

Fall 2002. 10.34. Numerical Methods Applied to Chemical Engineering

Homework # 2. Nonlinear algebraic equations

Assigned Friday 9/13/02. Due Wednesday 9/25/02

Problem 1. Tank-draining problem

Let us consider the system below, in which a cylindrical tank of diameter D_{tank} is drained by a cylindrical pipe of length L and diameter D_{pipe} . The fluid in the tank is water, and the tank is exposed to standard atmospheric conditions.

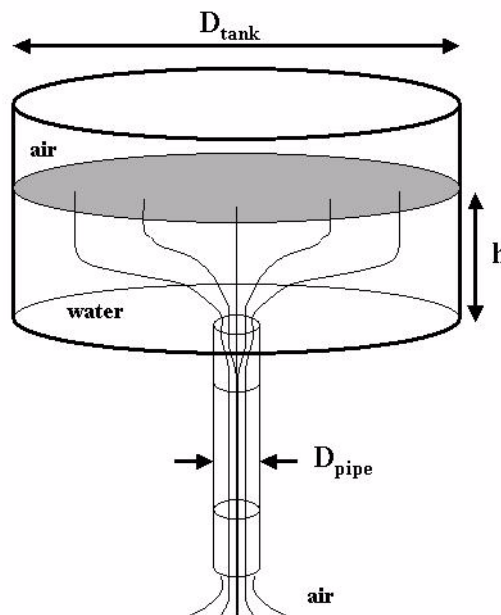


FIGURE 1. Geometry for tank draining problem

To calculate the resistance to flow of the pipe, use the relation from fluid mechanics that the change in dynamic pressure $P = p + \rho gz$ across a pipe of length L and diameter D for flow with a mean velocity v is

$$-\Delta P = f_D \left(\frac{L}{D} \right) \left(\frac{1}{2} \rho V^2 \right) \quad (\text{EQ 1})$$

The Darcy friction factor f_D is related to the Reynolds' number in laminar flow by

$$f_D = \frac{64}{Re} \quad Re < 2100 \quad (\text{EQ 2})$$

and in turbulent flow is related to the Reynolds' number and the surface roughness e by the Colebrook equation,

$$\frac{1}{\sqrt{f_D}} = (-2)\log_{10}\left[\frac{(e/D)}{3.7} + \frac{2.51}{Re\sqrt{f_D}}\right] \quad Re > 2100 \quad (\text{EQ 3})$$

Our pipe is assumed to be commercial steel, for which the effective surface roughness e is 0.045 mm.

You may neglect viscous effects within the bulk of the tank, but include the minor loss due to entrance flow into the pipe,

$$-(\Delta p)_{(entrance)} = 0.5\left(\frac{1}{2}\rho V^2\right) \quad (\text{EQ 4})$$

Question 1.A. Plot the volumetric flow rate out of the tank as a function of h . The diameter of the tank is 2.5 m, the diameter of the drain pipe is 5 cm, and the length of the drain pipe is 2 m.

Question 1.B. From the results of 1.A, starting with an initial depth of water in the tank of 2 m, plot as a function of time the height of water in the tank until it empties.

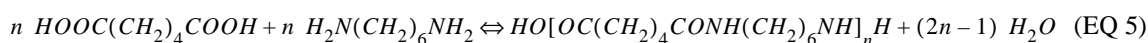
Hint: Try rearranging the equation $h(t + \Delta t) = h(t) + (\Delta t)\frac{dh}{dt}\Big|_{t, h(t)}$.

Problem 2. Modeling steady-state behavior of a Nylon reaction system

Background

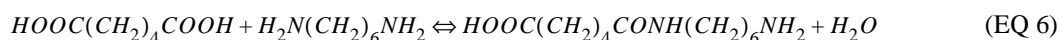
This question considers the application of numerical methods for solving nonlinear algebraic equations to the study of a continuous process for the polymerization of Nylon. The problem statement gives a sufficient description of polycondensation kinetics to answer the questions; however, a more general formulation of a polycondensation kinetic model may be found in Beers and Ray, *J. Appl. Polym. Sci.*, v 79, 246-265, 2001.

The most common form of Nylon, *Nylon-6,6*, is made by polycondensation of the two monomers hexamethylene diamine (HMD) and adipic acid (ADA). The general reaction for the formation of polymer from the diamine and diacid monomers is



The \Leftrightarrow symbol denotes that this reaction is reversible, and is driven to the right by the removal, through evaporation, of the water coproduct. Here, we show n moles of diacid monomer and n moles of diamine producing a polymer that contains (on average) n number of repeat units (the quantity within the brackets that is comprised of one monomer unit each of diacid and diamine). Such a polymer contains $2n$ monomer units, and is said to have a *chain length* of $2n$, or to be a $2n$ -mer.

Because water is produced as a condensate (i.e. a volatile species that evaporates and is recovered through condensation), the method used to synthesize *Nylon-6,6* is known as *condensation polymerization*, although a name that better describes the nature of the process is *stepwise polymerization*. In this approach, we build up high molecular weight polymer step-by-step, where the first step is the combination of two monomer units to form a dimer according to the reaction,



The double-sided arrow denotes that this reaction is reversible, with an equilibrium constant on the order of 100. The mechanism of this reaction under acid catalysis is shown in the figure below. The acid catalyst may be either supplied externally (e.g. *HCl*) or the reaction may be self-catalyzed by the carboxylic acid end groups. The equilibrium constant of this reaction is on the order of 100 because in the amide linkage, $-\text{CONH}-$, the less-electronegative nitrogen is able to donate some electron density to the electron-deficient carbon of the carbonyl group.

The dimer produced by this reaction still has functional groups on both ends, and so may react further to produce even larger molecules. Condensation among larger molecules occurs through the same mechanism as that shown below for monomers, and the reactivity of an end group ($-\text{COOH}$ or $-\text{NH}_2$) is essentially independent of the size of the molecule to which it is attached.

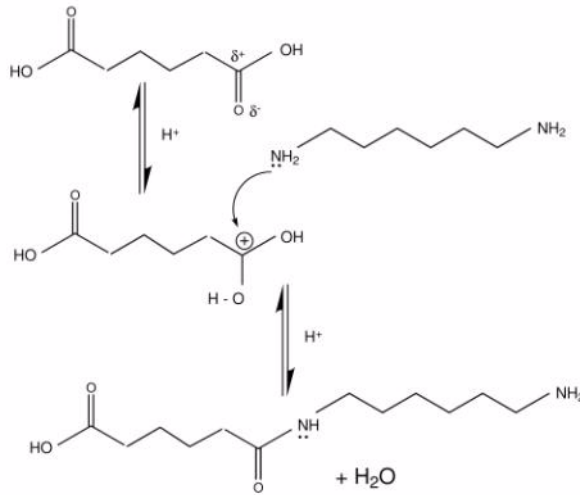
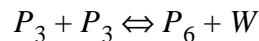
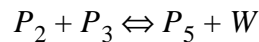
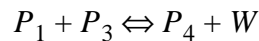
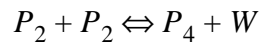


FIGURE 2. Acid-catalyzed condensation among diamine and diacid monomers

To simplify our description, we use the following short-hand notation to represent the reaction among monomers,



P_1 refers to a polymer chain comprised of one monomer unit (i.e., a monomer), and P_2 refers to a chain comprised of two monomer units (a dimer). W represents a water condensate molecule. Because the dimer itself has acid and base groups on both ends, it may react with other monomers, dimers, trimers, etc., to produce larger molecules. The hierarchy of additional reactions that occur during polymerization is



and so on, or in general for $m = 1, 2, 3, \dots$ $n = 1, 2, 3, \dots$,



In the forward direction, the condensation reaction takes the form



Because the reaction may be catalyzed by either an added, “external” acid or be self-catalyzed by the carboxylic acid end groups, the rate constant is written as

$$k_{(fc)} = k_{(fc)}^{(ext)} + k_{(fc)}^{(self)} [A] \quad (\text{EQ 10})$$

[A] is the total concentration of acid end groups. Since each chain contains on average one acid group and one base group, at a given conversion, the total concentration of chains of any length is equal to the concentration of unreacted acid (base) end groups,

$$\sum_{x=1}^{\infty} [P_x] = [A] = [B] \quad (\text{EQ 11})$$

Here we have assumed that the concentrations of acid and base end groups are equal throughout the course of the polymerization. If their initial concentrations are equal and there is no significant loss of either monomer to side-reactions or evaporation, the stoichiometry of the reaction will retain the equimolar balance.

The net rate of change of the m -mer concentration due to the forward-direction condensation reaction among all species is

$$r_{P_m(fc)} = -2k_{(fc)} [P_m] \sum_{n=1}^{\infty} [P_n] + k_{(fc)} \sum_{n=1}^{m-1} [P_n] [P_{m-n}] \quad (\text{EQ 12})$$

The first term is the rate of disappearance of m -mer from reaction with all other species, and the second term is the rate of m -mer creation through the reaction of two smaller species. The factor of 2 in the first term refers to the fact that two modes of addition (at the acid and base ends of the m -mer) both deplete m -mer.

The rates of change of the concentrations of amide linkages [L], water condensate [W], acid end groups [A], and base end groups [B] are easy to calculate,

$$\left. \frac{d[L]}{dt} \right|_{(fc)} = \left. \frac{d[W]}{dt} \right|_{(fc)} = - \left. \frac{d[A]}{dt} \right|_{(fc)} = - \left. \frac{d[B]}{dt} \right|_{(fc)} = k_{(fc)} [A] [B] \quad (\text{EQ 13})$$

In the reverse direction, the condensation reaction becomes



with a reverse rate constant,

$$k_{(rc)} = k_{(fc)} K_{eq}^{-1} \quad (\text{EQ 15})$$

K_{eq} is the equilibrium constant of the reaction, and for Nylon is on the order of 100. This equilibrium constant relates at equilibrium the concentrations of the active end groups, the linkages, and the condensate.

$$K_{eq} = \frac{[CONH]_{eq}[H_2O]_{eq}}{[COOH]_{eq}[NH_2]_{eq}} = \frac{[L]_{eq}[W]_{eq}}{[A]_{eq}[B]_{eq}} \quad (\text{EQ 16})$$

If we assume that the concentrations of acid and base groups are equal throughout the polymerization, we can define a fractional conversion p of the end groups as

$$[A] = [B] = (1 - p)[A]_0 \quad (\text{EQ 17})$$

$[A]_0$ is the initial concentration of acid groups before reaction. If $[P_1]_0$ is the initial concentration of monomers (both diacid and diamine), then since each pair of monomers (one diacid and one diamine) contains two acid groups and two base groups, the initial acid and base group concentrations are

$$[A]_0 = [B]_0 = [P_1]_0 \quad (\text{EQ 18})$$

and the concentration of acid groups at a conversion p is

$$[A] = (1 - p)[P_1]_0 \quad (\text{EQ 19})$$

At complete conversion, each pair of diamine and diacid monomer units contribute two amide linkages. Therefore, the linkage concentration at a conversion p is

$$[L] = p[P_1]_0 \quad (\text{EQ 20})$$

The equilibrium constant, written in terms of the conversion at equilibrium, is therefore

$$K_{eq} = \frac{p_{eq}[P_1]_0[W]_{eq}}{(1 - p_{eq})^2[P_1]_0^2} \quad (\text{EQ 21})$$

If no water is removed from the reaction medium, $[W] = p[P_1]_0$, and the conversion at equilibrium becomes

$$p_{eq} = \frac{2[K_{eq} - \sqrt{K_{eq}}]}{2(K_{eq} - 1)} \quad \text{no removal of W} \quad (\text{EQ 22})$$

The rates of change of the linkage, end group, and condensate concentrations from the reverse reaction are

$$-\left. \frac{d[L]}{dt} \right|_{(fc)} = -\left. \frac{d[W]}{dt} \right|_{(fc)} = \left. \frac{d[A]}{dt} \right|_{(fc)} = \left. \frac{d[B]}{dt} \right|_{(fc)} = k_{(fc)} K_{eq}^{-1} [L][W] \quad (\text{EQ 23})$$

The net rate of change of m -mer concentration due to the reverse reaction is

$$r_{P_m(rc)} = k_{(rc)} W \left[2 \sum_{n=m+1}^{\infty} [P_n] - (m-1)[P_m] \right] \quad (\text{EQ 24})$$

The first term is the rate of production of m -mer through the scission of larger molecules, and the second term is the rate at which m -mer disappears itself when one of its linkages is attacked by water. Since a larger chain can be split in two places to produce a m -mer, the first term carries a factor of 2. Since a m -mer has $(m-1)$ linkages, the second term carries a factor of $(m-1)$.

Using these two expressions, we can calculate the time evolution of the chain length distribution during a batch polymerization by integrating the following set of ordinary differential equations. Since this is an infinite set of equations, we specify a cutoff chain length, m_{cut} , and assume that $[P_m] = 0$ for $m > m_{cut}$.

$$\frac{d[P_m]}{dt} = r_{P_m(fc)} + r_{P_m(rc)} = r_{P_m} \quad m = 1, 2, \dots \quad (\text{EQ 25})$$

In a continuous stirred tank reactor (CSTR), such as those shown in the process diagram below, these rate equations are replaced by the following mass balance on each species, including the fluxes from the inlet and outlet flows.

$$\frac{d}{dt}(V[P_m]) = F\{[P_m]_{(in)} - [P_m]\} + Vr_{P_m} \quad (\text{EQ 26})$$

Dividing by the flow rate through the reactor yields at steady state the following set of nonlinear algebraic equations for the concentrations of each chain length,

$$[P_m]_{(in)} - [P_m] + \theta r_{P_m} = 0 \quad (\text{EQ 27})$$

θ is the residence time of the reactor.

We need also an algebraic equation for the concentration of water in the reaction medium within the CSTR. We assume that each reactor is purged with nitrogen, but that the removal of water is mass-transfer limited. The mass balance for the concentration of water becomes,

$$V \frac{d[W]}{dt} = F\{W_{(in)} - W\} - (k_m A) W + Vr_w \quad (\text{EQ 28})$$

The first term is the net flux into the reactor with the flow and the second is the mass transfer rate of water into the purge gas stream. We assume that the product of the mass transfer coefficient and the area are specified model parameters. The rate of water production due to reaction is

$$r_w = k_{(fc)}[A][B] - k_{(fc)}K_{eq}^{-1}[L][W] \quad (\text{EQ 29})$$

At steady state, the balance on water becomes

$$0 = W_{(in)} - W - [(k_m A/V)\theta]W + \theta r_w \quad (\text{EQ 30})$$

In this problem, we will use various approaches to calculate the properties of the polymer produced in each reactor of the three CSTR system diagrammed below.

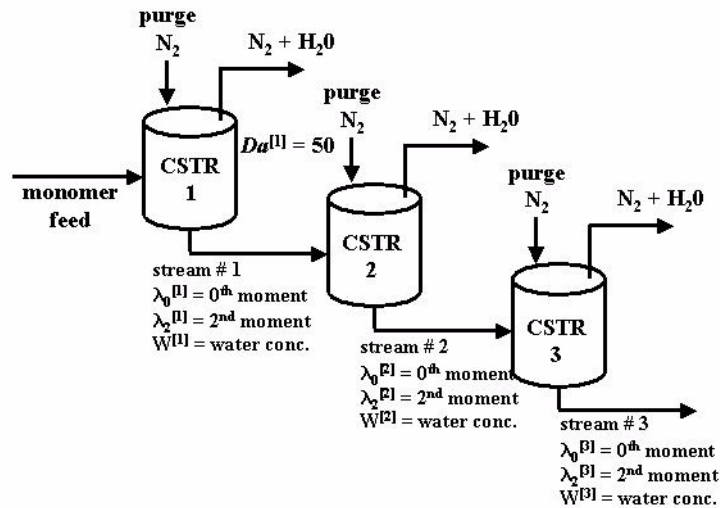


FIGURE 3. Diagram of 3 CSTR process for the production of moderate molecular weight Nylon

PART 2.A. Plots of chain length distribution from batch reaction

Before computing the properties of the polymer produced in the continuous process, we first employ a simple statistical model (developed by Paul Flory, the Nobel laureate chemist who laid much of the foundation of modern polymer science) to calculate the concentrations of each chain length as a function of conversion in a batch reaction. Again, we assume that at all times, the concentrations of acid and base end groups are equal. We now use statistical arguments to reconstruct the chain length distribution (the concentrations of each chain length) from the conversion and the initial monomer concentration.

Let us say that we select, at random, a chain end with an unreacted acid end group and ask the question - what is the length of chain that is attached to this end? At a conversion of p , the probability that the chain is terminated with only one monomer unit is $(1-p)$ and the probability that the other end group of the terminal monomer unit is attached to another unit (so that the chain length is at least two) is p . Let us assume the latter case, and then ask - what is the probability that the second monomer unit is also attached to something else? Again, the probability that the second monomer unit is attached to another, third monomer unit is p , so that the total probability that a randomly-chosen end is attached to a

chain of length 3 or greater is p^2 . We can extend this process to calculate that the probability that a randomly chosen chain end is attached to a chain comprised of at least $x-1$ monomer units is p^{x-1} . At this point, we see that if the next acid group considered remains unreacted, we will have a chain with a total of x monomer units, so that the probability that a randomly chosen acid end group is attached to a chain of exactly x monomer units is $p^{x-1}(1-p)$. The concentration of polymer chains of length x is therefore

$$[P_x] = [A]p^{x-1}(1-p) \quad (\text{EQ 31})$$

Relating $[A]$ to the initial monomer concentration yields the Flory chain length distribution,

$$[P_x] = [P_1]_0 p^{x-1} (1-p)^2 \quad (\text{EQ 32})$$

Question 2.A.1., using this statistical model, plot the chain length distributions at conversions of 25%, 50%, 75%, 90%, 92.5%, 95%, 97.5%, 99%, 99.5%, 99.75%, and 99.9%.

Often we do not need to know the entire chain length distribution, but only wish to know the average size of the polymer chains and some measure of the breadth of the chain length distribution. We can characterize the average size of the molecules and the breadth of the distribution by calculating a few moments of the chain length distribution. We define the k^{th} moment of the chain length distribution, λ_k , as

$$\lambda_k = \sum_{m=1}^{\infty} m^k P_m \quad (\text{EQ 33})$$

Of particular interest are the three leading moments, the zeroth moment (the total number per unit volume of polymer chains)

$$\lambda_0 = \sum_{m=1}^{\infty} P_m \quad (\text{EQ 34})$$

the first moment (the total “mass” per unit volume of polymer chains)

$$\lambda_1 = \sum_{m=1}^{\infty} m P_m \quad (\text{EQ 35})$$

and the second moment,

$$\lambda_2 = \sum_{m=1}^{\infty} m^2 P_m \quad (\text{EQ 36})$$

From these three values, we can calculate the *number-averaged chain length*, $\bar{x}_n = \lambda_1/\lambda_0$, and the *weight-averaged chain length*, $\bar{x}_w = \lambda_2/\lambda_1$. Since the weight-averaged chain length biases more the contributions of the larger chains, $\bar{x}_w \geq \bar{x}_n$, with the equality holding only if all chains are of the same length. The ratio of these two averages, $Z = \bar{x}_w/\bar{x}_n$ (the *polydispersity*), provides a simple measure of the breadth of the chain length distribution. The larger the polydispersity, the greater is the disparity in the lengths (molecular weights) of individual chains. A polydispersity value of one means that all of the polymer chains are of the same length. A large polydispersity means that there are significant numbers of both “small” and “large” chains.

From knowledge of the moments of the chain length distribution, we can also obtain the concentrations of end groups and linkages,

$$[A] = [B] = \lambda_0 \quad [L] = (\lambda_1 - \lambda_0) \quad (\text{EQ 37})$$

Question 2.A.2, use your results from 2.A.1 to plot, as functions of the conversion, the number and weight average chain lengths and the polydispersity. Make sure that you consider high-enough chain lengths in your summation that the weight-averaged chain length and polydispersity converge closely to their true values.

Note that we can calculate directly the number-average chain length since each polymer chain has, on average one acid end group.

$$\bar{x}_n = \frac{[P_1]_0}{[A]} = \frac{[P_1]_0}{[P_1]_0(1-p)} = \frac{1}{1-p} \quad (\text{EQ 38})$$

Question 2.A.3. From your results in 2.A.2, propose the corresponding formulas for \bar{x}_w and Z .

Part 2.B. Modeling the continuous polymerization process

In this section, we compute the properties of the polymer in each of the reactors in the 3-CSTR process shown above. To do so, we derive “mass” balances on each of the three leading moments of the chain length distribution that will allow us to compute the number and weight average molecular weights of polymer in each reactor. We take the mass bal-

ance for each species P_m , multiply it by m^k , and sum over all m to obtain the following “balance” for λ_k ,

$$\frac{d}{dt} \left(V \sum_{m=1}^{\infty} m^k [P_m] \right) = F \sum_{m=1}^{\infty} m^k \{ [P_m]_{(in)} - [P_m] \} + V \sum_{m=1}^{\infty} m^k r_{P_m} \quad (\text{EQ 39})$$

which, after division by the reactor volume, yields,

$$\frac{d\lambda_k}{dt} = \theta^{-1} [\lambda_k^{(in)} - \lambda_k] + r_{\lambda_k} \quad (\text{EQ 40})$$

At steady state, we obtain a nonlinear algebraic equation by setting the time derivative to zero. In these equations, r_{λ_k} is the rate of change, due to reaction, of the k^{th} moment of the chain length distribution. It is computed directly from the rates of change of each species,

$$r_{\lambda_k} = \sum_{m=1}^{\infty} m^k [r_{P_m(fc)} + r_{P_m(rc)}] \quad (\text{EQ 41})$$

After some math, we obtain the following rates of change of the three leading moments due to forward and reverse condensation.

$$r_{\lambda_0} = -k_{(fc)}\lambda_0^2 + k_{(fc)}K_{eq}^{-1}W(\lambda_1 - \lambda_0) \quad (\text{EQ 42})$$

$$r_{\lambda_1} = 0 \quad (\text{EQ 43})$$

$$r_{\lambda_2} = 2k_{(fc)}\lambda_1^2 + k_{(fc)}K_{eq}^{-1}W\frac{1}{3}(\lambda_1 - \lambda_3) \quad (\text{EQ 44})$$

We see that the equation for the second moment calls for the value of the third moment; however, we have not derived an equation for this moment. To “close” the set of equations, we use an approximation for the third moment based on assuming a certain mathematical form of the chain length distribution that is fitted to the values of λ_0 , λ_1 , and λ_2 . We then use the computed third moment of this approximate distribution as the estimate of the third moment in our system. This yields the following closure approximation, the use of which is found to introduce very little error,

$$\lambda_3 \approx \frac{\lambda_2(2\lambda_2\lambda_0 - \lambda_1^2)}{\lambda_1\lambda_0} \quad (\text{EQ 45})$$

Since we can calculate the value of λ_3 directly from the values of λ_0 , λ_1 , and λ_2 , this equation is called an *auxiliary equation* and is not added to the system of nonlinear algebraic equations.

Question 2.B.1. Write a MATLAB program that computes p , \bar{x}_n , \bar{x}_w , and Z for each reactor in the 3 CSTR process shown in the diagram above.

The program should set the values of the constant first moment λ_1 , the equilibrium constant K_{eq} , and the value of the Dämkohler number for the first reactor. The *Dämkohler number* is defined as the dimensionless ratio of the reactor residence time divided by the characteristic time of the reaction, and for this system takes the form,

$$Da = k_{(fc)}\theta\lambda_0^{(in)} \quad (\text{EQ 46})$$

$\lambda_0^{(in)}$ is the value of the zeroth moment in the reactor inlet stream. We specify the value $Da^{[1]}$ of the Dämkohler number for the first reactor only, and assume that all subsequent reactors have the same mean residence time θ . Therefore, if $\lambda_0^{(in,j)}$ is the zeroth moment of the chain length distribution to reactor # j , the value of Da for this reactor is

$$Da^{[j]} = Da^{[1]}\left(\frac{\lambda_0^{(in,j)}}{\lambda_0^{(in,1)}}\right) \quad (\text{EQ 47})$$

The program should ask the user to input one of more values of the cluster of parameters $(k_m A/V)\theta$. k_m is the mass transfer coefficient for the removal of water from the reaction medium to the gas phase, A/V is the mass transfer area per unit volume of the reaction medium, and θ is the residence time of the reactor. The larger is the value of $(k_m A/V)\theta$, the greater is the mass transfer rate relative to the flow through the reactor. When the value of $(k_m A/V)\theta$ is very small, the reaction medium passes through the reactor so quickly that there is insufficient time for the water to be removed to the purge stream.

For each of the input values of $(k_m A/V)\theta$, the program should compute the values of p , \bar{x}_n , \bar{x}_w , and Z in each reactor.

While in practice the reaction is self-catalyzed, assume in this example that an external catalyst has been added so that the rate constant is independent of the acid end group concentration.

Question 2.B.2. Using a Dämkohler number of 50 for the first CSTR, plot as functions of $(k_m A/V)\theta$ the number-averaged and weight-averaged chain lengths, the polydispersities, and the conversions in the product streams from each reactor.

Explain why one observes limiting values of the chain lengths as $(k_m A/V)\theta \rightarrow 0$ and $(k_m A/V)\theta \rightarrow \infty$.

Why is the polydispersity greater for large mass transfer rates than would be expected for a batch polymerization, where the chain length distribution follows the Flory statistical model?

Why does the polydispersity decrease as the mass transfer rate decreases?

In actuality, the polydispersity never becomes as large as this model suggests, even when the mass transfer rate is infinitely fast. The reason is that there are additional reactions, known as *interchange reactions*, in which the end groups react with a linkage in another molecule to “trade” parts of their chains. Since larger molecules contain more linkages, they are more likely to lose part of their chain to another molecule. This has the effect of narrowing the chain length distribution, but since the total number of chains remains constant during interchange, the number-averaged chain length is not affected. When the interchange reactions occur infinitely fast, one observes the same Flory chain length distribution computed above from statistical arguments.

HINTS:

1. When working with nonlinear equations, it is often difficult to converge to a solution when you do not know *a priori* what to use for an initial guess. In this case, a useful tool is *homotopy*, in which one varies the system parameters to obtain a limiting case with an easily-determined solution. You can use the expected solution in this limit as an initial guess, and then vary the system parameters slowly to move towards the solution for the parameter values of interest. The key idea is that for each step, you are only modifying the parameters by a small amount so that your initial guess should be close to the solution. If you find you have difficulties getting the nonlinear equation solver **fsolve()** in MATLAB to converge, you might consider this approach.
2. It is also helpful to validate your program by performing a simulation for which you know the answer. In this problem, we know that if the Daemkohler number is very large and no water is removed, the conversion from the final product stream should be that expected at equilibrium. Also, we know that if the residence time is very small, there is little time for reaction to occur, and the outlet concentrations should be nearly equal to the inlet concentrations.
3. Note that the outlet from reactor 1 is the inlet to reactor 2, and reactor 2 output flows into reactor 3 as input. How can you use this observation to make the solution process easier and more robust?
4. On the 10.34 website, I include a problem `SS_CSTR_2_rxn_scan_Q.m`, that shows how to solve sets of nonlinear algebraic equations with the MATLAB built-in (as part of the optimization toolkit) nonlinear equation solver **fsolve()**.