

# Reactor Engineering Week 5 Problem Set

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## Question 1a

The following second-order, isothermal, liquid phase reaction is conducted in two MFR's in series:



The volume of the first reactor is  $V_1$ , the volume of the second is  $V_2$ , the volumetric flow rate is  $v$  and the initial concentration of  $A$  is  $C_{A0}$ . Find an expression for the final conversion,  $X_A$ , as a function of  $V_1$  and  $V_2$ .

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## Question 1b

If the total volume of the two reactors was constrained to equal  $V_1 + V_2 = V$ , find volumes  $V_1$  and  $V_2$  which maximise the final conversion  $X_A$ .

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## Question 1c

If the final conversion was constrained to equal  $X_A$ , find reactor volumes  $V_1$  and  $V_2$  which minimise the total volume  $V = V_1 + V_2$ , while still obtaining the necessary reaction conversion. Demonstrate how you would find this optimum *graphically*.

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## Question 2

The liquid phase, isothermal reaction,

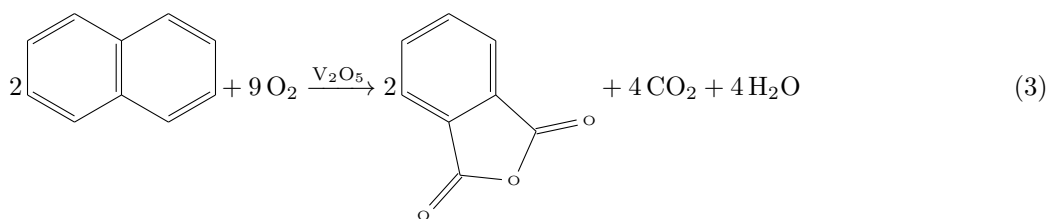


occurs inside two plug flow reactors placed in series. The volume of the first reactor is  $V_1$ , and the volume of the second is  $V_2$ . If the initial concentration of  $A$  and  $B$  were equal (so  $C_{A0} = C_{B0}$ ), if the volumetric flow rate is  $v$ , and if the reaction is first order in both  $A$  and  $B$  with reaction constant  $k_2$ , find a relationship between outlet conversion  $X_A$  and reactor volumes  $V_1$  and  $V_2$ . Does the conversion depend on the individual reactor volumes, or only on the sum,  $V_1 + V_2$ ? Provide some physical and/or graphical intuition to justify your finding.

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## Question 3

Jenny is reminiscing about the 'good-old days'. When she was young, men were men, women were women, and engineers didn't waste time worrying about anything as mundane as process safety. She remembers working on the production of phthalic anhydride by the oxidation of naphthalene:



This reaction occurred in the gas phase inside long tubes containing the peletized catalyst  $\text{V}_2\text{O}_5$ . Even though it was an extremely exothermic reaction, the temperature was controlled very accurately at around  $355^\circ\text{C}$  by submerging the tubes in a bath of boiling mercury. (This is true! Here's the patent: <https://tinyurl.com/ya6nhg5a>.) The mercury vapor was continually captured, condensed and returned to the bath, and in this way, provided the pressure stayed constant, the temperature of the bath couldn't change by so much as  $1^\circ\text{C}$ . Those were the days!

Jenny has challenged you to figure out how long the tubes had to be for some degree of conversion to occur. Rather than accounting for the exact dynamics of the catalyst (we'll cover this later!) simply assume that the reaction is first order in both naphthalene and oxygen with reaction rate constant  $k_2$ . The inlet volumetric flow rate was  $v_0$ , the tube radius was  $R$ , and the inlet contained a stoichiometric mixture of oxygen and naphthalene with naphthalene concentration equal to  $C_{A0}$  (and, of course, oxygen concentration equal to  $9/2 \times C_{A0}$ .) Assuming perfect plug flow, find a relationship between the reaction conversion and the length of the tubes.

*Bonus:* Thinking back, Jenny is wondering whether adding extra  $\text{O}_2$ , beyond the stoichiometric minimum, would increase the rate of reaction and in turn shorten the length of the tubing. If the molar flow rate of  $\text{O}_2$  were multiplied by some factor  $\alpha$ , while the molar flow rate of naphthalene were held constant (note that this will increase the inlet volumetric flow rate!), how would this affect the length of the tubing required? Find a relationship between  $\alpha$  and the tube length.

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**Question 4**

Alice has realised that it may be possible to conduct the reaction she was working on last week more efficiently using a combination of a plug flow and a MFR reactor in series! To jog your memory, she had found that for the isothermal, liquid phase reaction



with initial concentration  $C_{A0}$ , the reaction rate varied according to:

$$r_A = -\frac{k}{((X_A - 0.5)^2 + 0.5)}. \quad (5)$$

If Alice can place an MFR and a PFR in series (in either order), and if she requires a final reaction conversion of  $X_{Af}$  (for this problem we will assume  $X_{Af} > 0.5$ ) find the volumes of each reactor,  $V_{MFR}$  and  $V_{PFR}$  which minimise the total volume  $V = V_{MFR} + V_{PFR}$ . Assume the volumetric flow rate is  $v$ , and initial concentration  $C_{A0}$ . If she could use more MFR's or PFR's in series, could she reduce the total volume further? You may solve this algebraically, but (*hint!*) a graphical solution may be simpler.

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**Super-Duper-Tricky-Fredo-Frog-Challenge-Question!**

**Note:** This is a challenging problem. Any student who can solve this by next week's tutorial will be eligible for a Fredo Frog.

*After the runaway success of his auto-inflating balloons, Erico is on the hunt for more inventive party paraphernalia! His housemate Kevin has a disco party coming up next week, and he wants to incorporate some glow-in-the-dark colours into the party decorations. He's identified the following reaction:*



*which occurs in the aqueous phase, and which is first order in A and also in B. The reaction is isothermal, but it releases a beautiful pink light as long as it is occurring, which will match Erico's favourite dancing shoes perfectly! There's only one problem. The reaction doesn't last long, and Erico needs a way to continually resupply the reactants. He's come up with the following idea.*

*Erico has placed two large tanks on the roof of the house - one contains a solution of A, the other a solution of B. These tanks each have a tap at their base, and through the course of the disco, equimolar amounts of A and B will flow out of these taps, and will be mixed together into one thin, transparent, long pipe. Erico will wrap this pipe all around the walls of the disco party, and as A and B flow through the pipe, they'll react and cause the whole room to glow pink!*

*Erico's trying to figure out how long his pipe should be. The reaction is quite fast, and if the pipe is too long, it's end won't glow. Erico has modelled his pipe as a plug flow reactor, however you're convinced that's a bad idea! Laminar flow inside thin pipes does not obey perfect plug flow. Plug flow assumes the velocity at the middle of the pipe and near the wall are the same, but in laminar flow this isn't true: the flow is slow near the pipe wall (and in fact it is zero at the wall) and fast in the middle of the pipe. You know that the velocity in the pipe is related to the radius by the following expression:*

$$v(r) = \frac{2\nu}{\pi R^2} \left( 1 - \left( \frac{r}{R} \right)^2 \right). \quad (7)$$

*where  $v$  is the liquid velocity,  $R$  the internal radius of the pipe, and  $\nu$  is the volumetric flow rate of the liquid (be careful not to get this confused with  $v$ : the SI units of  $\nu$  will be  $\text{m}^3 \text{s}^{-1}$ , while the SI units of  $v$  will be  $\text{m s}^{-1}$ .) In laminar flow, we ignore radial mixing: reactants that enter near the middle of the pipe stay in the middle, and travel through the pipe very quickly (they're on the fast lane in the highway!) Reactants that enter the pipe near the wall are stuck in the slow lane and travel through the pipe much more slowly. In general, in laminar flow, as a molecule travels through the pipe, the distance it is from the wall stays constant. We may assume that A and B are large molecules, so diffusion effects may be ignored in this problem.*

*If the initial concentrations of A and B (after the two streams have been mixed) are the same and are both equal to  $C_{A0}$ , and if the second-order reaction rate constant is  $k_2$ , find an expression for the average reaction conversion inside the pipe as a function of the pipe length. How does this compare with the assumption of perfect plug flow? Has Erico under or overestimated the length of pipe he can use?*

## Solutions

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### Question 1a

The design equation for a CSTR is

$$\tau = \frac{V}{v} = \frac{C_{A0} - C_A}{-r_A} \quad (8)$$

and for a second order reaction,

$$\frac{V}{v} = \frac{C_{A0} - C_A}{k_2 C_A^2} \quad (9)$$

Over our first reactor, then,

$$\frac{V_1}{v} = \frac{C_{A0} - C_{Am}}{k_2 C_{Am}^2} \quad (10)$$

where  $C_{Am}$  is the concentration coming out of the first reactor and entering the second reactor, i.e. the middle concentration between the reactors. For the second reactor,

$$\frac{V_2}{v} = \frac{C_{Am} - C_A}{k_2 C_A^2} \quad (11)$$

where  $C_A$  is the concentration coming out of the second reactor. We can also write these in terms of the conversion at the midpoint,  $X_{Am} = 1 - C_{Am}/C_{A0}$ , and the final conversion  $X_A = 1 - C_A/C_{A0}$ :

$$\frac{V_1}{v} = \frac{C_{A0} X_{Am}}{k_2 C_{A0}^2 (1 - X_{Am})^2} \quad (12)$$

and

$$\frac{V_2}{v} = \frac{C_{A0} (X_A - X_{Am})}{k_2 C_{A0}^2 (1 - X_A)^2} \quad (13)$$

In problems like this with reactors in series, we typically get several equations - one for each reactor - and we want to use these equations to eliminate the ‘internal’ variables - i.e. the concentrations, conversions, etc. in the internal streams between the reactors. For this problem, the one internal variable we have in (12) and (13) is  $X_{Am}$ , and we can combine both of these equations to eliminate  $X_{Am}$ . In particular, rearranging (13) we get:

$$X_{Am} = X_A - \frac{V_2}{v} k_2 C_{A0} (1 - X_A)^2 \quad (14)$$

and substituting this into (12) we get

$$k_2 C_{A0} \frac{V_1}{v} = \frac{(X_A - \frac{V_2}{v} k_2 C_{A0} (1 - X_A)^2)}{(1 - (X_A - \frac{V_2}{v} k_2 C_{A0} (1 - X_A)^2))^2} \quad (15)$$

This is the relationship between  $V_1$ ,  $V_2$  and  $X_A$  we were looking for. Note that the conversion only depends upon 2 dimensionless volumes,  $\alpha \equiv k_2 C_{A0} \frac{V_1}{v}$  and  $\beta \equiv k_2 C_{A0} \frac{V_2}{v}$ .

$$\alpha = \frac{(X_A - \beta(1 - X_A)^2)}{(1 - (X_A - \beta(1 - X_A)^2))^2} \quad (16)$$

It would be interesting to make a plot of  $X_A$  vs these two parameters and see how it varies.

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### Question 1b

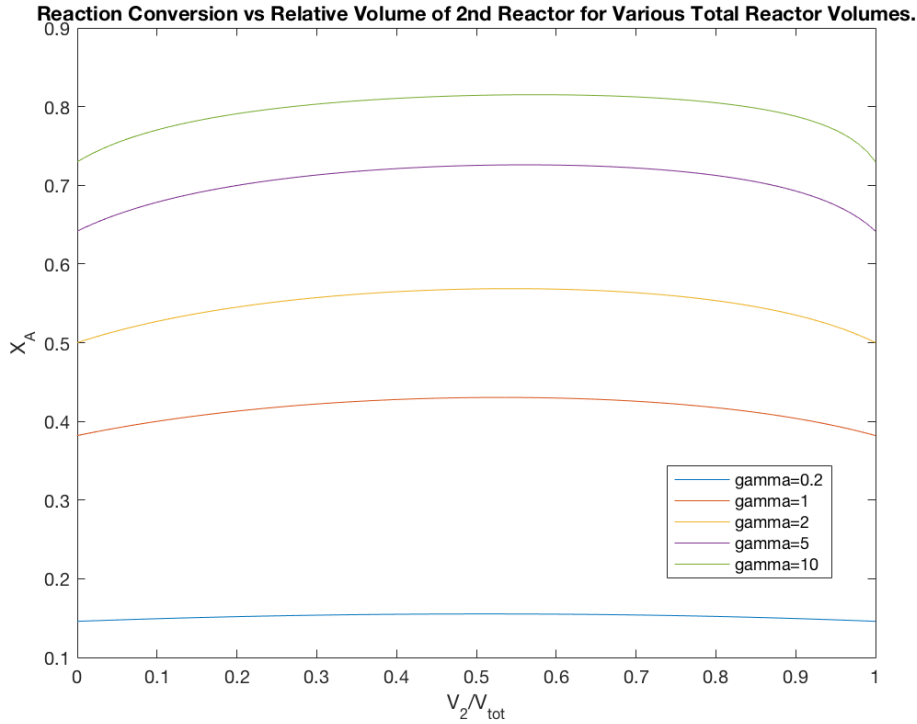
To solve this question, we note that constraining  $V_1 + V_2 = V_{tot}$  is equivalent to constraining  $\alpha + \beta = \gamma$ , where  $\gamma$  is some constant. Thus we can write

$$\gamma - \beta = \frac{(X_A - \beta(1 - X_A)^2)}{(1 - (X_A - \beta(1 - X_A)^2))^2} \quad (17)$$

which, for any given  $\gamma$ , gives us a relationship between  $X_A$  and  $\beta$ . We can then solve this equation for various values of  $\beta$  with  $0 \leq \beta \leq \gamma$  to see what values of  $\beta$  maximise  $X_A$ . Doing this in MATLAB gives the following graph, where  $V_2/V_{tot}$  (i.e.  $\beta/\gamma$ ) is plotted against the conversion  $X_A$ . We see that it looks like having slightly larger second reactor gives better conversion than spreading the volume out equally. It should also be possible to find a numerical expression for this maximum value, though the calculus is a bit messy.

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### Question 1c



For this question, we want to constrain  $X_A$  to some constant value, and find  $\beta$  that minimises  $\gamma$ . Once again, the simplest approach is just to plot  $\gamma$  vs  $\beta$  for constant  $X_A$  (based on (17)) and see where the minimum is. Doing this in the figure below, we see that the volume of the two MFR's is typically minimised when the second tank is about 60% of the total volume, and the first tank is about 40%. We also see that when only 50% conversion is required, the two CSTR's require about 75% of the volume of a single CSTR achieving the same conversion, but when 90% conversion is required, the two CSTR's need only be 30% of the total volume of a single CSTR. Thus, when very large conversions are required, having multiple CSTR's (or a PFR) becomes more and more important. A more sophisticated approach would be to take fix  $X_A$  as constant in (17) and solve  $d\gamma/d\beta = 0$ .

Once again, this is all a little messy, and we're dealing with a relatively simple kinetic expression ( $r_A = -kC_A^2$ ) and only 2 CSTR's in series! This is the benefit of a graphical approach: it simplifies a lot of the mathematics. The graphical solution to this problem is described in the notes. Do you see the simple analytical trick that the graphical solution suggests?

## Question 2

It is relatively simple to show that two plug flow reactors in series with identical internal conditions (i.e. identical temperature, reaction rate constants, etc.) are equivalent to a single plug flow reactor. The design equation for the first reactor in the series is:

$$\tau = \int_{C_{Am}}^{C_{A0}} \frac{dC_A}{-r_A} \quad (18)$$

where  $C_{Am}$  is the concentration in the middle stream between the two reactors. For the second reactor in the series

$$\tau_2 = \int_{C_A}^{C_{Am}} \frac{dC_A}{-r_A} \quad (19)$$

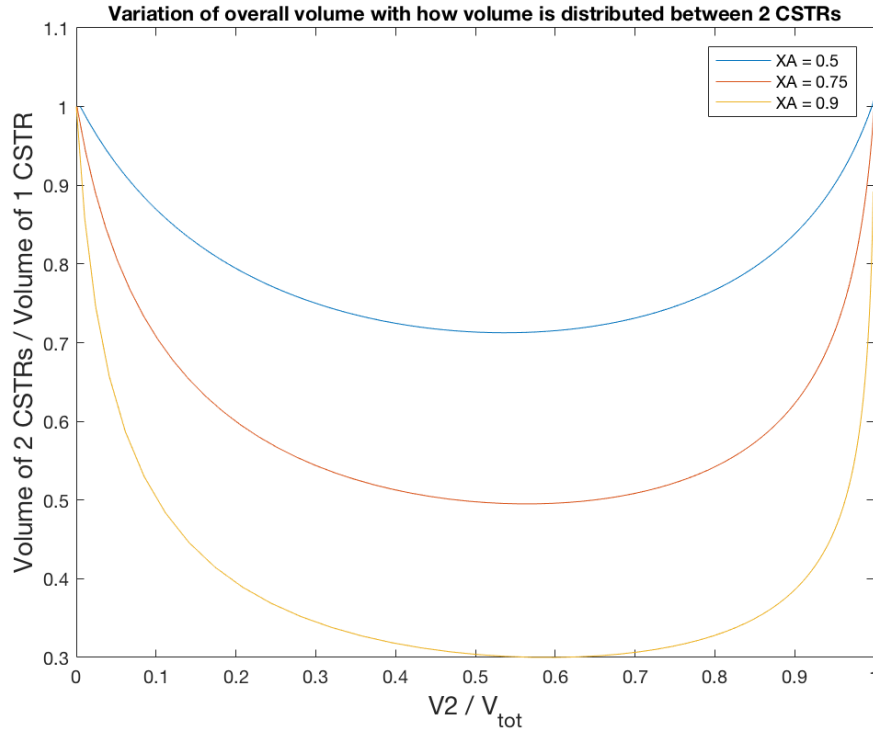
It is clear that the total volume of the two reactors is

$$\tau_{tot} = \tau_1 + \tau_2 = \int_{C_{Am}}^{C_{A0}} \frac{dC_A}{-r_A} + \int_{C_A}^{C_{Am}} \frac{dC_A}{-r_A} = \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A} \quad (20)$$

which is just the design equation for a single PFR. Thus all that matters for the conversion is the total volume  $V = V_1 + V_2$ , and the question reduces to a standard question, where we try to find the volume of a single plug flow reactor with volume  $V = V_1 + V_2$ . Note that this is not the same as in the MFR case, where the conversion for two reactors of volume  $V_1$  and  $V_2$  in series was *not* the same as the conversion in a single MFR of volume  $V_1 + V_2$ .

For this problem,  $C_B = C_{A0} - 2(C_{A0} - C_A) = 2C_A - C_{A0}$  and the design equation is

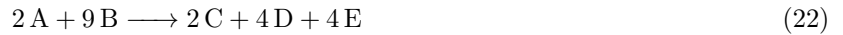
$$\tau = \frac{V_1 + V_2}{v} = \int_{C_{Af}}^{C_{A0}} \frac{dC_A}{k_2 C_A (2C_A - C_{A0})} \quad (21)$$



which can be integrated to find the final outlet concentration  $C_{Af}$  in terms of  $V_1 + V_2$ .

### Question 3

We can rewrite the chemical equation as



This is a gas phase equation, and so there will be a small degree of volume change due to the reaction. For this case, complete conversion of  $A$  will reduce the volume by a factor of 10/11, and so  $\varepsilon_A = -1/11$ . If we have a stoichiometric mixture  $X_A = X_B$ , and  $C_{B0} = 9/2C_{A0}$  and so, for perfect batch flow we have

$$\frac{\tau}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A(1 + \varepsilon X_A)} = \int_0^{X_A} \frac{dX_A}{9/2 \times C_{A0}^2 (1 - X_A/11)(1 - X_A)^2} \quad (23)$$

We can then evaluate this integral to find  $V$  as a function of the final concentration.

### Question 4

The volume of a MFR is given by:

$$V = vC_{A0} \frac{X_{Af} - X_{A0}}{-r_A(X_{Af})} \quad (24)$$

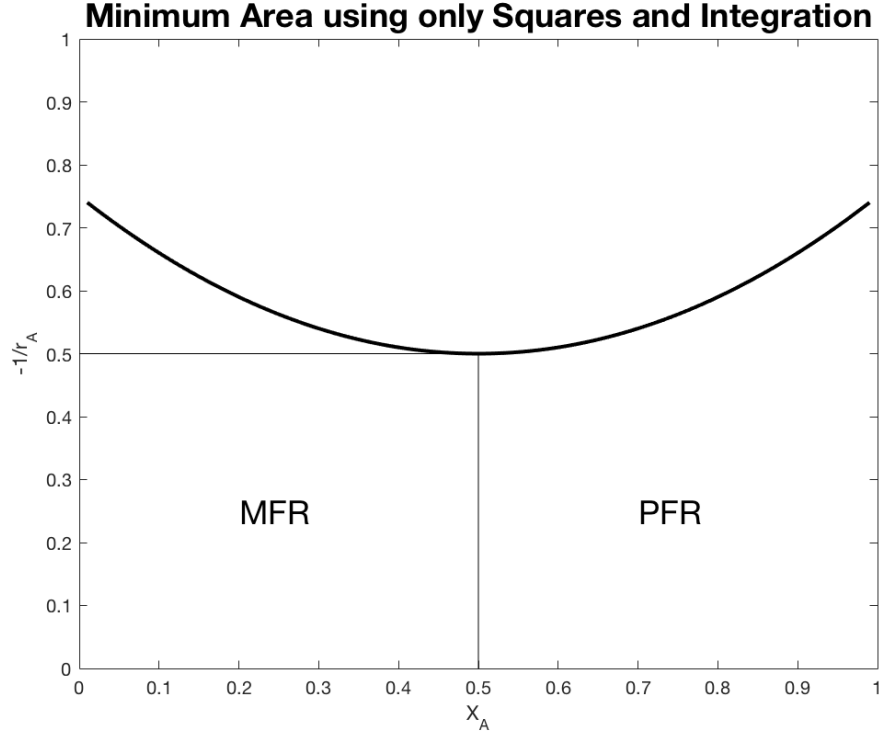
while for a PFR,

$$V = vC_{A0} \int_{X_{A0}}^{X_{Af}} \frac{dX_A}{-r_A}. \quad (25)$$

In other words, for a PFR the volume is proportional to the area under a plot of  $-r_A$  vs  $X_A$  from  $X_{A0}$  up to the final conversion, while the volume of an MFR is proportional to the area of a square on the same plot with corners at  $(X_{A0}, 0)$  and  $(X_{Af}, -1/r_A(X_{Af}))$ . We want to minimise the area. It is clear graphically that the area is minimised when we first place an MFR so that the conversion coming out of the MFR is 0.5, and we then place a PFR after this to reach the final conversion  $X_{Af}$ .

### Fredo-Frog-Challenge-Question

The simplest way to approach to this problem is to realise that the laminar pipe can be divided into many small annuluses, of length  $L$ , internal radius  $r$  and external radius  $r + \Delta r$ , where  $\Delta r$  is very, very small. The liquid flowing down the pipe flows at constant velocity and stays at constant radius, never leaving its little annulus. Thus, each annulus may be thought of as a little plug flow reactor. We will use ' $|_r$ ' below to refer to values specific to a specific annulus at radius  $r$ . The volume of an annulus will be  $V|_r \equiv 2\pi r \Delta r \times L$ , the liquid velocity



inside the annulus will be  $2\nu/(\pi R^2)(1 - r^2/R^2)$ , and the volumetric flow rate inside the annulus is given by  $\nu|_r \equiv 2\pi r \Delta r \times 2\nu/(\pi R^2)(1 - r^2/R^2) = 4\pi r \Delta r \nu/R^2(1 - r^2/R^2)$ . The design equation for our reactor is:

$$\tau = \int_{C_{A0}}^{C_A} \frac{dC_A}{-r_A} \quad (26)$$

and as  $C_A = C_B$  we have  $r_A = -k_2 C_A C_B = -k_2 C_A^2$ , so

$$\tau k_2 = \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = \frac{1}{C_A} - \frac{1}{C_{A0}} \quad (27)$$

or

$$C_A = \frac{C_{A0}}{1 + \tau k_2 C_{A0}}. \quad (28)$$

Now, the residence time for an annulus at radius of  $r$  is

$$\tau|_r = \frac{V|_r}{\nu|_r} = \frac{2\pi r \Delta r \times L}{2\pi r \Delta r \times 2\nu/(\pi R^2)(1 - r^2/R^2)} = \frac{L}{2\nu/(\pi R^2)(1 - r^2/R^2)} \quad (29)$$

and substituting (29) into (28) will give us the concentration of the liquid coming out of the annulus at radius  $r$ ,  $C_A|_r$ . We now need to convert this to an average concentration from all the annuluses. This will be given by summing up all the  $A$  coming out of all the annuluses and dividing by the total flow rate:

$$\frac{\sum C_A|_r \times \nu|_r}{\nu} = \frac{1}{\nu} \int_0^R \frac{C_{A0}}{1 + \tau|_r k_2 C_{A0}} \cdot 2\pi r \times 2\nu/(\pi R^2)(1 - r^2/R^2) dr = \frac{1}{\nu} \int_0^R \frac{4C_{A0} r \nu/R^2}{1 + \tau|_r k_2 C_{A0}} \left(1 - \frac{r^2}{R^2}\right) dr \quad (30)$$

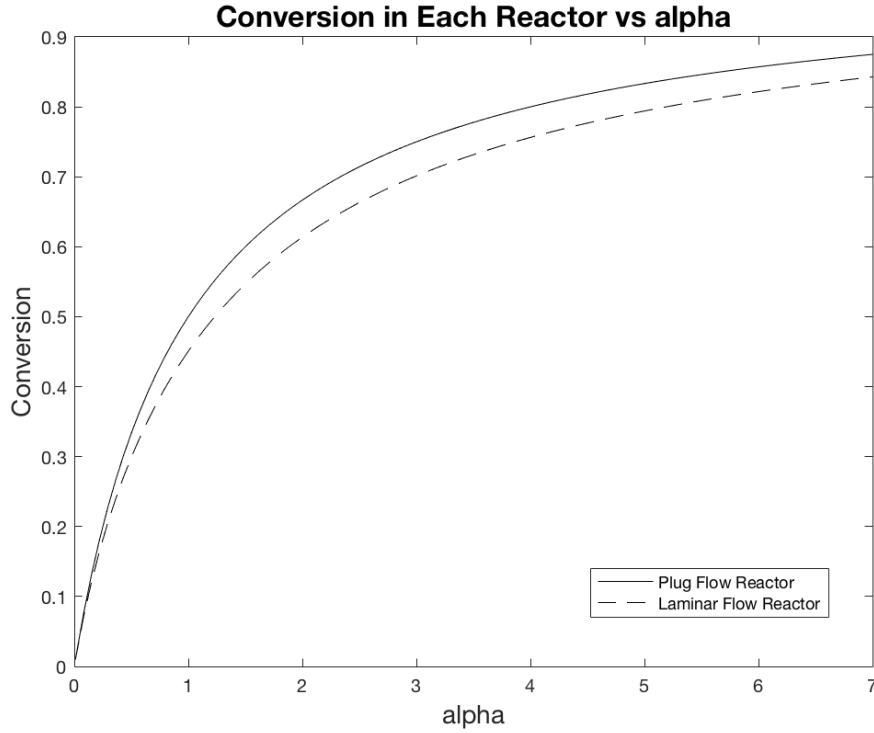
$$\bar{C}_A = \frac{4C_{A0}}{R^2} \int_0^R \frac{r}{1 + \tau|_r k_2 C_{A0}} \left(1 - \frac{r^2}{R^2}\right) dr \quad (31)$$

subbing in (29),

$$\bar{C}_A = \frac{4C_{A0}}{R^2} \int_0^R \frac{r}{1 + \frac{k_2 C_{A0} \pi R^2 L}{2\nu(1 - r^2/R^2)}} \left(1 - \frac{r^2}{R^2}\right) dr \quad (32)$$

We can rearrange this to a dimensionless form:

$$\bar{X}_A = 1 - 4 \int_0^1 \frac{\bar{r} (1 - \bar{r}^2)^2}{1 + \alpha/2 - \bar{r}^2} d\bar{r} \quad (33)$$



where  $\bar{r} = r/R$ ,  $\bar{X}_A$  is the mean conversion of  $A$  coming out of the pipe, and the one parameter that determines the conversion,  $\alpha$ , is

$$\alpha = \frac{k_2 C_{A0} \pi R^2 L}{\nu} = \tau k_2 C_{A0} \quad (34)$$

where  $\tau$  is the mean residence time in the reactor.

This should be compared with the normal plug flow reactor,

$$\frac{\tau}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} = \int_0^{X_A} \frac{dX_A}{k_2 C_{A0}^2 (1 - X_A)^2} \quad (35)$$

$$\tau k_2 C_{A0} = \int_0^{X_A} \frac{dX_A}{(1 - X_A)^2} = \frac{1}{1 - X_A} - 1 = \frac{1}{1 - X_A} - \frac{1 - X_A}{1 - X_A} = \frac{X_A}{1 - X_A} \quad (36)$$

Or, in other words,

$$\frac{X_A}{1 - X_A} = \alpha \quad (37)$$

$$X_A = \frac{\alpha}{\alpha + 1} \quad (38)$$

We now may now compare the laminar-flow reactor conversion given by (33) with the plug flow conversion given by (38). It is simplest to do this numerically, calculating the conversions as a function of  $\alpha$ . The results are plotted below. We see that, for a given conversion, the laminar flow reactor requires a slightly larger  $\alpha$  - typically around 10% bigger. This corresponds to 10-20% greater volume, and suggests that, if Erico had based his calculations on a plug flow assumption, the last 10-20% of his reactor may be dark, with no chemical reaction occurring :(