Technical Memorandum

To: Client X
From: Daniel Wang
Subject PBR Simulation
Date: 19/04/2022

Hello Client, I have outlined the quantitative analysis of your PBR in this memo. I have conducted data analysis to determine the rate law of your reaction and analysis of the cylindrical catalysts contained within your PBR. I have developed some curves to quantify the performance of your PBR and effectiveness of your coolant, and provided the expressions to estime the internal and overall effectiveness factors.

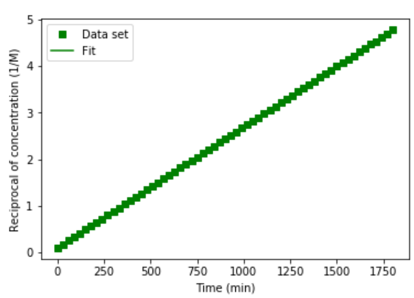
The experimental data was fitted using linear regression, and it was found that the rate law is second order with respect to species A:

$$-r_A = k_{ov} C_A^2$$

The two sets of data was combined to calculate the parameters in the Arrhenius equation:

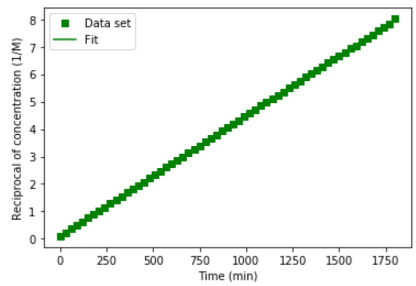
$$k_{ov} = Ae^{\frac{-E_A}{RT}}$$

The value for $k_{ov} = 0.1598991487$ at $T = 150^oC$. The rate constant derived k_{ov} has units of $\frac{m^3}{mol-sec}$. The plots are shown below:



The coefficient of determination for the fit for the dataset is 0.9999940936683402
The model for the dataset 1/C = 0.10135397375444688 + [0.00259469] * time

Figure 1: Reciprocal of concentration vs time graph for experiment 1 (T = 50)

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The coefficient of determination for the fit for the dataset is 0.9999822252064176
The model for the dataset 1/C = 0.10733849751221491 + [0.00437959] * time
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Figure 2: Reciprocal of concentration vs time graph for experiment 1 (T = 60)

It is a good idea to run the PBR at high pressures as this ultimately will increase the reaction rate as summarized by the equation below,

$$\begin{aligned} -r_A &= kC_A^2 \\ &= k\Big(C_{A_o}(1-X_A)\Big(\frac{P}{P_o}\Big)\Big(\frac{T_o}{T}\Big)\Big)^2(1-\mathcal{E}X_A)^{-2} \\ -r_A &\propto \Big(\frac{P}{P_o}\Big)^2 \end{aligned}$$

The ODE used to describe the concentration of species A within the catalyst is shown below:

$$\begin{aligned} \frac{d^2C_A}{dr^2} + \frac{1}{r}\frac{dC_A}{dr} &= \frac{k_{ov}}{D_{eff}}C_A^2 \\ &= \frac{k_{ov}R^2C_{A,surf}}{D_{eff}} \times \frac{C_A^2}{R^2C_{A,surf}} \\ \frac{d^2C_A}{dr^2} + \frac{1}{r}\frac{dC_A}{dr} &= \frac{\Phi^2}{R^2C_{A,surf}}C_A^2 \end{aligned}$$

The expression of the Thiele modulus of the cylindrical catalyst is:

$$\Phi^2 = \frac{k_{ov}R^2C_{A,s}}{D_{eff}}$$

It is important to note that the length of the described cylindricaln catalyst has no bearing on the Thiele Modulus. The expression of the internal and overall effectiveness factors can be summarized below:

$$\begin{aligned} \eta &= \frac{\left| -2D_{eff}\frac{dC_A}{dr}\Big|_{r=R} \right|}{k_{ov}C_{A,surf}R} \\ \Omega &= \frac{k_{conv}\eta}{k_{conv} + \eta k_{conv}(1-\phi_{cat})} \end{aligned}$$

Considering both effectiveness factors are dependant on $C_{A,surf}$ which is a function of $C_{A,bulk}$ that changes along the reactor, both effectiveness factors would vary along reactor as well. There is a significantly higher concentration of species A in the bulk at the inlet of the reactor compared to the outlet due to lack of catalyst and residence time.

Due to the lack of time, a python curve could not be generated to quantify this relationship, however, considering the nature of each expression, we can predict the behaviour of the effectiveness factors. Along the length of the reactor, we can establish that the surface concentration decreases due to the overall decrease in species A. A decrease in $C_{A,surf}$ decreases the $\frac{dC_A}{dr}\Big|_{r=R}$ as shown in the shooting method. A unit decrease in $C_{A,surf}$ decreases $\left.\frac{dC_A}{dr}\right|_{r=R}$ by a greater amount, hence we will see an overall decrease in internal effectiveness as we move along the length of the reactor.

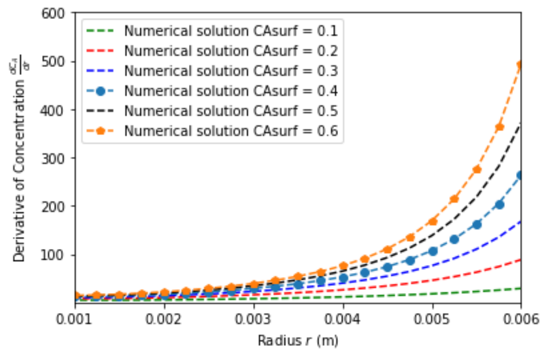

Figure 3: Derivative of concentration at the surface of the catalyst with varying surface concentrations

From the figure above, we see an increase in $\left.\frac{dC_A}{dr}\right|_{r=R}$ as the value of $C_{A,surf}$ which supports the predictions mentioned prior. Similarly, the same can be sad about the overall effectiveness factor. A decrease in η in the numerator superseads the decrease in the denominator, hence there will be an overall decrease in Ω as η decreases along the length of the reactor.

The system of equations and ODEs used to investigate this PBR is shown below:

$$
\begin{aligned}
k_{ov} &= Ae^{\frac{-E_A}{RT}} \\
C_{A,surf} &= \frac{k_{conv}C_{A,bulk} + D_{eff}\left.\frac{dC_A}{dr}\right|_{r=R}(1-\phi_{cat})}{k_{conv}} \\
\eta &= \frac{2D_{eff}\left.\frac{dC_A}{dr}\right|_{r=R}}{k_{ov}C_{A,surf}R} \\
\Omega &= \frac{k_{conv}\eta}{k_{conv} + \eta k_{conv}(1-\phi_{cat})} \\
-r_A &= \Omega k_{ov}C_A^2 \\
\frac{dX_A}{dW} &= \frac{1}{\rho_B}\frac{-r_A}{F_{A_o}} \\
\frac{dy}{dW} &= \frac{-\alpha}{2}\left(\frac{1}{y}\right)\left(\frac{T}{T_o}\right)(1+\mathcal{E}X_A) \\
\frac{dT}{dW} &= \frac{1}{\rho_B}\frac{U\alpha(T-Tc) - (-r_A)[\Delta^o H_{rxn} + \Delta Cp_{rxn}(T-T_{ref})]}{F_{A_o}[\sum\theta_i Cp_i + X_A\Delta Cp_{rxn}]} \\
\frac{dTc}{dW} &= \frac{1}{\rho_B}\frac{U\alpha(T-Tc)}{\dot{m}_c Cp_{cool}}
\end{aligned}
$$

Due to errors in python, a generalized model was unable to be produced, however I have provided an example model below where we assume an initial $C_{A,surf}$ to be used in the shooting method. From the plots shown in the figure below, the heavier the catalyst bed, a greater conversion can be achieved and a higher pressure drop is achieved. The increase in conversion is due to the increase in contact with the catalyst bed. The latter is due to the increase in the physical barrier between the inlet and outlet flows. Assuming the porosity of the bed is constant, a longer catalyst bed will achieve a greater pressure drop. Note that the pressure drop is small at this catalyst bed weight. This could be attributed to the porosity of the bed.

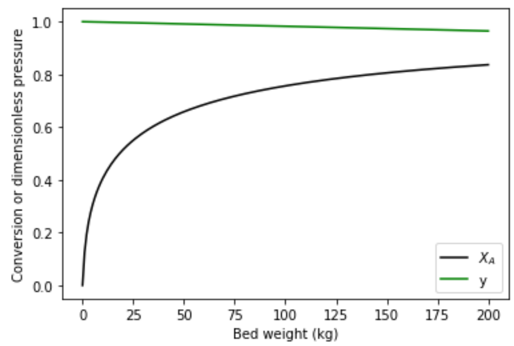

Figure 4: Conversion and Dimensionless Pressure

From the plot above, we can see at a 200kg bed weight, the final conversion of species A is 0.8366788. The exit tempertaure of the coolant is calculated to be 274.45391369K. Although this is a low temperatue given that an incoming feed of hot reactant at 150^{o}C is making contact with a coolant feed of 0^{o}C. However it is important to note, the heat capacity of this coolant is significantly higher than that of the heat capacities of species A, B and inert (200,000 J/mol-K compared to 2000-5000 J/mol-K). In addition, the entering flow rate of this coolant is 500kg/s which promotes the heat transfer convection from the reactor to the coolant. This temperature profile can be shown in the figure below.

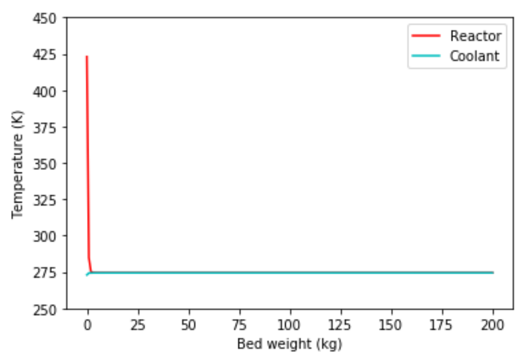

Figure 5: Temperature Profile

As mentioned prior a generalized model was unable to be produced, however to produce a robust model a range of $C_{A,surf}$ should have been used solve the shooting method initially to determine $\frac{dC_A}{dr}\Big|_{r=R}$. Therefore, a relationship can be used to describe how C_{A_bulk} is related to $C_{A,surf}$ and consequently $\frac{dC_A}{dr}\Big|_{r=R}$. Therefore, like the system of ODEs and equations encoded into python above, we will have a function of C_{A_bulk} which are to be solved for the PBR system. This will also support the claim that the internal and overall effectiveness factors will vary along the the reactor.

To further improve the profitability of your reactor, a higher inlet temperature should be investigated. As shown from the plot below, there is an evident increase in relationship between inlet temperature and conversion at a fixed catalyst bed weight.

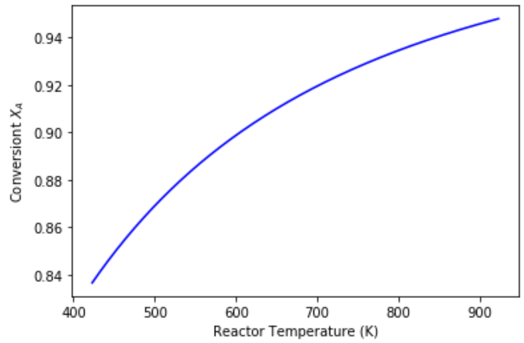

Figure 6: Conversion and Reactor Temperature

From the figure above and python calculations, if the inlet temperature was increased from 150^{o}C to 250^{o}C the total conversion would increase from 0.8366788 to 0.9479098.

1 Ethics Statement

This dedicated section is to confirm that this report, related calculations and the final examination as a whole was completed without any collaboration.