Modeling Reactor for Methanol Dehydration to Dimethyl Ether

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Introduction

We attempt to model a novel gas process using waste as reactants and producing valuable fuel (dimethyl ether). The reaction equations and constants are taken from previous work done by other researchers that are studying this process. The original intention was to use industry data to build a more complex model of the system, but alas, we were unable to obtain the data. The model would have made use of compressors and coolers to keep the process at constant temperature (isothermal). Now we are going to be controlling temperature and pressure as if we had a system in place to regulate it. The parameter tuning process is done with the temperature and pressure to find out the optimal values to produce the most dimethyl ether as possible in a single continuous reaction. We implemented gekko for the optimization process.

Literature Review

Aaron Gillette and Trent Okeson [2], performed optimization of an ethanol bioreactor system. The model they used is based on the work and equations provided in Wei et al. [3]. The model is based on previous work by others, parameters estimated from industrial plant data, and the energy balance equation for the reactor. Gillete et al. added a head exchanger to their model and used the APOPT solver. They noted that there needs to be bounds on temperature because the optimizer will request unreasonable temperatures in order to reach optimal products. For this they had an integer controller that would turn a chiller on or off. Lastly, they saw that small changes in temperature would cause a big difference in concentration output. The sensitivity analysis they ran would have several different temperatures run as constants in various simulations. The results of the final concentrations differed greatly. In our work we will take a similar approach by finding the best temperature to maximize desired product and keeping the reaction isothermic.

Guffanti et al. (2021) investigated the optimal parameters for the synthesis of DME, modeling the sorption process inside the PBR and determining the necessary conditions to overcome the usual thermodynamic limitations in this process, considering the mass and energy transference

phenomena. In this case, the modeling of the PBR was carried out considering no limitations in terms of mass and energy transference. Additionally, the kinetic model and kinetic parameters reported by Guffanti were implemented in this case.

Reactor modeling and assumptions

The reactor was modeled as a Packed Bed Reactor (PBR) according to the literature review. To model this process, the reactor was calculated as ideal, therefore, gases are assumed to behave according to the ideal gas law, the pressure drop along the reactor is negligible and the process is assumed to be isothermal due to the presence of a cooling jacket.

- **Reaction Equations**

In order to carry out the synthesis of dimethyl ether (DME) and methanol (MetOH), four reactions are considered. First of all, the synthesis of methanol is achieved from reactions 1 and 3, using carbon monoxide, carbon dioxide and hydrogen (syngas) as reagents. Second, the obtention of dimethyl ether is achieved by the dehydration of methanol (reaction 4). Finally, an undesired reaction, known as the water was shift reaction (represented by reaction 2) is considered. These reactions are carried out using a dual catalyst of copper, zinc and alumina and gamma-alumina in a Packed Bed Reactor (PBR).

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (1)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (2)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad (3)$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \quad (4)$$

- **Kinetics of the reaction**

To model the production of DME and MetOH, the kinetics of the four reactions are considered. This kinetic model follows a LHHW reaction type and has been widely investigated by many authors experimentally. Therefore, kinetic parameters, equilibrium constants for chemical reactions and adsorption constants are reported in the literature. The kinetic model is reported below.

$$R_1 = k_1 \frac{K_{CO}\left(f_{CO} f_{H_2}^{3/2} - f_{CH_3OH} / \left(f_{H_2}^{1/2} K_{eq,1}\right)\right)}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}\right)\left(f_{H_2}^{1/2} + K_{H_2O/H_2} f_{H_2O}\right)}$$

$$R_2 = k_2 \frac{K_{CO_2}\left(f_{CO_2} f_{H_2} - f_{H_2O} f_{CO} / K_{eq,2}\right)}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}\right)\left(f_{H_2}^{1/2} + K_{H_2O/H_2} f_{H_2O}\right)}$$

$$R_3 = k_3 \frac{K_{CO_2}\left(f_{CO_2} f_{H_2}^{3/2} - f_{CH_3OH} f_{H_2O} / \left(f_{H_2}^{3/2} K_{eq,3}\right)\right)}{\left(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2}\right)\left(f_{H_2}^{1/2} + K_{H_2O/H_2} f_{H_2O}\right)}$$

$$R_4 = k_4 \frac{K_{CH_3OH}^2 C_{CH_3OH}^2 \left(1 - C_{H_2O} C_{CH_3OCH_3} / \left(C_{CH_3OH}^2 K_{eq,4}\right)\right)}{\left(1 + 2\sqrt{K_{CH_3OH} C_{CH_3OH}} + K_{H_2O} C_{H_2O}\right)^4}$$

Some of the kinetic parameters are reported in the *Previously Measured Coefficients and Parameters* section.

- **Previously Measured Coefficients and Parameters**

Kinetic parameters, equilibrium constants, and adsorption constants were investigated by several authors, thus, its constants are reported below. It is necessary to mention that these parameters follow an Arrhenious-Type relationship.

	A		B	
k_1	1.07	(mol/(kg_{cat} s bar^2))	36,696	(J/mol)
k_2	3.45×10^3	–	0	(J/mol)
$(k_3)^{0.5}$	0.499	($bar^{-0.5}$)	17,197	(J/mol)
k_4	6.62×10^{-11}	(bar^{-1})	124,119	(J/mol)
k_5	1.22×10^{10}	(mol/(kg_{cat} s bar))	−94,765	(J/mol)
k_6	5.35×10^{13}	(kmol/(kg_{cat} h))	−143665.92	(J/mol)
K_{CH_3OH}	5.39×10^{-4}	(m^3/kmol)	70560.918	(J/mol)
K_{H_2O}	8.47×10^{-2}	(m^3/kmol)	42151.98	(J/mol)

$$A(i)exp(B(i)/RT)$$

- **Material Balance:**

Material balances are considered to model the molar flows inside the PBR reactor. Additionally, the molar flow of each component is modeled by implementing kinetic reactions. These material balances are modeled considering the catalyst mass.

$$\frac{dF_i}{dW} = r_i'$$

$$r'_{DME} = \frac{R_4}{2}$$

$$r'_{MetOH} = R_1 + R_3 - R_4$$

$$r'_{H_2O} = R_2 + R_3 + \frac{R_4}{2}$$

$$r'_{H_2} = -2R_1 - R_2 - 3R_3$$

$$r'_{CO_2} = -R_2 - R_3$$

$$r'_{CO} = -R_1 + R_2$$

- **Process**

The model, as it was intended, is represented in the figure below (Diagram.1). The initial chemical concentrations would run through a compressor that would be used to control the pressure in the reactor. Then the concentrations would travel through a chamber that had fans to cool down the entering fluid. Since the project will not be using data to simulate the compressor and cooler, we now control the temperature and pressure directly.

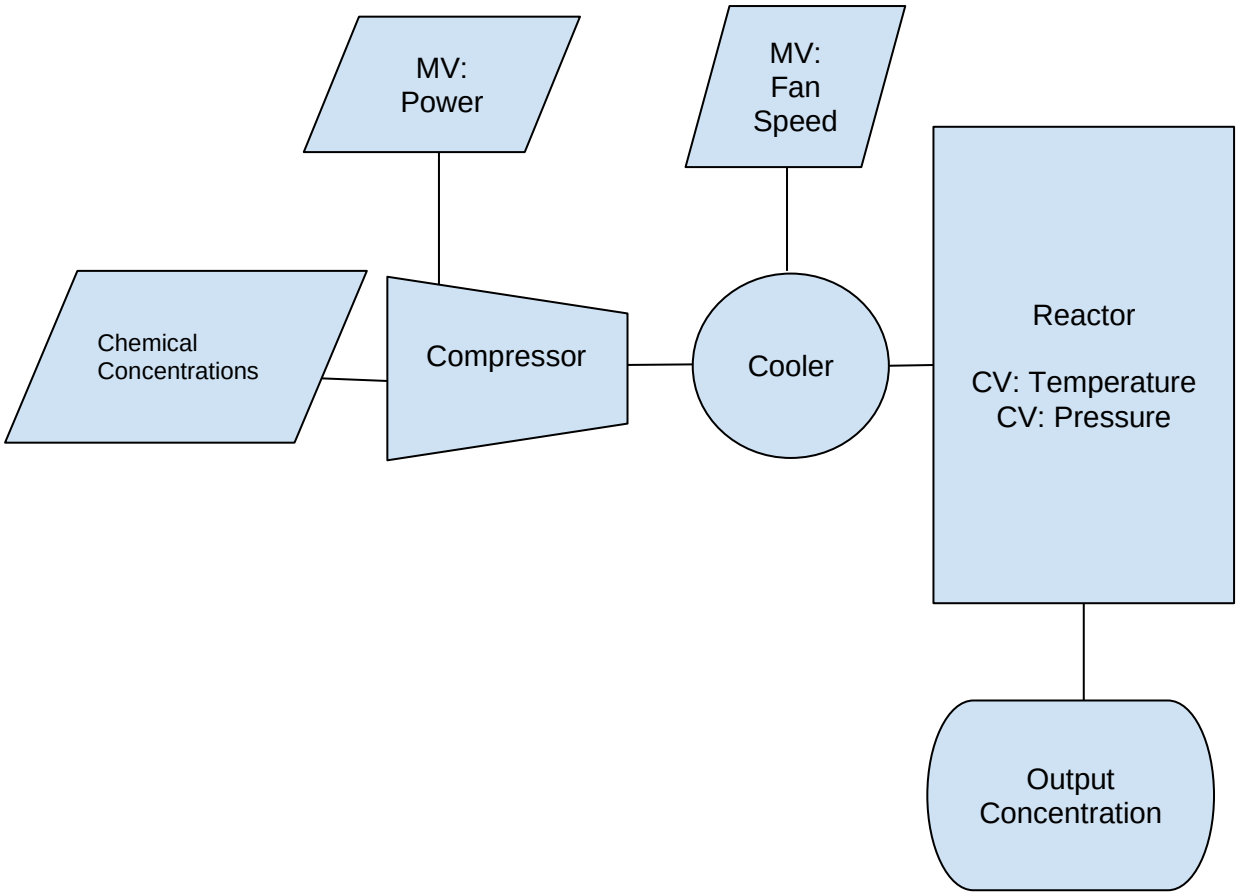

Diagram 1. Reactor Model Components and Process

- **Variables:**

Variable	**Type**	**Unit**	**LB and UP**
Power	MV	kW	(0%, 100%)
Fan Speed	MV	Percent	(0%, 100%)
Temperature	CV	Kelvin	(323.15,673.15)
Pressure	CV	Bar	(1,80)
K_i	Param		
Molar flow rate	Variable	mol/s	-
InitialConcentration	Param		(0,1)
Bi / Ai	Constants		

Unoptimized reactions

The simulation of this process was carried out implementing Python. First of all, the reactor was calculated implementing the simulation mode, in this case, the temperature of the reactor was assumed to be 250°C and the pressure of the reactor was assumed to be 20 bar, obtaining the results presented in figure 1. It is necessary to mention that these values of pressure and temperature are unoptimized values.

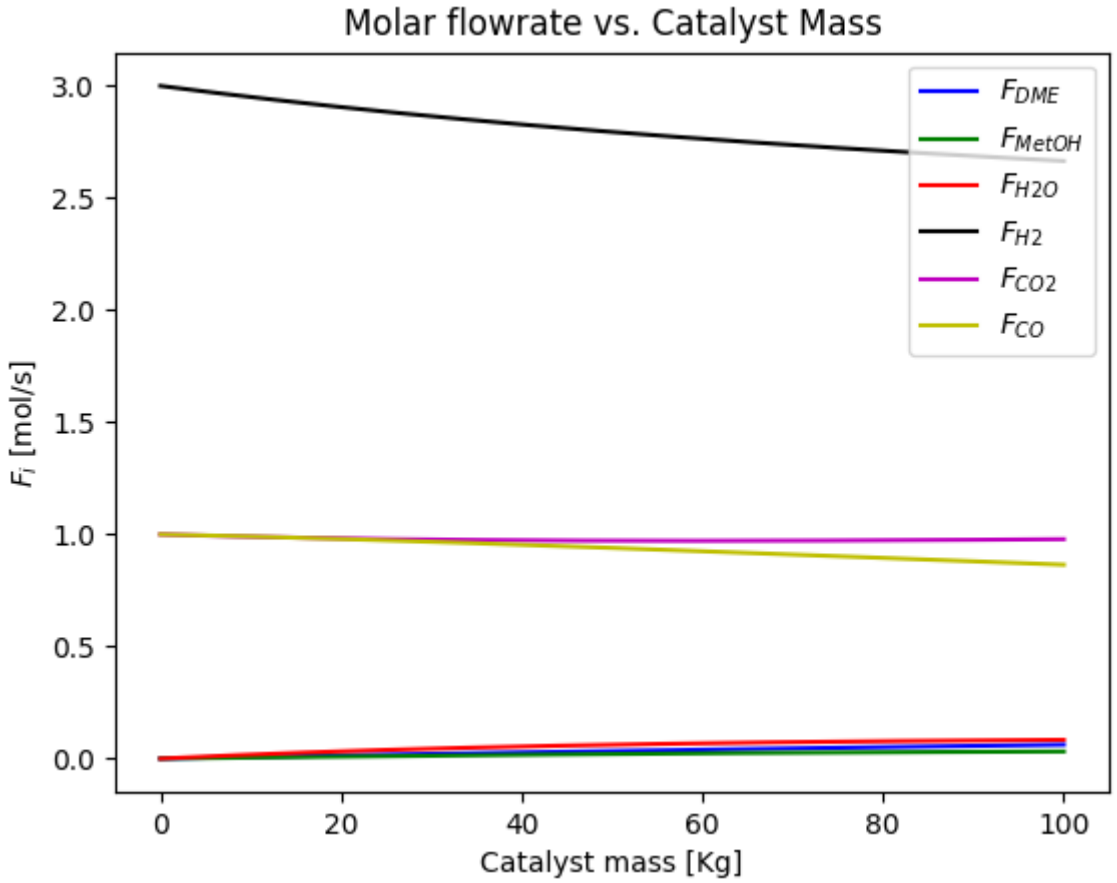

Figure 1: Component flow rate vs. catalyst mass - PBR reactor.

It can be observed in figure 1 that the production of the fuels (represented by the blue and green lines) are null, therefore, it can be concluded that the process should be optimized to find a suitable temperature and pressure.

Optimization

In this work, the optimization problem is solved using the GEKKO package in Python where the main variables of the process are pressure and temperature as mentioned before. In order to set the optimization boundaries for pressure and temperature, a sensitivity analysis is carried out. The results for the sensitivity analysis in terms of the outlet molar flow rate of the fuels are presented in figures 2 and 3. The catalyst mass for the sensitivity analysis, inlet molar flow rates and composition were kept constant as in figure 1.

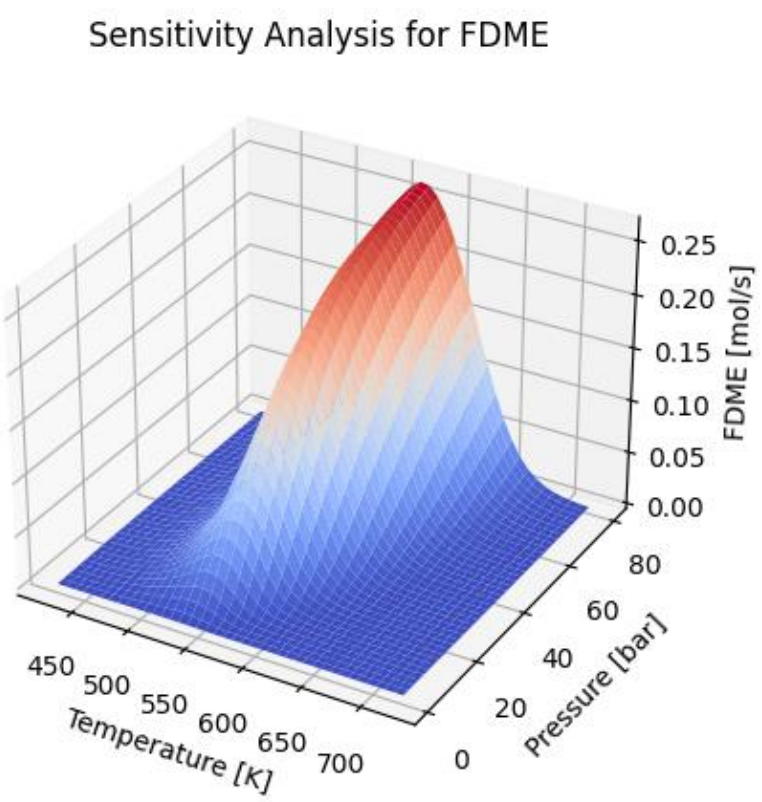

Figure 2: Sensitivity analysis for the production of DME considering pressure and temperature.

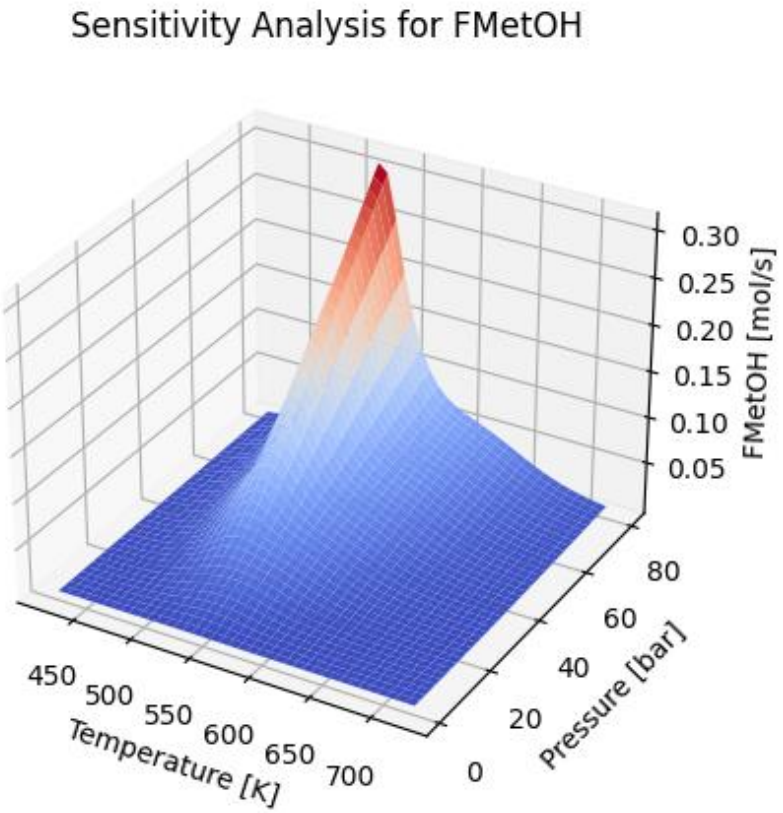

Figure 3: Sensitivity analysis for the production of MetOH considering pressure and temperature.

As a conclusion of the sensitivity analysis carried out for the production of DME and MetOH, it can be said that in terms of pressure, the outlet concentration of both products increases as the pressure increases. On the other hand, the optimal temperature should take a value between 550K and 600K.

Optimization of FDME using pressure and temperature as fixed parameters had a few difficulties. The process that is being modeled is quite complex which made it difficult for gekko to run efficiently. We lowered the concentrations to make it easier for the simulation to run. This made the time to compute much faster.
Another difficulty we ran into was having the too large of a lower and upper bound for the temperature and pressure which made the program produce less than a previous attempt inside of the bounds. We used bounds that were specified in a previous paper [1]. The results are shown in the figure below.

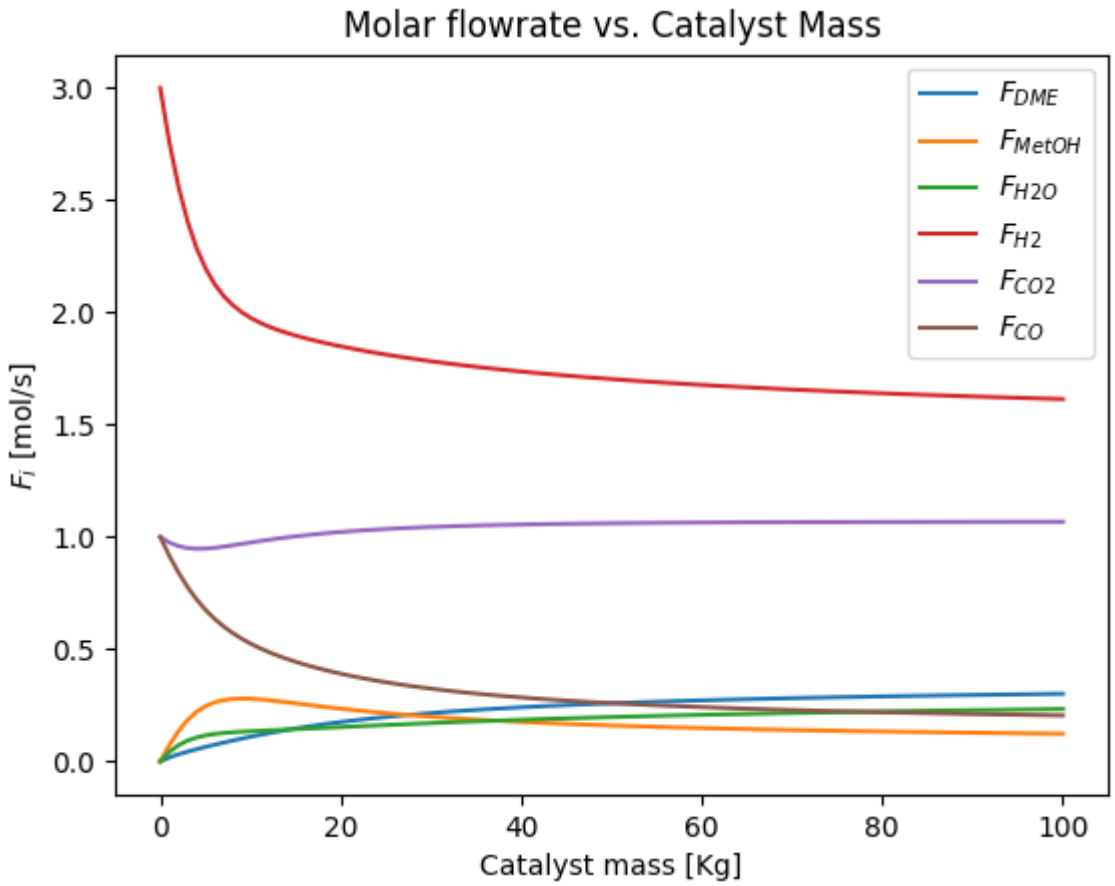

Figure 4: Optimized results for the DME production.

Temperature and pressure were then treated as fixed variables to determine the optimal isothermal temperature and pressure.
Optimal value for temperature is equals to 577.7K and optimal value for pressure is equals to 80bar. These results were obtained using the GEKKO package, implementing IMODE 6. These operation conditions yield a production of approximately 0.30 mol/s.

Future Work

The first principles model could be improved with data collected from compressors, coolers, and reactors. We would also like to try to have interactive model predictive control as part of our model once we understand better the production capabilities of the reactor. Additionally, it would be good to have quantifiable benefits (profit, use of materials, eco-friendly, etc.) of this reaction as part of our analysis to motivate the benefits of this process. The process can be adjusted to maximize both desired output products based on the need of the company or based on maximizing profits.

References

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