In-Situ Resource Utilization on Mars

Rishav Choudhary & Mohammed Ayub

June 12, 2017

Abstract

The objective of this project was to investigate the effectiveness of a methanation reactor in converting carbon dioxide drawn from the Martian atmosphere to methane. The appropriate operating conditions of the reactor were determined by simulation of a simple model of the reactor over a wide range of operating conditions. The state-of-the-art gaseous separation systems were researched, and a liquefaction system was proposed and analyzed. In order to accommodate for an appropriate mixture model for methane and other gases, a framework was made to get the desired physical properties for methane based on temperature and density fits for Helmholtz energy.

1 Introduction

Production and cryogenic storage of propellants and oxidizer on Mars is imperative to the success of future manned exploration missions. In-Situ Resource Utilization (ISRU) will reduce the constraints on the quantity and the kind of payload that has to be lifted off the Earth on a Mars bound rocket. Owing to the abundance of carbon dioxide in the Martian atmosphere, and the ease of liquefaction, methane seems to the only viable choice for the mass produced propellant. [1].

The first part of the project involved design and simulation of the methanation reactor for a range of operating conditions. Due to competition from the reverse Water Gas Shift (rWGS) reaction, methanation of carbon dioxide has to be carried out at low temperature, high pressure, and in the presence of a catalyst that can block the pathways leading to competing reactions. Since a catalyst lowers the activation energy of certain reaction pathways without affecting the equilibrium, the exact operating conditions can be ascertained by choosing a temperature that maximizes the equilibrium constant of methanation reaction. The pressure can be further adjusted to maximize conversion of carbon dioxide. [2].

Since the methanation reaction is exothermic, the heat released can raise the temperature of the reactor significantly, which, in the absence of active cooling, can increase the rate of rWGS. This would lead to reduction in the selectivity of the reaction. Thus, finding out the appropriate rate of heat removal is important. This is one of the many important quantities that the simulations must reveal.

Simulation of the reactor requires integration of transport equation with surface and gas phase chemistry. The kinetics used in the simulation of the

reactor in this project pertain to the experimentally obtained curve fits for methantion over a 50% $Nickel - Al_2O_3$ catalyst, obtained by Xu et. al [3]. The spatial distribution of the concentration of species and temperature within the reactor were obtained from the simulation. This helped in deciding the final geometry of the reactor.

After fixing the geometry of the reactor and its operating conditions, the energy input to the supporting systems, i.e.preheater, compressors, etc. was calculated. Another important aspect of the methanation system is the fate of its products. The product gas stream is expected to be rich in methane and water vapor with carbon monoxide, carbon dioxide, and hydrogen present in trace quantities. Separation of multi-component gas mixtures would prove challenging to analyze. While flash distillation seems to be the most plausible solution, the weight of the distillation columns might be prohibitive. Additionally, the behavior of fluid at phase boundaries cannot be known accurately. In order to simplify the analysis for this project, the separation systems was treated as a black box.

Assuming that the mixture only consists of hydrogen and methane at the exit of the separation chamber, a Heylandt liquefaction system was used for liquefaction of methane. The net work input, coefficient of performance, and other relevant performance parameters were calculated. The properties of methane and hydrogen used in the simulation were obtained from the temperature and density fits for the Helmholtz free energy.

2 Questions

2.1 Reactor Simulation

The objective of this part is to identify the theoretical limits to the conversion of carbon dioxide. This would set the targets for the reactor simulation. The system is constrained to attain equilibrium with only five species i.e. $CO_2, CO, H_2O, CH_4, and H_2$, by editing the *'gasification.xml'* file used in the fifth assignment of $ME - 370B$.

Plot the equilibrium constant for carbon dioxide methanation, carbon monoxide methanation, and reverse water gas shift reactions as a function of temperature in the aforementioned temperature range. Additionally, plot the heat of reaction for these three reactions as a function of temperature on a separate plot.

Solve the system of coupled first-order ordinary differential equations in MATLAB with initial gas temperature being 473 K for stoichiometric carbon dioxide, hydrogen mixture, without any external heat removal rate. On three separate plots, show the spatial distribution of species, spatial distribution of temperature, and percentage of conversion of carbon dioxide to methane, within the reactor. Compare the predicted asymptotic concentrations with the equilibrium concentrations.

Determine the effect of flow velocity, catalyst density, and initial temperature by plotting mole fraction of methane at the reactor exit with velocity, catalyst density, and initial temperature, respectively.

Calculate the energy input needed for compression and preheating of the reactant mixture.

2.2 Methane Properties

Use the empirical fits for specific heat capacity, and residual Helmholtz function to for methane and tweak the existing property codes to get the desired properties for methane at any given state. Test the code by generating contour plots of the first and second derivatives of pressure with specific volume to compare the numerical and experimental critical point.

Generate the P-v plot with isotherms, and generate the T-s plot with isobars and isenthalphs.

2.3 Liquefaction & Separation

Generate the P-T saturation curve, and Duhring plot for carbon dioxide, methane and hydrogen. Survey the proposed methods for separation of carbon dioxide from methane.

Assume an ideal mixture of methane and hydrogen, and use a Heylandt liquefaction system, operating between $2atm$ and $100atm$ with an expander bleed of 60% to liquefy methane. Obtain the properties at each state of the liquefaction system. Show the process on a T-s diagram. Calculate the work done by the expander, work input to the compressor, yield, and coefficient of performance of the liquefaction system. Compare the work input per unit mass of the liquid produced to that of hydrogen.

3 Deliverables

3.1 Reactor Simulation

1. Plot of species concentration v/s distance along the catalyst bed
2. Plot of temperature v/s distance along the catalyst bed
3. Plot of carbon dioxide selectivity and conversion v/s distance along the catalyst bed
4. Plot equilibrium concentrations on the same plot
5. Plot the equilibrium constants, and heat of reaction for the three reactions, with temperature

3.2 Methane Properties

1. Contour plot of first and second derivatives of pressure with specific volume, showing the numerical and experimental critical point
2. P-v plot for methane with isotherms
3. T-s plot for methane with isobars and isenthalps

3.3 Liquefaction

1. T-s diagram showing the each of the states in the liquefaction system

References

[1] Mars ISRU for Production of Mission Critical Consumables – Options, Recent Studies, and Current State of the Art, G.B. Sanders, A. Paz, L. Oryshchyn, K. Araghi, A.C. Muscatello, D.L. Linne, J. E. Kleinhenz, and T. Peters, AIAA SPACE 2015 Conference and Exposition, AIAA SPACE Forum, (AIAA 2015-4458), http://dx.doi.org/10.2514/6.2015-4458

[2] The development of models for Carbon Dioxide Reduction Technologies for Spacecraft Air Revitalization, M. J. Swickarth, M. Anderson, Proceedings of the 42nd International Conference on Environmental Systems, AIAA, http://dx.doi.org/10.2514/6.2012-3586

[3] Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics, Xu, Jianguo and Froment, Gilbert F., AIChE Journal,volume 35, number 1, pages 88–96, 1989, http://dx.doi.org/10.1002/aic.690350109