

# Kinetics and Reactor Design HW4

Daniel Naumov

Assigned: February 16, 2023

Due: February 23, 2023

## 1 Problem Statement

### 1.1 P5-14<sub>A</sub> (a-c)

**P5-14<sub>B</sub>** The dehydration butanol of alumina is carried out over a silica-alumina catalyst at 680 K.



The rate law is

$$-r'_{\text{Bu}} = \frac{kP_{\text{Bu}}}{(1 + K_{\text{Bu}}P_{\text{Bu}})^2}$$

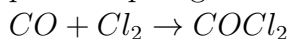
with  $k = 0.054 \text{ mol/gcat}\cdot\text{h}\cdot\text{atm}$  and  $K_{\text{Bu}} = 0.32 \text{ atm}^{-1}$ . Pure butanol enters a thin-tubed, packed-bed reactor at a molar flow rate of 50 kmol/hr and a pressure of 10 atm (1013 kPa).

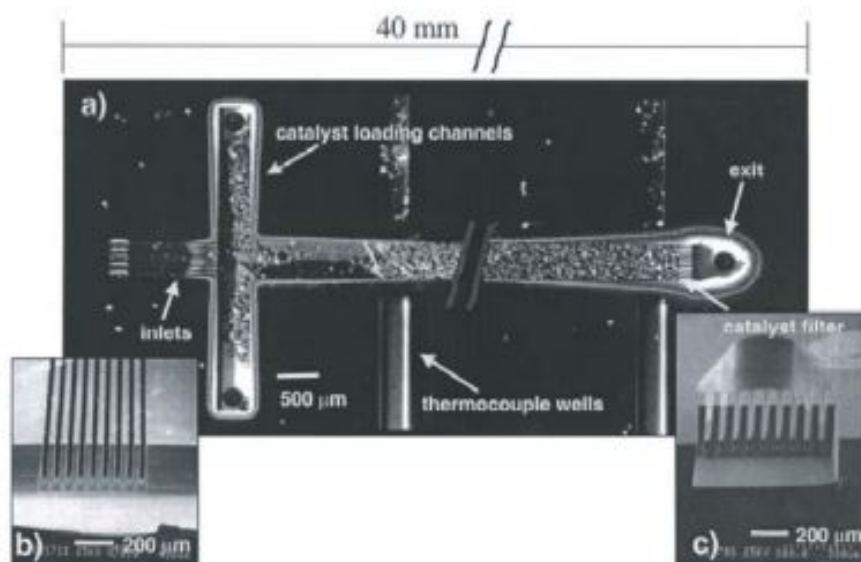
- (a) What PBR catalyst weight is necessary to achieve 80% conversion in the absence of pressure drop? Plot and analyze  $X$ ,  $p$ ,  $f$  (i.e.,  $(v/v_0)$ ) and reaction rate,  $-r'_A$ , as a function of catalyst weight.
- (b) What "fluidized CSTR" catalyst weight is necessary to achieve 80% conversion?
- (c) Repeat (a) when there is pressure drop, with the pressure-drop parameter  $\alpha = 0.0006 \text{ kg}^{-1}$ . Do you observe a maximum in the rate of reaction, and if so, why? What catalyst weight is necessary to achieve 70% conversion? Compare this weight with that for no pressure drop to achieve the same conversion.

Figure 1

### 1.2 P5-21<sub>B</sub> (a-d)

A microreactor from the MIT group similar to the one shown in Figure P5-21<sub>B</sub> was used to produce phosgene in the gas phase.





**Figure P5-21<sub>B</sub>** Microreactor. Source: Courtesy of S. K. Ajmera, M. W. Losey, K. F. Jensen, and M. A. Schmidt, *AIChE J.* 47, 1639 (2001). (Article titled "Microfabricated cross-flow chemical reactor for catalyst testing.")

The microreactor is 20 mm long, 500  $\mu\text{m}$  in diameter, and packed with catalyst particles 35  $\mu\text{m}$  in diameter. The entering partial pressure of A is 231 kPa (2.29 atm), and the entering flow to each microreactor is equimolar. The molar flow rate of CO is  $2 \times 10^{-5}$  mol/s and the volumetric flow is  $2.83 \times 10^{-7}$  m<sup>3</sup>/s. The weight of catalyst in one microreactor:  $W = 3.5 \times 10^{-6}$  kg. The reactor is kept isothermal at 120°C. Because the catalyst is also slightly different than the one in Figure P5-21<sub>B</sub>, the rate law is different as well:

$$-r'_A = k_A C_A C_B$$

*Additional information:*

$$\alpha = 3.55 \times 10^5 / \text{kg catalyst (based on properties of air and } \phi = 0.4)$$

$$k = 0.004 \text{ m}^6 / (\text{mol} \cdot \text{s} \cdot \text{kg catalyst}) \text{ at } 120^\circ\text{C}$$

$$u_0 = 2.83 \cdot 10^{-7} \text{ m}^3/\text{s}, \rho = 7 \text{ kg/m}^3, \mu = 1.94 \cdot 10^{-5} \text{ kg/m} \cdot \text{s}$$

$$A_c = 1.96 \cdot 10^{-7} \text{ m}^2, G = 10.1 \text{ kg/m}^2 \cdot \text{s}$$

- Plot the molar flow rates  $F_A$ ,  $F_B$ , and  $F_C$ , the conversion  $X$ , and pressure ratio  $p$  along the length (i.e., catalyst weight,  $W$ ) of the reactor.
- Calculate the number of microreactors in parallel needed to produce 10,000 kg/year phosgene.
- Repeat part (a) for the case when the catalyst weight remains the same but the particle diameter is cut in half. If possible, compare your answer with part (a) and describe what you find, noting anything unusual.
- How would your answers to part (a) change if the reaction were reversible with  $K_C = 0.4 \text{ dm}^3/\text{mol}$ ? Describe what you find.

Figure 2

### 1.3 P6-5<sub>B</sub> (a, b)

**P6-5<sub>B</sub>** For the reaction and data in P6-4<sub>B</sub>, we now consider the case when the reaction is reversible with  $K_C = 0.025 \text{ dm}^6/\text{mol}^2$  and the reaction is carried out at 300 K in a membrane reactor where  $\text{C}_2\text{H}_6$  is diffusing out. The membrane transport coefficient is  $k_C = 0.08 \text{ s}^{-1}$ .

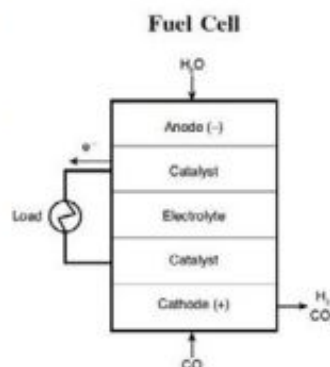
- What is the equilibrium conversion and what is the exit conversion in a conventional PFR? (Ans.:  $X_{eq} = 0.52$ ,  $X = 0.47$ )
- Plot and analyze the conversion and molar flow rates in the membrane reactor as a function of reactor volume up to the point where 80% conversion of di-tert-butyl peroxide is achieved. Note any maxima in the flow rates.

Figure 3

### 1.4 P6-7<sub>B</sub>

**P6-7<sub>B</sub> Fuel Cells Rationale.** With the focus on alternative clean-energy sources, we are moving toward an increased use of fuel cells to operate appliances ranging from computers to automobiles. For example, the hydrogen/oxygen fuel cell produces *clean energy* as the products are water and electricity, which may lead to a hydrogen-based economy instead of a petroleum-based economy.

A large component in the processing train for fuel cells is the water-gas shift membrane reactor. (M. Gummala, N. Gupta, B. Olsomer, and Z. Dardas, *Paper 103c*, 2003, AIChE National Meeting, New Orleans, LA.)



Here, CO and water are fed to the membrane reactor containing the catalyst. Hydrogen can diffuse out the sides of the membrane, while CO,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$  cannot. Based on the following information, plot the concentrations and molar flow rates of each of the reacting species down the length of the membrane reactor. Assume the following: The volumetric feed is  $10 \text{ dm}^3/\text{min}$  at 10 atm, and the equimolar feed of CO and water vapor with  $C_{T0} = 0.4 \text{ mol/dm}^3$ . The equilibrium constant is  $K_c = 1.44$ , with  $k = 1.37 \text{ dm}^6/\text{mol kg-cat} \cdot \text{min}$ , bulk density,  $\rho = 1,000 \text{ kg/m}^3$ , and the mass transfer coefficient  $k_{\text{H}_2} = 0.1 \text{ dm}^3/\text{kg-cat} \cdot \text{min}$  (Hint: First calculate the entering molar flow rate of CO and then relate  $F_A$  and  $X$ .)

- What is the membrane reactor catalyst weight necessary to achieve 85% conversion of CO?
- Sophia wants you to compare the MR with a conventional PFR. What will you tell her?
- For that same membrane reactor catalyst weight, Nicolas wants to know what would be the conversion of CO if the feed rate were doubled?

Figure 4

## 2 Problem Solution

### 2.1 P5-14<sub>A</sub> (a-c)

a)

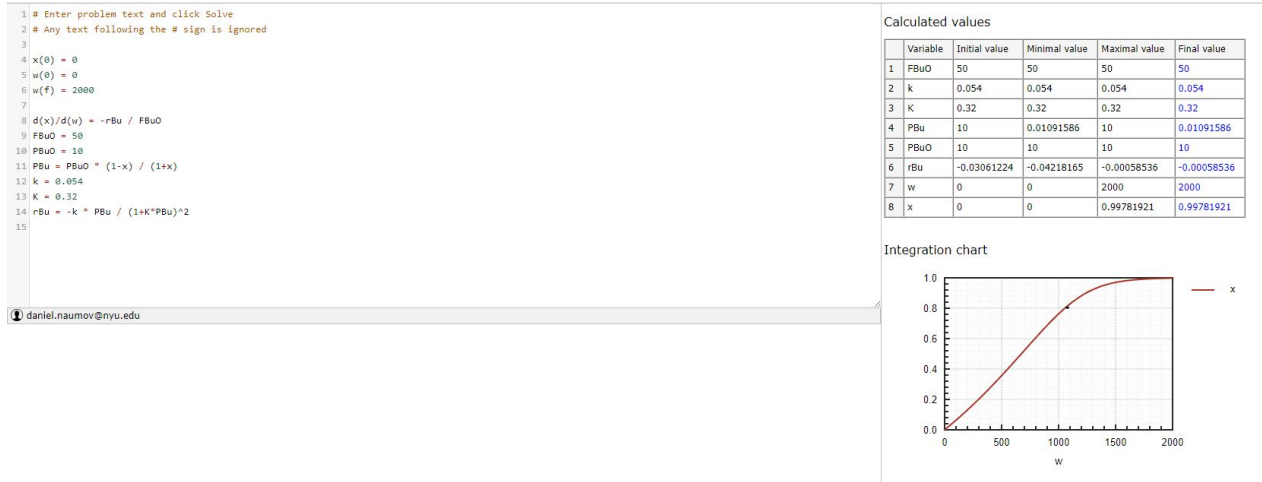


Figure 5: My setup for Polymath Online to solve the Differential Equation

Roughly speaking, 1050 kg of catalyst is necessary for 80 percent conversion without pressure drop.

b) For a fluidized CSTR:

$$F_{AO} = \frac{dX}{dW} - r'_{Bu} \quad (1)$$

$$P_{Bu} = P_{BuO} \frac{(1-x)}{(1-\epsilon x)} \quad (2)$$

$$\epsilon = 1 \quad (3)$$

$$-r'_{Bu} = K \times P_{Bu} \frac{1}{(1 + KBu + PBu)^2} \quad (4)$$

$$\frac{W}{F_{BuO}} = \frac{x}{r_{Bu}} \quad (5)$$

$$w = F_{BuO} \times X \times \frac{(1 + KBu + PBuO \frac{(1-X)}{(1+X)})^2}{K \times PBuO \frac{(1-X)}{(1+X)}} \quad (6)$$

Plugging in given values ( $X = 0.8$ ,  $F_{BuO}$ ,  $KBu$ ,  $PBuO$ ), we get  $w = 1225$  kg of catalyst needed for fluidized CSTR.

c) Coupled ODE. Looking at the data for maximum rate of the reaction (smallest value of  $r_{Bu}$ ), I found it to be around 600 kg of catalyst. Also looking at the data, a conversion of 70 percent would be reached at 932 kg of catalyst (for part a, 915 kg).



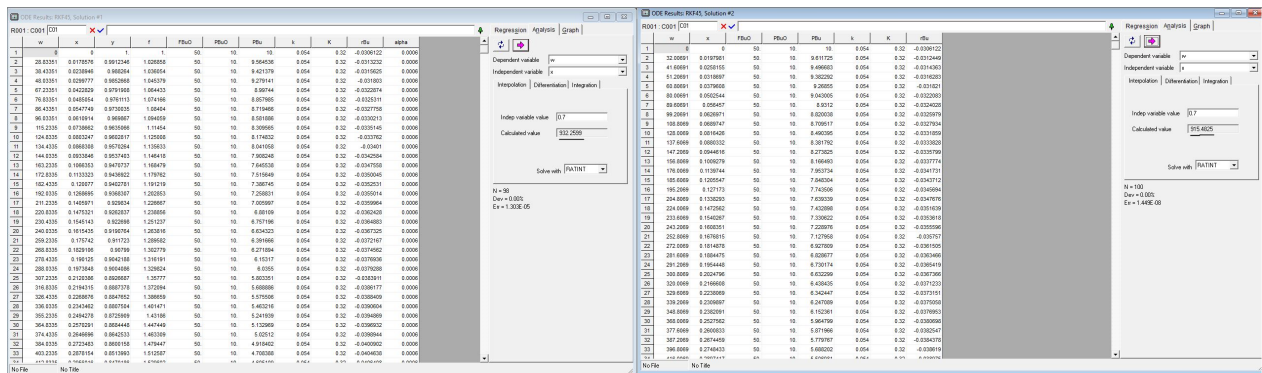


Figure 6: My data for solving for catalyst weight in the Polymath program

## 2.2 P5-21<sub>B</sub> (a-d)

a) Epsilon is equal to 1/2.

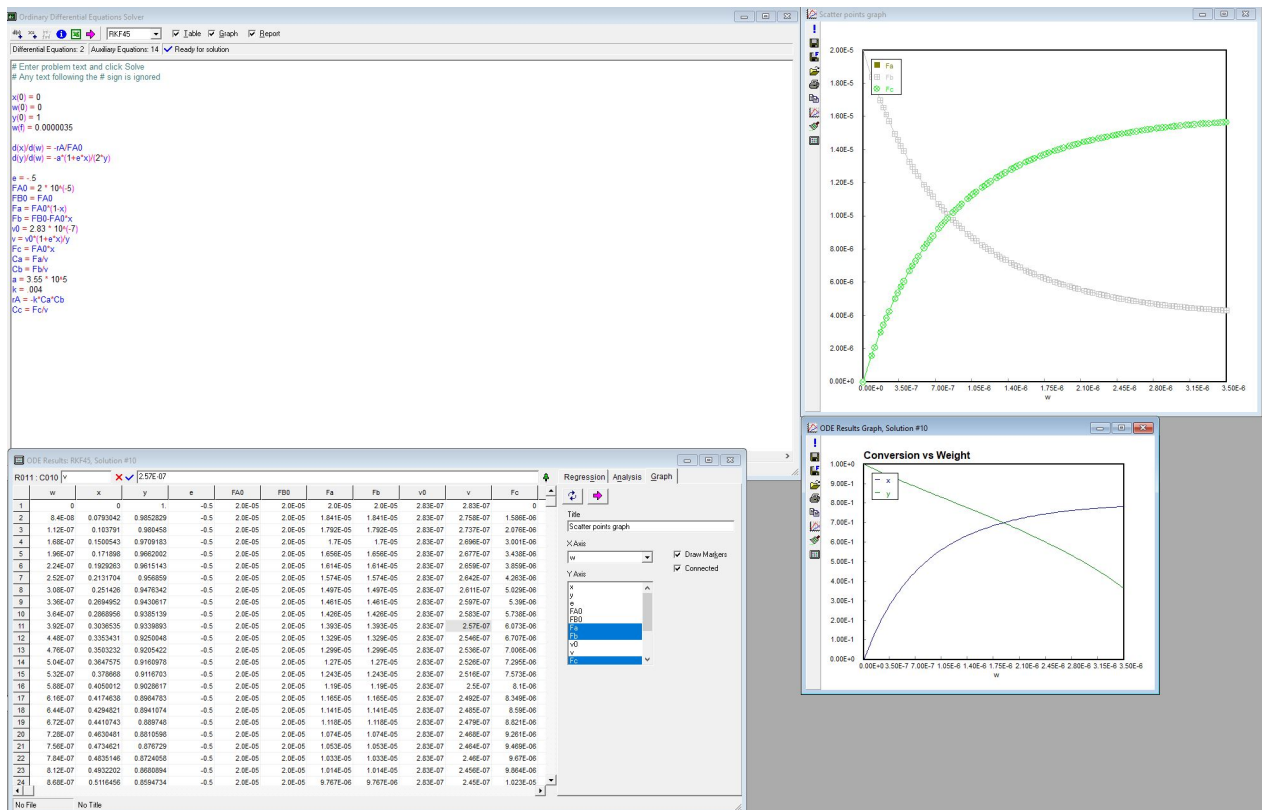


Figure 7: My data for solving for molar flow rates and the conversion in the Polymath program

b) At  $w = 3.5 \times 10^{-6}$  kg, conversion is 78.4 percent according to the data. Thus the yield is the molar weight of phosgene multiplied by the flow rate multiplied by 0.784, then

multiplying by 86,400 seconds per day times 365 days per year. This yields 48.9 kg per year. So for 10000 kg per year, we need 204.5 microreactors (so 205 microreactors).

c) Halving the particle diameter causes  $\beta_0$  to increase by around 3.48 times.  $\alpha$  increases proportionately to  $\beta_0$  therefore the new value for  $\alpha$  is  $12.35 \times 10^5 / \text{kg catalyst}$ . Plugging that into Polymath:

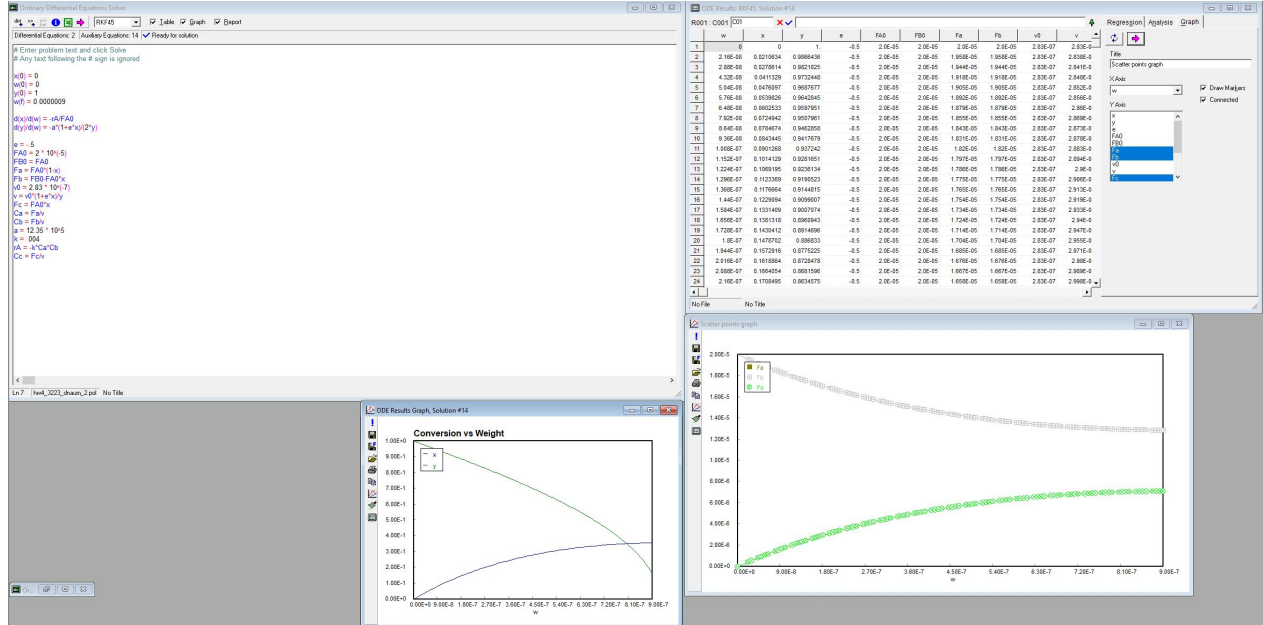


Figure 8: My data for solving for molar flow rates and the conversion in the Polymath program with new  $\alpha$

(For the record, Polymath didn't want to plot up to  $w = 3.5 \times 10^{-6} \text{kg}$ , but the trend is pretty clear - there's a flattening out of the conversion and the conversion rate slows down very quickly due to pressure drop).

d) I made the rate reversible and added the Kc term.

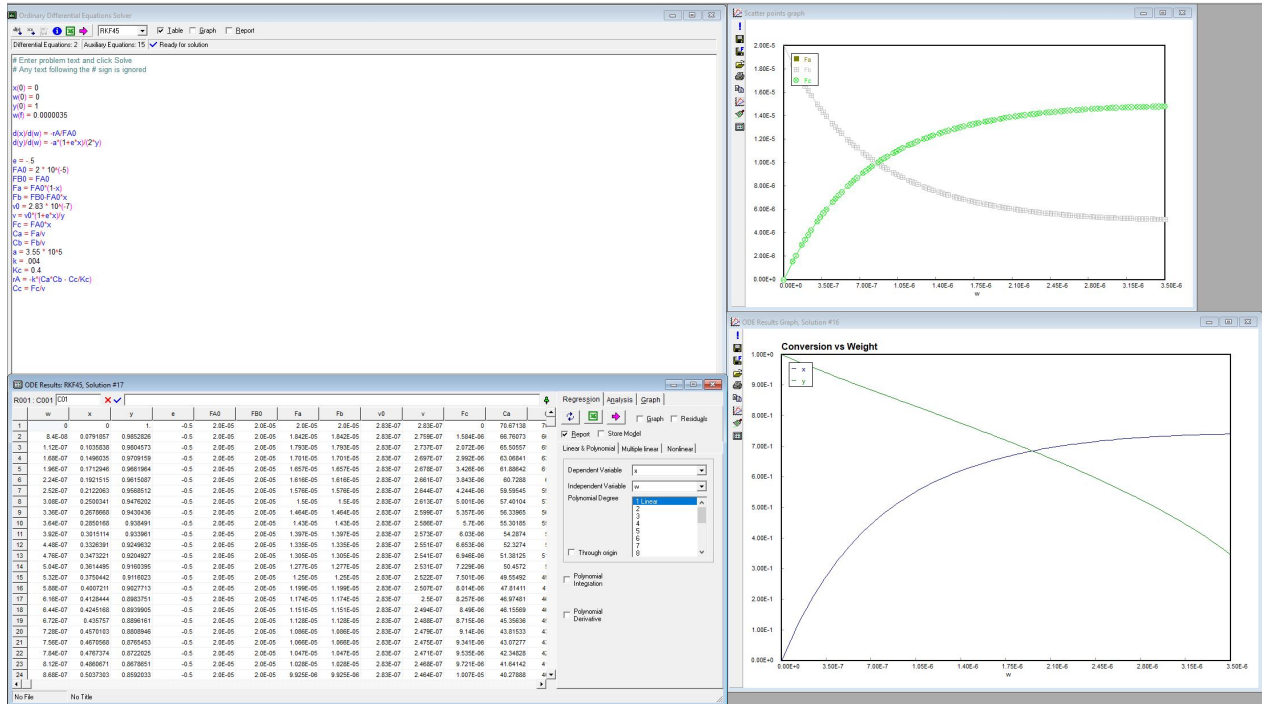


Figure 9: My data for solving for molar flow rates and the conversion in the Polymath program with reversibility accounted for

There's a similar effect here as in part c, except instead of pressure drop being the primary cause, it's both pressure drop and reversibility.

## 2.3 P6-5<sub>B</sub> (a, b)

a) Equilibrium conversion and exit conversion in a conventional PFR, using givens from 6-4. Partial solution of 6-4 below:

$$V = F_{A0} \int_0^x \frac{dX}{-r_A} \quad (7)$$

$$-r_A = kC_A \quad (8)$$

$$\epsilon = y_{A0}\delta = 1 \times 2 = 2 \quad (9)$$

$$C_A = C_{A0} \frac{(1 - X)}{(1 + \epsilon X)} \quad (10)$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{10 \text{ atm}}{0.082 \text{ L atm/(K mol)} \times 400 \text{ K}} = 0.3 \frac{\text{dm}^3}{\text{mol}} \quad (11)$$

$$V = \frac{F_{A0}}{kC_{A0}} \int_0^x \frac{(1 + \epsilon X)}{(1 - X)} dX \quad (12)$$

$$V = \frac{F_{A0}}{kC_{A0}} \left[ (1 + \epsilon) \ln \frac{1}{1 - X} - \epsilon X \right] \quad (13)$$

We're given a  $K_C$  and  $k_c$  For this problem, we modify the rate law:

$$-r_A = -k(C_A - \frac{C_B C_C^2}{K_C}) = 0 \text{ at equilibrium} \quad (14)$$

Stoichiometry:

$$C_A = \frac{C_{A0}(1 - X)}{1 + \epsilon X} \quad (15)$$

$$C_B = \frac{C_{A0}X}{1 + \epsilon X} \quad (16)$$

$$C_C = \frac{2C_{A0}X}{1 + \epsilon X} \quad (17)$$

$$K_C = \frac{C_B C_C^2}{C_A} = \frac{4C_{A0}^2 X^3}{(1 + \epsilon X)^2 (1 - X)} \quad (18)$$

Since  $K_C$  at equilibrium is 0.025, we can evaluate  $X$  at that value as  $X_{eq}$ . This yields a value of 0.52. For the conventional PFR which is mentioned in 6-4, there is a conversion of 90 percent. So here it would be 90 percent of  $X_{eq}$ , or 0.47.

b) 80 percent conversion of A for equilibrium reaction means 80 percent of 0.52, so 0.416. Using Polymath to solve for  $V$ , I got a volume of 191.5  $\text{dm}^3$ .

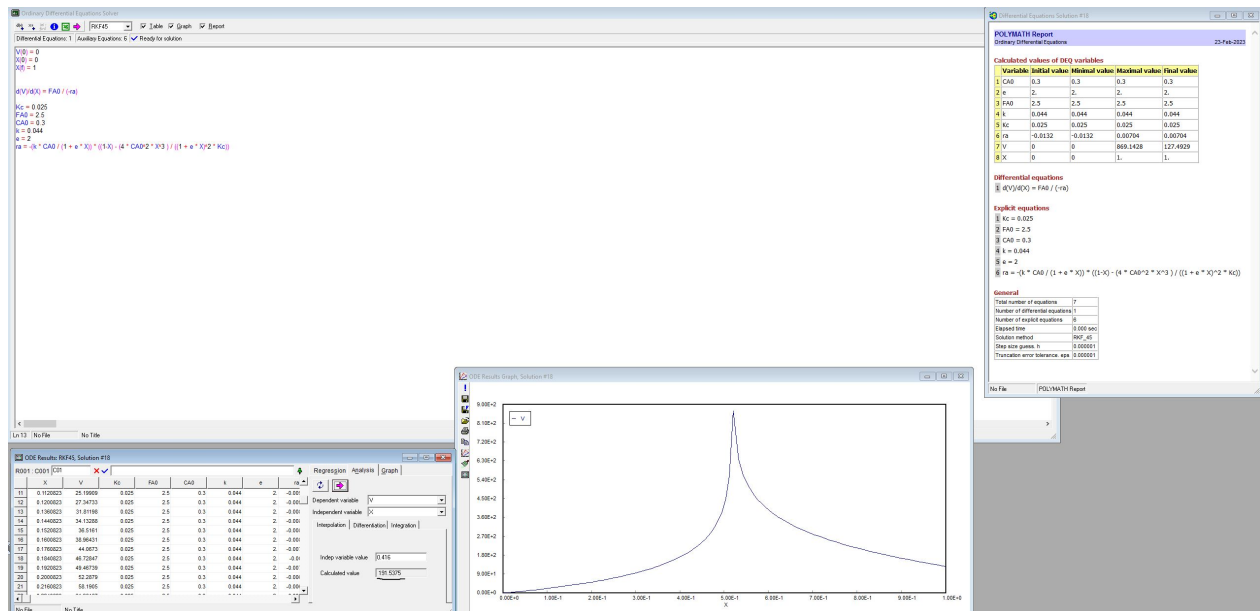


Figure 10: My data for solving for reactor sizing in the Polymath program with reversibility accounted for



## 2.4 P6-7<sub>B</sub>

Membrane reactor mole balance:

$$\frac{dF_A}{dW} = r \quad (19)$$

$$\frac{dF_B}{dW} = r \quad (20)$$

$$\frac{dF_C}{dW} = -r \quad (21)$$

$$\frac{dF_D}{dW} = -r - R_{H_2} \quad (22)$$

Rate law:

$$r = -k \left[ C_A C_B - \frac{C_C C_D}{K_{eq}} \right] \quad (23)$$

Stoichiometry:

$$C_A = C_{T0} \frac{F_A}{F_T} \quad (24)$$

$$C_B = C_{T0} \frac{F_B}{F_T} \quad (25)$$

$$C_C = C_{T0} \frac{F_C}{F_T} \quad (26)$$

$$C_D = C_{T0} \frac{F_D}{F_T} \quad (27)$$

$$F_T = F_A + F_B + F_C + F_D \quad (28)$$

Via Polymath:

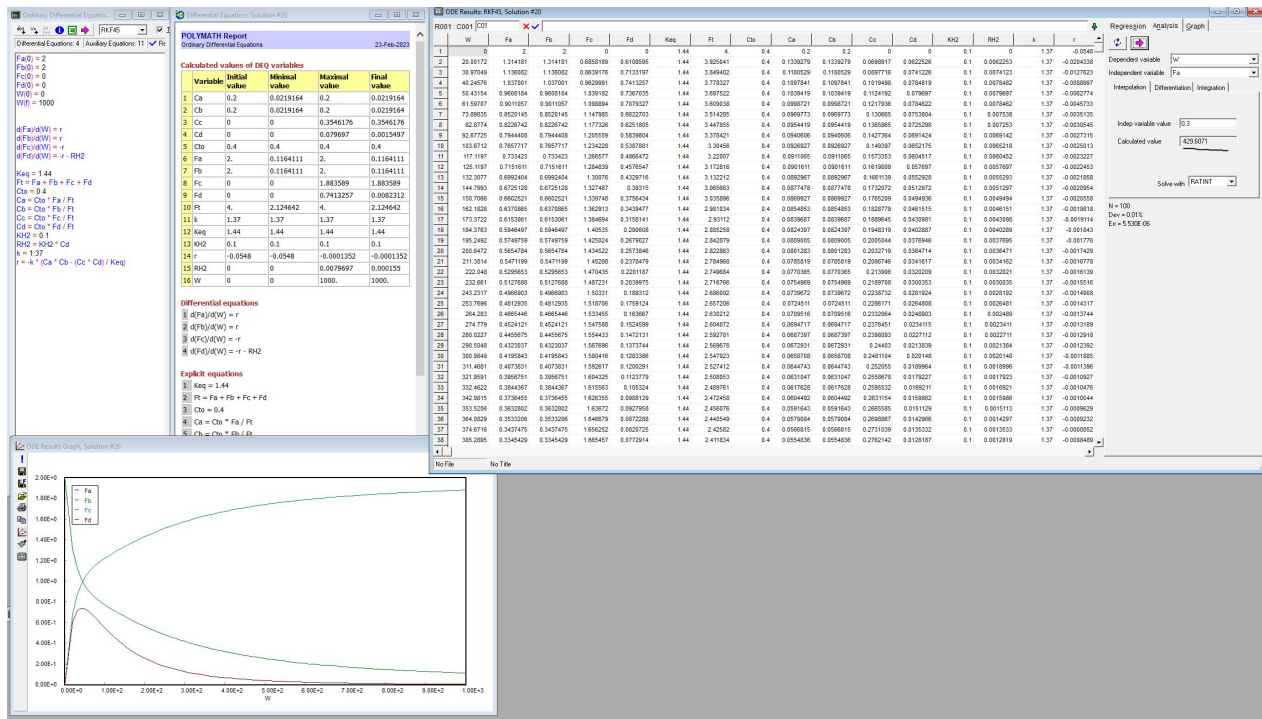


Figure 11: My data for solving for catalyst weight in the Polymath program with reversibility accounted for

Since I wanted to know the weight at 85 percent conversion, I knew that  $C_A$  had to have a flow that was 85 percent less than initial (so  $2 \times 0.3$ ). Solving for the weight  $W$  lead to 430 kg of catalyst.

b) This could be evaluated analytically. However I evaluated it in Polymath by just removing the terms associated with the removal of hydrogen gas. Then I divided  $F_C$  (or  $F_D$  would also work) over  $F_T$ , and got  $X = 0.5454$ .

c) Doubling the feed rate means that more hydrogen forms that has to be vented off, which slightly slows the reaction down. Evaluating at 430 kg, the conversion rate is around 73 percent.