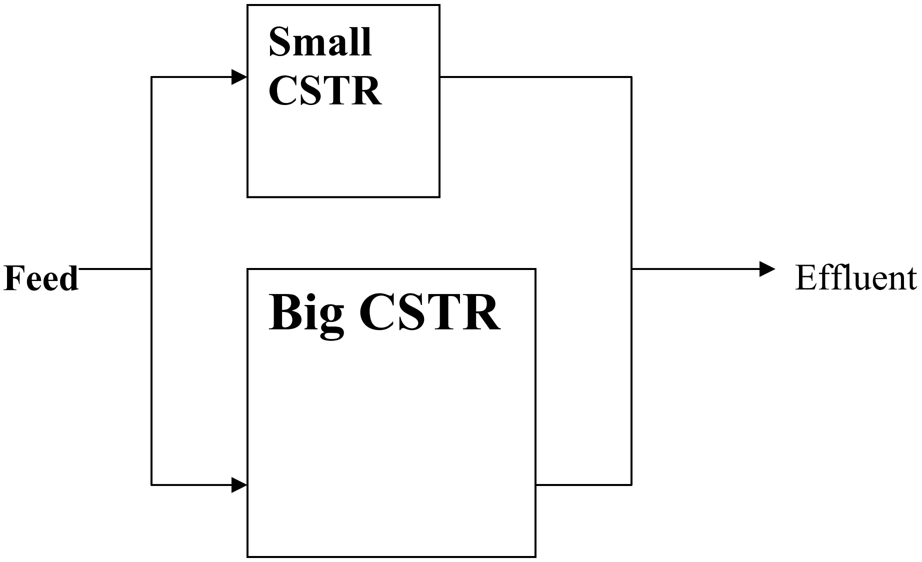
10.37 Final Exam
Spring 2007

There are 4 problems**. Pick any 3 of these problems** to do and turn in. (If you turn in solutions to 4 problems, we will not count the problem where you earned the lowest score.) Please turn in your solution for each problem separately. Write your name on every blue book or sheet of paper you turn in.

Problem 1. (100 points) A reactant stream is split to feed, in parallel, two CSTRs, one of which is twice the volume of the other. The effluents from the two CSTRs are combined. The reaction of interest follows a first-order rate law.

a) (50 points). How should the feed stream be split in order to maximize the total reactant conversion in the combined effluent from the two CSTRs?



b) (50 points). Using the same feed, what overall conversion would be obtained by placing these same two CSTRs in series (i.e. the effluent of the first is the feed of the second)? (Consider both possible topologies – one where the large CSTR feeds the smaller, and one where the small CSTR feeds the larger.) Is this conversion superior or inferior to the best case calculated in a)?

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Problem 2. (100 points) An appealing partial solution to the greenhouse gas problem is to convert biomass into liquid fuels. Most of biomass is composed of linked C6 sugars ($C_6H_{12}O_6$) and C5 sugars ($C_5H_{10}O_5$), which can be broken down by an enzyme secreted by fungi. Ideally, the sugars could then be converted into ethanol or other liquids in subsequent reactions.

This mechanism is proposed for the enzymatic breakdown:

$C_{11}H_{22}O_{11}$ + Enzyme → Complex (reaction 1)
Complex → Enzyme + $C_6H_{12}O_6 + C_5H_{10}O_5$ (reaction 2)

Reaction 1 is expected to be reversible under some conditions, but reaction 2 is expected to be irreversible.

Experimental rate data on this enzyme from low-conversion batch-reactor experiments can be fit to this expression:

$$d[C_5H_{10}O_5]/dt = r = a[C_{11}H_{22}O_{11}]_0[\text{Enzyme}]_0/\{1 + b*[C_{11}H_{22}O_{11}]_0\} \qquad \text{(Eqn 3)}$$

$a = 2\text{x}10^4$ liter/mole-second $\quad b=10^8$ liter/mole.

where $[C_{11}H_{22}O_{11}]_0$ and $[\text{Enzyme}]_0$ are the initial concentrations added to the mixture, i.e. (moles added / volume of solution), not necessarily the actual concentrations of these species in the beaker when the reaction is running, since some of the enzyme will exist in the form of the complex.

(a) (20 points) Is the observed rate law (Eqn 3) consistent with the mechanism shown above? If so, give an expression for b in terms of k_1, k_{-1}, and k_2. If not consistent, explain.

Suppose we could tether 10^{-9} mole of enzyme within a 4 mm diameter porous particle without affecting the rate law (i.e. r is given by Eqn. 3). The diffusivity inside the porous particles is 10^{-10} m^2/s. In the bulk fluid $D = 7\text{x}10^{-10}$ m^2/s. Suppose we then filled a packed bed reactor (internal diameter 2 cm, length 30 cm) with many particles like this, and flowed an aqueous solution of $C_{11}H_{22}O_{11}$ through the reactor at rate of 1 liter/minute. The void fraction of the packed bed $\phi=0.4$. For concentrations of $C_{11}H_{22}O_{11}$ below 0.5 M, the viscosity and density of the solution is essentially the same as that of water.

(b) (30 points) Write an equation for the Thiele modulus for this system, as a function of $[C_{11}H_{22}O_{11}]$. Over what range of $[C_{11}H_{22}O_{11}]$ is it reasonable to neglect diffusive transport limitations?

(c) (30 points) If $[C_{11}H_{22}O_{11}]$ is always in the range where transport limitations are negligible, what differential equation(s) should be solved to compute the conversion? What Matlab program would you use to solve the equation(s) numerically? Write the differential equation(s) in the form dY/dt = F(Y) required by the Matlab solvers.

(d) (20 points) Write (but do not attempt to solve) the differential equation(s) with boundary conditions that would have to be solved to compute the effectiveness factor Ω if $[C_{11}H_{22}O_{11}]_{bulk}$ had a value outside the range specified in part (b). Are you missing any data needed to calculate Ω?

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Problem 3. (100 points) A biosensor experiment is performed with a small amount of immobilized protein and flowing soluble ligand. The observed rate constant during the association phase, and the signal output at equilibrium, are given as a function of ligand concentration in the table below. The equilibrium signal RU_{eq} is proportional to the concentration of protein/ligand complex at the surface. During the association phase the signal follows the following function: $RU = RU_{eq}(1 - e^{-k_{obs}t})$.

$[L]_o$ (nM)	k_{obs} (s^{-1})	RU_{eq}
0.14	0.00177	1.63
0.84	0.00186	9.34
2.1	0.00201	21.5
5.60	0.00245	47.1
14.00	0.00350	82.5
35.0	0.00612	118
84.00	0.0122	141
210.00	0.0280	155
560.00	0.0718	161
1400.00	0.177	163

A) (60 points) Determine K_d, k_{on}, and k_{off}. Are these data self-consistent?

B) (40 points) In a separate experiment, soluble protein (2 nM) and ligand (0.1 nM) are mixed. At equilibrium, what fraction of ligand is complexed with the protein? At what time following mixing will 95% of this equilibrium value be attained?

Problem 4. (100 points total) "Clean Coal" technology is based on first converting the coal into syngas (an $H_2 + CO$ mixture). The syngas can then be purified and used to make clean synthetic fuels, or to generate electricity (with CO_2 sequestration). The largest and most expensive reactor in a "clean coal" plant is the gasifier. The main reactions are:

$C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ (Reaction 1) $\Delta H_{rxn1} = -110$ kJ/mole

$r_1 = k_1(T)[O_2]^2[H_2]/([H_2O] + a[H_2])$

$k_1(T) = (10^7$ liter/mole-s$)\exp(-2000/T)$ $a = 0.0113\exp(10000/T)$

$C(s) + H_2O(g) \rightarrow H_2(g) + CO(g)$ (Reaction 2) $\Delta H_{rxn2} = +130$ kJ/mole

$r_2 = k_2[O_2][H_2O]/([H_2O] + a[H_2])$ $k_2 = 5\text{x}10^4\ s^{-1}$ at T=1100 K
$a=100$ at T=1100 K

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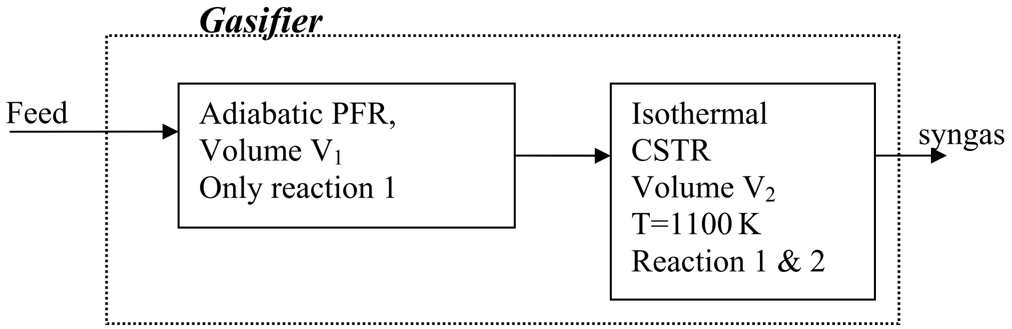
Problem 4 (continued) The peculiar-looking rate laws come from a quasi-steady-state-approximation treatment of the radicals which are the reactive intermediates in these reactions. Reaction 1 is much faster than reaction 2 at low T, so the gasifier system can be modeled as an adiabatic PFR (volume V_1) where most of the O_2 is consumed but the H_2 formation is negligible, followed by an isothermal CSTR (volume V_2) where both reactions occur.



The final 1100 K output stream coming out of the gasifier has no carbon and a negligible concentration of $O_2(g)$, but large concentrations of CO, H_2, and steam. Assume that the heat capacity of the feed stream is 3 MJ/ton-Kelvin and that the heat capacity per ton does not change significantly with temperature or the change in composition through the reactions. The process is carried out at P_{total}=40 bar. The input stream is at 700 K, and consists of 120 tons per hour of C(s), 120 tons per hour of steam, 64 tons per hour of O_2, and 0.02 tons per hour of H_2.

(a) (20 points) What is the molar flow rate of CO, H_2, and H_2O at the output? What is the volumetric flow rate of the output?

(b) (25 points) How much heat must be transferred per second to maintain the output at 1100 K? Is the heat flowing into or out of the reactor? How could you adjust the composition of the feed to reduce the amount of heat transfer required, while still maintaining the same Carbon feed rate and output temperature?

(c) (30 points) Write the equation(s) that should be solved to compute the conversion of O_2 in the adiabatic PFR, V_1=1 m^3, in a form that can be solved numerically by Matlab. What Matlab program would you use to solve these equations?

(d) (25 points) What CSTR reactor size V_2 is required so that 99% of the initial feed O_2 and 99% of the initial feed carbon will be consumed by the time the mixture leaves the isothermal (1100 K) CSTR? Hint: How much carbon was consumed by reacting with O_2? So how much carbon must be consumed by reaction 2?

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