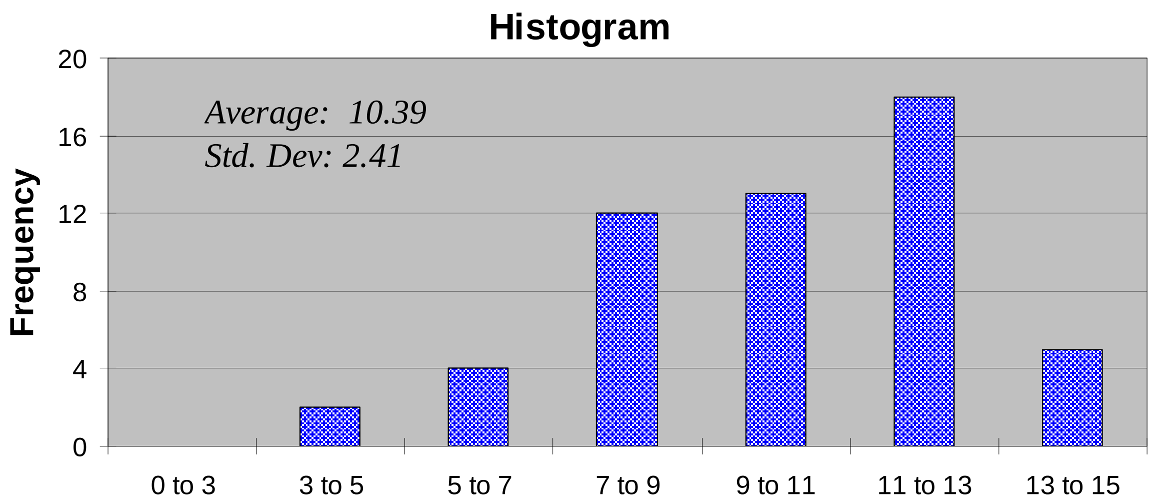
10.34 - Quiz 2

Statistics



Question Point Values:

1) **3 points**
2) **6 points**
3) **1 point**
4) **2 points**
5) **2 points**
6) **1 point**

Total: 15 points

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An isomerase (an enzyme that catalyzes an isomerization reaction) is used to convert a cheap unpalatable substrate S into its isomer, a delicious high-value product P called fructose (used to make soft drinks and candy).

The enzyme reaction is expected to follow the Michaelis-Menton rate law:

$$R = n_E V_m \left(\frac{[S] - \frac{[P]}{K_{eq}}}{K_m + [S]} \right) \quad [=] \quad \frac{moles\ S \rightarrow P}{\sec} \qquad \text{Eq.(1)}$$

where V_m and K_m depend on the enzyme, and K_{eq} is for the equilibrium S=P, and n_E is the moles of enzyme in the reactor.

Note that throughout the isomerization process [S]+[P] = constant. We therefore suggest you use the dimensionless concentration C = [Substrate]/[Substrate]$_o$ rather than tracking S and P separately.

1) Simulate the batch conversion of S into P by writing a couple of short Matlab functions. Your Matlab functions should take $[S]_o$, n_E, V, Km, and Keq as inputs. Feel free to call any built-in Matlab functions.

A microreactor for accomplishing this process continuously is constructed this way: a coating of the isomerase is chemically bonded to two flat plates. The coating density is 10^{-11} moles enzyme/cm^2. The two plates are then bonded to a thin spacer, to create a very thin channel (gap between the plates Y=0.01 cm (0.005 cm from the centerline to the wall), length X=5 cm, width of channel Z=2 cm), see figure. Inside the channel, flow can be accurately modeled as being laminar and two-dimensional, i.e. we only need to be concerned about gradients in x and y directions, not z, don't worry about what happens close to z=0 or z=Z. The enzyme's substrate, initial concentration $[S]_o$ is flowed at a rate of 0.1 ml/second through the channel from x=0, and the output stream (hopefully rich in product P) exits at x=X.

2) Write the finite difference equations that can be solved to compute $C_i = C(x_i,y_i)$ at a set of N_x*N_y mesh points (x_i,y_i) inside the channel when the system is running in steady state, in the limit where the enzyme reaction is so fast that the Substrate and Product are in equilibrium at the walls. That is, at the inlet C=1, and along the walls $C = (1+K_{eq})^{-1}$. At the outlet assume von Neumann boundary conditions. What is the boundary condition along the centerline of the channel Y=0 cm? Write the special equations that apply for the mesh points at or near the boundaries (the centerline is one of the boundaries).

3) Is the system of equations you wrote in part 2 linear or nonlinear in the unknowns? What Matlab function would you use to solve this system of equations?

4) It would be interesting to compute values of X,Y,Z which would maximize the yield, i.e. the moles of P made per second, subject of course to a couple of practical constraints:

a) safety: the total pressure drop cannot exceed some maximum set by our pump and the materials used to construct the microreactor.
b) product specifications: the [P] in the output stream must be at least $[P]_{min}$

Explain whether or not one should expect this maximum productivity to occur at the point where:

$$\partial(\text{yield})/\partial X = 0 \quad \text{and} \quad \partial(\text{yield})/\partial Y = 0 \quad \text{and} \quad \partial(\text{yield})/\partial Z = 0$$

Note no computations are required, just a sentence or two.

5) In reality, the enzymatic reaction will not be fast enough to achieve perfect equilibrium at the walls. Instead, the rate of conversion per unit area at the walls will be (with n_E now being in moles Enzyme/cm^2)

$$(\text{moles converted /second/ } cm^2) = R \qquad \text{Eq.(3)}$$

Write the new boundary condition at the walls that replaces $C=(1+K_{eq})^{-1}$ and the corresponding finite difference equation for a point (x_n,y_n) near the wall.

6) If you were solving the BVP problem using non-uniform grid points, where would you want to make the density of grid points the largest? Explain with a sentence or to why that is the case.

Quiz 2 Solutions

15 November 2006

1. Let us assume that the volume of the reactor is V_R. Then the rate of the reaction, R is given in Equation(1).

$$R = n_E V_m \left(\frac{[S] - \frac{[P]}{K_{eq}}}{K_m + [S]} \right) \tag{1}$$

But the rate of the reaction is also equal to the rate of change of concentration of the substrate (the volume of the reactor remains constant). Thus the differential equation that we have to solve for this problem is given in Equation(2). For the given differential equation, the initial condition is; at $t = 0$, $C = 1$.

$$\begin{aligned} [S]_0 \frac{dC}{dt} &= -\frac{n_E V_m}{V_R} \left(\frac{[S]_0 C - \frac{[S]_0 (1-C)}{K_{eq}}}{K_m + [S]_0 C} \right) \\ \frac{dC}{dt} &= -\frac{n_E V_m}{V_R} \left(\frac{C - \frac{(1-C)}{K_{eq}}}{K_m + [S]_0 C} \right) \end{aligned} \tag{2}$$

Now we can solve the differential equation by using the following matlab function.

```
function(S,P,time) = batch_rtr(S0,Keq,Km,Vm,nE,Vr)
C0 = 1;
tspan = [0 tfinal]; % tfinal will depend on the problem
[time C] = ode15s(@odefun, tspan, C0, [], S0, Keq,Km,Vm,nE,Vr);
S = S0*C;
P = So*(1-C);
return;


function dC = odefun(t,C,S0, Keq,Km,Vm,nE,Vr)
dC = -nE*Vm/Vr*((C - (1-C)/Keq)/(Km + S0*C));
return;
```

2. The differential equation governing the concentration of substrate in the microreactor is given by Equation(2). The term on the left hand side of the equation is the convective term and the term on the right hand side is the diffusive term. The reaction term in not present because the reaction is instantaneous on the boundary and in incorporated into the boundary conditions.

$$v_x \frac{\partial C}{\partial x} = D_i \left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right] \tag{3}$$

Since the flow is laminar, the velocity profile is given in Equation(4), where U_0 is the centerline velocity. We can calculate the value of U_0 by using the fact that the total volumetric flow rate of the substrate is 0.1 ml/sec.

$$v_x(y) = U_0 \left(1 - \frac{y^2}{0.005^2}\right) \tag{4}$$

Based on Equation(4) we can calulate the total flow rate as shown in Equation(5) and then use this eqation to calculate the value of U_0.

$$\begin{aligned} 0.1 &= \int_0^2 \int_{-0.005}^{0.005} v_x dy dz \\ &= \frac{4}{3} U_0 \times 2 \times 0.005 \end{aligned} \tag{5}$$

$U_0 = 7.5$ cm/s. At the centerline we apply the symmetry condition, which tells us that $\frac{\partial C}{\partial y} = 0$. The discretized analog of this equation is given in Equation(6). The boundary conditions at $x = 0$ is that all the dimensionless variable $C = 1$ (see Equation(7)) and at $x = 5$ cm $\frac{\partial C}{\partial x} = 0$ (see Equation(8)). Also according to the problem statement the reaction is instantaneous at the boundary and $C = (1 + K_{eq})^{-1}$ (see Equation(9)).

At $y = 0$ cm

$$C(i,0) - \frac{4}{3}C(i,1) + \frac{1}{3}C(i,2) = 0 \tag{6}$$

At $x = 0$ cm

$$C(0,j) = 1 \tag{7}$$

At $x = 5$ cm

$$C(N_x,j) - \frac{4}{3}C(N_x-1,j) + \frac{1}{3}C(N_x-2,j) = 0 \tag{8}$$

At $y = 0.005$ cm

$$C(i,N_y) = (1 + K_{eq})^{-1} \tag{9}$$

The equation that applies at non-boundary mesh points is shown in Equation(10).

$$7.5\left(1 - \frac{(j\Delta x)^2}{0.005^2}\right)\frac{C(i,j) - C(i-1,j)}{\Delta x} = D\left(\frac{C(i+1,j) - 2C(i,j) + C(i-1,j)}{\Delta x^2} + \frac{C(i,j+1) - 2C(i,j) + C(i,j-1)}{\Delta y^2}\right) \tag{10}$$

3. The system of equations in part 2 are linear in the unknowns. One could use command to solve the system of equations or if one wants take advantage of the sparcity of the system of equations then one could use `GMRES`.

4. This is a constrained minimization problem and hence the minimum of the problem will in general not lie at a point where $\frac{\partial yield}{\partial x} = 0$, $\frac{\partial yield}{\partial y} = 0$ and $\frac{\partial yield}{\partial z} = 0$. Instead the gradient yield will be normal to one of the inequality constraints if the constraint is active. Thus there wont be any decrease in the yield if we have to satisfy the constraints. Only in the scenario that none of the inequlity constraints are active will the partial derivative of yield be 0.

5. If the reaction is not instantaneous then instead of having a diriclet boundary condition at the wall we will have a neumann boundary condition, the flux towards the wall will be equal to the rate of reaction on the surface of the wall. The boundary condition is expressed in Equation(11).

$$
\begin{aligned}
[S]_0 D \frac{\partial C}{\partial y} &= -R \\
-\left(\frac{3C(i,N_y) - 4C(i,N_y-1) + C(i,N_y-2)}{2\Delta y}\right) &= \frac{-R}{D[S]_0} \\
&= \frac{-n_E V_m}{D}\left(\frac{C - \frac{1-C}{K_{eq}}}{K_m + [S]_0 C}\right)
\end{aligned} \tag{11}
$$

6. The density of grid points should be highest at the walls and if we are taking into account entrance effects then at the entrance of the channel.