/2002	0.5	0.5	400	45	99.99	(0% closed)
6/10/2002	1.5	1.5	400	45	82.92	(0% closed)

A brief description of the equations used to model the RWGS system is provided in this section. A more detailed description of the modeling equations and associated theory can be found in the 1999 NASA/ASEE Summer Faculty Program Research Report [3]. While the basic modeling equations are the same as in the 1999 report some modifications to the membrane model have been made and are discussed below.

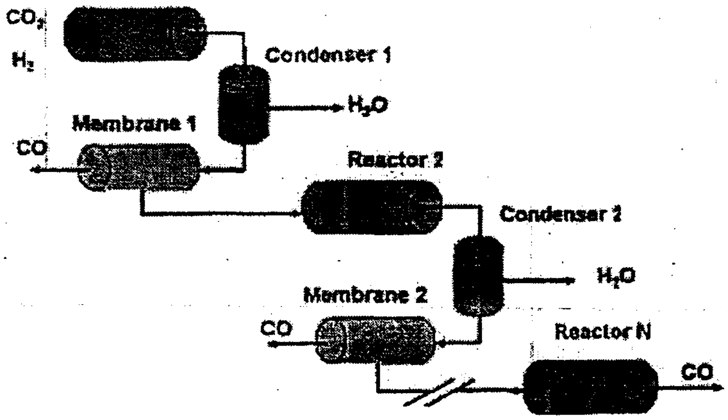

Figure 2 Alternative Staged RWGS Process Flow Diagram

The chemical equilibrium constant K for the reaction is given as a function of temperature by the expression: [4]

$$K = e^{13.148 \frac{5639.5}{T} \; 1.077 \ln T \; 5.44 \times 10^{4} T + 1.125 \times 10^{7} T^{2} + \frac{49170}{T^{2}}} \qquad (1)$$

The equilibrium constant is also written in terms of product and reactant concentrations which subsequently can be expressed in terms of conversion of the limiting reactant hydrogen by the expression:

$$K = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{(\Theta_{CO} + x_{eq})(\Theta_{H_2O} + x_{eq})}{(\Theta_{CO_2} - x_{eq})(1 - x_{eq})} \qquad (2)$$

The values of Θ_{CO}, Θ_{H_2O}, Θ_{CO_2} represent the molar ratios of those components to the limiting reactant hydrogen in the inlet to the reactor. Given a reaction temperature, the value of K can be determined from equation 1 and the equilibrium conversion, x_{eq} determined by solving equation 2. The equilibrium conversion is the maximum conversion, which can be achieved, in a single pass through the reactor. For the simulation models it is assumed that equilibrium is reached for simplicity. The experimental results given in Table 1 have shown the single pass approach to equilibrium to be in the range between 86 and 97 % depending on the total feed flow rate. While it may not be feasible to reach total equilibrium in practice, proper design of the reactor bed should allow the system to come close based on the experimental findings.

The exit gases from the reactor are sent to a condenser where most of the water is removed. For modeling purposes, the compositions of the liquid and vapor streams leaving the condenser are determined by employing Raoult's Law to determine the amount of water in the vapor phase and Henry's Law to determine the solubility and hence concentration of the gasses dissolved in the condensed phase.

The gases leaving the condenser are fed into a hollow fiber polymeric membrane which separates the components of a gas mixture based on a given components permeability to the polymer. The membrane operates in a countercurrent fashion, and is modeled based on a 1998 publication, [5] which depicts the membrane as an N stage process as shown in Figure 3. Here, $L_{,k}$ and $x_{j,k}$ are the total molar flow and mole fraction of component j in the feed/reject leaving stage k, while $V_{,k}$ and $y_{j,k}$ are the total molar flow and mole fraction of j in the permeate leaving stage k. For each stage the mass transferred of a component j on a given stage $m_{j,k}$ is given by the permeability coefficient of that component times the difference in partial pressures in component j across the membrane. For N stages, a system of N nonlinear simultaneous equations is yielded for each component j requiring an iterative solution.

The permeability coefficients in the membrane model for each component (excluding water) were refined based on a set of RWGS operating data from July 18,2001. [6] Although the actual dimensions and data associated with the membrane are unknown and proprietary, the permeability coefficients were forced to fit the data and hence the values used have good predictive capabilities.

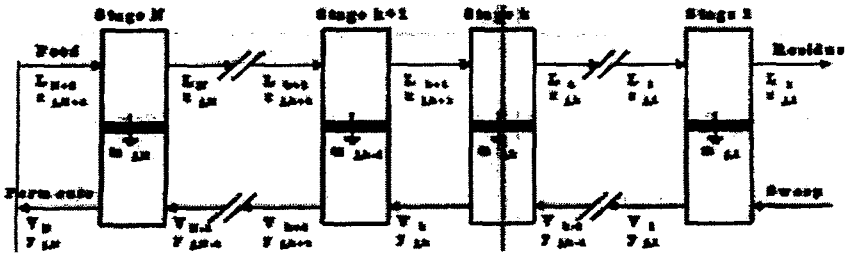

Figure 3 Flow Diagram for an N Stage Counter-Current Membrane

The membrane model has been modified from the model used in previous work to allow the introduction of a sweep stream into the system as shown in Figure 3. In addition the pressure drop across stage k on the permeate side of the membrane has been accounted for by using the Hagen-Poiseuille equation for laminar flow of an incompressible fluid in an impermeable tube:

$$\Delta P_k = \frac{8\mu_{mix} V_k R T \, \Delta z}{\Pi R_i^4 P_{Vk}} \tag{3}$$

Here μ_{mix} is the viscosity of the gas mixture, Δz is the length of the fibers for the given stage, Ri is the inner radius of the fibers, V_k is the permeate flow on stage k, R is the universal gas constant, T is the absolute temperature and P_{Vk} is the permeate pressure on stage k.

4. SIMULATION RESULTS AND DISCUSSION

For a given stage there are many variables which affect the operation and hence the simulation results These variables include reaction temperature, condenser temperature, pressure drop across the membrane, absolute pressure in the membrane, membrane area, CO_2 and H_2 feed rates, CO_2 to H_2 ratio and sweep flow rate. Since each of these can be altered in each subsequent stage the task of finding optimum operating conditions is difficult at best. After multiple simulation runs a base case was determined which gave good results in terms of overall H_2 utilization and conversion as well as met the hypothetical design constraints for the system in terms of limiting operating pressure and number of overall stages. The base case which is presented in Table 3 was used to evaluate the sensitivity of the overall H_2 conversion to the system variables listed above. As can be observed from the base case results an overall H_2 conversion including loss in the membrane reject, equal to 99.5% can be achieved in only 5 stages. An inlet pressure of only 80 psia is needed for a 6 stage configuration to achieve a 99.8% conversion of H_2.

By performing additional simulations and comparing them to the base case the following information was obtained. The overall H_2 conversion increases with increasing reaction temperature as expected however increasing the temperature above the base case value of 400 C gives limited improvement as shown in Figure 4. This is significant in that it may be possible to use a single heating zone and temperature controller for all reactors with appropriate geometrical configuration with limited consequences. Increasing the condenser temperature above 5 C decreases the overall conversion as expected but it is not until values greater than 40 C are used that a substantial drop in conversion is seen leading to the conclusion that a single condensation zone may be employed for all stages with again, a single temperature control point. It also indicates that the condensers may be able to operate at temperatures higher than originally believed thus resulting in energy savings.

The introduction of a CO_2 sweep into the permeate side of the membrane had the greatest positive effect on the simulations in terms of increasing the conversion while both reducing stages and system pressure requirements. It can be seen in Figure 5 that as the flow of sweep increases the overall conversion generally increases, however an optimum is reached near the base flow rate of 3 slpm. Another variable observed to have a significant optimum is the ratio of CO_2 to H_2 in the initial feed as shown in Figure 6.

Table 3 Base Case for Six Stage RWGS Alternative Configuration

	Stage 1	**Stage 2**	**Stage 3**	**Stage 4**	**Stage 5**	**Stage 6**	**Exit**
Reactor Temperature (C)	**400**	**400**	**400**	**400**	**400**	**400**	
Condenser Temperature (C)	**5**	**5**	**5**	**5**	**5**	**5**	
Reactor Pressure (psia)	**80**	**64**	**48**	**32**	**20**	**12**	
Membrane Delta P (psia)	**16**	**16**	**16**	**12**	**8**	**8**	
Permeate Delta P (psia)	**0.15**	**0.21**	**0.36**	**0.70**	**1.31**	**3.28**	
Membrane Area (m^2)	**27**	**27**	**27**	**27**	**27**	**27**	
Permeate CO2 Sweep (slpm)	**3**	**3**	**3**	**3**	**3**	**3**	
H2 Reactor Feed (slpm)	**4**	**2.50**	**1.38**	**0.60**	**0.16**	**0.01**	**0.00**
CO2 Reactor Feed (slpm)	**12.00**	**13.24**	**14.87**	**16.83**	**19.01**	**21.21**	**23.27**
CO Reactor Feed (slpm)	**0.000**	**0.147**	**0.101**	**0.053**	**0.012**	**0.002**	**0.000**
H2 in Reject (slpm)	**0.00006**	**0.00007**	**0.00013**	**0.00358**	**0.00212**	**0.00008**	
CO in Reject (slpm)	**1.35638**	**1.15943**	**0.83380**	**0.47623**	**0.15234**	**0.01543**	
Reactor H2 Conversion	**37.59**	**44.60**	**56.81**	**72.97**	**89.87**	**98.21**	
Overall H2 Conversion	**37.44**	**65.28**	**84.92**	**95.90**	**99.50**	**99.84**	

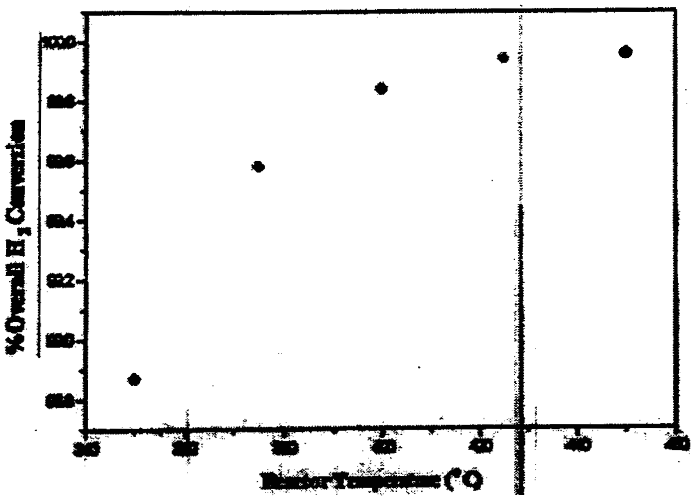

Figure 4 Simulation Results for Overall H_2 Conversion versus Reaction Temperature

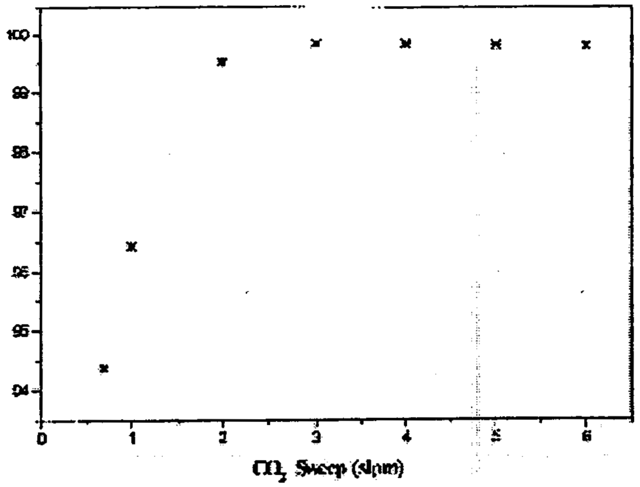

Figure 5 Simulation Results for Overall H_2 Conversion versus CO_2 Sweep

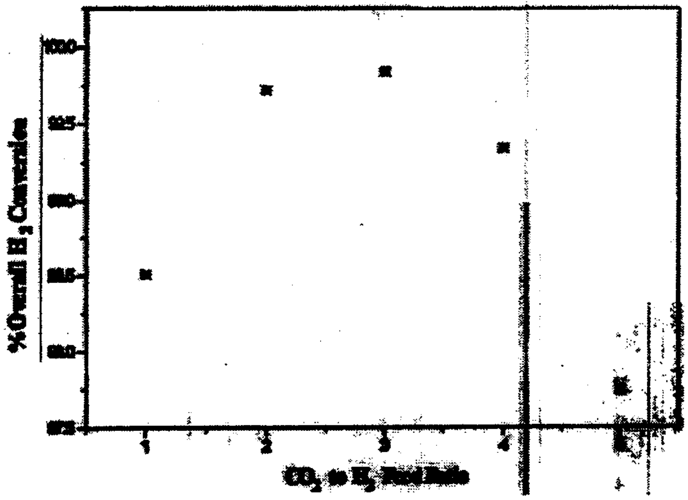

Figure 6 Simulation Results for Overall H_2 Conversion versus Feed Ratios

Although additional figures could not be included due to space limitations, it was also found that an optimum exists in the membrane area used close to the value used in the base case simulations. It was also found that as membrane pressure drop is reduced to a fractional value of 0.8 to 0.9 of the values used for each stage in the base case an optimum is found. If this was done the overall system pressure could be reduced even further.

While the simulation results have shown that using the alternative staged configuration of RWGS has much promise, experimental verification is needed. Hopefully additional funds will be obtained to perform the experimental work and validate the modeling results.

4. REFERENCES

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