Electrochemicalpolymerization problem

The following problem comes from Scott, K., *Electrochemical Reaction Engineering*, Academic Press, New York (1991).

A polymerization takes place between two organic compounds, *A* and *H*, according to the reaction

$A + 3H$ -> polymer

The reaction rate is

Rate r (in mol m^{-2} s^{-1}) = $k_1 \sigma C_A C_H$ when C_A and C_H are expressed in kmol m^{-1}.

The parameter k_1 takes the value 2.2e-7 m s^{-1}; the parameter σ is the specific electrode area, which is 50 m^{-1}. The reactor is described by Scott as a rotating cylindrical electrolyser with wiper blades to prevent fouling of the electrode surface. Unwanted side reactions need to be minimized by limiting the electrode potential. The equation for compound *A* in the *n*-th electrolyser is thus (refer to Eq. 8.15, page 140)

$$Q(C_{A,n} - C_{A,n-1}) = -Vk_1\sigma C_{A,n}C_{H,n}$$

The equation for compound *H* is different, since the stoichiometry is different.

$$Q(C_{B,n} - C_{B,n-1}) = -3Vk_1\sigma C_{A,n}C_{H,n}$$

The inlet concentrations to the first electrolyser are C_A = 0.8 kmol m^{-3} and C_H = 2 kmol m^{-3}. The volume of each reactor is 1e-2 m^3 and the volumetric federate is 5e-4 m^3 s^{-1}. (These numbers are changed slightly from those in Scott. See that book for a graphical way to solve the problem.)

Solution

The stoichiometry is such that for every mole of compound *A* that reacts three moles of compound *H* reacts. The amount of A that has reacted is $C_{A,in} - C_{A,n}$. Thus the amount of *H* that has reacted is $3\left(C_{A,in} - C_{A,n}\right)$. The amount of *H* remaining in the *n*-th reactor is then $C_{H,in} - 3\left(C_{A,in} - C_{A,n}\right)$. This assumes that there is more *A* than needed in the reaction, as is the case for this problem. This also means that one need only solve the reactor equation for compound *A* since the concentration of compound *H* can be found from the concentration of compound *A*. The resulting equation is

$$Q(C_{A,n} - C_{A,n-1}) = -Vk_1\sigma C_{A,n}\left[C_{H,in} - 3\left(C_{A,in} - C_{A,n}\right)\right]$$

It is more convenient to work in terms of the conversion, $X_n = 1 - C_{A,n} / C_{A,in}$. The final equation is

$$Q(X_{A,n-1} - X_{A,n}) = -Vk_1\sigma C_{A,in}\left[1 - X_n\right]\left[C_{H,in} / C_{A,in} - 3X_n\right]$$

With the parameters inserted this is

$$5 \bullet 10^{-4}(X_{A,n-1} - X_{A,n}) = -10^{-2} \bullet 2.2 \bullet 10^{-7} \bullet 50 \bullet 800\left[1 - X_n\right]\left[2 / 0.8 - 3X_n\right]$$

This gives

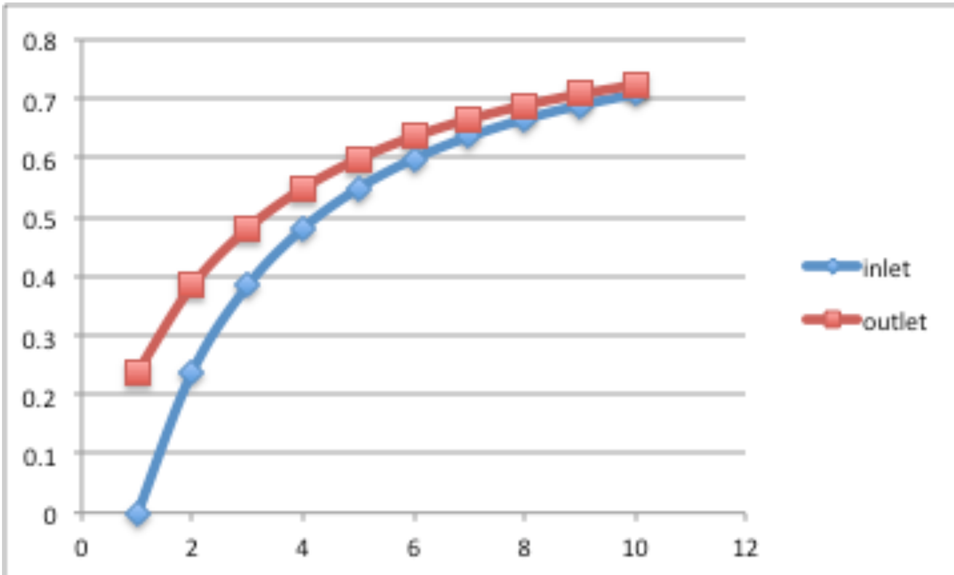
$$(X_{A,n-1} - X_{A,n}) = -0.176\left[1 - X_n\right]\left[2.5 - 3X_n\right]$$

with $X_{in} = X_{n=0} = 0$.

The first solution is done with Excel. In the *n*th reactor, the inlet conversion is the outlet conversion of the previous reactor, the rate is calculated using the equation above. The reactor equation is typically =B2−C2+D2 where B2 is the inlet conversion, C2 is the outlet conversion and D2 is the rate calculated with the outlet conversion. Then Goal Seek is used to make the reactor equation of the first reactor (E2) zero by changing the outlet conversion of the first reactor. The equation for the first reactor is solved using Goal Seek (under Data Tools Group, What-if analysis). Then the second reactor is solved, etc. The results are shown below. This would be easier if you have more sophisticated equation solving software on your version of Excel, but it does work. The spreadsheet is shown below.

reactor	inlet	outlet	rate	reactor equation
1	0.000	0.239	0.239	0.000534
2	0.239	0.384	0.146	0.000237
3	0.384	0.481	0.097	0.000011
4	0.481	0.549	0.068	0.000043
5	0.549	0.598	0.050	0.000095
6	0.598	0.636	0.038	0.000160
7	0.636	0.666	0.030	0.000232
8	0.666	0.689	0.024	0.000306
9	0.689	0.708	0.019	0.000379
10	0.708	0.723	0.016	0.000448

A plot of the conversion vs. reactor number is:



It is easily seen that you reach a point of diminishing returns – as the number of reactors increases each one makes a smaller contribution to the conversion.

The MATLAB version of the solution is done using the *fzero* function to solve the equation and doing it in a loop from the first to the last tank.

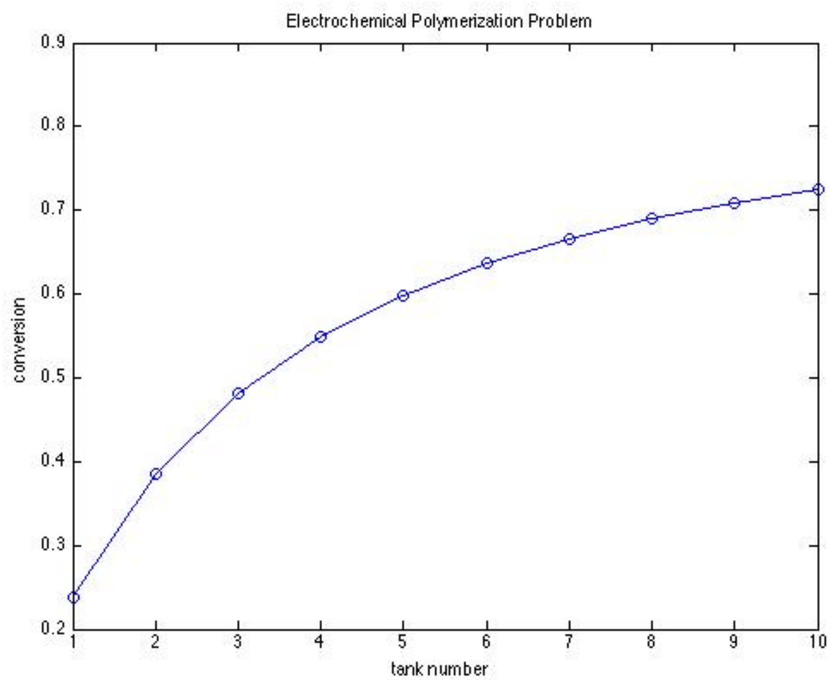
```
% function for polymerization in stirred tanks
function y=tank(x)
global xin
y = xin-x+0.176*(1-x)*(2.5-3*x);

% poymerization problem
global xin
n = 10
xin = 0;
for i=1:n
   x(i) = fzero('tank',xin);
   eq(i)=xin-x(i)+0.176*(1-x(i))*(2.5-3*x(i));
   xin = x(i);
   axis(i) = i;
end
plot(axis,x,'ob-')
xlabel('tank number')
ylabel('conversion')
title('Electrochemical Polymerization Problem')
x
eq
```

The results are:

```
x =
  Columns 1 through 7
    0.2389    0.3847    0.4811    0.5489    0.5986    0.6364    0.6660
  Columns 8 through 10
    0.6895    0.7087    0.7245
eq =
   1.0e-15 *
  Columns 1 through 7
   -0.0555   -0.0278   -0.0139   -0.0694   -0.0139   -0.0763   -0.0208
  Columns 8 through 10
    0.0798   -0.1076    0.0347
```

and



The results are almost the same, but the solution of the equations in Excel using Goal Seek is not as accurate as that from MATLAB.

It is easily seen that you reach a point of diminishing returns – as the number of reactors increases each one makes a smaller contribution to the conversion.