Identification of CVD kinetics by the method of Komiyama, et al. *Comparison to 1D model R. K. Herz, rherz@ucsd.edu (2012) filename: CVD Komiyama 1D model*

Komiyama, et al. (1999) discussed methods to identify the important steps in a CVD reaction system. In one method, they considered CVD on the internal wall of a cylindrical tube. They proposed that the limiting process in a CVD reaction system could be determined by the pattern of plots of the log of the experimental growth rate vs. tube length for tubes of different length.

In their Equations 1 and 2, Komiyama, et al. presented a 1D model of the system. The convection of the reactant is represented by the mean velocity. For the diffusion limited case, the wall reaction is fast relative to the other processes. The rate of diffusion of reactant B to the wall can be represented by a mass transfer coefficient that is appropriate for laminar flow.

Below we develop equations for the 1D approximation of the diffusion limited case. A dimensionless mass transfer coefficient, the Sherwood number, is defined. The plot below was produced by this 1D approximation. The equations and Matlab programs are listed at the end of this document.

The pattern shown in this plot agrees with the diffusion limited plot in Komiyama et al. This plot is also similar to the pattern produced by the 2D model that we developed in separate set of notes.



Reference

H. Komiyama, Y. Shimogaki, and Y. Egashira, "Chemical reaction engineering in the design of CVD reactors," *Chemical Engineering Science*, vol. 54, no. 13–14, pp. 1941–1957, Jul. 1999.

Introduction of the Sherwood number to laminar flow reactor

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Start with the 2D equations shown previously for species A and B using dimensionless variables with the primes dropped.

$$0 = -Da_A^g c_A - u \frac{\partial c_A}{\partial x} + \frac{4}{\left(\text{ReSc}\right)^2} \frac{\partial^2 c_A}{\partial x^2} + \left(\frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r} \frac{\partial c_A}{\partial r}\right) \text{ for species A (dimensionless)}$$

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Now, <u>neglect axial diffusion</u> for large ReSc and specify that there is <u>no reaction of A at</u> <u>the wall</u>. The product ReSc can be expressed as the ratio of convective mass transport rate to diffusive mass transport rate, and as the characteristic time for diffusion across the tube diameter divided by the mean residence time of fluid in the tube. See my notes on flow patterns in chemical reactors.

Also, instead of describing radial diffusion and reaction at the wall exactly, we will approximate these combined processes using a mass transfer coefficient. This will convert the equations into ordinary differential equations.

Since convection and reaction at the wall are both linear in the concentration, we can use the mean velocity, \overline{u} , and mean concentrations, \overline{c} , to develop balances around a disk-shaped control volume instead of our original ring-shaped control volume. Using the original dimensioned variables:

$$0 = -k_A^g \overline{c}_A - \overline{u} \frac{d\overline{c}_A}{dx}$$
$$0 = k_A^g \overline{c}_A - \overline{u} \frac{d\overline{c}_B}{dx} + \left(\frac{2}{R}\right) k_m \left(c_B^{wall} - \overline{c}_B\right)$$

These equations are approximations for gas reaction in laminar flow (they describe plug flow) and over-predict conversions by about 10%. See my course notes on chemical reaction engineering, flow patterns in chemical reactors, for ReSc >> 1 in laminar flow.

The last term on the right in the lower equation is the net rate at which B diffuses into the disk-shaped control volume from the wall. This rate is approximated as being proportional to the difference between the wall and bulk-mean concentrations of B, where the proportionality coefficient, k_m , is called the mass transfer coefficient. The mass transfer coefficient k_m has units (m/s). The term (2/*R*) is the wall area per unit volume of reactor, where *R* is the radius of the reactor.

Since B is being consumed at the wall, and $c_B^{wall} < \overline{c}_B$, this term is negative, so it is conventional to reverse the concentration terms:

$$0 = k_A^g \overline{c}_A - \overline{u} \, \frac{d\overline{c}_B}{dx} - \left(\frac{2}{R}\right) k_m \left(\overline{c}_B - c_B^{wall}\right)$$

Now we convert back to dimensionless variables to get:

$$0 = Da_A^g \dot{c_A} - u' \frac{d\dot{c_B}}{dx} - Sh(\dot{c_B} - c_B^{wall'})$$

where

$$Da_{A}^{g} = k_{a}^{g} / (D/R^{2}); \quad u' = \frac{\overline{u}}{\overline{u}} = 1 \quad ; \quad x' = (2x/R) / (ReSc); \quad c_{i}' = \frac{\overline{c_{i}}}{c_{A,0}} \quad ; \quad c_{B}^{wall'} = \frac{c_{B}^{wall'}}{c_{A,0}}$$

and where the Sherwood number is:

$$Sh = \frac{2Rk_m}{D}$$

Now we have a system of two ODEs. Dropping the primes:

)

$$\frac{dc_A}{dx} = -Da_A^g c_A$$
$$\frac{dc_B}{dx} = Da_A^g c_A - Sh(c_B - c_B^{wall})$$

Our only problem now is that we don't know c_B^{wall} . Since both mass transfer and <u>this</u> reaction are first-order processes, we can do something about this.

The flux of B from the bulk gas to the wall equals the rate at which B reacts at the wall:

$$k_m\left(\overline{c}_B-c_B^w\right)=k_B^w c_B^w$$

A little algebra gives us:

$$k_m \left(\overline{c}_B - c_B^w\right) = \left(\frac{k_m k_B^w}{k_m + k_B^w}\right) \overline{c}_B = k^* \overline{c}_B \qquad Sh^* = \frac{2Rk^*}{D}$$

<u>Mass-transfer limited case</u>: For the limiting case where the rate of reaction at the wall is fast, $k_B^w >> k_m$, $k^* \approx k_m$ and $\overline{c}_B >> c_B^w$. $Sh^* = Sh = 2Rk_m/D$. In Komiyama et al. this case is loosely called "diffusion limited." The film growth rate equals k_m (m/s) \overline{c}_B (mol/m³). Since *Sh* and, therefore, *Sh*^{*} does not vary with *R*, k_m is proportional to (1/*R*).

<u>Surface-reaction limited case</u>: For the limiting case where the rate of reaction at the wall is relatively slow, $k_B^w \ll k_m$, $k^* \approx k_B^w$ and $\overline{c}_B \approx c_B^w$. $Sh^* = 2Rk_B^w/D$. Note that, whereas $\overline{c}_B \approx c_B^w$, $\overline{c}_B > c_B^w$ such that $k_m(\overline{c}_B - c_B^w) > 0$. Note that k_B^w is independent of R such that Sh^* for this case is proportional to R. Also note that the value of Sh^* for this case is much less than the value of Sh^* for the mass-transfer limited case, since $k_B^w \ll k_m$. The film growth rate equals $k_B^w(m/s)\overline{c}_B(mol/m^3)$. The surface reaction rate constant k_B^w does not vary with R.

Now our dimensionless equations are:

$$\frac{dc_A}{dx} = -Da_A^g c_A$$
$$\frac{dc_B}{dx} = Da_A^g c_A - Sh^* c_B$$

The initial conditions are, at x = 0, dimensionless $c_A = 1$, dimensionless $c_B = 0$.

The equations are in the form of those for a standard series reaction system. The equation for A can be integrated easily by separating variables, and then the solution for c_A as a function of x can be substituted in the equation for B. This equation can be integrated using the integrating factor approach.

<u>Gas-phase reaction limited case</u>: $Da_A^g \ll Sh^*$.

Sh for the mass-transfer limited case:

The values of the Sherwood number can be determined from analytical solution of the equations for laminar flow and radial diffusion, or solution of the equivalent heat transfer problem to obtain the Nusselt number for heat transfer (the Sherwood number is sometimes called the Nusselt number for mass transfer).

For fully developed laminar flow entering a tube in which mass transfer to the wall occurs with constant concentration at the wall, e.g., fast reaction such that the wall concentration is approximately zero, the Sherwood number varies with dimensionless axial position x' in the following way, as obtained from the solution of the governing partial differential equations:

dimensionless x': 0, 0.002, 0.02, 0.2, 0.4, ∞ Sh: ∞ , 12.8, 6.0, 3.71, 3.66, 3.66

where dimensionless x' = (2x/R)/(ReSc), $Sh = \frac{2Rk_m}{D}$

Since *Sh* does not vary with tube radius *R*, k_m is proportional to (1/*R*).

[e.g., Kays and Crawford, "Convective heat and mass transfer," 2nd ed., McGraw-Hill (1980), p. 111, for analogous heat transfer case]

1D SYSTEM - Matlab listing

When you copy to Matlab do not include page footers & may need to add return between end end

```
\% model CVD reactions in tube \% A(q)->B(q)
% B (g) -> film at wall (s) %
% this program requires the following m-files:
웅
    cvd_1D_derivs.m
8
    cvd 1D sherwood.m
2
% THIS PROGRAM CURRENTLY IS FOR MASS-TRANSFER LIMITED CASE
% since function Sherwood, which is used by
% function cvd 1D derivs, supplies only Sh for
% mass-transfer limited case
warning('off') % otherwise get warnings from taking log for plot
% share global variable values with main and functions
global Da Rratio GTL
 5 INPUT VALUE - GTL IS 1 for Gas Transport Limited Case
% other for Surface Reaction Limited Case
GTL = 1;
% Rratio = ratio of tube radius R to a reference radius
for Rratio = [0.5 \ 1 \ 2]
  % Damkoehler number for A->B rxn in gas
  % Da for gas rxn prop to R<sup>2</sup>
  Da = 200 * Rratio^2;
  % initial conditions of dependent integration variables of ODEs
  % dimensionless inlet concentrations
  cA0 = 1;
  cB0 = 0;
  c0 = [cA0 \ cB0];
  % specify span in independent integration variable of ODEs
  % dimensioned tube length relative to a reference tube length
  xd0 = 0;
  xdL = 2;
  xdspan = [xd0 xdL];
  \ for constant-length tube, dimensionless x prop. to 1/R^2
  xspan = xdspan/Rratio^2; % span in dimensionless tube length
  % integrate using standard matlab function ode45
  [x c] = ode45('cvd 1D derivs', xspan, c0);
  cA = c(:, 1);
cB = c(:,2);
  [row col] = size(cA);
  cAf = cA(row);
  XA = (cA0 - cAf)/cA0;
  cBf = cB(row);
  % convert from dimensionless x to
  % dimensioned xd relative to reference tube length
  xd = x*Rratio^2;
  if GTL == 1
    % calculate film deposition rate (mol/m2/s) = km(m/s)*cB(mol/m3)
    % km = Sh*D/(2*R), so km and film deposition rate prop to cB/R
    frate = cB/Rratio;
else
    % for surface reaction limited, rate = kw(m/s)*cB(mol/m3)
    % kwall is independent of R
    frate = cB;
end
  % probably a better way in matlab than this to have different color
  % curves for each case on plot but this comes to mind
  if Rratio == 0.5
    RateMin = frate;
    xdMin = xd;
```

```
cAMin = cA;
    cBMin = cB;
  elseif Rratio == 2.0
    RateMax = frate;
    xdMax = xd;
    cAMax = cA;
cBMax = cB;
else
    RateMid = frate;
    xdMid = xd;
    cAMid = cA;
    cBMid = cB;
  end
end
% plot rate and distance down tube as dimensioned values
% relative to reference dimensioned values of rate and tube length
plot(xdMin,log10(RateMin),'g',xdMid,log10(RateMid),'r',xdMax,log10(RateMax),'b')
title('green = 0.5 * Rref, red = Rref, blue = 2 * Rref, Rref = reference tube
radius')
ylabel('log10(film deposition rate) (arbitrary dimensional units)')
xlabel('distance down tube (arbitrary dimensional units)')
axis([0 xdL -5 0.5])
% TAKE A LOOK AT GAS PHASE CONC
figure(2), plot(xdMin,cAMin,'g',xdMid,cAMid,'r',xdMax,cAMax,'b')
title('cA: green = Rref/2, red = Rref, blue = 2Rref, Rref = reference tube radius')
ylabel('dimensionless cA')
xlabel('distance down tube (arbitrary dimensional units)')
figure(3), plot(xdMin,cBMin,'g',xdMid,cBMid,'r',xdMax,cBMax,'b')
title('cB: green = Rref/2, red = Rref, blue = 2Rref, Rref = reference tube radius')
ylabel('dimensionless cB')
xlabel('distance down tube (arbitrary dimensional units)')
```

LISTING OF FUNCTION FILE cvd_1D_derivs.m

```
function dcdx = cvd 1D derivs(x,c)
% function cvd 1D derivs uses function cvd 1D sherwood
% share global variable values with main and functions
global Da Rratio GTL
cA = c(1);
cB = c(2);
if GTL == 1
  % for gas-transport limited case, kwall >> km
   \text{so Sh}^* = 2 \times \mathbb{R} \times \mathbb{m}/\mathbb{D} 
  \% and km is proportional to (1/R), so Sh* indep of R
  % here take into account variation of Sherwood number
  % in entrance length - not much change from using constant 3.66
  Sh = cvd 1D sherwood(x);
else
  % for surface-reaction limited, kwall << km</pre>
  % so Sh* = 2*R*kwall/D
  \ensuremath{\$} and Sh* is proportional to R
  ShRef = 0.3; % arbitrary value but must be << 3.66
  Sh = ShRef*Rratio;
end
dcAdx = -Da*cA;
dcBdx = Da*cA - Sh*cB;
dcdx = [dcAdx; dcBdx]; % return as column vector
```

LISTING OF FUNCTION FILE cvd_1D_sherwood.m

```
function Sh = cvd \ 1D \ sherwood(x)
% this function supplies the Sherwood number
% for mass-transfer to cylindrical tube wall
% for fully developed laminar flow and
% constant wall concentration, e.g.,
% a wall concentration near zero for fast wall reaction
% variation of Sh in entrance region
% has small effect vs. using limiting value of 3.66 everywhere
% for the values of inputs in main program cvd 1D
% account for variation of Sh in entrance region
% where concentration profiles are developing
% fit curve to Sh vs. dimensionless x in entrance region
% coefficients of 3rd order polynomial
% fit of log(x) vs. log(Sh) see below
coef = [0.0053 0.0995 0.2862 1.5122];
if (x<0.001)
     Sh = infinity at x = 0 but don't bother
    Sh = 12.8;
elseif x < 0.2
    % use fit in entrance region
    lnSh = polyval(coef,log(x));
    Sh = exp(lnSh);
else
    % past entrance region, use limiting Sh
Sh = 3.66;
end
% % fit Sh in entrance region
9
% Sh = [12.8 6.0 3.71 3.66 3.66];
% x = [0.001 \ 0.01 \ 0.1 \ 0.2 \ 0.3];
9
% lnSh = log(Sh); % matlab log = ln
% lnx = log(x);
% coef = polyfit(lnx,lnSh,3); % 3rd order polynomial
S
% % check curve at more points than were fit
% % to see if have deviations between fit points
8
 \ln xp = \log(0.001):0.1:\log(0.3); 
% lnShp = polyval(coef,lnxp);
8
% plot(lnx,lnSh,'b',lnxp,lnShp,'k')
% title('blue = data, blk = fit')
8
% BE CAREFUL with 2 factors
2
% If change dimensionless x' = (2x/R)/(ReSc) to
% get rid of 2's in ODEs, then have to re-fit the function in Sherwood.m!!!!
% Sherwood.m dimensionless x' = (x/R)/(ReSc)
```