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MODELING AND ANALYSIS OF THE REVERSE WATER GAS SHIFT PROCESS FOR IN-SITU PROPELLANT PRODUCTION

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ABSTRACT

This report focuses on the development of mathematical models & simulation tools developed for the Reverse Water Gas Shift (RWGS) process. This process is a candidate technology for oxygen production on Mars under the In-Situ Propellant Production (ISPP) project. An analysis of the RWGS process was performed using a material balance for the system. The material balance is very complex due to the downstream separations and subsequent recycle inherent with the process. A numerical simulation was developed for the RWGS process to provide a tool for analysis and optimization of experimental hardware, which will be constructed later this year at Kennedy Space Center (KSC). Attempts to solve the material balance for the system, which can be defined by 27 nonlinear equations, initially failed. A convergence scheme was developed which led to successful solution of the material balance, however the simplified equations used for the gas separation membrane were found insufficient. Additional more rigorous models were successfully developed and solved for the membrane separation. Sample results from these models are included in this report, with recommendations for experimental work needed for model validation.

ACKNOWLEDGMENT

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. ISPP is a joint effort through various NASA and contractor organizations aimed at producing fuel for Mars sample return missions. The primary candidate for fuel production is the Sabatier/Electrolysis process. Sabatier/Electrolysis produces methane and water from carbon dioxide and hydrogen in a catalytic reactor. The water is split with electrolysis producing oxygen and hydrogen, which is recycled back to the reactor feed. The product ratio of oxygen to methane produced is less than that required for a methane rocket, thus giving the need for an additional process to meet the oxygen requirements. RWGS is a candidate technology for oxygen production on Mars. This report details this process and describes a simulation model developed to aid in the analysis and optimization of experimental RWGS hardware which is to be constructed at KSC later this year. The RWGS design and inherent assumptions are taken from a report prepared by Pioneer Astronautics, who determined the RWGS process to be a viable candidate for ISPP in a SBIR project performed in 1997. [1] The RWGS process flow sheet is presented in Figure 1 below. An analysis of the process and each of its components follows. Details of the solution procedure used to solve the conservation equations for the system and sample results from the simulations performed are also presented.
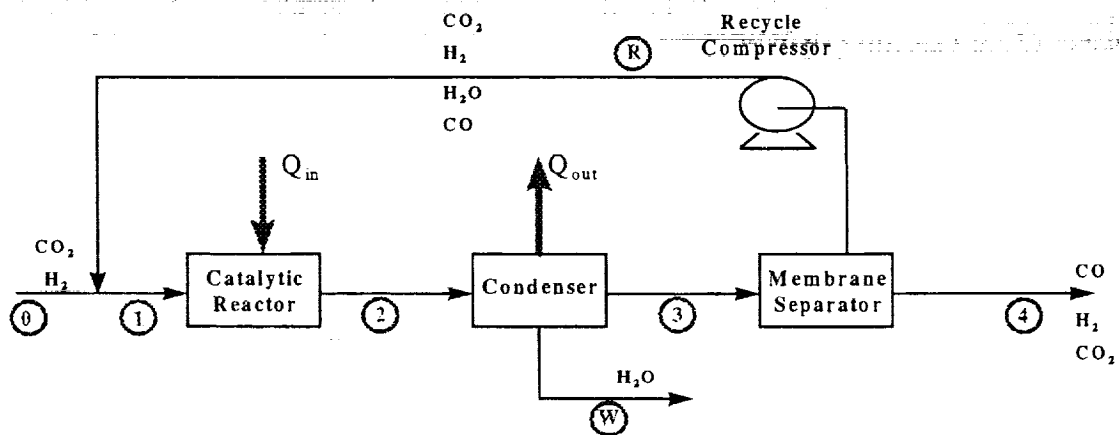

Figure 1 RWGS Process Flow Diagram

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AN OVERVIEW OF THE REVERSE WATER GAS SHIFT PROCESS

The Reactor

RWGS uses carbon dioxide and hydrogen as reactants just as the Sabatier/Electrolysis process, however the desired products are oxygen and carbon monoxide. The selectivity of this reaction over the Sabatier reaction or some other side reaction is an issue in the development of RWGS. Previous work done on the RWGS reaction identified several catalysts with good selectivity. [2] The selection of catalyst can affect the selectivity, rate of reaction and rate of deactivation, however the chemical equilibrium for any reaction is governed by thermodynamics, in particular the Gibbs free energy. The expression relating the chemical equilibrium coefficient to the Gibbs free energy, can be expressed by definition in terms of enthalpy and entropy as:

$$\Delta G = \Delta H - T \Delta S = R T \ln K \tag{1}$$

For the RWGS reaction equation 1 can be employed to obtain a value of the equilibrium constant K as a function of temperature: [3]

$$K = e^{13.148 - \frac{5639.5}{T} - 1.077 \ln T - 5.44 \times 10^4 T + 1.125 \times 10^7 T^2 + \frac{49170}{T^2}} \tag{2}$$

The value of K is thus solely a function of temperature and is related to the concentrations of the products and reactants and in terms of conversion of a limiting reactant by the expressions:

$$K = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{(\Theta_{CO} + x_{eq})(\Theta_{H_2O} + x_{eq})}{(\Theta_{CO_2} - x_{eq})(1 - x_{eq})} \tag{3}$$

The values of Θ_{CO}, Θ_{H2O}, Θ_{CO2} represent the molar ratios of those components to the limiting reactant in the inlet stream to the reactor (assumed to be H_2 in the given case). It should be noted that the limiting reactant is based on the total feed to the reactor, (recycle stream + fresh feed) instead of the fresh feed to the reactor. Given a reaction temperature, the value of K can be determined from equation 2 and the equilibrium conversion determined by solving equation 3, which is a quadratic in x_{eq}. The equilibrium conversion is the maximum conversion, which can be achieved, in a single pass through the reactor.

The Condenser

Upon leaving the reactor, the exit gases are sent to a condenser where most of the water is removed. In determining the compositions of the liquid and vapor streams leaving the condenser, idealities were assumed. Raoult's Law was used to determine the amount of water in the vapor

phase by assuming that the partial pressure of the water was equal to its vapor pressure, which is readily available in the literature. Henry's Law and corresponding Henry's Law constants were used to determine the solubility and hence concentration of the gasses dissolved in the condensed water. A more rigorous calculation could have been performed for the condenser, however it was felt that the effort involved was not justified since it would have required the knowledge of equilibrium ratios which are not readily available, to solve the 10 equations shown in Figure 2.
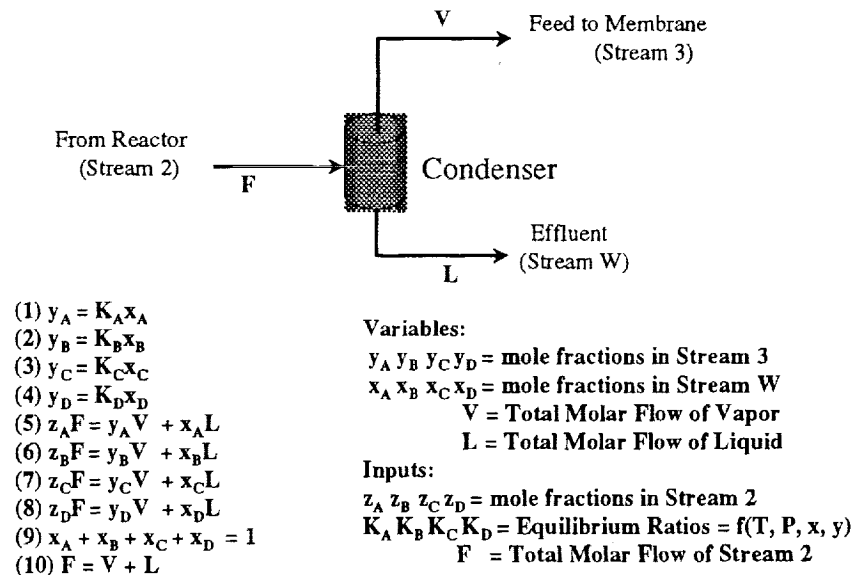

$(1)\ y_A = K_A x_A$

$(2)\ y_B = K_B x_B$

$(3)\ y_C = K_C x_C$

$(4)\ y_D = K_D x_D$

$(5)\ z_A F = y_A V + x_A L$

$(6)\ z_B F = y_B V + x_B L$

$(7)\ z_C F = y_C V + x_C L$

$(8)\ z_D F = y_D V + x_D L$

$(9)\ x_A + x_B + x_C + x_D = 1$

$(10)\ F = V + L$

Variables:

$y_A\ y_B\ y_C y_D$ = mole fractions in Stream 3

$x_A\ x_B\ x_C x_D$ = mole fractions in Stream W

V = Total Molar Flow of Vapor

L = Total Molar Flow of Liquid

Inputs:

$z_A\ z_B\ z_C z_D$ = mole fractions in Stream 2

$K_A\ K_B\ K_C K_D$ = Equilibrium Ratios = f(T, P, x, y)

F = Total Molar Flow of Stream 2

Figure 2 Equations Required for Rigorous Condenser Calculations

Gas Separation Membrane

As shown in Figure 1 the membrane is directly downstream of the condenser. The use of membranes for separation of gases is a relatively new technology. In theory, the gas components can be adsorbed onto the surface of the polymer and providing that there is a concentration gradient across the membrane, they will diffuse to the low pressure or permeate side. At that point the gas desorbs from the membrane into the bulk fluid permeate. The type of membrane specified for this process is composed of hollow fiber polymers. This type of membrane is the most economical on a surface area per cost basis however other membrane types such as spiral wound and plate and frame have superior fouling and pressure drop characteristics. [4]

The polymeric membranes separate the components of a gas mixture based on a given components permeability to the polymer. Permeability for this type of membrane can be defined as the product of a given components solubility and its molecular diffusion coefficient in the polymeric membrane. Fick's law of diffusion is the principle governing this separation technique

as the permeation flux through the membrane is proportional to the concentration gradient across the membrane. Since both solubility and diffusion are temperature dependent, permeability and hence mass transfer across the membrane are likewise temperature dependent.

In developing a model for the polymeric hollow fiber membranes several approaches can be taken. Three distinct models are presented here, namely complete mixing, cross flow and counter-current flow. The simplest model, which is known as complete mixing, assumes the membrane as a single stage in which the feed is split into the permeate and retentate or residue. The mass transfer rate for a given component j across the membrane is given by the equation:

$$m_j = Q_j A (P^*_{L,j} - P^*_{V,j})$$ (4)

Here m_j is the mass transfer of component j across the membrane, Q_j is an effective permeability for component j and $P^*_{L,j}$ and $P^*_{V,j}$ are the partial pressure of j in the feed and permeate respectively. Specifying the feed to the membrane, the transport equations given in equation 4 can be rewritten in terms of mole fractions and solved. The solution requires the simultaneous solution of the overall balance, the component mole balances around the membrane and one of the constraints that the mole fractions in both the residue and permeate equal unity.

This complete mixing model does not account for the fact that the partial pressures on both sides of the membrane change as the entering gas mixture proceeds along the length of the membrane to the exit. In the cross flow model, the membrane is treated as a series of stages in which the gas is transferred from the residue stream into the permeate, and a variation in the residue concentration down the membrane is introduced. This adds complexity to the model in that instead of having a single equation for each component describing the mass transfer across the membrane, N equations must be written for each component. For a given stage k, equation 1 can be redefined in terms of mole fractions for component j as:

$$y_{j,k} = \frac{Q_j (P_{Lk} x_{j,k} - P_{Vk} y_{j,k})}{\sum_{m=1}^{R} Q_m (P_{Lk} x_{m,k} - P_{Vk} y_{m,k})}$$ (5)

Here $P_{L,k}$ and $x_{j,k}$ are the total pressure and mole fraction of j in the feed while $P_{V,k}$ and $y_{j,k}$ are the total pressure and mole fraction of j in the permeate. For this model the composition of gas produced on a stage depends on the upstream compositions, permeances and pressures, however is independent of the composition of the gas produced downstream in other stages. Discussion of solving this model is presented later when the algorithm developed is presented.

The counter-current model depicted in Figure 3 is the most rigorous model and also best describes the true system, which is operated as a counter-current separation membrane. Here as with the cross-flow model, the system is divided into N stages.

Unlike the cross-flow model however the compositions change on both permeate side as well as the residue side. Hence a material balance can be written on any stage k as:

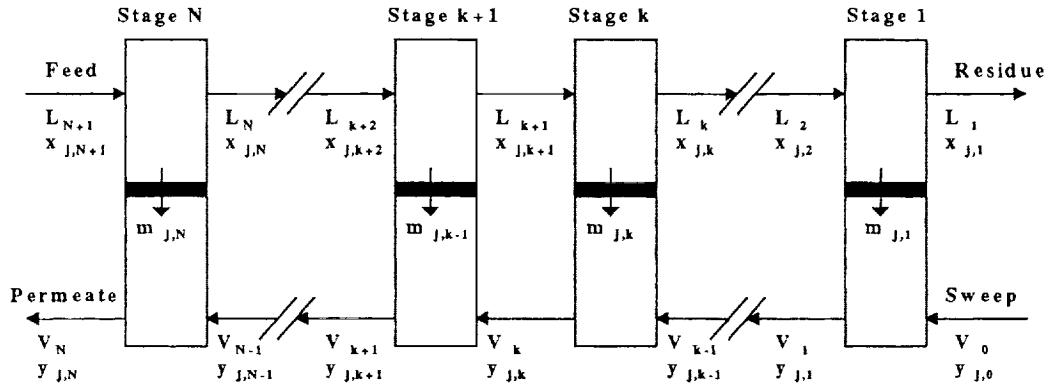$$l_{j,k+1} - l_{j,k} + v_{j,k-1} - v_{j,k} = 0 \qquad (6)$$

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

Here l & v represent the residue & permeate molar flows for component j leaving or entering stage k. The convention for use of the subscripts referring to k in the above equation is based on the stage the component is leaving, hence $l_{j,k}$ is leaving the k+1 stage but it is entering the kth stage. The transport of component j across the membrane on stage k can be denoted as $m_{j,k}$ which is equal to the difference in $l_{j,k+1}$ and $l_{j,k}$. The driving force for the transport is the difference in partial pressures of the component on each side of the membrane as was given in equation 4. If equation 4 is written for a general stage k using mole fractions instead of partial pressures the resulting equation is:

$$m_{j,k} = Q_j \Delta A (P_{Lk} x_{j,k} - P_{Vk} y_{j,k}) \qquad (7)$$

A is the total surface area divided by the number of stages while the other quantities have been previously defined. If the mole fractions on a given stage in equation 7 are redefined as a component flow rate divided by the total flow rate the resulting equation is:

$$m_{j,k} = l_{j,k+1} - l_{j,k} = Q_j \Delta A \left(\frac{P_{Lk} l_{j,k}}{l_k} - \frac{P_{Vk} y_{j,k}}{V_k} \right) \qquad (8)$$

When this expression is rearranged and solved for the component flow rate in the permeate $v_{j,k}$ the expression becomes:

$$v_{j,k} = \frac{-V_k}{P_{Vk}\,Q_j\,\Delta A}\,[l_{j,k+1} - (1 + \frac{Q_j\,\Delta A\,P_{Lk}}{L_k})\,l_{j,k})] \tag{9}$$

Using equation 9 and substituting for $v_{j,k}$ and $v_{j,k-1}$ in equation 6 results in the equation:

$$B_{j,k}\,l_{j,k-1} + C_{j,k}\,l_{j,k} + D_{j,k}\,l_{j,k+1} = 0 \tag{10}$$

where:

$$B_{j,k} = \frac{-V_{k-1}}{P_{Vk-1}\,Q_j\,\Delta A}\,(1 + \frac{Q_j\,\Delta A\,P_{Lk-1}}{L_{k-1}})$$

$$C_{j,k} = 1 + \frac{-V_{k-1}}{P_{Vk-1}\,Q_j\,\Delta A} + \frac{V_k}{P_{Vk}\,Q_j\,\Delta A}\,(1 + \frac{Q_j\,\Delta A\,P_{Lk}}{L_k})$$

$$D_{j,k} = \frac{-V_k}{P_{Vk}\,Q_j\,\Delta A} - 1$$

If equation 10 is applied to each of the N stages, a system of N nonlinear simultaneous equations is yielded for each component j. Written in matrix form results in a tridiagonal coefficient matrix where the values for $C_{j,k}$ are on the main diagonal with the values of $B_{j,k}$ and $D_{j,k}$ occupying the adjacent columns. Since the elements of coefficient matrix, $B_{j,k}$, $C_{j,k}$ and $D_{j,k}$ are functions of the variable, residue molar flow rates, nonlinearity is present in the system. The methods for solution of this model is based on recent literature [5], in which successive approximations for the molar flow rates $l_{j,1}$, to $l_{j,N}$ are used to evaluate, the values of $B_{j,k}$, $C_{j,k}$ and $D_{j,k}$ until the system converges. The initial guesses for the molar flow rates in the residue are based on the solution of the cross flow case.

The RWGS system can be defined by 27 independent material balance equations if the complete mixing model is assumed for the membrane. Initial attempts to solve the system of nonlinear equations, which have not been included for brevity, proved unsuccessful. This resulted in the development of an iterative algorithm in which the recycle stream molar flow rates were used as tear variables. In other words, an initial estimate was made for these variables and then the rest of the system equations were solved in succession until new values of the tear variables were generated. Convergence could then be achieved when the values guessed matched the values calculated. The first attempts at implementing the algorithm, which is presented in Figure 4, involved successive substitution of the calculated values of the recycle stream into the guessed values.

This method diverged and hence required an alternative tearing method. The Wegstein method was employed for this task with success, as it is more stable than successive substitution. [6] The Wegstein method is based on the algorithm:

$$x_{n+1} = \frac{x_{n-1} \, g(x_n) - x_n \, g(x_{n-1})}{x_{n-1} - g(x_{n-1}) - x_2 + g(x_n)}$$
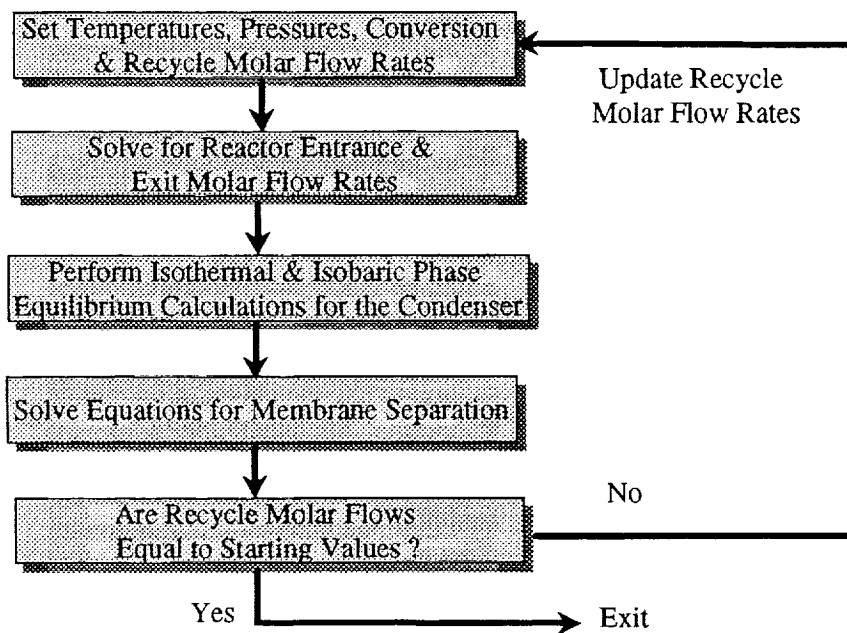
(11)

Figure 4 RWGS Material Balance Solution Algorithm

While the system converged with the aforementioned algorithm, the values of permeability supplied by Pioneer,[11] had to be reduced for all components except carbon monoxide, in order to prevent the mole fractions of those components in the residue, from being less than zero. This ultimately led to the use of the cross flow and counter-current methods previously described, for estimating the material balance around the membrane. The number of stages used in the simulation was 100, which is recommended as a minimum value by the developers of the method.

All programming for the RWGS material balance solution was implemented in MATLAB code. While convergence was obtained using the rigorous calculations, the convergence was very time consuming. In addition, the area of the membrane had to be slightly reduced for convergence. In this case, as with the solution using the complete mixing model, the permeability's used resulted in numerical stability problems. Sample results obtained from the algorithm based on a reactor temperature of 370 °C and a condenser temperature of 2 °C are presented in Figure 5. The convergence for this case required in excess of 300 iterations of the RWGS algorithm and took on the order of 2 hours to complete.

REACTOR CALCULATIONS: (Reactor Temperature = 370 Centigrade)
The Single Pass Equilibrium Conversion is 0.2127
The Molar Flow of H2 in Reactor Feed is 53.6990 gmoles/hr
The Molar Flow of CO2 in Reactor Feed is 23.6718 gmoles/hr
The Molar Flow of CO in Reactor Feed is 5.8846 gmoles/hr
The Molar Flow of H2O in Reactor Feed is 0.1734 gmoles/hr
The Molar Flow of H2 in Reactor Exit is 48.6642 gmoles/hr
The Molar Flow of CO2 in Reactor Exit is 18.6370 gmoles/hr
The Molar Flow of CO in Reactor Exit is 10.9194 gmoles/hr
The Molar Flow of H2O in Reactor Exit is 5.2082 gmoles/hr

CONDENSER CALCULATIONS: (Condenser Temperature = 2 Centigrade)
The Total Molar Feed Flow is 83.428827 gmoles/hr
The Molar Flow of H2 in the Vapor is 48.6640 gmoles/hr
The Molar Flow of CO2 in the Vapor is 18.6324 gmoles/hr
The Molar Flow of CO in the Vapor is 10.9193 gmoles/hr
The Molar Flow of H2O in the Vapor is 0.1734 gmoles/hr
The Total Molar Flow of the Vapor is 78.3891 gmoles/hr
The Molar Flow of H2 in the Liquid is 0.0002 gmoles/hr
The Molar Flow of CO2 in the Liquid is 0.0046 gmoles/hr
The Molar Flow of CO in the Liquid is 0.0001 gmoles/hr
The Molar Flow of H2O in the Liquid is 5.0348 gmoles/hr
The Total Molar Flow of the Liquid is 5.0397 gmoles/hr

MEMBRANE CALCULATIONS: (Total Area Used = 29.98 m^2)
The Molar Flow of H2 in the Permeate is 48.4826 gmoles/hr
The Molar Flow of CO2 in the Permeate is 18.3818 gmoles/hr
The Molar Flow of CO in the Permeate is 5.8844 gmoles/hr
The Molar Flow of H2O in the Permeate is 0.1734 gmoles/hr
The Total Molar Flow of the Permeate is 72.9222 gmoles/hr
The Molar Flow of H2 in the Residue is 0.1814 gmoles/hr
The Molar Flow of CO2 in the Residue is 0.2506 gmoles/hr
The Molar Flow of CO in the Residue is 5.0349 gmoles/hr
The Molar Flow of H2O in the Residue is 0.0000 gmoles/hr
The Total Molar Flow of the Residue is 5.4669 gmoles/hr

OVERALL MASS BALANCE CALCULATIONS:
The Overall pct. Conversion of H2 is 96.5192
The Overall pct. Conversion of CO2 is 95.1757
The Overall error in the mass balance based on Hydrogen is 0.0007 gmoles
The Overall error in the mass balance based on Carbon in -0.0002 gmoles

RECYCLE STREAM
The Recycle Flow of H2 to the Reactor is: 48.4826 gmole/hr
The Recycle Flow of CO2 to the Reactor is: 18.3818 gmole/hr
The Recycle Flow of CO to the Reactor is: 5.8844 gmole/hr
The Recycle Flow of H2O to the Reactor is: 0.1734 gmole/hr
The Total Recycle Flow to the Reactor is: 72.9222 gmole/hr

Figure 5 Sample Results for Solution of the RWGS Material Balance

CONCLUSIONS

The material balance for the RWGS process was successfully solved in MATLAB using the iterative algorithm and rigorous calculations for the gas separation membrane. Model validation is required to employ the simulation tool developed for use in analysis and optimization of the RWGS hardware, which will be constructed at KSC. The validation process should include experimental determination of permeability through the polymeric membrane for each component. Performance degradation, which can sometimes accompany the hollow fiber membranes, should also be evaluated. Additional model validation tasks should include analysis of the reactor kinetics and confirmation that equilibrium is obtained for the RWGS reaction, as well as evaluation of the phase distribution of components in the condenser.

To complete the model, energy balance calculations should be incorporated into the RWGS simulation. The development of a rigorous process model for the RWGS system could have significant impact on the development of the technology for this system. In addition to the analysis and optimization aspects previously discussed, this type of model can lead to abstraction of deeper knowledge for use in autonomous control. The development of virtual sensors could also be a by- product of this type of modeling effort. This would prove useful due to the mass constraint, which will be place on missions to Mars.

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