

Reactor Engineering Week 4 Problem Set

Question 1

The following reaction,



occurs in a constant pressure, variable volume, isothermal batch reactor. The forward reaction is first order in A and in B , while the backward reaction is second order in R . Initially, $C_{A0} = 3C_{B0}$, while $C_{R0} = 0$. Find a relationship between X_A and time in terms of the variables of the problem.

Question 2a - Alice's new reactor.

Alice is back on the hunt for another get-rich-quick scheme. She's noticed that the following liquid-phase reaction:



is always conducted in a mixed flow reactor. However, she's heard that plug flow reactors are much more efficient, and she thinks she may be able to design a new reactor that's much smaller than the CSTR (this is another name for a mixed flow reactor - a **C**ontinuously **S**tirred **T**ank **R**actor.) If she can patent a smaller, more efficient design, it might be her big break!

To help with her design, Alice measured the reaction rate, r_A , at various conversions $X_A = 1 - C_A/C_{A0}$, where C_{A0} is the concentration of the feed going into the reactor. She found they fit the following equation quite well:

$$r_A = -\frac{k}{((X_A - 0.5)^2 + 0.5)} \quad (3)$$

where k is a reaction rate constant. This clearly isn't an elementary reaction!

Assuming that the feed concentration and flow rates are identical in each case, use the design equations for the mixed flow reactor,

$$\frac{V}{F_{A0}} = \frac{X_{Af}}{-r_A|_{X_A=X_{Af}}} \quad (4)$$

and the plug flow reactor,

$$\frac{V}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}, \quad (5)$$

to calculate the ratio of the reactor volumes, V_{PFR}/V_{CSTR} , as a function of final reaction conversion X_{Af} . Is a plug flow reactor clearly better than a mixed flow reactor at all conversions? Find the point where the two reactors will be of equal volume. If only 50% conversion is required in the final product stream, how promising is Alice's PFR design?

Question 2b

Illustrate what's happening graphically in a plot of $-1/r_A$ vs X_A (the plot of $-1/r_A$ may just be qualitative, but it should have the right shape). Show how the reactor volumes can be represented as areas on this plot.

Question 3 - At least Alice's idea was good...

Most reactions are not as strange as the one Alice encountered in the last question. Usually, $-r_A$ increases with C_A , or mathematically, $-\partial r_A / \partial C_A > 0$. If this is true for a liquid-phase, irreversible, isothermal reaction of the form:



prove (either graphically or mathematically) that for the same feed flow rates and conditions, and to achieve the same outlet conversion X_{Af} , the plug flow reactor will have smaller volume than the mixed flow reactor.

Question 4 - Derivations

Derive equations (4) and (24) above from first principles. Memorising them is useless. *Understanding* them and how to derive them is one of the most important parts of this course.

Question 5 - Exam Training! Every Kind of Reactor!

The following reaction,



occurs at a constant temperature. The forward reaction is first order in A and in B , and the backwards reaction is first order in C .

Question 5a

If the reaction occurs in a constant volume batch reactor with $C_{B0} = 2C_{A0}$, while $C_{R0} = 0$, find an expression relating X_A and time.

Question 5b

If the reaction occurs in the gas phase in a variable volume batch reactor at constant pressure with $C_{B0} = 2C_{A0}$, while $C_{R0} = 0$, find an expression relating X_A to time.

Question 5c

If the reaction occurs in the liquid phase in a mixed flow reactor with inlet flows such that $F_{B0} = 2F_{A0}$ and $F_{R0} = 0$, find an expression relating the conversion in the product stream, X_{Af} , to the reactor volume V .

Question 5d

If the reaction occurs in the liquid phase in a plug flow reactor with inlet flows such that $F_{B0} = 2F_{A0}$ and $F_{R0} = 0$, find an expression relating the conversion at the reactor outlet, X_{Af} to the reactor volume V .

Question 5e

If the reaction occurs in the gas phase in a constant pressure mixed flow reactor with inlet flows such that $F_{B0} = 2F_{A0}$ and $F_{R0} = 0$, find an expression relating the conversion in the product stream, X_{Af} , to the reactor volume V .

Question 5f

If the reaction occurs in the gas phase in a constant pressure plug flow reactor with inlet flows such that $F_{B0} = 2F_{A0}$ and $F_{R0} = 0$, find an expression relating the conversion at the reactor outlet, X_{Af} to the reactor volume V .

Super-Tricky-Fredo-Frog-Challenge-Question

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

Jeremy has just received his brand new mixed flow reactor from Amazon, the MFR-3000[®]! Stuffing his old batch reactors in his brother's bedroom, he sets up his MFR and wonders at all the things he could do.

A particular question has bothered him since he took reactor engineering last semester. Why do MFR's run continuously, at constant volume? Would it be better if they ran in an oscillatory way? Jeremy's going to find out! He's going to investigate the first-order, isothermal, liquid-phase reaction:



Jeremy's reactor has a volume of V and the inlet flow-rate and inlet concentration are held constant at Q_0 and C_{A0} . The outlet flow-rate, on the other hand, will oscillate (Jeremy's installed a valve to control the flow rate) according to

$$Q = Q_0 - \frac{2V\omega}{5} \cos \omega t. \quad (9)$$

Where ω is the oscillation frequency. The tank will start half-full with concentration C_{A0} , so that with the oscillatory motion (9) the tank will fill to 90% of V then empty to 10% each cycle. Assume that at all times the tank remains well mixed. Over many cycles, what is the mean conversion of A in the outlet liquid stream? How does this compare with the standard situation, where the volume was held constant at V ?

Solutions

Question 1 The reaction rate of A is given by:

$$r_A = -k_1 C_A C_B + k_2 C_R^2 \quad (10)$$

and for a constant volume batch reactor,

$$t = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A(1 + \varepsilon_A X_A)} \quad (11)$$

If we can express r_A in terms of X_A , we will be able to solve the problem. For a start, we know that

$$C_A = C_{A0} \frac{1 - X_A}{1 + \varepsilon_A X_A} \quad (12)$$

We know from the stoichiometry that the amount of A and B reacted are related by:

$$2N_{A0}X_A = N_{B0}X_B \quad (13)$$

and, as $N_{A0} = 3N_{B0}$,

$$6X_A = X_B. \quad (14)$$

Similarly, the amount of R produced is double the amount of A consumed, so

$$2N_{A0}X_A = N_R \quad (15)$$

and so

$$C_R = \frac{N_R}{V} = 2C_{A0} \frac{1 - X_A}{1 + \varepsilon_A X_A} \quad (16)$$

Finally, we need ε_A . Lets take a basis of $N_{B0} = 1$ mole. Then initially, we have 4 moles of gas. When all the B is consumed, we will have 2.5 moles of A , no moles of B and 1 mole of R . Conversion of A is $1 - 2.5/3 = 1.6$, and the moles changes to 3.5. Thus,

$$V = V_0(1 + \varepsilon X_A) \quad (17)$$

$$3.5 = 4(1 + \varepsilon \times 1/6) \quad (18)$$

$$\varepsilon_A = -0.75. \quad (19)$$

Substituting everything in,

$$t = \int_0^{X_A} \frac{dX_A}{\left(k_1 C_{A0} \frac{1 - X_A}{1 - 0.75X_A} \times C_{A0}/3 \frac{1 - 6X_A}{1 - 0.75X_A} - k_2 \left(2C_{A0} \frac{1 - X_A}{1 - 0.75X_A} \right)^2 \right) (1 - 0.75X_A)}. \quad (20)$$

That's a nasty expression - we'd probably want to integrate that numerically!

Question 2a

The CSTR is relatively easy to size. We have

$$\frac{V}{F_{A0}} = \frac{X_{Af}}{-r_A|_{X_A=X_{Af}}}. \quad (21)$$

and we know that

$$r_A = -\frac{k}{((X_A - 0.5)^2 + 0.5)} \quad (22)$$

so, substituting this in,

$$\frac{V_{MFR}}{F_{A0}} = \frac{X_A((X_A - 0.5)^2 + 0.5)}{k}. \quad (23)$$

For the PFR, we have

$$\frac{V}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}, \quad (24)$$

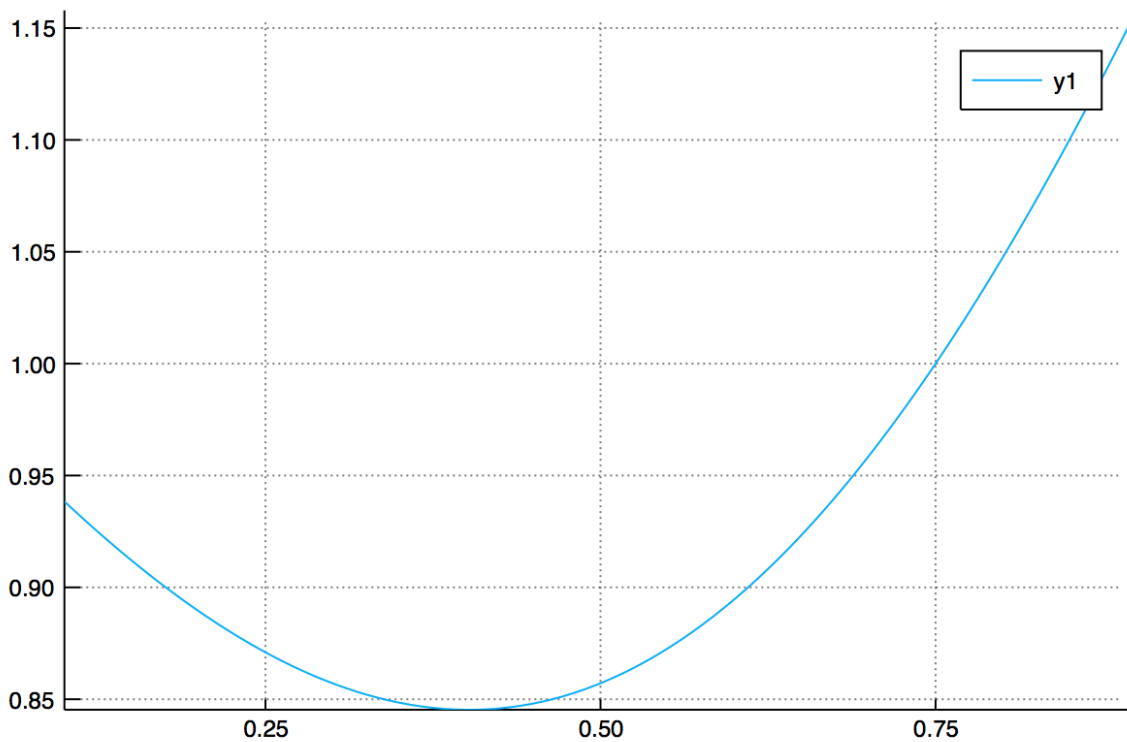


Figure 1: V_{MFR}/V_{PFR} vs X_A for Alice's Reaction.

which gives

$$\frac{V_{PFR}}{F_{A0}} = \int_0^{X_{Af}} \frac{((X_A - 0.5)^2 + 0.5)dX_A}{k} = \frac{1}{k} \left[\frac{(X_A - 0.5)^3}{3} + 0.5X_A \right]_0^{X_A} = \frac{1}{k} \left(\frac{(X_A - 0.5)^3}{3} + 0.5X_A + \frac{1}{24} \right). \quad (25)$$

The ratio of the volumes is then

$$\frac{V_{MFR}}{V_{PFR}} = \frac{X_A(X_A - 0.5)^2 + 0.5X_A}{\frac{(X_A - 0.5)^3}{3} + 0.5X_A + \frac{1}{24}} \quad (26)$$

This is plotted in the figure below. It is clear that the break-even point occurs at $X_A = 0.75$, and the CSTR is actually better than the PFR at 50% conversion.

The reason for this is the strange nature of the reaction. It is faster at lower concentrations of reactants, so the more dilute CSTR mixture is better! This can occasionally happen in practice, and indeed one of the benefits of CSTR is excellent concentration control.

Question 2b

A plot of $-1/r_A$ vs X_A is shown in the figure below. The volume of a PFR that can achieve conversion X_A is equal to the area under this curve from 0 up to X_A , while the volume of the MFR that can achieve conversion X_A is equal to the area of a square with bottom-left vertex at $(0, 0)$ and upper-right vertex lying on the curve at $(-1/r_A, X_A)$. It is clear that for smaller X_A , the squares are smaller than the area under the curve, while for larger X_A , the area under the curve will be smaller.

Question 3

The Figure in Question 2b is odd: typically the reaction rate decreases with X_A , and so the graph of $-1/r_A$ vs X_A will be continually increasing as we go from left to right. Graphically it is clear that, in that case, the area of the square that gives the volume of the CSTR will always be larger than the area under the curve, which gives the volume of the PFR. Thus for any 'normal' decomposition reaction a PFR will have smaller volume than a CSTR.

Question 4

These can be found on p.45-48 of your notes, and also in any textbook on reactor engineering.

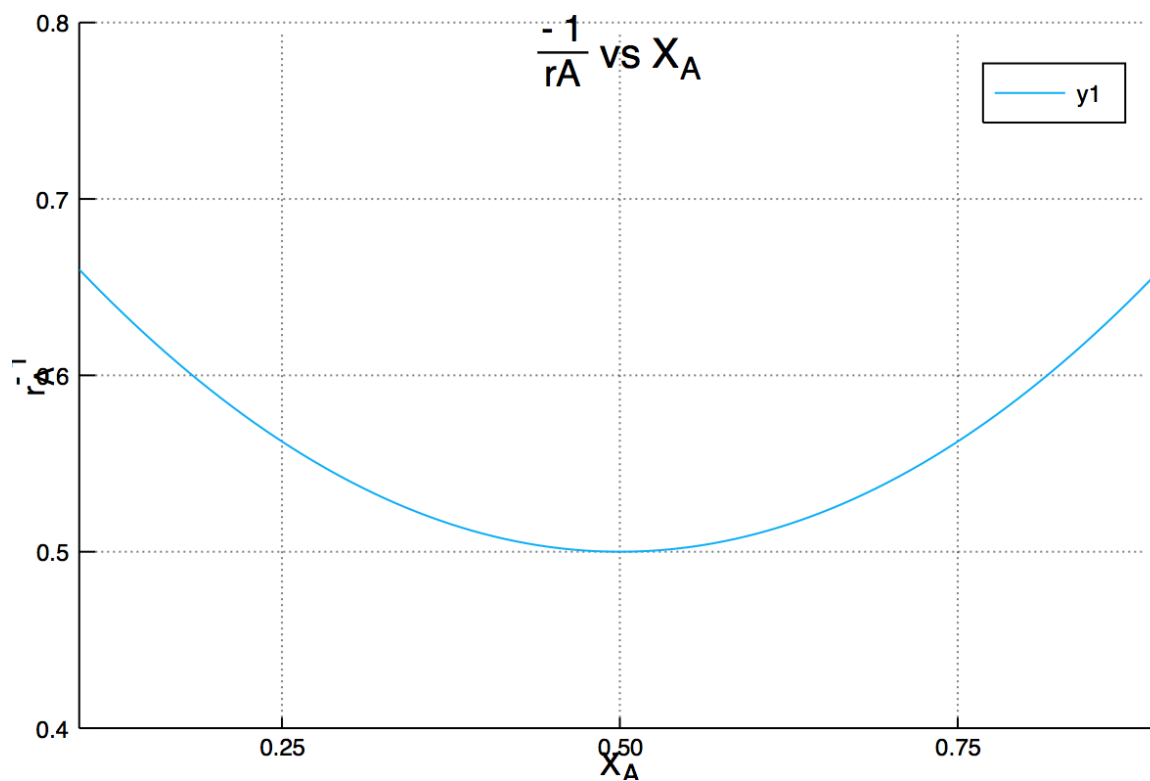


Figure 2: $-1/r_A$ vs X_A for Alice's Reaction.

Question 5

I'm not going to go through all of these. The method is the same as for the various tutorial problems / Q1. If you would like to go through a solution to one of these, please contact me.

Super-Tricky-Fredo-Frog-Challenge-Question

OK, I have a confession to make. This was a little messier than I thought. I hope you had fun! Whenever you're faced with a new problem in chemical engineering, it's good to start with some sort of balance - a mole balance, a mass balance, an energy balance: just find a conserved quantity and look at how it moves around. In our reactor, we can do a mole balance for A :

$$\text{Accumulation of } A = A_{\text{in}} - A_{\text{out}} + A_{\text{created}} - A_{\text{consumed}} \quad (27)$$

or, mathematically,

$$\frac{dN_A}{dt} = F_{A0} - F_A - kC_A V_l(t). \quad (28)$$

where C_A is the concentration in the reactor (which we assume is well mixed and homogeneous throughout) and $V_l(t)$ is the volume of liquid inside the reactor at time t . We know that $F_{A0} = Q_0 C_{A0}$ is a constant, but the other terms will vary with time. The flow out will vary as $F_A = Q(t)C_A = Q(t)N_A/V_l(t)$. Similarly, we can write $kC_A V_l(t) = kN_A/V_l(t) \cdot V_l(t) = kN_A$, giving

$$\frac{dN_A}{dt} = Q_0 C_{A0} - \frac{Q(t)}{V_l(t)} N_A - kN_A. \quad (29)$$

We know that $Q(t)$ is given by

$$Q = Q_0 - \frac{2V\omega}{5} \cos \omega t. \quad (30)$$

and $V_l(t)$ can be calculated by integrating this. According to the question, the liquid volume starts at $V/2$, and it will grow or shrink depending on the difference between the inlet and outlet liquid flows:

$$V_l(t) = \int_0^t (Q_0 - Q) dt + \frac{V}{2} \quad (31)$$

which gives

$$V_l(t) = \frac{V}{2} \left(1 + \frac{4}{5} \sin \omega t \right). \quad (32)$$

We see that the liquid volume does indeed oscillate between $V_l = 0.9V$ and $V_l = 0.1V$ every cycle.

Returning to the mole balance, (29), this is a single differential equation for N_A , that only depends on N_A and time, and has initial condition $N_A|_{t=0} = C_{A0}V/2$. In a sense, deriving (29) is the engineer's job done - now just give the problem to the mathematician in your closet.

Alas, we must continue nonetheless. Numerical integration would be the easiest approach, however as we don't have values for the parameters, we shall proceed analytically. We can rearrange (29) to:

$$\frac{dN_A}{dt} + N_A \left(\frac{Q(t)}{V_l(t)} + k \right) = Q_0 C_{A0} \quad (33)$$

Now, this is a differential equation of the form

$$y' + f(t)y = b \quad (34)$$

and the general solution to these equations is of the form:

$$y(t) = e^{-F(t)} \left(C + b \int_0^t e^{F(t)} dt \right). \quad (35)$$

where C is an integration constant and $F(t)$ is an antiderivative of f , so $F' = f$. In our case

$$f(t) = \frac{Q(t)}{V_l(t)} + k = \frac{2Q_0 - 0.8V\omega \cos \omega t}{V(1 + 0.8 \sin \omega t)} + k \quad (36)$$

so

$$F(t) = \int_0^t \left(\frac{2Q_0 - 0.8V\omega \cos \omega t}{V(1 + 0.8 \sin \omega t)} + k \right) dt \quad (37)$$

and

$$b = Q_0 C_{A0}. \quad (38)$$

Finally, the constant of integration, C , will be equal to $N_A|_{t=0} = C_{A0}V/2$ (as all other values in (35) will either cancel or equal 1 at $t = 0$). Overall, then (hold your breath!):

$$N_A(t) = \exp\left(-\int_0^t \left(\frac{2Q_0 - 0.8V\omega \cos \omega t}{V(1 + 0.8 \sin \omega t)} + k\right) dt\right) \times \left(C_{A0}V/2 + Q_0C_{A0} \int_0^t \exp\left(\int_0^t \left(\frac{2Q_0 - 0.8V\omega \cos \omega t}{V(1 + 0.8 \sin \omega t)} + k\right) dt\right) dt\right). \quad (39)$$

and we're not done yet! That just gives how the moles of A in the reactor change with time. We need to work out the mean outlet concentration over many cycles. But that's quite straightforward. The flow of liquid out is given by:

$$F_A = C_A(t)Q(t) = N_AQ(t)/V_l(t) \quad (40)$$

and we know $N_A(t)$, $Q(t)$ and $V_l(t)$ from the equations above. Finally, the average outlet concentration for some period of time will be the total amount of A that leaves the reactor in that time divided by the total volume leaving the reactor in that time, which will be given by:

$$C_A^{av} = \frac{\int_0^t F_A dt}{\int_0^t Q dt} \quad (41)$$

or,

$$C_A^{av} = \frac{\int_0^t C_A Q dt}{\int_0^t Q dt} = \frac{\int_0^t N_A Q / V_l dt}{\int_0^t Q dt} \quad (42)$$

where once again $N_A(t)$, $V_l(t)$ and $Q(t)$ are given by the equations above. The mean conversion is then given by:

$$X_A^{av} = 1 - \frac{C_A^{av}}{C_{A0}}. \quad (43)$$

When you're stuck with extremely messy equations like this, two paths of action often prove fruitful. The first is to substitute in some real numbers, put it into a computer, and see what the solutions look like. Change some variables, make some plots, and get some intuition. The second often-fruitful approach is to see if you can identify the *dimensionless variables* that actually govern the system's behaviour. If you look back at previous weeks, every challenge question has ultimately reduced to a solution in terms of a few dimensionless numbers: call it my secret subliminal message to you. Often, in dimensionless form, you can *understand* what's actually happening in a system.

In this system, we have lots and lots of variables, but only a few quantities actually matter. If we perform a dimensionless analysis on our system, we find that the mean conversion X_A^{av} (which itself is a dimensionless number) only depends upon a few dimensionless variables: $\alpha = V\omega/Q_0$, $\beta = Vk/Q_0$ and $\bar{t} = Q_0t/V$. Each of these variables has a physical interpretation: α represents the ratio of the typical residence time of a molecule in the reactor to the period of the oscillations in the liquid volume, and β represents the ratio of the residence time to the typical time the reaction takes to occur. The third dimensionless variable is a measure of time, however as we're interested in the average over long time, only α and β will ultimately be important for calculating X_A^{av} .

On the other hand, in a normal CSTR with volume V in which a first order reaction takes place, the conversion is given by:

$$\frac{X_A}{1 - X_A} = \frac{kV}{Q_0} = \beta. \quad (44)$$

In this case, there are no oscillations in volume, so α doesn't matter, and β is the only factor in the system that affects the conversion.

We can compare the two systems by calculating the average conversion for various X_A^{av} in the oscillating tank at large t (i.e. $t \gg 1/\omega, 1/k$) for various values of α and β . We can actually just use the equations above: just set $\omega = \alpha$ and $k = \beta$, and set all other constants equal to 1: this will ensure $\omega V/Q_0 = \alpha$; $kV/Q_0 = \beta$, which is what we require. We then calculate the mean conversion for various values of α and β , and plot them against the ideal CSTR reactor with constant volume equal to $V/2$ (this is the mean liquid volume of our oscillating tank). This plot is shown in the Figure below.

It looks like the oscillating tank never gives as good conversion as the constant-volume CSTR. Faster oscillations in the volume increase average conversion, but never help us to reach the optimal conversion. I don't have a physical explanation for this as yet. But at least we now know the answer to Jeremy's question: not only is oscillatory motion worse than simply using the full tank with volume V , it's worse than using even just half the tank! Nonetheless, there may be other situations where oscillatory CSTR's are useful.

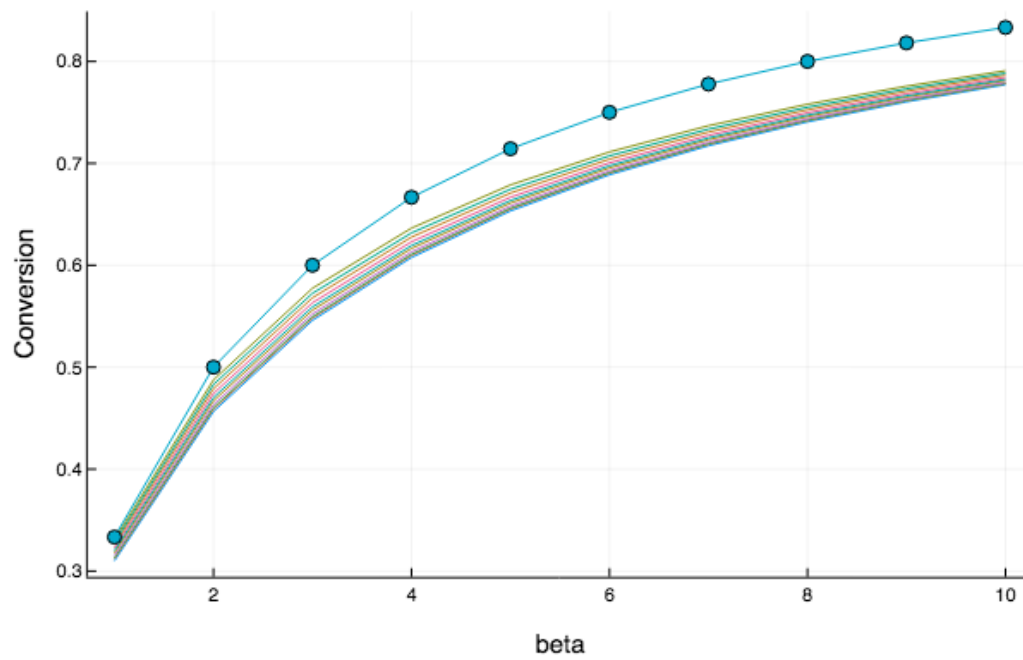


Figure 3: Conversion as a function of α and β . Higher-conversion lines are larger values of α , ranging from 0.5 to 2.5. The top line is a constant-volume CSTR with volume $V/2$.