10.37 Spring 2007
Problem Set 10 Solutions

1. a) Yes, the reaction is limited by external diffusion.

b) Table 12-1 shows that external diffusion-limited ra varies with $U^{1/2}$ and nearly linearly with T. This is the case for:

F_{T0} = 10 mol/hr, all T
F_{T0} = 100 mol/hr, about 362K < T < 375K

c) Yes, the reaction is "reaction-rate-limited".

d) According to Fogler, r_A varies exponentially with both reaction-rate-limitations and internal-diffusion-limitations, and is nearly independent of F_{T0}. However, rA varies more with T more strongly in the reaction-rate limited regime. So, the reaction-rate-limitation is overcome before the internal-diffusion-limitation as T is increased. This is the case for:

T < 362K, F_{T0} = 100 mol/hr
T < 365K, F_{T0} > 1000 mol/hr

e) Yes, the reaction is limited by internal diffusion.

f) Internal-diffusion limitations are seen at:

367K < T > 377K, F_{T0} > 1000 mol/hr

g) $$\Omega = \frac{actual\_rate(external\_\lim)}{ideal\_rate(rxn\_\lim)} = \frac{-r_A'\left(10\frac{mol}{hr},360K\right)}{-r_A'\left(5000\frac{mol}{hr},360K\right)} \approx \frac{.25}{.70} = 0.36$$

h) $$\eta = \frac{\text{actual\_rate(internal\_lim)}}{\text{ideal\_rate(rxn\_lim)}} = \frac{-r_A'\left(5000\frac{mol}{hr},367K\right)}{-r_A'\left(5000\frac{mol}{hr},367K\right)}$$

Extrapolate the reaction-rate limited portion of the F_{T0} = 5000 mol/hr curve up to 367 K.

$$\eta \approx \frac{1.2}{1.5} = 0.8$$

i) Fort a first order reaction with spherical pellets:

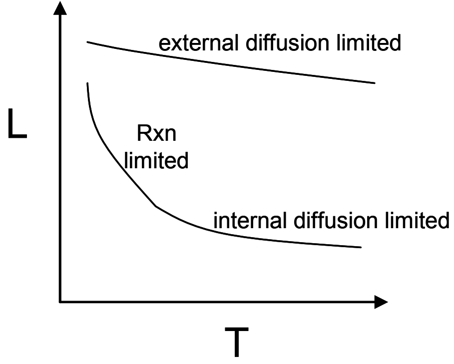
$$\eta = \frac{3}{\phi_1^2}\left(\phi_1 \coth\phi_1 - 1\right) = 0.8$$

Solve: $\phi_1 = 2.0$

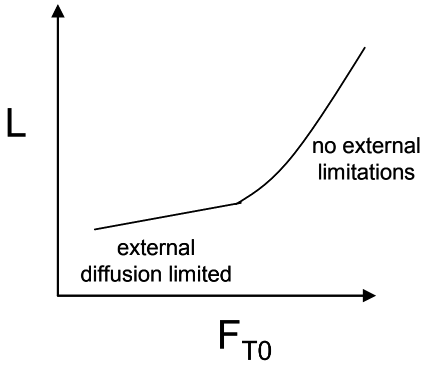
$$\Psi = \frac{C_A}{C_{A,S}} = \frac{1}{\lambda}\left(\frac{\sinh(\phi_1 \lambda)}{\sinh \phi_1}\right) \quad \text{with } \lambda = r/R = 1/2$$

$$C_A = C_{A,S}\frac{1}{\lambda}\left(\frac{\sinh(\phi_1 \lambda)}{\sinh \phi_1}\right) = 1\frac{mol}{L}(2)\left(\frac{\sinh(1)}{\sinh(2)}\right) = 0.65\frac{mol}{L}$$

j) For a given F_{T0}, the reaction rate will increase either exponentially or linearly with T (meaning the needed pipe length to achieve a certain conversion will decrease either exponentially or linearly with T).



For a given T, increasing the flowrate will increase the pipe length needed for a given conversion. However, while in the external diffusion limited region, an increase in F_{T0} also increases the reaction rate (i.e. decreases the pipe length). The higher r_A will offset somewhat the effect of the higher flow rate, and therefore the needed pipe length will increase slowly with F_{T0} while in the external-diffusion limited region. When the process is internal-diffusion or rxn-rate limited, r_A no longer increases with F_{T0}, so the pipe length needed for a given conversion will increase sharply.



2. a)

$$r_{\lim} = k\theta_{NO-M}\theta_{CO-M}\left(\frac{\text{Area of noble metal}}{\text{Volume of porous material}}\right)$$

where $\theta_{i-M} = \frac{[i-M]}{[M]_o}$

Use the adsorption steps (rapid equilibrium) to find θ_{i-M}.

$$K_{eq,1} = \frac{[CO-M]}{P_{CO}[M]} = \frac{\theta_{CO-M}[M]_o}{P_{CO}[M]} \qquad \Rightarrow \qquad \theta_{CO-M} = \frac{K_{eq,1}P_{CO}[M]}{[M]_o}$$

$$K_{eq,2} = \frac{[NO-M]}{P_{NO}[M]} = \frac{\theta_{NO-M}[M]_o}{P_{NO}[M]} \qquad \Rightarrow \qquad \theta_{NO-M} = \frac{K_{eq,1}P_{NO}[M]}{[M]_o}$$

Use and overall site balance to find [M] (concentration of empty sites).

$$[M]_o = [M] + [CO-M] + [NO-M] = [M] + \theta_{CO-M}[M]_o + \theta_{NO-M}[M]_o$$

Substitute in the equations for θ_{i-M}:

$$[M]_o = [M] + \frac{K_{eq,1}P_{CO}[M]}{[M]_o}[M]_o + \frac{K_{eq,2}P_{NO}[M]}{[M]_o}[M]_o$$

Solve for [M] and use the simplifications given in the problem statement ($K_{eq2}P_{NO} << K_{eq1}P_{CO}$ and $P_{CO} = P_{CO,S}$):

$$[M] = \frac{[M]_o}{1 + K_{eq,1}P_{CO} + K_{eq,2}P_{NO}} = \frac{[M]_o}{1 + K_{eq,1}P_{CO,S}}$$

Substitute θ_{i-M} and [M] into given rate equation:

$$-r_{NO} = r_{\lim} = k\frac{K_{eq,1}P_{CO,S}}{[M]_o}\frac{K_{eq,2}P_{NO}}{[M]_o}\left(\frac{[M]_o}{1 + K_{eq,1}P_{CO,S}}\right)^2\left(\frac{\text{Area of noble metal}}{\text{Volume of porous material}}\right)$$

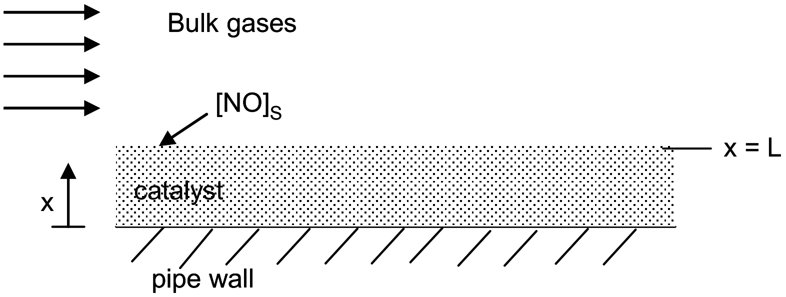
$$-r_{NO} = k\frac{K_{eq,1}P_{CO,S}K_{eq,2}}{(1 + K_{eq,1}P_{CO,S})^2}\left(\frac{\text{Area of noble metal}}{\text{Volume of porous material}}\right)P_{NO} = k' P_{NO}$$

or, in terms of NO concentration:

$$-r_{NO} = k' RT[NO] = k''[NO]$$

where $k'' = k\dfrac{K_{eq,1}K_{eq,2}P_{CO,S}}{(1+K_{eq,1}P_{CO,S})^2}\left(\dfrac{\text{Area of noble metal}}{\text{Volume of porous material}}\right)RT$

b) We now have a rate expression that is first order in [NO]. The thickness of the catalyst on the surface is small, so the curvature can be ignored and the catalyst is modeled as a slab:



At steady state, diffusion of NO inside the catalyst is governed by:

$$D_{pores}\frac{\partial^2[NO]}{\partial x^2} + r_{NO} = 0$$

$$D_{pores}\frac{\partial^2[NO]}{\partial x^2} - k''[NO] = 0$$

Non-dimensionalize:

$$\psi \equiv \frac{[NO]}{[NO]_S} \qquad \lambda \equiv \frac{x}{L} \qquad \Rightarrow \qquad \frac{\partial^2\Psi}{\partial\lambda^2} - \left(\frac{k'' L^2}{D_{pores}}\right)\Psi = 0$$

So, the Thiele modulus is defined as:

$$\phi^2 \equiv \frac{k'' L^2}{D_{pores}}$$

The equation: $\dfrac{\partial^2\Psi}{\partial\lambda^2} - \phi^2\Psi = 0$

Has a solution of the form: $\psi = Ae^{-\lambda\phi} + Be^{\lambda\phi}$

The boundary conditions are:

1. $\Psi\big|_{\lambda=1} = 1$ ([NO] = [NO]$_S$ at the surface)

2. $\left.\dfrac{\partial \Psi}{\partial \lambda}\right|_{\lambda=0} = 0$ (no flux at pipe wall)

From the second boundary condition:

$$\frac{\partial \psi}{\partial \lambda} = -A\phi e^{-\lambda\phi} + B\phi e^{\lambda\phi}$$

$$0 = -A\phi e^{0} + B\phi e^{0} \qquad \Rightarrow \qquad \mathrm{A = B}$$

From the first boundary condition:

$$1 = Ae^{-\phi} + Ae^{\phi} \qquad \Rightarrow \qquad A = \frac{1}{e^{-\phi} + e^{\phi}}$$

Solution of the concentration profile of NO inside the catalyst (treated as a slab):

$$\psi = \frac{e^{-\lambda\phi} + e^{\lambda\phi}}{e^{-\phi} + e^{\phi}}$$

We want the internal effectiveness factor (η) as a function of the thiele modulus (ϕ).

$$\eta = \frac{\text{actual rxn rate}}{\text{rxn rate is all catalyst was exposed to }[\mathrm{NO}]_{\mathrm{S}}}$$

The actual reaction rate is the integral of the concentration times the first order rate constant over the entire slab thickness. However, an easier way to find this is to use the fact that the flux at the surface of the catalyst has to be equal to the total reaction occurring inside.

$$\text{actual rxn rate} = (\text{flux})(\text{surface area}) = D_{pores}\frac{\partial[NO]}{\partial x}A_{surface} = D_{pores}\frac{[NO]_S}{L}\left.\frac{\partial \Psi}{\partial \lambda}\right|_{\lambda=1}A_{surface}$$

$$\text{actual rxn rate} = D_{pores}\frac{[NO]_S}{L}\left(\frac{-\phi e^{-\phi} + \phi e^{\phi}}{e^{-\phi} + e^{\phi}}\right)A_{surface}$$

$$\text{rxn rate if all catalyst was exposed to }[\mathrm{NO}]_{\mathrm{S}} = k''[NO]_S V_{catalyst}$$

$$\eta = \frac{D_{pores}\frac{[NO]_S}{L}\left(\frac{-\phi e^{-\phi}+\phi e^{\phi}}{e^{-\phi}+e^{\phi}}\right)A_{surface}}{k''[NO]_S V_{catalyst}} = \frac{D_{pores}}{k''L^2}\left(\frac{-\phi e^{-\phi}+\phi e^{\phi}}{e^{-\phi}+e^{\phi}}\right) = \frac{1}{\phi}\left(\frac{e^{\phi}-e^{-\phi}}{e^{\phi}+e^{-\phi}}\right)$$

(note that the surface area exposed to the bulk gas divided by the volume of porous material is equal to 1/L)

c) $$\Omega = \frac{\text{actual rxn rate}}{\text{rxn rate is all catalyst was exposed to }[\text{NO}]_{\text{bulk}}} = \frac{\eta k''[NO]_S V_{catalyst}}{k''[NO]_{bulk} V_{catalyst}} = \frac{\eta [NO]_S}{[NO]_{bulk}}$$

Need to use flux balance to find $[NO]_S$.

At steady state:

$$\text{flux to the catalyst surface} = \text{rxn inside catalyst}$$

$$k_c A_{surface}\left([NO]_{bulk} - [NO]_S\right) = \eta k''[NO]_S V_{catalyst}$$

Solve for $[NO]_S$:

$$[NO]_S = \frac{k_c A_{surface}[NO]_{bulk}}{\eta k'' V_{catalyst} + k_c A_{surface}} = \frac{k_c [NO]_{bulk}}{\eta k'' L + k_c}$$

Substitute into the omega equation:

$$\Omega = \frac{\eta k_c [NO]_{bulk}}{[NO]_{bulk}\left(\eta k'' L + k_c\right)} = \frac{\eta k_c}{\eta k'' L + k_c}$$

where $k_c = D_{bulk}/\text{delta}$

d) Design equation for a PFR:

$$\frac{dX_{NO}}{dz} = \frac{-r_{NO} A_c V_{porous\_material}}{F_{NO,0} V_{reactor}} = \frac{\Omega k''[NO] A_c V_{porous\_material}}{F_{NO,0} V_{reactor}} = \frac{\Omega k''[NO]_0\left(1 - X_{NO}\right) A_c V_{porous\_material}}{F_{NO,0} V_{reactor}}$$

Note that the change in the number of moles can be ignored because epsilon ≈ 0 (mole fraction of NO in the feed is extremely small).

The $V_{porous\_material}/V_{reactor}$ term is needed because the rate expression derived in part a) is per volume of porous material, but the rate expression in the PFR design equation needs to be on a per volume of reactor basis.

In order to calculate kc, need to first calculate delta using the equation given in the problem statement:

$$\delta = \frac{.001m}{\mathrm{Re}^{0.5}} \qquad \text{where } \mathrm{Re} = \frac{\rho U d_{pipe}}{\mu}$$

To calculate the superficial velocity (U) in each pipe, use the equation:

$$U = \frac{q_o}{A_c} = \frac{F_{NO,o}}{[NO]_o A_c}$$

The feed molar flow rate of NO in each pipe is found by dividing the total feed molar flow rate of NO by the number of pipes:

$$F_{NO,o} = \frac{F_{NO,o,total}}{N_{pipes}}$$

The concentration of NO in the feed is found by multiplying the feed mole fraction by the total concentration:

$$[NO]_o = y_{NO,o} C_{tot} = \frac{F_{NO,o}}{\sum_i F_{i,o}} \frac{P}{RT}$$

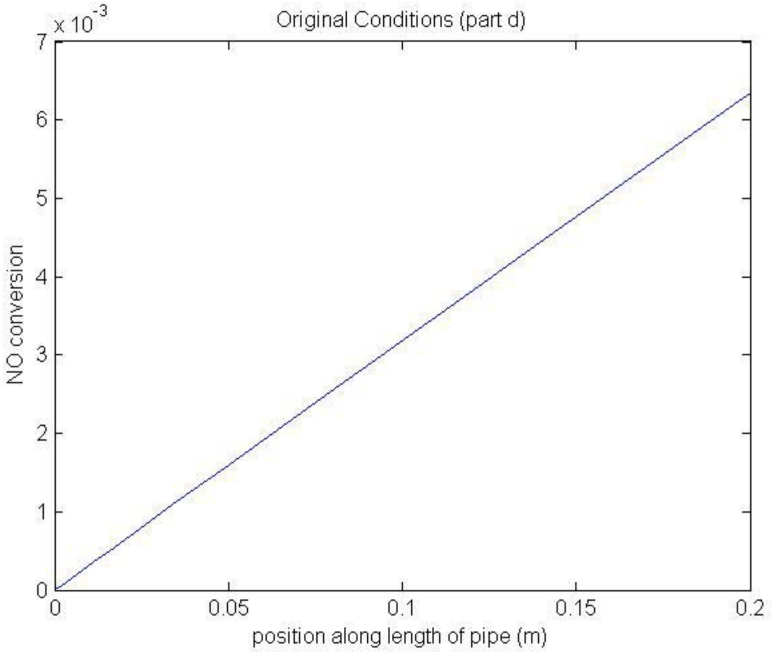
See matlab code below:

```
function [X1f,X2f,X3f,X4f,X5f] = HW10_P2_allparts();
%[X] = HW10_P2_allparts()

[z1,X1] = reactorsimulation(1E-6, 2000, 0.2);
[z2,X2] = reactorsimulation(2E-6, 2000, 0.2);
[z3,X3] = reactorsimulation(1E-6, 4000, 0.2);
[z4,X4] = reactorsimulation(1E-6, 2000, 0.4);
[z5,X5] = reactorsimulation(.4E-6, 5000, 0.2);

%[z,X] = reactorssimulation(catalyst thickness, number of pipes, length of
%pipes, total mol/hr in feed)

X1f = X1(length(z1));
X2f = X2(length(z2));
X3f = X3(length(z3));
X4f = X4(length(z4));
X5f = X5(length(z5));

figure(1);
plot(z1,X1);
xlabel(['position along length of pipe (m)'])
```

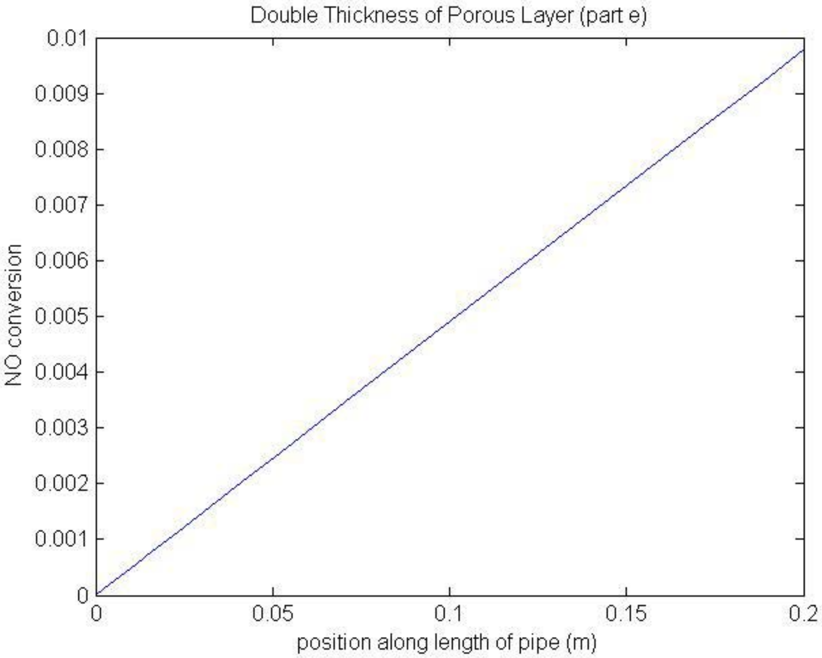
```
ylabel('NO conversion')
title('Original Conditions (part d)')

figure(2);
plot(z2,X2);
xlabel(['position along length of pipe (m)'])
ylabel('NO conversion')
title('Double Thickness of Porous Layer (part e)')

figure(3);
plot(z3,X3);
xlabel(['position along length of pipe (m)'])
ylabel('NO conversion')
title('Double Number of Parallel Pipes (part f)')

figure(4);
plot(z4,X4);
xlabel(['position along length of pipe (m)'])
ylabel('NO conversion')
title('Double Length of Pipes (part g)')

figure(5);
plot(z5,X5);
xlabel(['position along length of pipe (m)'])
ylabel('NO conversion')
title('Thinner Catalyst Layer, More Pipes (same amount of noble metal)(part
h)')

return;

function [z,X] = reactorsimulation(thicknessofcatalyst,numberofpipes,...
lengthofpipes);

%a = NO
%b = CO
%Reactor/Catalyst Geometry and Chemistry
param.L = thicknessofcatalyst; %m
N = numberofpipes;
Lp = lengthofpipes; %m
param.T = 700; %in Kelvin
dpipe = 8/1000; %inner diameter of each pipe 8 mm, in m
param.Ac = pi*(dpipe/2)^2; %cross sectional area of each pipe, m^2

%Reactor/Feed Conditions
P = 1*101325; %pressure = 1atm, in Pa
param.R = 8.314; %gas constant, J/(K mol)
Ctot = P/param.R/param.T; %total concentration of gas, moles/m^3
ya0 = 4/1624; %feed mole fraction of NO
yb0 = 20/1624; %feed mole fraction of CO
Ftot = (1200+200+200+20+4)/60/60/N; %total feed flow rate per pipe (mol/s)
param.Fa0 = ya0*Ftot; %NO feed molar flow rate into each pipe, in mol/s
Fb0 = yb0*Ftot; %CO feed molar flow rate into each pipe, in mol/s
param.Ca0 = ya0 * Ctot; %feed concentration of NO, in mol/m^3
Cb0 = yb0 * Ctot; %feed concentration of CO, in mol/m^3
param.theta_b = yb0/ya0; %feed ratio for CO
```

```
q=param.Fa0/param.Ca0;  %volumetric flow rate into each pipe, in m^3/s
U = q/param.Ac; %superficial velocity in each pipe, in m/s

%Physical Property Data
Dbulk = 1E-8; %in m^2/s
mu = 3E-5; %viscosity in Pa*s = kg/m/s
rho = 0.5; %density in kg/m^3
Re = rho*U*dpipe/mu; %Reynolds number
delta = 0.001/(Re^0.5); %thickness of boundary layer, in m
param.kc = Dbulk/delta; %m/s
param.Vporous_mat = pi*dpipe*param.L*Lp; %volume of catalyst (m^3)
param.Vreactor = param.Ac*Lp; %volume of reactor (m^3)

odeoptions = odeset('AbsTol',1e-9,'RelTol',1e-12);
[z,X]=ode15s(@diffeqs,[0 Lp],0,odeoptions,param);
return

function dXdz = diffeqs(z,X,param);

%unpack the parameters
T = param.T;
R = param.R;
kc = param.kc;
Ac = param.Ac;
L = param.L;
theta_b = param.theta_b;
Vporous_mat = param.Vporous_mat;
Vreactor = param.Vreactor;
Ca0 = param.Ca0;
Fa0 = param.Fa0;

Dpores = 1E-9; %in m^2/s
Area_metal_per_Vol_porous_material = 0.1*100^3; %m^2 platinum/m^3 porous
material
Keq1 = 1/101325; %Pa^-1
Keq2 = 3/101325; %Pa^-1
k = 400/60/60; %reaction rate constant, in mol/s/m^2(of noble metal)

Ca = Ca0*(1-X);
Cb = Ca0*(theta_b-X);
Pbs = Cb*R*T; %CO pressure in pores (Pa)

k_double_prime =
k*R*T*Keq1*Keq2*Pbs/(1+Keq1*Pbs)^2*Area_metal_per_Vol_porous_material;
%mol/s/m^3(catalyst)*1/Pa

phi = (k_double_prime/Dpores)^.5*L;
eta = 1/phi*(exp(phi)-exp(-phi))/(exp(phi)+exp(-phi));
omega = eta*kc/(eta*k_double_prime*L+kc);

r = k_double_prime*Ca*omega; %mol/s/m^3(catalyst)

dXdz = r/Fa0*Vporous_mat/Vreactor*Ac; %m^-1
return
```

d) Original conditions (does not meet emission specifications).



e) Double thickness of porous layer - more conversion (more catalyst).



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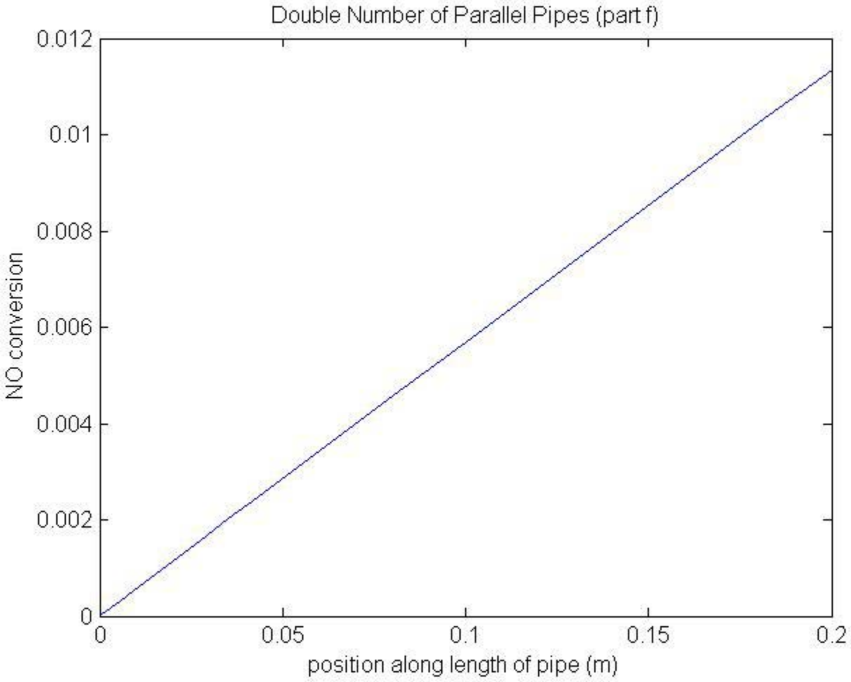
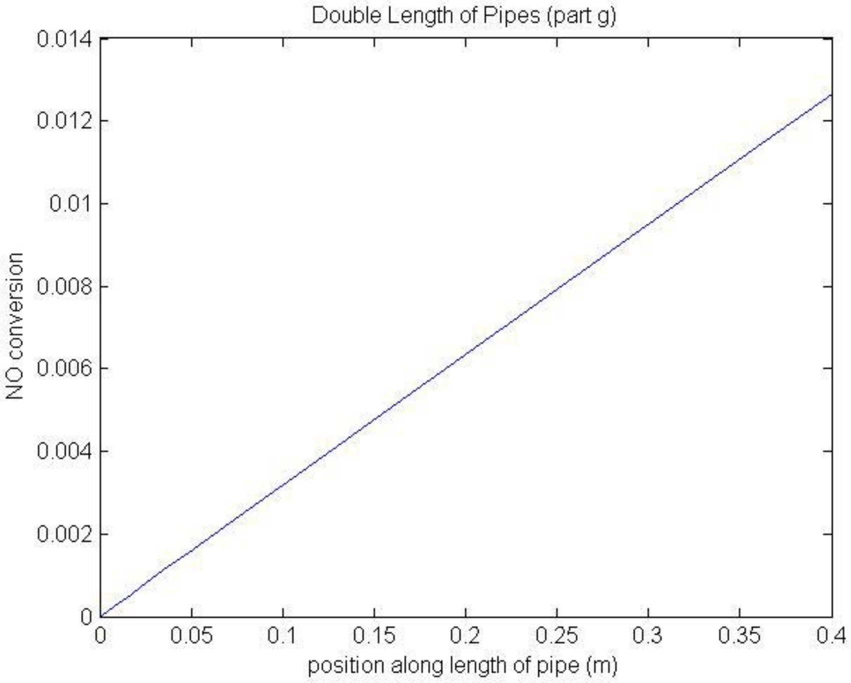
f) Double number of parallel pipes – more conversion (lower flow rate).



g) Double length of pipes – higher conversion.



h) Open ended.

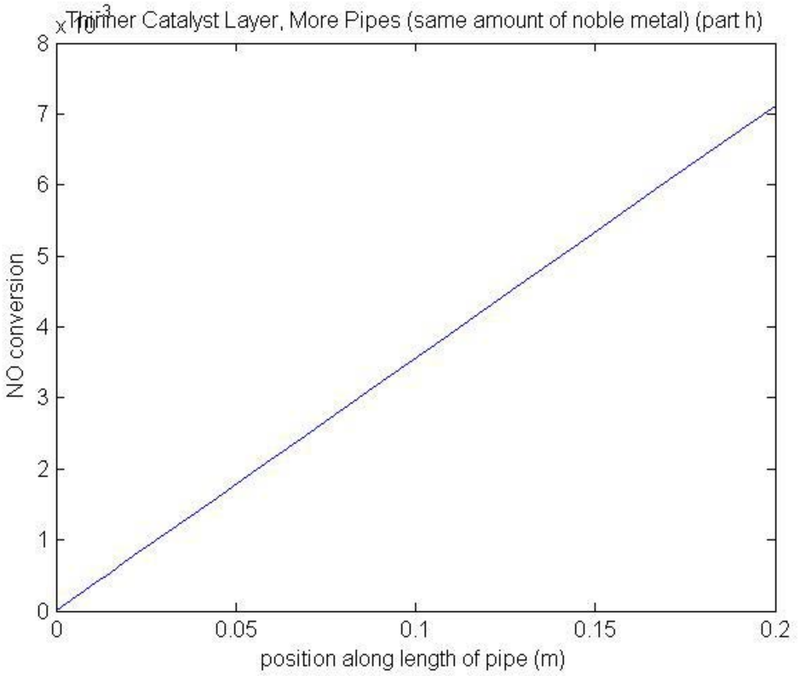
Improve reaction rate by increasing T or changing the catalyst to improve surface area to volume ratio.

Improve external mass transfer by making more turbulent flow.

Improve internal mass transfer by making a larger number of shallower pores.

Many other answers possible. Equation 4-36 in Fogler gives an equation for calculating pressure drop in pipes. Whether pressure drop changes significantly or not will depend on the parameters changed.

The figure below is for a thinner catalyst layer (0.4 um) and more pipes, but with the same total amount of noble metal. The conversion is slightly higher (71%) than the base case (64%). For the case shown below, an increase in the total number of pipes (i.e. decrease in the superficial velocity through each individual pipe) would decrease the pressure drop compared to the base case. The pressure drop in the base case is assumed to be negligible, so an increase in the total number of pipes should have no significant effect on the pressure drop.



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