# $CO_2$ Conversion via the Sabatier Reaction

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## 1. Executive Summary

The team was tasked with the evaluation of using the Sabatier reaction as a means of carbon dioxide reduction for space applications. The Sabatier reaction converts carbon dioxide and hydrogen into methane and water; this is called a methanation of carbon dioxide. Of the two reactants, carbon dioxide is obtained directly from the exhalation of the astronauts aboard the spacecraft. The other reactant, hydrogen, must be shipped to the spacecraft or obtained via pyrolysis. The products can be used for various things, like electrolyzing the water to obtain oxygen for the astronauts to breathe or pyrolyzing the methane to produce more of the hydrogen reactant. The goal of this project was to design a reactor to support a crew of at least 10 people.

The reactor was modeled, under isobaric conditions, as a catalyst-filled plug flow reactor, with ruthenium pellets serving as the catalyst. The model will account for the reactor's operation at steady state. Due to the ruthenium catalyst's high selectivity for methane, all other side reactions within the reactor are neglected. The selectivity of the ruthenium catalyst for methane is over 90 percent.[1]

Our finalized, 10 mL reactor is capable of supporting a 10-person crew on the International Space Station (the space station has a maximum capacity of 10 astronauts) with a carbon dioxide inlet flow rate of 0.15 moles per hour and an overall volumetric flow rate of 0.0474 $m^3$/hr. The feed must be preheated to 217 ℃ in order to achieve the highest conversion of 84.23 percent. This will result in an outlet effluent temperature of 423.46 ℃. The reactor is to be operated at a constant pressure of 0.9 atmospheres.

In order to achieve the highest conversion of methane with the reactor, the parameters, inlet feed temperature and flow rate, were optimized.

## 2. Introduction

The Sabatier reaction is:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

The Sabatier reaction requires both a catalyst and feed preheating to get started. A modern application of the Sabatier reaction is the production of methane for use in fuel. On Earth, carbon dioxide is taken from the atmosphere, and hydrogen, like in space, is obtained via electrolysis.[2] In fact, in 2012, a fully functional 250 kW demonstration plant was built in Germany as proof of concept.[3]

Many different metals have been used as catalysts for the Sabatier reaction, but Ruthenium has been found to work the best.[2] Although exothermic, the reaction does require its feed to be preheated to at least 250°C and no more than 400°C.[4]

The Sabatier reaction is highly advantageous for use in space due to the fact that it offers a way to reuse valuable oxygen atoms, and it (or a derivative of it) will likely be used in future expeditions to distant planets like Mars. Although the methane is best used in pyrolysis to generate more hydrogen reactant, it may also be used as a fuel, like is done on Earth.

Currently, astronauts aboard the International Space Station are breathing oxygen converted from water via electrolysis. The electrolysis of water converts liquid water into both hydrogen and oxygen gas. This is a pretty efficient system, but there is a major issue: how do you get more water on the International Space Station? The answer is to ship water from Earth to the International Space Station. This takes a lot of room to store and shipping extremely expensive. It costs over $5,500 to send 1 kilogram of material to space.[5] That comes out to over $20,000 per gallon.

As NASA continues to send astronauts to space, there is an ever-increasing interest in utilizing the carbon dioxide generated by the crew to produce useable molecules and compounds, like water and methane via the Sabatier reaction. As of current, the carbon dioxide is filtered out of the space station, resulting in a net loss of oxygen atoms. Designing a reactor that utilizes the Sabatier reaction will maximize the use of the oxygen atoms on the space station, and it will lessen the amount of materials

that need to be shipped to the station, as well as the amount of storage space necessary on the station (water is much denser than hydrogen).

The following assumptions fix the reactor's design specifications for application on the International Space Station:

| Assumption | Justification |
|---|---|
| Ideal Gas | Gas entering the reactor will be at moderate enough temperature and low enough pressure to permit the ideal gas law equation of state to be used |
| Isobaric | Negligible pressure drop in the reactor |
| Steady State | All time dependent variables are constant and/or negligible |
| No Product in Feed | Feed consists of only $CO_2$, $H_2$ and $N_2$ |
| No Side Reactions | Ruthenium has a very high selectivity for methane |

## 3. Methods

### 3.1 Potential Side Reactions

The following are possible reactions associated with the Sabatier reaction.

| |
|---|
| $CO_2 + 2H_2 \rightarrow C_{(solid)} + 2H_2O$ (Bosch) |
| $CO_2 + H_2 \rightarrow CO + H_2O$ (Reverse Water Gas Shift) |
| $CO + 3H_2 \rightarrow CH_4 + H_2O$ (Methanation of Carbon Monoxide) |

There are three potential side reactions. One of the side reactions is the Bosch reaction:

$$CO_2 + 2H_2 \rightarrow C_{(solid)} + 2H_2O$$

In the Bosch reaction, carbon dioxide and hydrogen react to form solid carbon and water. When solid carbon is deposited on a catalyst, the catalyst decreases in efficiency as the surface area for the reaction to occur decreases. The process of solid carbon deposition on a catalyst causes fouling of the catalyst, and is a primary concern for this reactor due to the difficulty of catalyst replacement in space.

The second potential side reaction is the reverse water gas shift reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

In the reverse water gas shift reaction, carbon dioxide and hydrogen react to form carbon monoxide and water. Though water is one of the desired products, carbon monoxide is not and is hazardous to have on the space station.
The final side reaction is the methanation of carbon monoxide:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

In the methanation, carbon monoxide and hydrogen are reacted to form methane and water. Though this reaction results in the desired products, it is important to avoid having carbon monoxide in the space station. The oxygen component of carbon monoxide is a waste of a valuable resource and carbon monoxide is hazardous and has no use on the space station.

**3.2 Catalyst Selection**

The Sabatier reaction is known as a methanation reaction. Many catalysts have been used for the methanation reaction, though Ru (ruthenium) and Ni (nickel) are two of the most efficient.[6] Since there is a catalysts involved in this reactor, there are some issues that must be of paramount concern due the reactor being located on the space station. Fouling is a very important issue when dealing with catalytic reactions. Fouling is the decrease in the number of active sites on the catalyst surface as a result of solid deposition. Fouling of the catalyst presents a significant problem in space, where more materials are in short supply and the cost for shipment to the space station is astronomical. Degradation of the catalyst is also important to avoid, for similar reasons. Degradation is a significant problem in the nickel catalyst.[7]

For this reactor, it was determined that ruthenium was the best choice of catalyst. The catalyst will be an alumina pellet coated in the Ru. Ideally the catalyst used would have been a ruthenium microlith catalyst, as it shows significantly higher conversion than the ruthenium pellets.[6] The microlith is a thin metal substrate, which has many short channels throughout. The microlith resembles a small screen. It has an extremely high surface area, allowing for high mass transfer and heat transfer, while still maintaining minimum pressure drops. Though NASA has used the microlith technology in prior

models, it is patented and information on the reactor is not readily available. For these reasons, the reaction catalyst chosen were ruthenium pellets, which have been shown to have a high selectivity for methane and a high conversion for the Sabatier reaction.[1] It is important to note that all side reactions are neglected in the model for this reactor. This assumption is a significant one, and was assumed valid due to previous research showing the ruthenium pellet catalyst selectivity for methane of greater than 90 percent.

The kinetics for the Sabatier reaction with a metal catalyst have been studied in-depth. There are various kinetic models for the Sabatier reaction over a ruthenium pellet catalyst. The kinetics used were developed by Hwang et al and can be seen listed below. The reaction kinetics were modeled with a Hougen-Waston type equation, resulting in a rate reaction rate and CO2 as the limiting reagent.[8]

The rate of disappearance of $CO_2$ is:

$$r_{CO_2} = \frac{kK_{CO_2}K_{H_2}^4 P_{CO_2}P_{H_2}^4}{\left(1 + K_{CO_2}P_{CO_2} + K_{H_2}P_{H_2}\right)^5}(1-\beta)$$

Where Beta, β, the approach to equilibrium constant is defined as:

$$\beta = \frac{1}{K_{eq}}\frac{(P_{CH_4}P_{H_2O}^2)}{(P_{CO_2}P_{H_2}^4)}$$

The equilibrium constant, $K_{eq}$, is:

$$K_{eq} = \frac{1}{2.06199512*10^{11}*e^{\frac{-22430}{T[K]}}}[=]$$

The adsorption equilibrium constant for carbon dioxide, $K_{CO_2}$, is:

$$K_{CO_2} = 9.099 * 10^{-7} * e^{\frac{69691.8}{R*T[K]}}$$

The adsorption equilibrium constant for hydrogen, $K_{H_2}$, is:

$$K_{H_2} = 9.6104 * 10^{-4} * e^{\frac{39942.0}{R*T[K]}}$$

Finally, the rate constant, k, is:

$$k = 1.0635 * 10^{11} * e^{\frac{-113497.4}{R*T[K]}}$$

### 3.3 Safety Concerns

Due to the reactor's location being the International Space Station, there is a significant concern regarding safety and operation. If the reactor malfunctions while in space, it will be difficult to fix and can have catastrophic consequences. With malfunctions and accidents being of paramount importance, many safety precautions will be in place. The reactor will operate at lower than atmospheric pressure to allow time for leak detection. In the case of a leak, gas will enter the reactor until the pressure inside the reactor reaches equilibrium with the space station. With multiple pressure sensors in place, leak detection should be almost immediate. The Sabatier reaction is highly exothermic. The temperature of the reactor and its housing will need to be monitored closely. The heat sink should be checked on a frequent basis to ensure that it is working correctly. It is very difficult to get rid of heat on the space station and the exothermicity of this reaction makes temperature monitoring even more important. Proper safety equipment must be used when handling anything on or around the reactor.

### 3.4 Reactor Scaling

The reactor modeled is has a volume of 10 milliliters. The volume was determined by modeling the reactor with a full 10-person crew and using the plot of conversion versus volume to determine a volume where the increase in conversion was negligible. There are a few issues that would present themselves if the reactor were scaled up for larger crews or a colony on Mars. First, the Sabatier reaction is highly exothermic and therefore will need a heat sink in order to get rid of the large amounts of heat produced. With a large reactor, it may be more difficult to manage the significant amount of heat in a space environment. Another concern would be the necessary amount of heat required to pre-heat the feed to the reactor. The Sabatier reaction works best with temperatures between 250 to 350 degrees Celsius.

## 4. Results and Discussion

### 4.1 Assumptions

The following assumptions for the material and energy balances were made:

| Assumptions | Consequence(s) |
|---|---|
| PFR kinetics | Reactor kinetics are identical to those of a PFR reactor |
| Isobaric | Pressure held constant |
| Steady State | Time dependent variables are constant and/or eliminated |
| No Product in Feed | No initial concentrations of products |
| No Side Reactions | No loss of products or reactants to secondary reactions |

### 4.2 Material and Energy Balances

Since everything about the Sabatier reaction's kinetics are temperature dependent an energy balance is required for the non-isothermal system. This is why isothermal conditions have not been assumed, along with the fact that it is a PFR based model, and PFRs are exceptionally difficult to maintain in isothermal conditions due to the

temperature change down the reactor. Additionally, recognize that the heat of reaction is negative and of large magnitude, indicating a strongly exothermic reaction, which will be confirmed by the analysis later in this section.

For a PFR, the design equation is:

$$\frac{dX}{dV} = \frac{r_{CO_2}}{F_{CO_2,0}}$$

Where $\frac{dX}{dV}$ is the change in conversion with respect to volume, $r_{CO_2}$ is the rate of disappearance of $CO_2$, and $F_{CO_2,0}$ is the initial flow rate of $CO_2$ in the feed.

The energy balance for the non-isothermal PFR in terms of conversion is:

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + r'_{CO_2}\Delta H_{Rx}(T)}{F_{CO_2,0}((C_{p_{CO_2}} + \theta_{H_2}C_{p_{H_2}} + \theta_{N_2}C_{p_{N_2}}) + \Delta C_p X)}$$

### 4.3 MATLAB

The analysis of the Sabatier reaction was conducted using MATLAB. An interactive script was written to ask the number of people the reactor is meant to by varying the initial flow rate of $CO_2$, with the ideal number of people it can support being 10. The MATLAB code tells the user to indicate this number, followed by a warning if a positive integer of people is not supplied. (See **Figure 4.3a**).

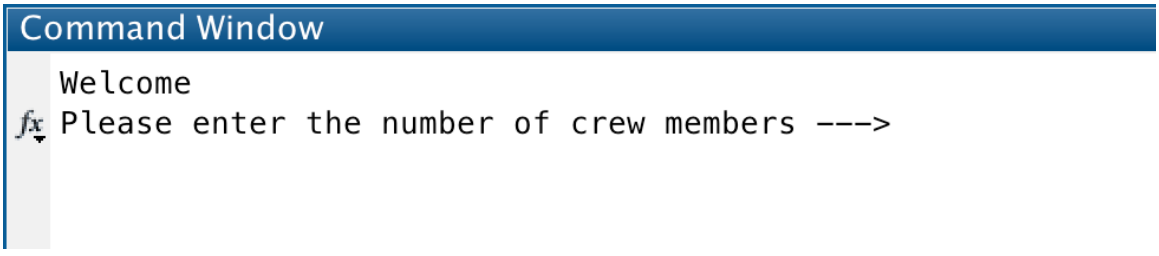


**Figure 4.3a**. Picture of the Command Window of MATLAB.

Using the kinetics found in section 4.2, and a basis of 10 people, various plots were constructed, shown in **Figures 4.3b** to **4.3e**.

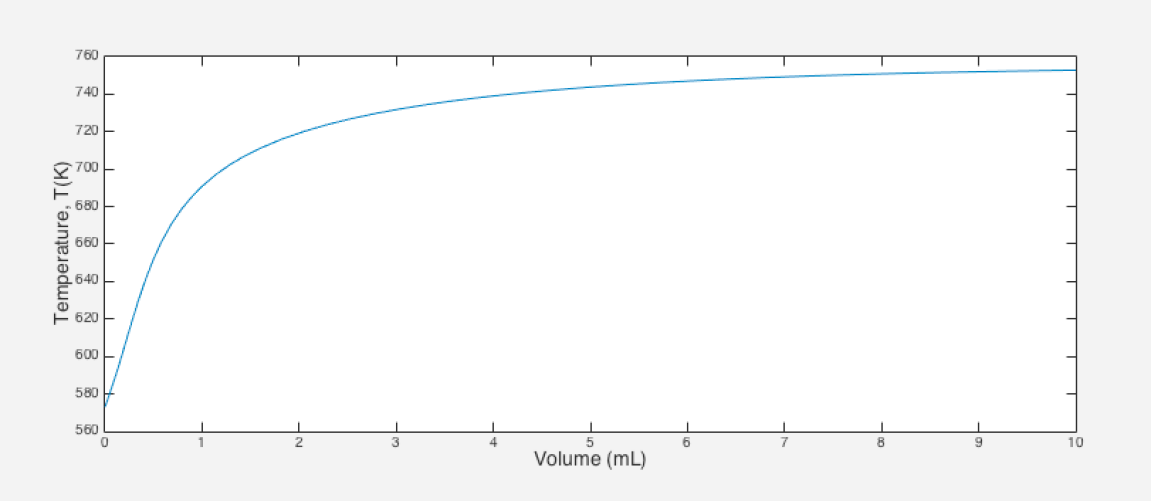


**Figure 4.3b**. Reactor Temperature vs. Reactor Volume

From **Figure 4.3b**, it can be seen that as the volume of the reactor increases, the temperature of the reactor also increases. That said, the reactor's temperature only varies slightly beyond volumes of ~2mL.

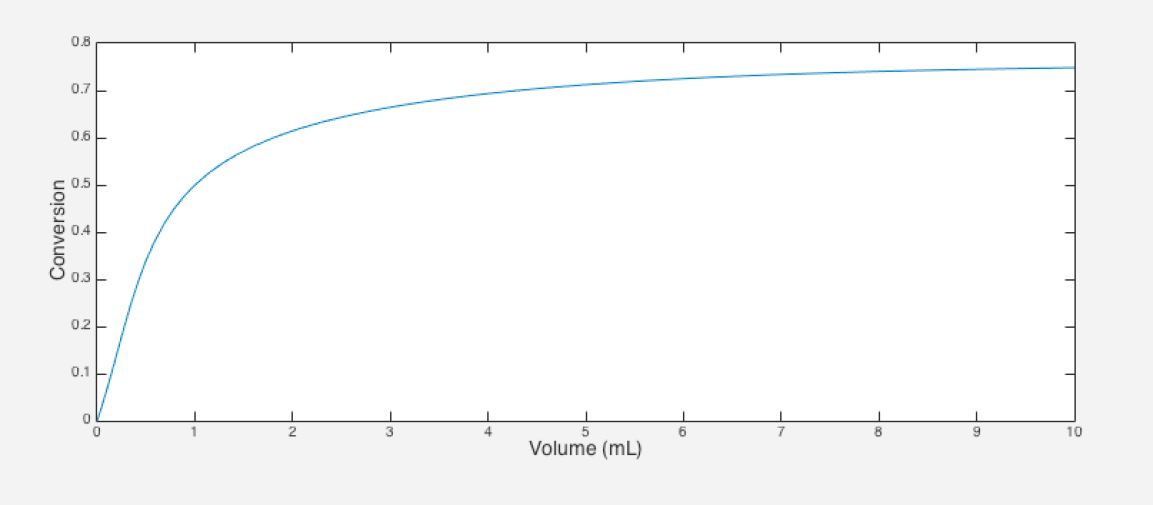


**Figure 4.3c**. Conversion vs. Reactor Volume

As seen with reactor temperature in **Figure 4.3b**, a similar response to the reactor volume is seen with conversion, as illustrated with **Figure 4.3c**. Just like reactor temperature, ~2mL is where the conversion doesn't vary much with increasing reactor volume.

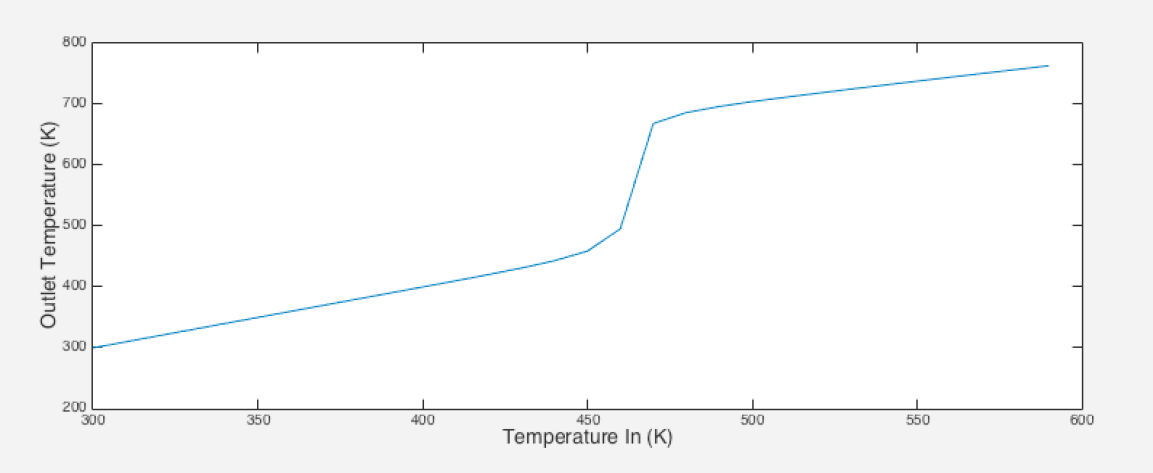


**Figure 4.3d**. Outlet Temperature vs. Feed Temperature

**Figure 4.3d** shows that for the lower magnitudes of the inlet temperature (feed temperature), the reactor temperature gradually increases, which is to be expected. However, when the inlet temperature falls between ~450K and ~480K, the reactor temperature varies considerably.

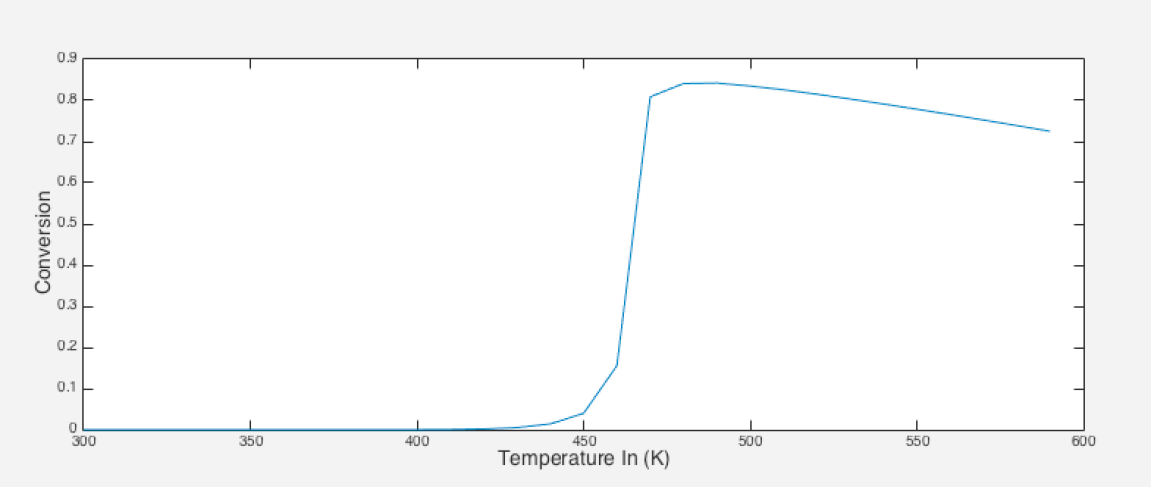


**Figure 4.3e**. Conversion vs. Feed Temperature

**Figure 4.3e** illustrates that the inlet temperature must be ~450K for a reaction to even take place. The highest conversion appears to occur at an inlet temperature of ~475K, so an inlet temperature of 500K was assumed.

The final MATLAB output is thus:

```
Command Window
  Welcome
  Please enter the number of crew members ---> 10


  Be advised the reactor size is 10 mL and is designed for 10 people

  Optimium Operating Parameters

  Please preheat the feed in degrees C to 217.0000

  Operating Conditions

  Max conversion achievable 0.8423
  Reactor Temperature in degrees C 423.4609
```

**Figure 4.3f**. Final MATLAB Command Window output after running the code

## 5. Conclusion

The Sabatier reaction is a useful reaction that is being considered as a potential method of converting carbon dioxide on the International Space Station. In this reaction, carbon dioxide and hydrogen are reacted to produce water and methane. The water can be reused on the space station, cutting down on supplies that are transported to the space station while maximizing the use of the available resources on the space station. Since this reactor will be located on the International Space Station, 258 miles above the Earth's surface, it is important to take all the possible problems and potential side reactions into consideration.

With a ruthenium pellet catalyst in a 10-milliliter reactor, this study showed that a relatively high conversion of carbon dioxide of 84 percent could be achieved, assuming complete capacity of a 10-person crew. With a high selectivity for methane, a high conversion of carbon dioxide, and the reactor's ability to help the space station conserve resources, the reactor in this study would be an efficient way to handle excess carbon dioxide and conserve oxygen atoms on the International Space Station.

## 6. References


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## Appendix

### A. Enthalpy Data for All Reactions at 298.15 K.[9]

Sabatier Reaction

Desired: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

$$\Delta H = [(-74.6) + (2 * (-241.826))] — [(-393.52) + (4 * 0)]$$

$$= -558.252 + 393.52$$

$$= -164.732 \text{ kJ/mol}$$

Undesired: $CO + 3H_2 \rightarrow CH_4 + H_2O$

$$\Delta H = [(-74.6) + (-241.826)] — [(-110.53) + (3 * 0)]$$

$$= -322.426 + 110.53$$

$$= -211.896 \text{ kJ/mol}$$

Undesired: $CO_2 + H_2 \rightarrow CO + H_2O$

$$\Delta H = [(-110.53) + (-241.826)] - [(-393.52) + 0]$$

$$= -352.356 + 393.52$$

$$= 41 \text{ kJ/mol}$$

Undesired (Bosch): $CO_2 + 2H_2 \rightarrow C_{(solid)} + 2H_2O$

$$\Delta H = [0 + (2 * (-241.826))] - [(-393.52) + (2 * 0)]$$

$$= -483.652 + 393.52$$

$$= -90.132 \text{ kJ/mol}$$

## B. List of Variables

| Variable | Description | Units |
|---|---|---|
| $r_i$ | Rate of disappearance of species "i" | mol/m$^3$-hr |
| k | Rate constant of Sabatier reaction | mol/m$^3$-hr |
| $K_{eq}$ | Equilibrium constant of Sabatier reaction | atm$^{-2}$ |
| $K_i$ | Adsorption equilibrium constant for species "i" | atm$^{-1}$ |
| $P_i$ | Partial pressure of species "i" | atm |
| $\beta$ | Approach to equilibrium constant | Dimensionless |
| $F_i$ | Feed molar flow rate of species "i" | mol/hr |
| $\frac{dX}{dV}$ | Change of conversion with respect to reactor volume | m$^{-3}$ |
| $\frac{dT}{dV}$ | Change of reactor temperature with respect to reactor volume | K/m$^3$ |
| $U$ | Overall heat transfer coefficient | W/m$^2$-K |
| $a$ | Heat transfer area on a per volume basis | m$^{-1}$ |
| $T_a$ | Ambient temperature (of the space station) | K |
| $T$ | Temperature (reactor, inlet, etc. – depends on context) | K |
| $r_i'$ | Rate of disappearance of species "i" on a per catalyst basis | mol/g$_{catalyst}$-hr |
| $\Delta H_{Rx}(T)$ | Enthalpy of reaction at temperature "T" | J/mol |
| $C_{p_i}$ | Specific heat (at constant pressure) of species "i" | J/mol-K |
| $\theta_i$ | Ratio of molar flows wrt $CO_2$ | Dimensionless |
| $\Delta C_p$ | Change in the specific heat | J/mol-K |
| $X$ | Conversion of methane | Dimensionless |