

## Identification of CVD kinetics by the method of Komiyama, et al.

### *Comparison to 2D models*

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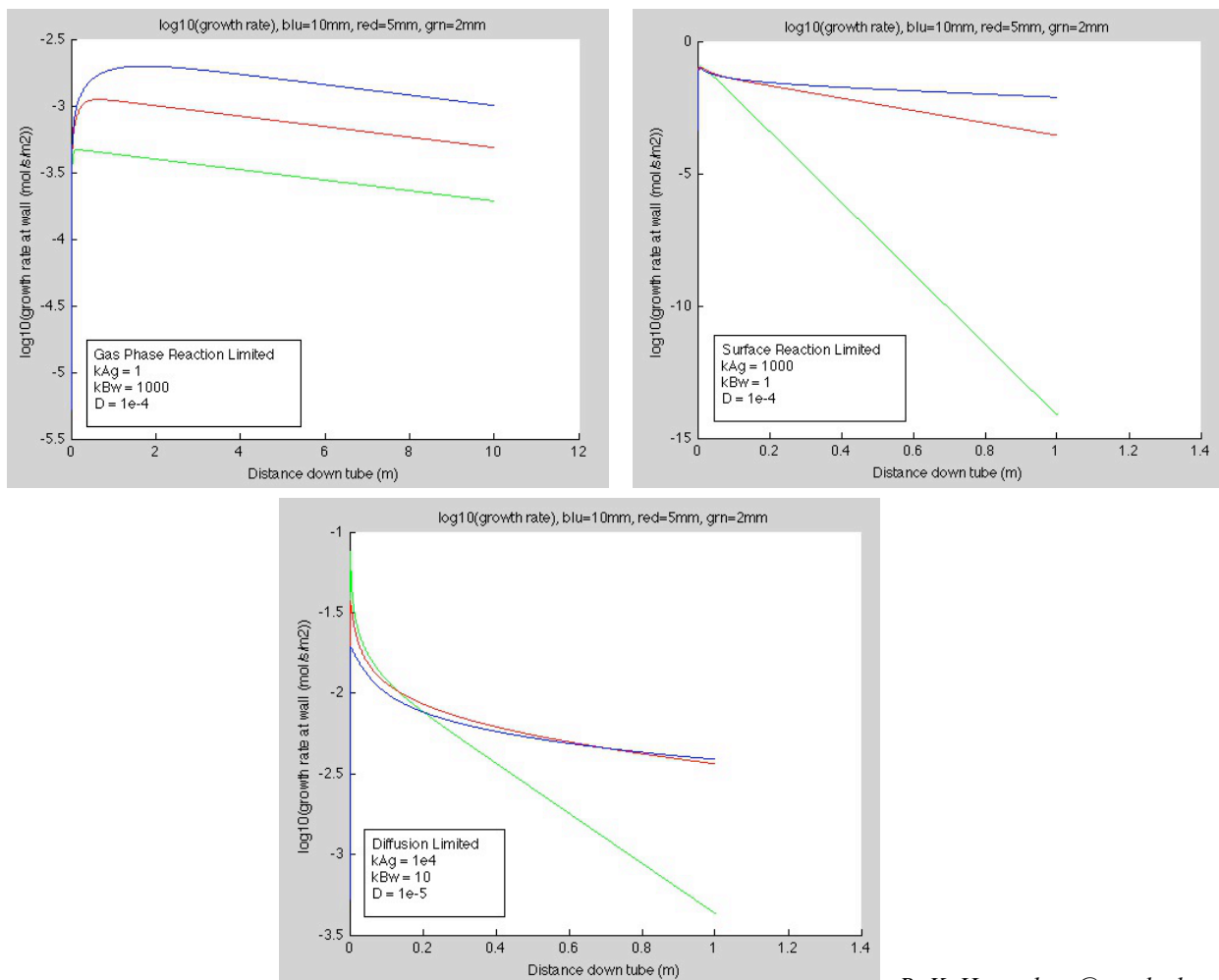
filename: CVD\_Komiyama\_2D\_model

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.

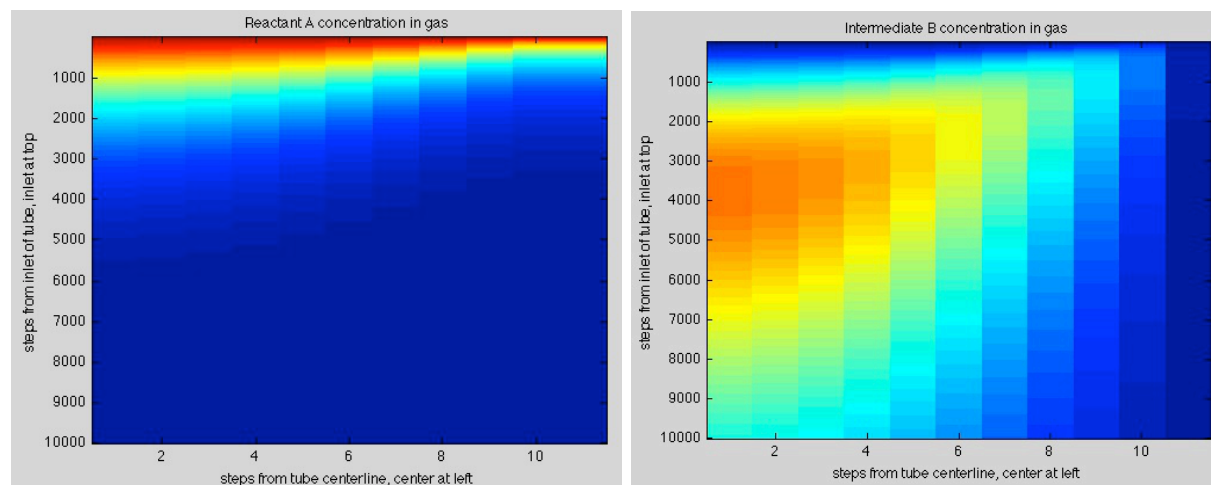
I wrote a 2D finite-difference numerical approximation of this system to see if it could generate the patterns presented in Komiyama, et al. Fig. 1. The equations and Matlab programs are listed at the end of this document.

The simplified system consists of fully developed laminar flow entering an isothermal, isobaric reactor. Equimolar counter-diffusion was assumed such that Fick's law of diffusion applied (e.g., A and B are dilute in an inert or each reaction does not change the total number of gas moles). Axial diffusion was assumed to be negligible. A reacts to B in the gas phase. B reacts on the tube wall to form a solid film.

The plots produced by our program look similar to the patterns at high conversion in the lower panels of Komiyama, et al. Fig. 1.



Below are representative 2D plots of the patterns of A and B concentrations in the gas phase. The inlet of the tube is at the top of the plot, the centerline of the tube is on the left, and the wall of the tube is on the right of each plot. Red is high concentration, blue is low concentration.



Do these patterns make sense to you? If A only reacts in the gas phase, why does its concentration stay higher along the centerline than along the wall for some distance into the reactor - it doesn't react at the wall. Hint, remember this is laminar flow.

In other work, we used the software program CHEMKIN (version 3.7) and it's application CRESLAF to simulate SiN film deposition from SiF<sub>4</sub> and NH<sub>3</sub>. CHEMKIN is a product of a San Diego, California based company, Reaction Design, [www.reactiondesign.com](http://www.reactiondesign.com)

The gas was in laminar flow in a tube at 300 °C and 1.8 Torr pressure. This was a 2D simulation. The surface reactions on the tube wall were:

```

REACTIONS
NH3          + HN_SIF(S) => HN_NH2(S) + SI(D) + HF    7.562E08  0.5 0.0
SiF4        + HN_NH2(S) => F3SI_NH2(S) + N(D) + HF    3.0967E8  0.5 0.0
F3SI_NH2(S)          => F2SINH(S) + HF    1.0E05  0.0 0.0
NH3          + F2SINH(S) => H2NFSINH(S) + HF    7.562E08  0.5 0.0
H2NFSINH(S) + F2SINH(S) => HN(FSINH)2(S) + HF    1.0E15  0.0 0.0
HN(FSINH)2(S) + F2SINH(S) => 3HN_SIF(S) + N(D) + HF    1.0E15  0.0 0.0
END

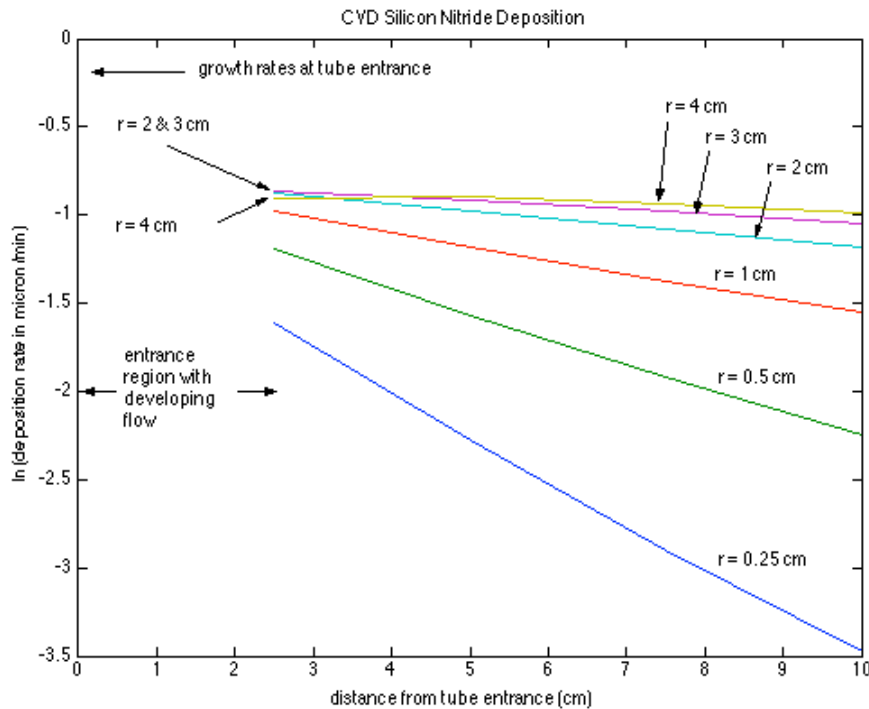
```

The (S) denotes Surface species and (D) denotes Deposit species which are in the layer under the surfaces species. Unmarked species are gas-phase species. The SI(D) and N(D) for the SiN deposit.

On the right side of the reaction list are the reaction rate coefficient values: pre-exponential, exponent on the temperature factor T in the rate coefficient, and the activation energy - zero here for this example of constant wall temperature. The => denotes that these reactions are considered essentially irreversible.

Not shown here is the list of 33 gas-phase elementary step reactions used in the simulation.

The figure below shows some results. For the small-diameter tubes (0.25-1 cm in diameter), Komiyama et al.'s analysis indicates that the reaction is "surface reaction limited." For the large-diameter tubes (2-4 cm in diameter), Komiyama et al.'s analysis indicates that the reaction is "diffusion limited."



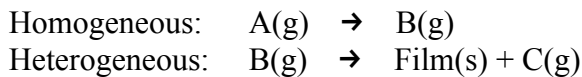
## Reference

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.

## DEVELOPMENT OF 2D EQUATIONS

Below are equations describing steady-state reaction and heat transfer in a laminar-flow reactor. The inlet flow is specified to be fully developed laminar flow with a radially uniform temperature and concentration as it enters the heated (or cooled) reaction section. The fluid density is constant.

### Reactions:



The heterogeneous reaction occurs at the tube wall. Specify that physical properties (density, heat capacity, etc.) are constant with composition and temperature.

### Dimensioned variables:

$c_A$  concentration of species A ( $\text{mol}/\text{m}^3$ )  
 $c_B$  concentration of species B ( $\text{mol}/\text{m}^3$ )

$C_p$	heat capacity of fluid (kJ/kg/K)
$D$	diffusion coefficient of components in fluid (m <sup>2</sup> /s)
$E_a^f$	activation energy of homogeneous reaction (kJ/mol)
$E_a^w$	activation energy of heterogeneous reaction at tube wall (kJ/mol)
$k^f$	rate coefficient of homogeneous reaction in fluid (1/s)
$k^w$	rate coefficient of heterogeneous reaction at tube wall (m/s)
$k_t$	thermal conductivity of fluid (kJ/m/s/K)
$r$	radial position (m)
$R$	radius of tube (m)
$R_g$	ideal gas constant (= 0.0083143 kJ/mol/K)
$T$	temperature of fluid (K)
$T_0$	inlet temperature of fluid (K)
$U$	fluid velocity at radial position $r$ and axial position $x$ (m/s)
$U_{mean}$	mean fluid velocity at axial position $x$ (m/s)
$x$	axial position (m)
$W$	heat flux imposed at tube wall (kJ/s/m <sup>2</sup> = kW/m <sup>2</sup> ), positive for heating fluid, constant with axial position
$\alpha$	thermal diffusivity $k_t/(\rho C_p)$ (m <sup>2</sup> /s)
$\mu$	dynamic viscosity of fluid (Pa s) (1 Poise = 0.1 kg/m/s = 0.1 N/m <sup>2</sup> = 0.1 Pa s)
$\rho$	density of fluid (kg/m <sup>3</sup> )
$\nu$	kinematic viscosity of fluid ( $\mu/\rho$ ) (m <sup>2</sup> /s)

Dimensionless variables:

$c_A'$	$c_A/c_{A0}$ , where $c_{A0}$ = concentration of A at inlet
$c_B'$	$c_B/c_{A0}$
$Da^f$	Damkoehler number for reaction in fluid = $k^f/(D/R^2)$ , varies with T.
$Da^w$	Damkoehler number for reaction at wall = $k^w/(D/R)$ , varies with T.
$Pr$	Prandtl number ( $\nu/\alpha$ )
$Re$	Reynolds number ( $2 R U_{mean}/\nu$ ) must be $\leq 2100$ for laminar flow
$r'$	$r/R$ = dimensionless radial position
$Sc$	Schmidt number ( $\nu/D$ )
$T'$	$T/T_0$ , where $T_0$ is inlet temperature of fluid.
$\theta^f$	$(-\Delta H^f c_{A0} D/k_t)/T_0$ = dimensionless T change by homogeneous reaction in fluid, positive for T increase due to exothermic reaction
$\theta^w$	$(-\Delta H^w c_{A0} D/k_t)/T_0$ = dimensionless T change by heterogeneous reaction at wall, positive for T increase due to exothermic reaction
$u'$	dimensionless fluid velocity, $U/U_{mean} = 2*(1 - r'^2)$ for fully developed laminar flow
$x'$	$(x/R)/(ReSc) = xD/(2R^2 U_{mean})$ = dimensionless distance down tube (axial position)
$\beta$	$WR/(k_t T_0)$ ; % dimensionless heat flux at wall, positive for heating fluid

**NOTE: drop ' on all dimensionless variables below.**

Material balances

Balances on the gas-phase components over ring-shaped control volume at steady state results in the following dimensionless equations:

$$0 = -Da^f c_A - \frac{u}{2} \frac{\partial c_A}{\partial x} + \frac{1}{(ReSc)^2} \frac{\partial^2 c_A}{\partial x^2} + \left( \frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r} \frac{\partial^2 c_A}{\partial r} \right)$$

$$0 = Da^f c_A - \frac{u}{2} \frac{\partial c_B}{\partial x} + \frac{1}{(ReSc)^2} \frac{\partial^2 c_B}{\partial x^2} + \left( \frac{\partial^2 c_B}{\partial r^2} + \frac{1}{r} \frac{\partial^2 c_B}{\partial r} \right)$$

$$0 = -\frac{u}{2} \frac{\partial c_C}{\partial x} + \frac{1}{(ReSc)^2} \frac{\partial^2 c_C}{\partial x^2} + \left( \frac{\partial^2 c_C}{\partial r^2} + \frac{1}{r} \frac{\partial^2 c_C}{\partial r} \right)$$

Terms from left to right:

*Accumulation = gas rxn, convection, axial diffusion, radial diffusion.*

The Damkohler number varies with  $T$ . The fluid velocity  $u$  varies with radius  $r$ . The axial diffusion term can be neglected for large  $ReSc$ . 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.

Initial Conditions:

$$c_A(0, r) = 1 \quad c_B(0, r) = c_C(0, r) = 0$$

Boundary Conditions (after neglecting axial diffusion)

At tube centerline

$$\left[ \frac{\partial c_A}{\partial r} \right]_{r=0} = \left[ \frac{\partial c_B}{\partial r} \right]_{r=0} = \left[ \frac{\partial c_C}{\partial r} \right]_{r=0} = 0$$

At wall

$$\left[ \frac{\partial c_A}{\partial r} \right]_{r=1} = 0 \quad ; \quad \left[ \frac{\partial c_B}{\partial r} \right]_{r=1} = -Da^w c_B(x, 1) \quad ; \quad \left[ \frac{\partial c_C}{\partial r} \right]_{r=1} = Da^w c_B(x, 1)$$

## Energy balance

$$0 = \theta^f Da^f c_A - \left( \frac{Pr}{Sc} \right) \frac{u}{2} \frac{\partial T}{\partial x} + \frac{1}{(ReSc)^2} \frac{\partial^2 T}{\partial x^2} + \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right)$$

In the second term on the right hand side,  $Pr/Sc = D/\alpha$ . The diffusion coefficient  $D$  comes in because of the way the axial position  $x$  was made dimensionless. The  $ReSc$  for the axial conduction term is correct and should not be  $RePr$ . The thermal conductivity,  $k$ , that originally appeared in the axial and radial conduction terms went into the  $Pr$  and  $\theta$  of the first two terms on making variables dimensionless.

The Damkohler number varies with  $T$ . The fluid velocity  $u$  varies with radius  $r$ . The axial conduction term can be neglected for large  $ReSc$ .

## Initial Conditions

$$T(0, r) = 1$$

## Boundary Conditions (after neglecting axial conduction)

$$\left[ \frac{\partial T}{\partial r} \right]_{r=0} = 0$$

$$\left[ \frac{\partial T}{\partial r} \right]_{r=1} = \beta + \theta^w Da^w c_B(x, 1)$$

On the right hand side, the first term is due to the constant heat flux imposed at the wall. The second term is due to the heat of reaction from the heterogeneous reaction at the wall under the assumption that the heat of reaction is released into the fluid. The Damkohler number varies with  $T$ .

## **2D SYSTEM - FINITE-DIFFERENCE APPROXIMATION - Matlab listing**

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

```
% Richard K. Herz <rherz@ucsd.edu> May 2002
% CVD simulation
% simulation of isothermal, laminar flow in tube with rxn in gas and rxn at wall
% flow is fully developed laminar flow when entering reaction section
% neglect axial diffusion (good for large ReSc)
% negligible pressure drop, therefore constant gas density and flow rate

% Reactions:
% A -> B in gas (rate has units mol/m^3/s)
% A -> solid film at wall (rate has units mol/m^2/s)
% B -> solid film at wall

% SET UP HERE to repeat for 2, 5, and 10 mm-diameter tubes
% at Umean fixed at 10 m/s for all tube diameters

clear
diam = [0.2e-2, 0.5e-2, 1e-2]; % m, diameters of tube
pcolor = ['g', 'r', 'b']; % colors for each diam for plots
```

```

for d = 1:3 % ***** start of main FOR repeat through the diameters *****
% ***** start of main input values to change *****
xdiv = 10000; % number of x divisions down reactor of dimensionless length xmax
rdiv = 10; % number of r divisions across tube radius
% Numerical solution stability considerations in picking xdiv and rdiv:
% for case of no reaction and plug flow in square channel: dx << dr^2, or rdiv^2 << xdiv
% for reaction in gas, dx*Dag << 1, or Dag << xdiv

% kAg = 1e4, kBw = 10 gives DaAg = DaBw = 100 for
% 2 mm tube (Da's change with diameter for same k's)

kAg = 1000; % (1/s), rate coefficient for A->B rxn in gas
kBw = 10; % (m/s), rate coefficient for B->film rxn at wall

kAw = 0; % (m/s), rate coefficient for A->film rxn at wall

len = 1; % m, length of tube
D = 1e-4; % m^2/s
vis = 1.2e-4; % (Pa s), 0.18e-4 = of N2 at 300 K, 1 atm (Perry's 3-247)
conc = 101325/(8314.3*300); % kmol/m3 = N/V = P/RT, P in Pa, R in units (Pa m3/kmol K)

% ***** end of main input values to change *****

dens = conc*28; % kg/m3 = kmol/m3 * kg/kmol
R = diam(d)/2; % m, radius of tube

% xxx below for fixed volumetric flow rate, variable Umean xxx
flow = 7.5e-5; % m3/s, volumetric flow rate at reaction conditions
area = pi*R^2; % m2, cross-sectional area of tube
Umean = flow/area; % m/s, mean linear velocity

% xxx below for fixed Umean at all diams xxx
Umean = 10; % m/s

% Dimensionless variables

% x' = (x/R)/(Re*Sc) = x*D/(2*R^2*Umean) = dimensionless distance down tube
% r' = r/R = dimensionless radial position in tube of radius R
% cA' = cA/cA0, where cA0 = concentration of A at inlet
% cB' = cB/cA0
% u' = U/Umean = dimensionless gas velocity, u' = 2*(1 - r'^2)
% drop ' on x', r', cA', cB', u' below
% DaAg = Damkoehler number for A->B rxn in gas = kAg/(D/R^2), kAg units (1/s)
% DaAw = Damkoehler number for A->film rxn at wall = kAw/(D/R), kAw units (m/s)
% DaBw = Damkoehler number for B->film rxn at wall = kBw/(D/R)
% where D = diffusion coefficient of gaseous A and B

% NOTE there's no reason d'less x'-max can't be less than or greater than 1
% x(meters) = x'*(2*R^2*Umean)/D )

Re = 2*R*Umean/(vis/dens); % Reynolds number
Sc = (vis/dens)/D; % Schmidt number
ReSc = Re*Sc; % product of Re and Sc
ReSc2 = ReSc^2; % square of ReSc needs to be large to neglect axial diffusion

xmax = len*D/(2*R^2*Umean); % dimensionless tube length = (x/R)/(Re*Sc)
dx = xmax/xdiv;
dr = 1/rdiv;

% NOTE similarity of Da to square of Thiele parameter

DaAg = kAg/(D/R^2) % Damkoehler number for A->B rxn in gas
DaBw = kBw/(D/R) % Damkoehler number for B->film rxn at wall
DaAw = kAw/(D/R); % Damkoehler number for A->film rxn at wall

x = [0:dx:xmax]'; % dimensionless distance down tube (ROWS)
r = [0:dr:1]'; % dimensionless distance from center to wall (COLUMNS)

cA = ones(xdiv+1, rdiv+1); % using ones() sets inlet cond for cA of reactant A entering
cB = zeros(xdiv+1, rdiv+1); % using zeros() sets inlet cond for cB of product B entering

```

```

for j = 1:xdiv
    i = 1; % r = 0, tube center BC of symmetry (zero flux)
    cA(j+1,i) = cA(j,i)+ dx*(1/(1-r(i)^2))*(-DaAg*cA(j,i)+2*(cA(j,i+1)-cA(j,i))/dr^2);
    cB(j+1,i) = cB(j,i)+ dx*(1/(1-r(i)^2))*(DaAg*cA(j,i)+2*(cB(j,i+1)-cB(j,i))/dr^2);
    % constrain cA and cB to physical values
    % this block of IFs repeated below so could make into a function
    if cA(j+1,i)>1;
        cA(j+1,i)=1;
    end
    if cA(j+1,i)<0;
        cA(j+1,i)=0;
    end
    if cB(j+1,i)>1;
        cB(j+1,i)=1;
    end
    if cB(j+1,i)<0;
        cB(j+1,i)=0;
    end
    for i = 2:rdiv % main PDE, step across tube between center and wall
        cA(j+1,i) = cA(j,i)+ dx*(1/(1-r(i)^2))*(-DaAg*cA(j,i)+(cA(j,i+1)-2*cA(j,i)+...
            cA(j,i-1))/dr^2+(cA(j,i+1)-cA(j,i-1))/(r(i)*2*dr));
        cB(j+1,i) = cB(j,i)+ dx*(1/(1-r(i)^2))*(DaAg*cA(j,i)+(cB(j,i+1)-2*cB(j,i)+...
            cB(j,i-1))/dr^2+(cB(j,i+1)-cB(j,i-1))/(r(i)*2*dr));
        if cA(j+1,i)>1;
            cA(j+1,i)=1;
        end
        if cA(j+1,i)<0;
            cA(j+1,i)=0;
        end
        if cB(j+1,i)>1;
            cB(j+1,i)=1;
        end
        if cB(j+1,i)<0;
            cB(j+1,i)=0;
        end
    end
end
i = rdiv+1; % tube wall BC of flux from gas = reaction at wall
cA(j+1,i) = cA(j+1,i-1)/(DaAw*dr + 1);
cB(j+1,i) = cB(j+1,i-1)/(DaBw*dr + 1);
if cA(j+1,i)>1;
    cA(j+1,i)=1;
end
if cA(j+1,i)<0;
    cA(j+1,i)=0;
end
if cB(j+1,i)>1;
    cB(j+1,i)=1;
end
if cB(j+1,i)<0;
    cB(j+1,i)=0;
end
end
filmRateA = kAw*cA(1:xdiv+1,rdiv+1); % rate with units mol/s/m2
filmRateB = kBw*cB(1:xdiv+1,rdiv+1);
filmRateTot = filmRateA + filmRateB;
xm = R*Re*Sc*x; % x in m, x' = (x/R)/(Re*Sc)

```



```

figure(1)
hold on
plot(xm, filmRateTot, pcolor(d))
title('film growth rate, blu=10mm, red=5mm, grn=2mm')
ylabel('film growth rate at wall (mol/s/m2)')
xlabel('Distance down tube (m)')

figure(2)
hold on
plot(xm, log10(filmRateTot), pcolor(d))
title('log10(growth rate), blu=10mm, red=5mm, grn=2mm')
ylabel('log10(growth rate at wall (mol/s/m2))')
xlabel('Distance down tube (m)')

% compute "mixed mean concentrations"
% (also "bulk fluid conc", "mixing-cup conc")
% need to "weight" conc at each radius by fluid velocity and cross-sectional
% area at that radius

cAmean = zeros(xdiv+1,1);
for j = 1:xdiv+1
    % at center, volume taken as pi*r^2, where r = half of dr
    cAmean(j) = cA(j,1) + cA(j,i)*(2*(1-r(1)^2))*pi*(dr/2)^2;
    for i = 2:rdiv
        % in central sections, flow area is approx. 2*pi*r*dr
        cAmean(j) = cAmean(j) + cA(j,i)*(2*(1-r(i)^2))*2*pi*r(i)*dr;
    end
    % at wall, flow area taken as half of that in central sections
    cAmean(j) = cAmean(j) + cA(j,i)*(2*(1-r(rdiv+1)^2))*pi*r(rdiv+1)*dr;
end

% now normalize by mean velocity times tube x-sect area = 1 * (pi*1^2) = pi
% using dimensionless variables for velocity and radius
% but cAmean(1) for A at inlet at this point is slightly off from pi (3.07 vs. 3.14)
% due to approximate integration, so use cAmean(1) for normalization

% note using cAmean(1) for normalization only works for case where inlet conc
% of A is 1 at all radii, otherwise, use pi for normalization
cAnorm = cAmean(1); % so can save and access orig cAmean(1) after normalization
cAmean = cAmean/cAnorm;

cBmean = zeros(xdiv+1,1);
for j = 1:xdiv+1
    % at center, volume taken as pi*r^2, where r = half of dr
    cBmean(j) = cBmean(j) + cB(j,i)*(2*(1-r(1)^2))*pi*(dr/2)^2;
    for i = 2:rdiv
        % in central sections, flow area is approx. 2*pi*r*dr
        cBmean(j) = cBmean(j) + cB(j,i)*(2*(1-r(i)^2))*2*pi*r(i)*dr;
    end
    % at wall, flow area taken as half of that in central sections
    cBmean(j) = cBmean(j) + cB(j,i)*(2*(1-r(rdiv+1)^2))*pi*r(rdiv+1)*dr;
end

% now normalize by mean velocity times tube x-sect area = 1 * (pi*1^2) = pi
cBmean = cBmean/cAnorm;

% note using cAmean(1) for normalization only works for case where inlet conc
% of A is 1 at all radii, otherwise, use pi for normalization

figure(3)
hold on
plot(xm, cAmean, pcolor(d), xm, cBmean, pcolor(d))
title('mean gas conc, cA starts at 1, cB at 0, blu=10mm, red=5mm, grn=2mm')
xlabel('Distance from inlet (m)')
ylabel('mean gas conc(mol/m3)')

end % ***** end of main FOR repeat through the diameters *****
fprintf('\n ***** three plots were produced ***** \n\n')

```