MATLAB Bootcamps 1, 2 and 3

- ✓ 1: Getting up to speed (or back up to speed) with MATLAB
- ✓ 2: Learning to use MATLAB to solve typical problem scenarios
- • 3: Detailed modeling of packed-bed and plug-flow reactors

Bootcamp 3 Outline

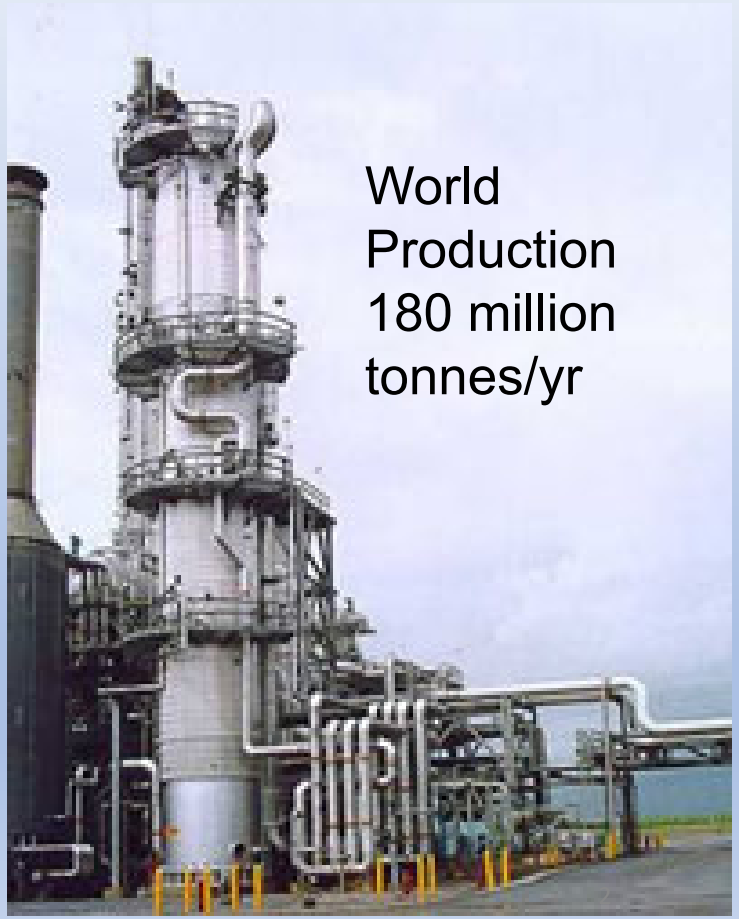
- Adiabatic, Packed-Bed, Plug-Flow Reactor
  - Ammonia Synthesis
- Tubular Reactor with Counter-current Heat Exchange
  - Acetone Cracking

Ordinary Differential Equation Models

Case Study 1

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis



World Production 180 million tonnes/yr

Ordinary Differential Equation Models

Case Study 1

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis

Reaction kinetics for main reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \Leftrightarrow NH_3$

Forward reaction: $r_f = k_f \cdot p_{N_2}^{1/2} \cdot p_{H_2}^{3/2}$

$$k_f = k_{0f} \cdot e^{-\frac{E_f}{R \cdot T}} \qquad k_{0f} = 10{,}000 \frac{kgmol}{m^3 s} \cdot \frac{1}{atm^2} \qquad E_f = 91{,}000 \frac{kJ}{kgmol}$$

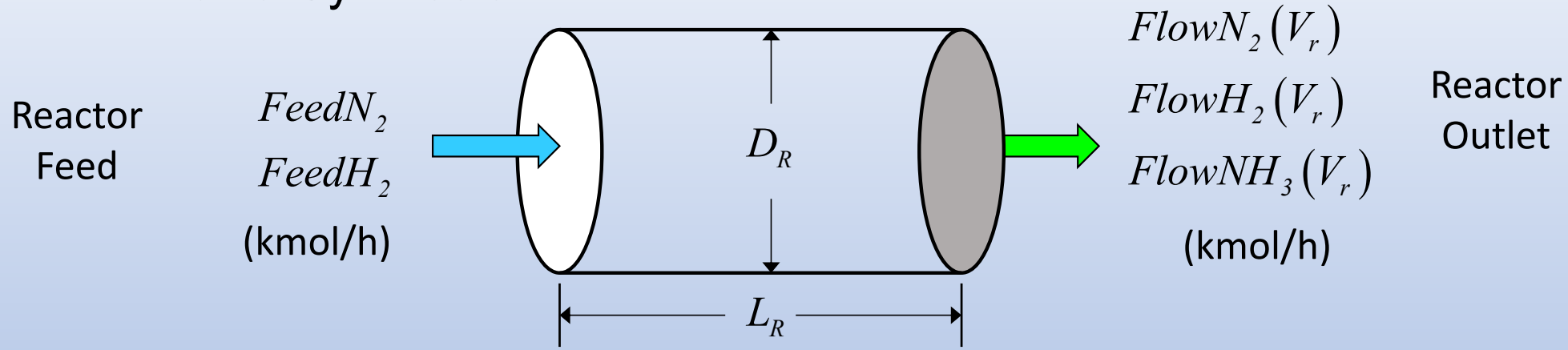
Reverse reaction: $r_r = k_r \cdot p_{NH_3}$

$$k_r = k_{0r} \cdot e^{-\frac{E_r}{R \cdot T}} \qquad k_{0r} = 1.3 \times 10^{10} \frac{kgmol}{m^3 s} \cdot \frac{1}{atm} \qquad E_r = 141{,}000 \frac{kJ}{kgmol}$$

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis



Differential Mole Balance on N_2

$$\frac{d[FlowN_2]}{dV} = (-r_f + r_r)\cdot\varepsilon$$

Note: $dV = A_r \cdot dz$

$$A_r = \pi\frac{D_r^2}{4} \qquad V_r = A_r \cdot L_r$$

Stoichiometric Balances on H_2 and NH_3

$$FlowH_2 = FeedH_2 - 3\cdot(FeedN_2 - FlowN_2)$$

$$FlowNH_3 = 2\cdot(FeedN_2 - FlowN_2)$$

dV is differential volume of empty reactor

ε is the void fraction of the packed bed

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis

Energy Balance

$$\frac{d}{dV}\left(\sum_i Flow_i \cdot H_i(T)\right) = 0$$

with constant heat capacity approximation

$$\frac{dT}{dV} \cong \frac{\left(r_f - r_r\right)\cdot\left(-\Delta H_{rxn}(T,P)\right)\cdot\varepsilon}{\left(\sum_i Flow_i \cdot C_{Pi}\right)}$$

pressure effect on enthalpy

$$H_i(T,P) = \int_{T_{ref}}^{T} C_{Pi}(T)\,dT + \int_{P_{ref}}^{P}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP + H_{fi}$$

$$\int_{T_{ref}}^{T} C_{Pi}(T)\,dT = \bar{C}_{Pi}(T)\cdot\left(T - T_{ref}\right)$$

$$\int_{P_{ref}}^{P}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]dP =$$

from eqn of state, analytically, or from P-V-T data. or using the Generalized Pitzer Correlation

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis

Pressure Drop – the Ergun equation for packed beds

$$\left[\frac{(P_0 - P_L)\cdot\rho}{G_0^2}\right]\cdot\left[\frac{D_P}{L}\right]\cdot\left[\frac{\varepsilon^3}{1-\varepsilon}\right] = 150\cdot\left[\frac{1-\varepsilon}{D_P\cdot G_0/\mu} + \frac{7}{4}\right]$$

written in terms of dimensionless groups

G_0 : mass flow rate per unit cross-sectional area of empty bed -- *constant with V*

Differential form:

$$\frac{dP}{dV} = \frac{1}{A_r}\cdot 150\cdot\left[\frac{1-\varepsilon}{D_P\cdot G_0/\mu} + \frac{7}{4}\right]\cdot\left[\frac{1-\varepsilon}{\varepsilon^3}\right]\cdot\left[\frac{G_0^2}{\rho\cdot D_P}\right]$$

P_0 : upstream pressure

P_L : downstream pressure at L

ρ : fluid density

G_0 : mass flux

D_P : effective particle diameter

ε : packing void fraction

μ : fluid viscosity

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis

Pressure Drop – the Ergun equation for packed beds

Fluid Density

$$\rho = \frac{\overline{MW}}{\tilde{V}} \qquad \overline{MW}: \text{avg molecular weight, } \frac{kg}{kmol} \qquad \tilde{V}: \text{specific volume, } \frac{m^3}{kmol}$$

$\tilde{V}$ from Peng-Robinson Equation of State

$$P = \frac{RT}{\tilde{V} - b_m} - \frac{a_m}{\tilde{V}\left(\tilde{V} + b_m\right) + b_m\left(\tilde{V} - b_m\right)}$$

Solve nonlinear, cubic equation for $\tilde{V}$

a_m, b_m : mixture coefficients

Ideal gas law approximation: $\rho = \frac{\overline{MW \cdot P}}{RT}$ 20% high at 150 atm

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis

Peng-Robinson EOS Mixture Coefficients

Coefficients for individual components

Units: K, kPa, kmol, kJ, m^3

$$a_i = 0.45724 \frac{R^2 T_c^2}{P_c}\left(1 + m_i\left(1 - \sqrt{\frac{T}{T_c}}\right)\right)^2 \qquad m_i = 0.37464 + 1.54226\,\omega_i - 0.26992\,\omega_i^2$$

$$b_i = 0.07780 \frac{R T_c}{P_c}$$

k_{ij} : binary interactor factors

ω_i : acentric factor for component i

$\mathbf{x}$: mole fractions

Mixture coefficients

$$\mathbf{Q} = \sqrt{\mathbf{a}\cdot\mathbf{a}'} \otimes (1 - \mathbf{K}) = \begin{bmatrix} 0 & k_{12}a_1a_2 & \cdots & k_{1n}a_1a_n \\ k_{12}a_1a_2 & 0 & k_{13}a_2a_3 & \vdots \\ \vdots & \vdots & \ddots & k_{n-1,n}a_{n-1}a_n \\ k_{1n}a_1a_n & \cdots & k_{n-1,n}a_{n-1}a_n & 0 \end{bmatrix}$$

$$a_m = \mathbf{x}'\cdot\mathbf{Q}\cdot\mathbf{x}$$

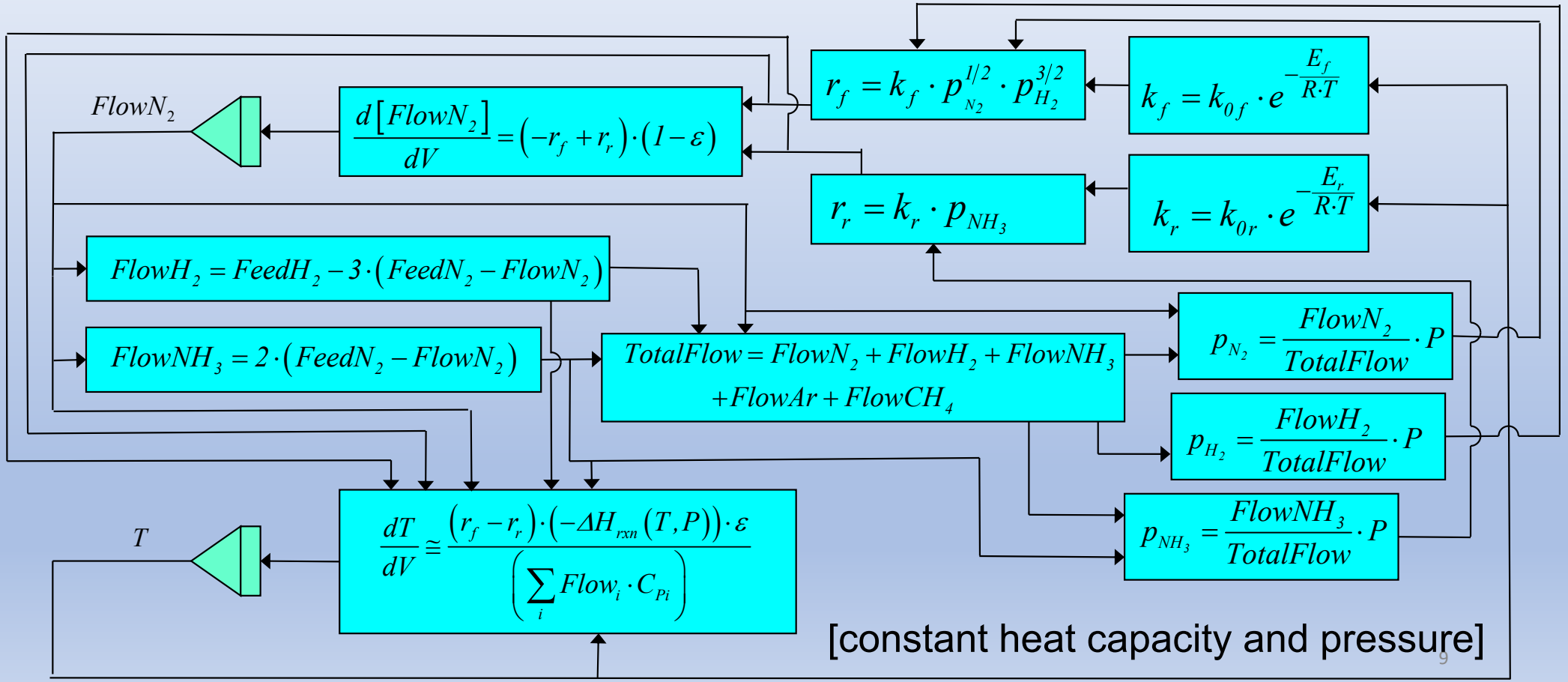
$$b_m = \mathbf{x}'\cdot\mathbf{b} = \sum_{i=1}^{n} x_i \cdot b_i$$

$\otimes$: item-by-item array multiplication

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Simplified Model Information Diagram



Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Simplified Model – Matlab Solution

AmmoniaPBRSimplified.m

```
% ammonia PBR simulation
% simplified model
% basic data
global Rgas
Rgas = 8.314; % kJ/kgmol/K
% molecular weights
MWN2 = 28.0134; % kg/kgmol
MWH2 = 2.016;
MWNH3 = 17.031;
MWAr = 39.948;
MWCH4 = 16.043;
% heat capacity coefficients from fit of Hysys properties at 150 atm
CpCoef = [ 40.442   -35.279      46.918     -19.41      0 ;
           28.75      1.86        0          0         0  ;
           1088.5   -5691.4     11787      -10900     3801.6 ;
           36.819    -53.01      63.973     -27.022    0 ;
           24.709    50.297       0          0         0 ];
% heat capacities at 350 degC
Tmid = 350;
CpN2 = HtCap(1,Tmid,CpCoef);
CpH2 = HtCap(2,Tmid,CpCoef);
CpNH3 = HtCap(3,Tmid,CpCoef);
CpAr = HtCap(4,Tmid,CpCoef);
CpCH4 = HtCap(5,Tmid,CpCoef);
```

```
% reaction kinetics from Hysys case
% forward reaction
k0f = 3.6e7; % kgmol/m3/h/atm^2
Ef = 9.1e4; % kJ/kgmol
% reverse reaction
k0r = 4.68e13; % kgmol/m3/h/atm
Er = 1.41e5; % kJ/kgmol
% reactor parameters
Dr = 3; % diameter, m
Lr = 1; % length, m
Ar = pi*Dr^2/4; % x-sectional area, m2
Vr = Ar*Lr; % volume, m3
% catalyst particles and packing
Dp = 1e-3; % particle diameter, m
eps = 0.4; % void fraction
% feed conditions from Hysys case
FeedN2 = 12348; % kgmol/h
FeedH2 = 37044;
FeedNH3 = 0;
FeedAr = 12391;
FeedCH4 = 5652;
FeedP = 150; % atm
FeedT = 270; % degC
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Simplified Model – Matlab Solution

```
% initial conditions
y0 = [ FeedN2 ; FeedH2 ; FeedNH3 ; FeedT ];
% mass matrix
M = [ 1 0 0 0 ;
      0 0 0 0 ;
      0 0 0 0 ;
      0 0 0 1 ];
% solution span
vspan = linspace(0,Vr,200);
% anonymous function
PFRanon = @(v,y) PBRSimplified(v,y,FeedN2,FeedH2,FeedAr,FeedCH4,FeedP
    ,k0f,Ef,k0r,Er,eps,CpN2,CpH2,CpNH3,CpAr,CpCH4);
options = odeset('Mass',M);
[ v , ysoln ] = ode15s(PFRanon,vspan,y0,options);
% unpack solution
MflowN2 = ysoln(:,1);
MflowH2 = ysoln(:,2);
MflowNH3 = ysoln(:,3);
T = ysoln(:,4);
Conv = (FeedN2 - MflowN2)/FeedN2 *100; % Conversion, N2 basis, in %
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Simplified Model – Matlab Solution

```
% create plots
figure(1) % Temperature Profile
plot(v,T,'k-')
grid
xlabel('Reactor Volume - m3')
ylabel('Temperature - degC')
title('Temperature Profile')
figure(2) % Molar Flows Profile
plot(v,MflowN2,'b-',v,MflowH2,'m-',v,MflowNH3,'g-')
grid
xlabel('Reactor Volume - m3')
ylabel('Molar Flow Rate - kgmol/h')
title('Molar Flow Profile')
legend('N2','H2','NH3','Location','northeastoutside')
figure(3)
plot(v,Conv,'k-')
grid
xlabel('Reactor Volume - m3')
ylabel('Conversion - %')
title('Conversion Profile')
format long g
disp([ v(end) ysoln(end,:) ])
disp(Conv(end))
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Simplified Model – Matlab Solution

PBRSimplified.m

```
function outvar = PBRSimplified(v,y,FeedN2,FeedH2,FeedAr,FeedCH4,P ...
    ,k0f,Ef,k0r,Er,eps,CpN2,CpH2,CpNH3,CpAr,CpCH4)
global Rgas
% unpack dependent variables
MflowN2 = y(1);
MflowH2 = y(2);
MflowNH3 = y(3);
T = y(4);
% total molar flow
TotFlow = MflowN2 + MflowH2 + MflowNH3 + FeedAr + FeedCH4;
% partial pressures in atm
PN2 = MflowN2/TotFlow*P;
PH2 = MflowH2/TotFlow*P;
PNH3 = MflowNH3/TotFlow*P;
% forward and reverse reaction rates
rf = k0f*exp(-Ef/Rgas/(T+273.15))*PN2^0.5*PH2^1.5;
rr = k0r*exp(-Er/Rgas/(T+273.15))*PNH3;
```

```
% differential balance on N2 in kgmol/h/m3
outvar(1) = -(rf-rr)*eps;
% algebraic equations from stoichiometry for H2 and NH3
outvar(2) = MflowH2 - ( FeedH2 - 3*( FeedN2 - MflowN2) );
outvar(3) = MflowNH3 - 2*( FeedN2 - MflowN2 );
HtRx = HtRxnP(T,P);  % heat of reaction
% differential energy balance
outvar(4) = (rf-rr)*(-HtRx)*eps/(MflowN2*CpN2+MflowH2*CpH2 ...
    +MflowNH3*CpNH3+FeedAr*CpAr+FeedCH4*CpCH4);
outvar = outvar';
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Simplified Model – Matlab Solution

HtCap.m

```
% function to compute heat capacity
function Cp = HtCap(component,T,CpCoef)
a = CpCoef(component,1);
b = CpCoef(component,2);
c = CpCoef(component,3);
d = CpCoef(component,4);
e = CpCoef(component,5);
TK = T + 273.15;
TK1 = TK/1000;
Cp = a + b*TK1 + c*TK1^2 + d*TK1^3 + e*TK1^4;
```

HtRxn.m

```
function Hrx = HtRxn(T)
% heat of reaction coefficients from spreadsheet fit
% basis: Hysys molar enthalpy predictions at 150 atm
aa = -1.9314e5;
bb = 4.8403e5;
cc = -9.944e5;
dd = 8.8054e5;
ee = -2.9078e5;
Tk1 = (T+273.15)/1000;
Hrx = aa + bb*Tk1 + cc*Tk1^2 + dd*Tk1^3 + ee*Tk1^4;
```

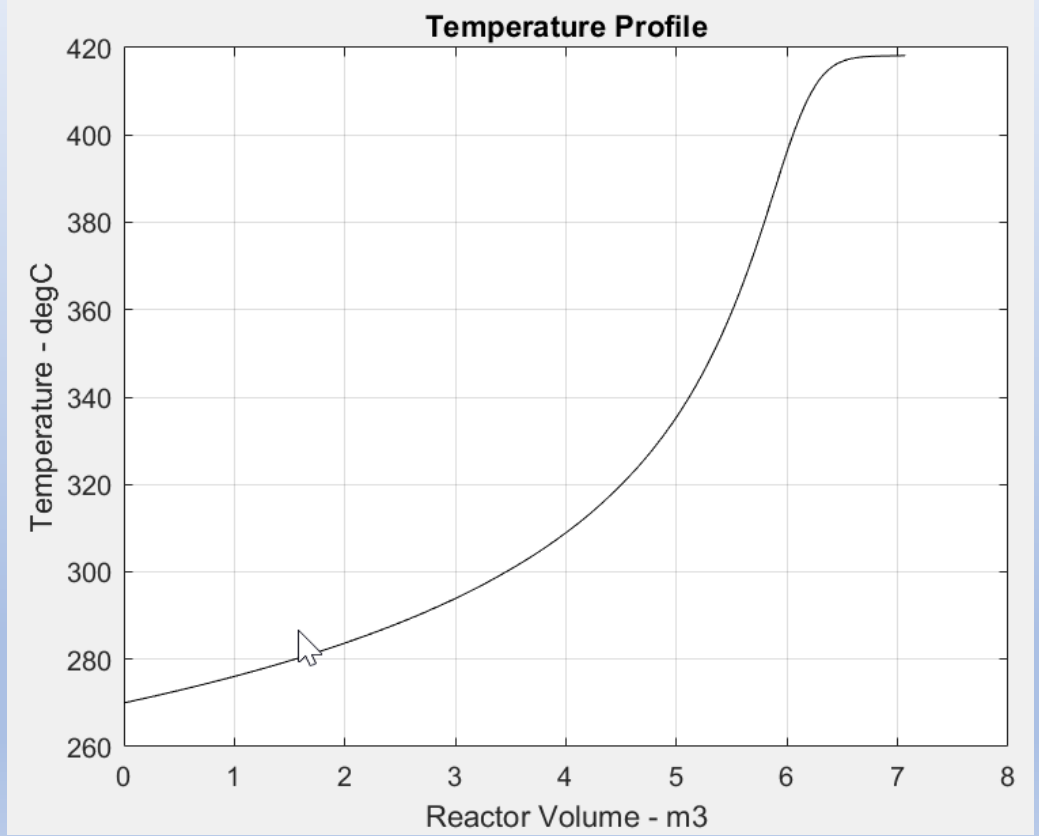
HtRxnP.m

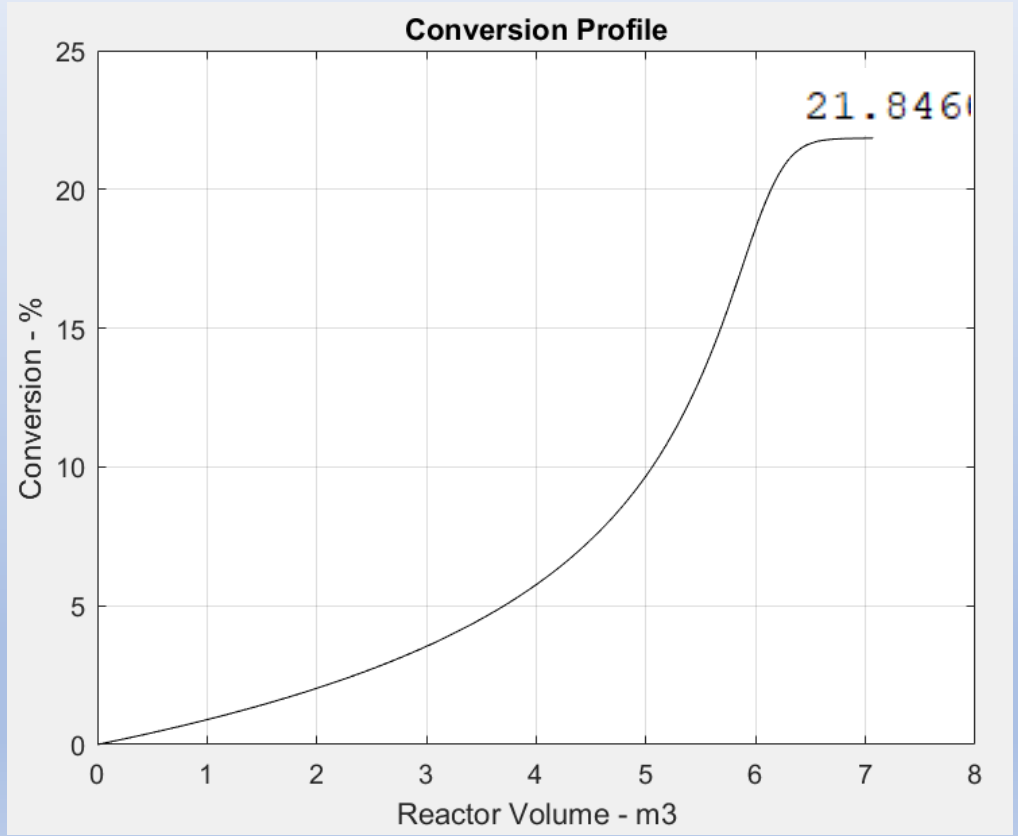
```
function Hrx = HtRxnP(T,P)
% heat of reaction coefficients from spreadsheet fit
% basis: Hysys molar enthalpy predictions at 150 atm
% includes pressure effect using Pitzer correlation
R = 8.31446;  % kJ/kgmol/K
aa = -1.9314e5;
bb = 4.8403e5;
cc = -9.944e5;
dd = 8.8054e5;
ee = -2.9078e5;
Tk = T + 273.15; % K
Tk1 = Tk/1000;
Pk = P *101.325; % kPa
HrxT = aa + bb*Tk1 + cc*Tk1^2 + dd*Tk1^3 + ee*Tk1^4;
Tc = [ 405.6 126.2 33.2 ];
Pc = [ 112.5 33.5 12.8 ];
Omega = [ 0.25 0.04 0.0 ];
Tr = Tk ./ Tc;
Pck = Pc * 101.325;
B0 = 0.1445 - 0.33 ./ Tr - 0.1385 ./ Tr.^2 - 0.0121 ./ Tr.^3;
B1 = 0.073 + 0.46 ./ Tr - 0.5 ./ Tr.^2 - 0.097 ./ Tr.^3 - 0.0073 ./ Tr.^8;
dB0 = 0.33 ./ Tr.^2 + 0.277 ./ Tr.^3 + 0.0363 ./ Tr.^4;
dB1 = -0.46 ./ Tr.^2 + 1 ./ Tr.^3 + 0.291 ./ Tr.^4 + 0.0584 ./ Tr.^9;
H = R * Tk * ( 1-Pk) ./ Pck .* ( (dB0 - B0 ./ Tr) + Omega .* (dB1 - B1 ./ Tr));
Hrx = HrxT + [ 2 -1 -3 ]*H';
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Simplified Model – Matlab Solution

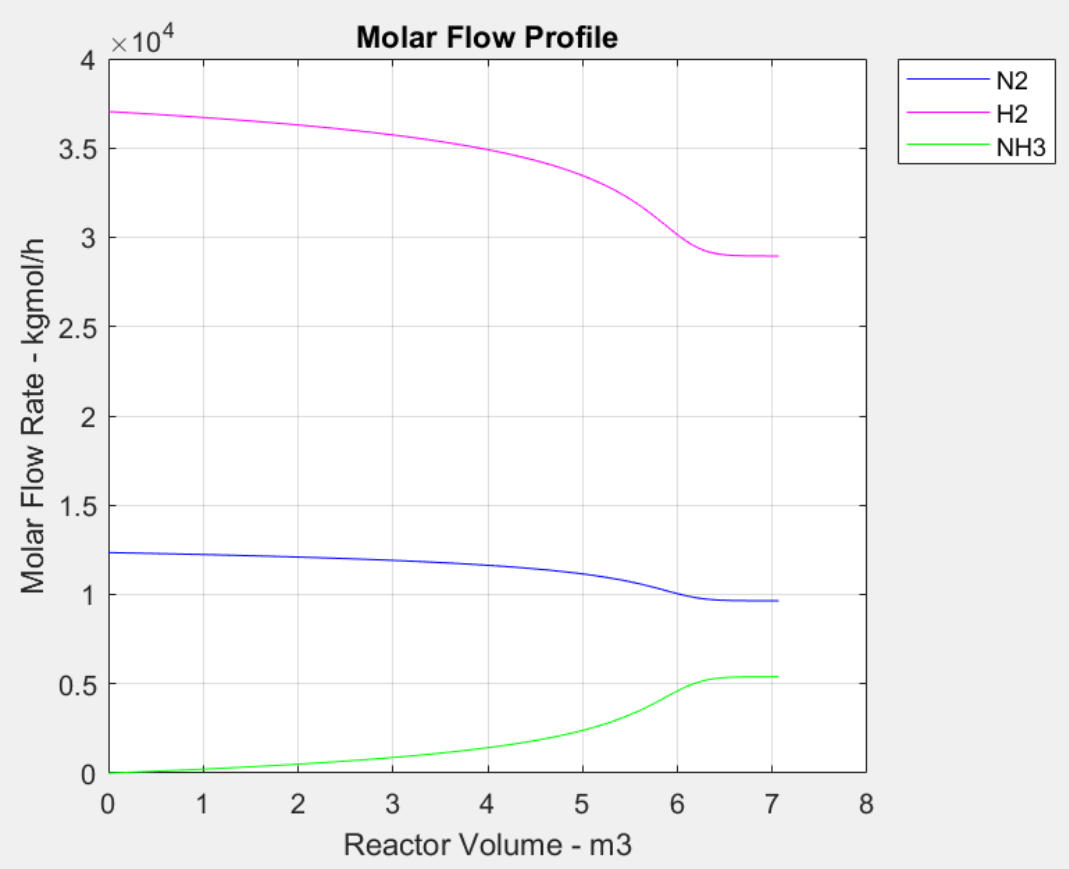




Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Simplified Model – Matlab Solution

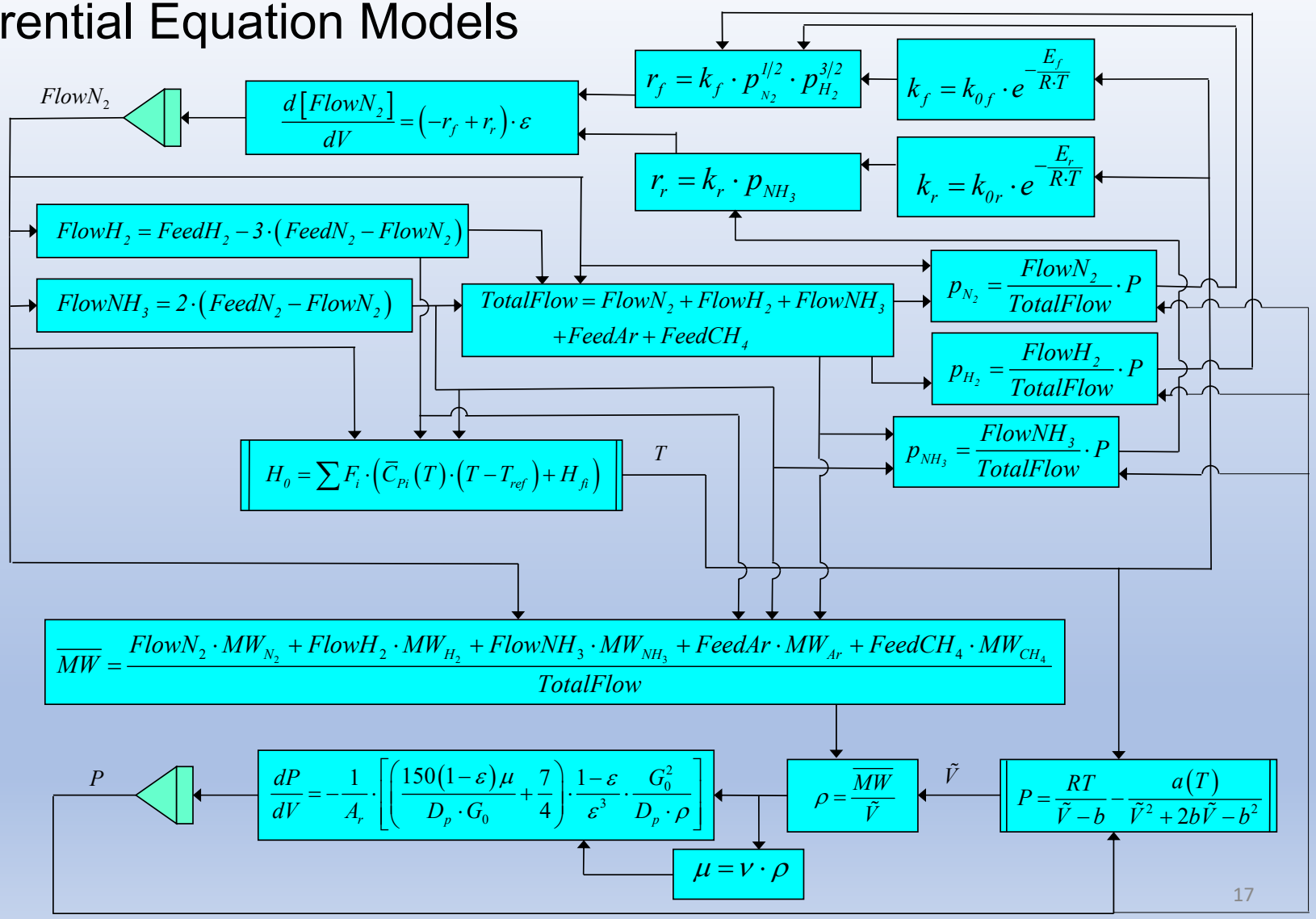


Ordinary Differential Equation Models

Modeling and Simulation of a PBR

Ammonia Synthesis

Full Model Information Flow Diagram



Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

AmmoniaPBRSimulationFullModel.m

```
% ammonia PBR simulation
% basic data
global Rgas Rgas2;
Rgas = 8.314; % kJ/kgmol/K
Rgas2 = 0.082057; % atm*m3/kgmol/K
% molecular weights
MWN2 = 28.0134; % kg/kgmol
MWH2 = 2.016;
MWNH3 = 17.02;
MWAr = 39.948;
MWCH4 = 16.043;
% heat capacity coefficients from fit of Hysys properties at 150 atm
CpCoef = [ 40.442   -35.279      46.918     -19.41      0 ;
           28.75      1.86        0          0         0  ;
           1088.5    -5691.4     11787      -10900     3801.6 ;
           36.819     -53.01      63.973     -27.022    0 ;
           24.709     50.297       0          0        0 ];
% reaction kinetics from Hysys case
% forward reaction
k0f = 3.6e7; % kgmol/m3/h/atm^2
Ef = 9.1e4; % kJ/kgmol
% reverse reaction
k0r = 4.68e13; % kgmol/m3/h/atm
Er = 1.41e5; % kJ/kgmol
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

```
% reactor parameters
Dr = 3; % diameter, m
Lr = 1; % length, m
Ar = pi*Dr^2/4; % x-sectional area, m2
Vr = Ar*Lr; % volume, m3
% catalyst particles and packing
Dp = 1e-3; % particle diameter, m
eps = 0.4; % void fraction
% gas kinematic viscosity estimate from Hysys case
nu = 5.075e-7; % m2/s
% feed conditions from Hysys case
FeedN2 = 12348; % kgmol/h
FeedH2 = 37044;
FeedNH3 = 0;
FeedAr = 12391;
FeedCH4 = 5652;
FeedP = 150; % atm
FeedT = 270; % degC
% mass flux
M0 = FeedN2*MWN2 + FeedH2*MWH2 + FeedNH3*MWNH3 + FeedAr*MWAr + FeedCH4*MWCH4;
G0 = M0/Ar/3600;  % kg/s/m2
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

```
% initial conditions
T0 = FeedT;
H0 = (FeedN2*HtCap(1,T0,CpCoef)+FeedH2*HtCap(2,T0,CpCoef) ...
    +FeedNH3*HtCap(3,T0,CpCoef)+FeedAr*HtCap(4,T0,CpCoef) ...
    +FeedCH4*HtCap(5,T0,CpCoef))*T0;
y0 = [ FeedN2 ; FeedH2 ; FeedNH3 ; FeedP ; FeedT ; H0 ];
% mass matrix
M = [ 1 0 0 0 0 0 ;
      0 0 0 0 0 0 ;
      0 0 0 0 0 0 ;
      0 0 0 1 0 0 ;
      0 0 0 0 0 0 ;
      0 0 0 0 0 1 ] ;
% solution span
vspan = linspace(0,Vr,200);
% anonymous function
PFRanon = @(v,y) PBRsysFullModel(v,y,FeedN2,FeedH2,FeedAr,FeedCH4 ...
    ,k0f,Ef,k0r,Er,eps,nu,G0,Dp,Ar,MWN2,MWH2,MWNH3,MWAr,MWCH4,CpCoef);
options = odeset('Mass',M);
[ v , ysoln ] = ode15s(PFRanon,vspan,y0,options);
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

```
% unpack solution
MflowN2 = ysoln(:,1);
MflowH2 = ysoln(:,2);
MflowNH3 = ysoln(:,3);
P = ysoln(:,4);
T = ysoln(:,5);
H = ysoln(:,6);
Conv = (FeedN2 - MflowN2)/FeedN2 *100; % Conversion, N2 basis, in %
% create plots
figure(1) % Temperature Profile
plot(v,T,'k-')
grid
xlabel('Reactor Volume - m3')
ylabel('Temperature - degC')
title('Temperature Profile')
figure(2) % Pressure Profile
plot(v,P,'m-')
grid
xlabel('Reactor Volume - m3')
ylabel('Presssure - atm')
title('Pressure Profile')
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

```
figure(3) % Molar Flows Profile
plot(v,MflowN2,'b-',v,MflowH2,'m-',v,MflowNH3,'g-')
grid
xlabel('Reactor Volume - m3')
ylabel('Molar Flow Rate - kgmol/h')
title('Molar Flow Profile')
legend('N2','H2','NH3','Location','northeastoutside')
figure(4)  % Conversion Profile
plot(v,Conv,'k-')
grid
xlabel('Reactor Volume - m3')
ylabel('Conversion - %')
title('Conversion Profile')
format long g
disp([ v(end) ysoln(end,:) ])
disp(Conv(end))
SaveVars = [v MflowN2 MflowH2 MflowNH3 P T H Conv];
save AmmoniaFullModel.txt SaveVars -ascii ;
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

```
function outvar = PBRsysFullModel(v,y,FeedN2,FeedH2,FeedAr,FeedCH4 ...
    ,k0f,Ef,k0r,Er,eps,nu,G0,Dp,Ar,MWN2,MWH2,MWNH3,MWAr,MWCH4,CpCoef)
global Rgas Rgas2;
% unpack dependent variables
MflowN2 = y(1);
MflowH2 = y(2);
MflowNH3 = y(3);
P = y(4);
T = y(5);
H = y(6);
% total molar flow
TotFlow = MflowN2 + MflowH2 + MflowNH3 + FeedAr + FeedCH4;
% partial pressures in atm
PN2 = MflowN2/TotFlow*P;
PH2 = MflowH2/TotFlow*P;
PNH3 = MflowNH3/TotFlow*P;
% forward and reverse reaction rates
rf = k0f*exp(-Ef/Rgas/(T+273.15))*PN2^0.5*PH2^1.5;
rr = k0r*exp(-Er/Rgas/(T+273.15))*PNH3;
```

PBRsysFullModel.m

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

```
outvar(1) = -(rf-rr)*eps;  % differential balance on N2 in kgmol/h/m3
% algebraic equations from stoichiometry for H2 and NH3
outvar(2) = MflowH2 - ( FeedH2 - 3*( FeedN2 - MflowN2) );
outvar(3) = MflowNH3 - 2*( FeedN2 - MflowN2 );
% average molecular weight
MWavg = (MflowN2*MWN2 + MflowH2*MWH2 + MflowNH3*MWNH3 + FeedAr*MWAr ...
    + FeedCH4*MWCH4) / TotFlow;
% gas density
z = [ MflowN2 ; MflowH2 ; MflowNH3 ; FeedAr ; FeedCH4 ]/TotFlow;
w = [ 0.039 ; -0.216 ; 0.25 ; 0.001 ; 0.011 ];
Tc = [ 126.2 ; 33.19 ; 405.65 ; 150.86 ; 190.564 ];  % K
Pc = [ 3394 ; 1297 ; 11277 ; 4870 ; 4641 ];  % kPa
K = [ 0       -0.036  0.222  0       0.036 ;
      -0.036  0       0      0       0.202 ;
      0.222   0       0      0       0 ;
      0       0       0      0       0.023 ;
      0.036   0.202   0      0.023   0 ];
SV = SpecVol(T,P,z,w,Tc,Pc,K) ;
RhoGas = MWavg / SV ; % kg/m3
% gas viscosity from kinematic viscosity and density
mu = nu * RhoGas; % Pa-s
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

```
% differential Ergun equation, dP/dV in atm/m3
outvar(4) = -(150*(1-eps)/Dp/G0*mu+7/4)*(1-eps)/eps^3/Dp/RhoGas*G0^2 ...
    /Ar/101325;
HtRx = HtRxnP(T,P);  % heat of reaction
outvar(5) = T - findT(H,T,MflowN2,MflowH2,MflowNH3,FeedAr,FeedCH4,CpCoef);
% differential energy balance
outvar(6) = (rf-rr)*(-HtRx)*eps;
outvar = outvar';
```

HtCap.m

```
% function to compute heat capacity
function Cp = HtCap(component,T,CpCoef)
a = CpCoef(component,1);
b = CpCoef(component,2);
c = CpCoef(component,3);
d = CpCoef(component,4);
e = CpCoef(component,5);
TK = T + 273.15;
TK1 = TK/1000;
Cp = a + b*TK1 + c*TK1^2 + d*TK1^3 + e*TK1^4;
```

HtRxn.m

```
function Hrx = HtRxn(T)
% heat of reaction coefficients from spreadsheet fit
% basis: Hysys molar enthalpy predictions at 150 atm
aa = -1.9314e5;
bb = 4.8403e5;
cc = -9.944e5;
dd = 8.8054e5;
ee = -2.9078e5;
Tk1 = (T+273.15)/1000;
Hrx = aa + bb*Tk1 + cc*Tk1^2 + dd*Tk1^3 + ee*Tk1^4;
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

HtRxnP.m

```
function Hrx = HtRxnP(T,P)
% heat of reaction coefficients from spreadsheet fit
% basis: Hysys molar enthalpy predictions at 150 atm
% includes pressure effect using Pitzer correlation
R = 8.31446;  % kJ/kgmol/K
aa = -1.9314e5;
bb = 4.8403e5;
cc = -9.944e5;
dd = 8.8054e5;
ee = -2.9078e5;
Tk = T + 273.15; % K
Tk1 = Tk/1000;
Pk = P *101.325; % kPa
HrxT = aa + bb*Tk1 + cc*Tk1^2 + dd*Tk1^3 + ee*Tk1^4;
Tc = [ 405.6 126.2 33.2 ];
Pc = [ 112.5 33.5 12.8 ];
Omega = [ 0.25 0.04 0.0 ];
Tr = Tk ./ Tc;
Pck = Pc * 101.325;
B0 = 0.1445 - 0.33 ./ Tr - 0.1385 ./ Tr.^2 - 0.0121 ./ Tr.^3;
B1 = 0.073 + 0.46 ./ Tr - 0.5 ./ Tr.^2 - 0.097 ./ Tr.^3 - 0.0073 ./ Tr.^8;
dB0 = 0.33 ./ Tr.^2 + 0.277 ./ Tr.^3 + 0.0363 ./ Tr.^4;
dB1 = -0.46 ./ Tr.^2 + 1 ./ Tr.^3 + 0.291 ./ Tr.^4 + 0.0584 ./ Tr.^9;
H = R * Tk * ( 1-Pk) ./ Pck .* ( (dB0 - B0 ./ Tr) + Omega .* (dB1 - B1 ./ Tr));
Hrx = HrxT + [ 2 -1 -3 ]*H';
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

SpecVol.m

```
function svol = SpecVol(T,P,z,w,Tc,Pc,K)
% find specific volume from the Peng-Robinson EOS
global Rgas
Tk = T + 273.15; % K
PkPa = P * 101.325; % kPa
m = 0.37464 + 1.54226 * w - 0.26992 * w .^ 2;
alpha = (1 + m .* (1 - (Tk ./ Tc) .^ 0.5)) .^ 2 ;
a = 0.45724 * Rgas^2 * (Tc .^ 2) ./ Pc .* alpha ;
b = 0.0788 * Rgas * Tc ./ Pc;
Q = ((a * a') .^ 0.5) .* (1 - K) ;
am = z'*Q*z;
bm = z'*b;
V1 = Rgas*Tk/PkPa;
tol = 1e-6;
while (1)
    del = 0.001*V1;
    V2 = V1 + del;
    Vnew = V1 - del * PR(V1,Tk,PkPa,am,bm)/(PR(V2,Tk,PkPa,am,bm)-PR(V1,Tk,PkPa,am,bm));
    if abs((Vnew-V1)/Vnew) < tol ; break ; end
    V1 = Vnew;
end
svol = Vnew;
```

PR.m

```
function er = PR(V,T,P,am,bm)
global Rgas
er = P - ( Rgas*T/(V-bm) - am / ( V^2 + 2*bm*V - bm^2));
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

```
function Tnew = findT(H,T1,MflowN2,MflowH2,MflowNH3,FeedAr,FeedCH4,CpCoef)
% find the temperature from the enthalpy value
tol = 1.e-7;
while (1)
    T2 = T1 + 0.1;
    Tnew = T1 - 0.1*fH(H,T1,MflowN2,MflowH2,MflowNH3,FeedAr,FeedCH4,CpCoef) ...
        / (fH(H,T2,MflowN2,MflowH2,MflowNH3,FeedAr,FeedCH4,CpCoef) ...
        - fH(H,T1,MflowN2,MflowH2,MflowNH3,FeedAr,FeedCH4,CpCoef));
    if abs((Tnew-T1)/Tnew)<tol ; break ; end
    T1 = Tnew;
end
```

findT.m

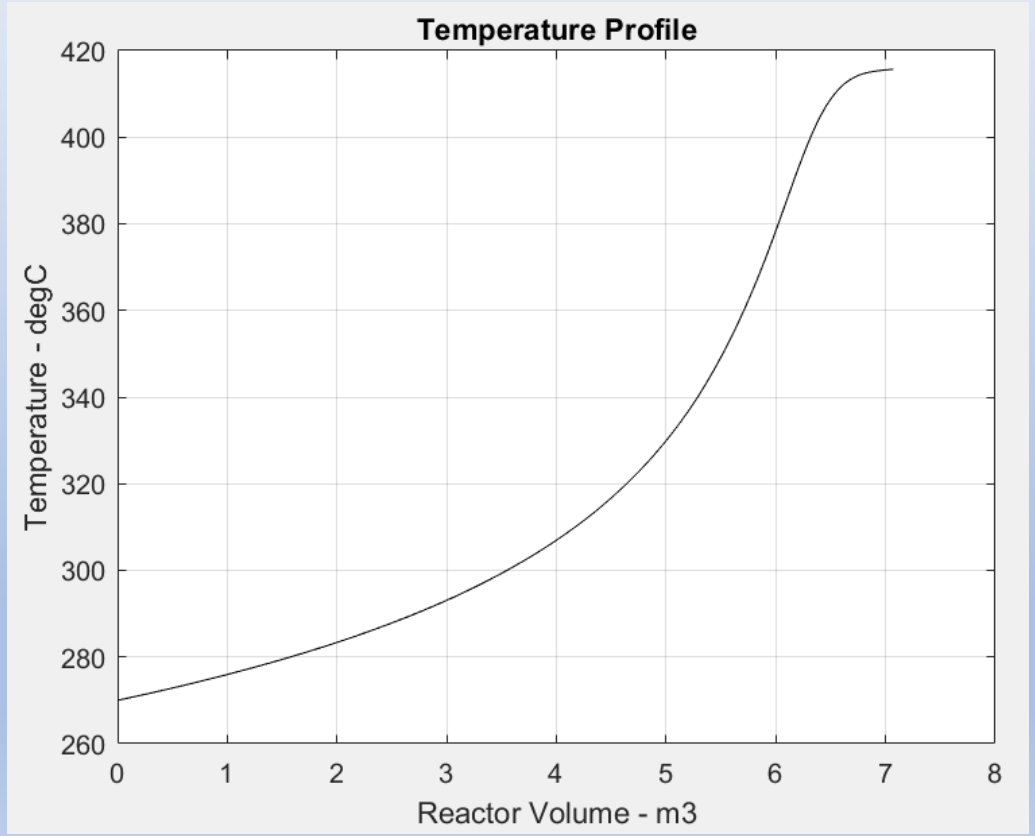
```
function result = fH(H,T,MflowN2,MflowH2,MflowNH3,FeedAr,FeedCH4,CpCoef)
result = H - (MflowN2*HtCap(1,T,CpCoef)+MflowH2*HtCap(2,T,CpCoef) ...
    +MflowNH3*HtCap(3,T,CpCoef)+FeedAr*HtCap(4,T,CpCoef) ...
    +FeedCH4*HtCap(5,T,CpCoef))*T;
```

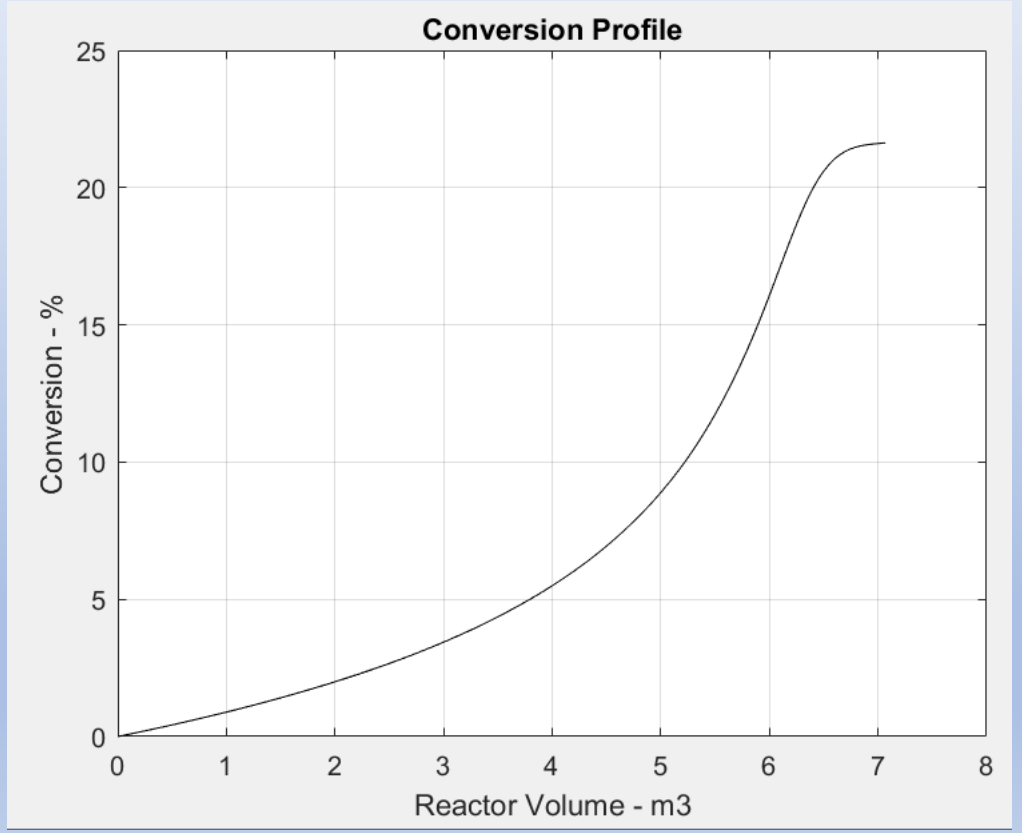
fH.m

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution

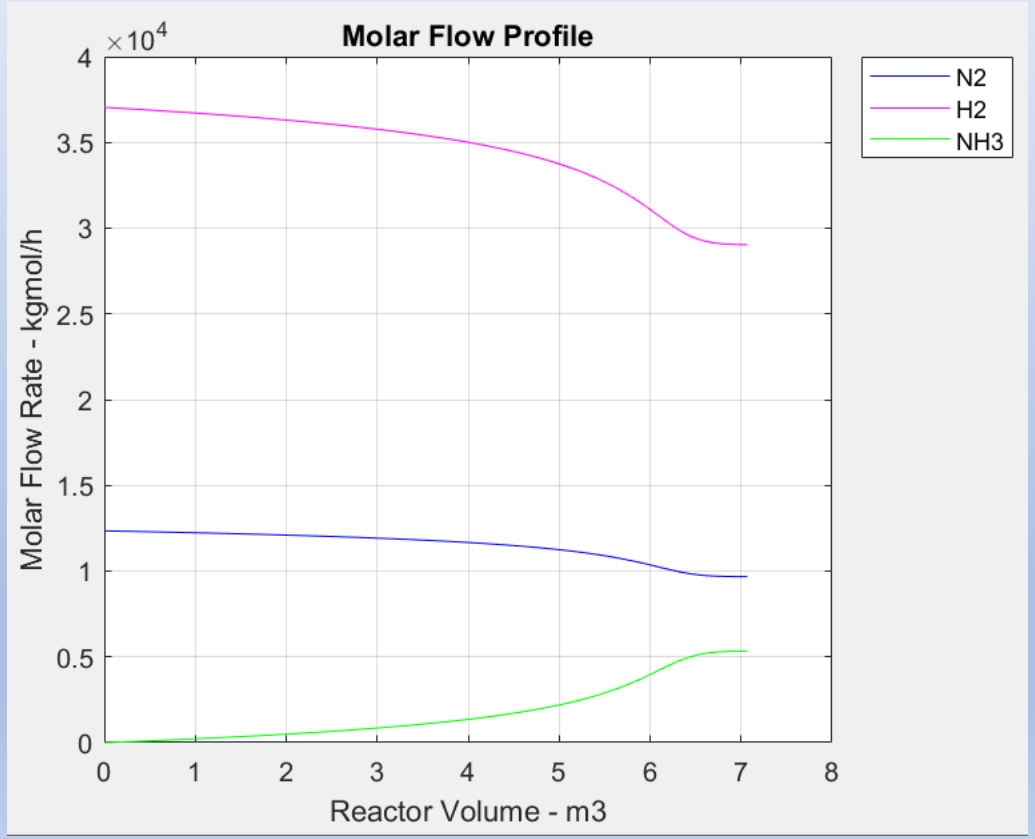


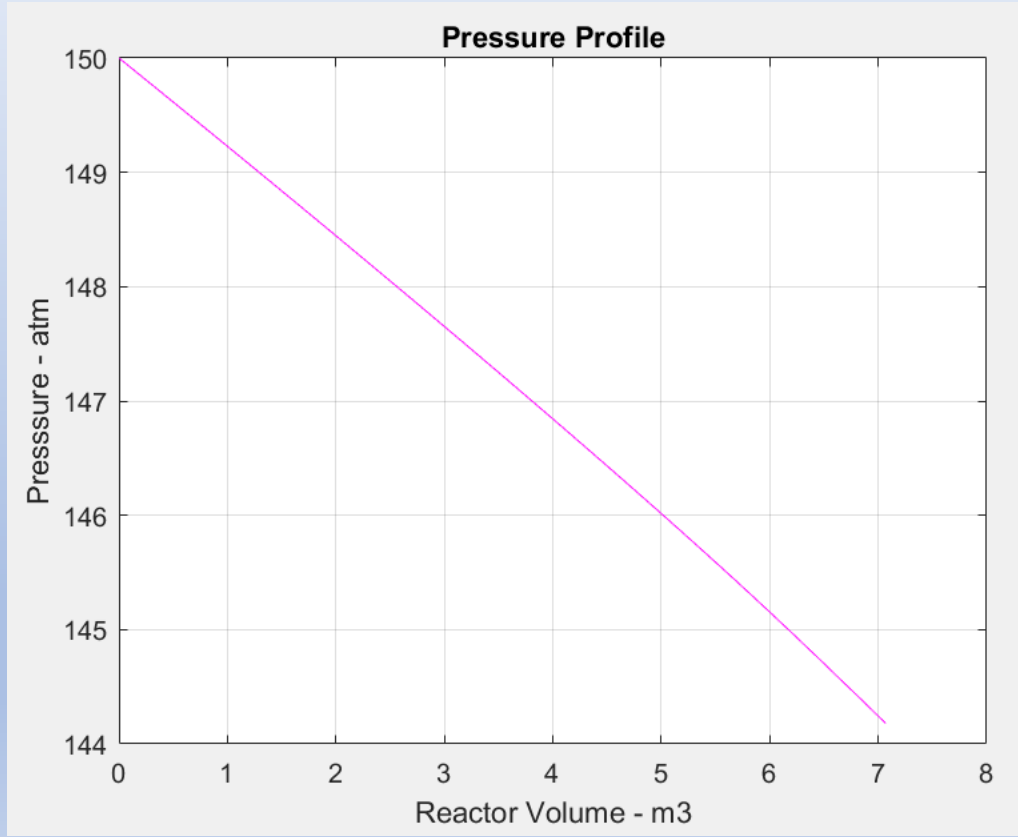


Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Full Model – Matlab DAE Solution





Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Comparison of Models – Matlab Solutions

```
% Ammonia Simulation
% Comparison of Full and Simplified Model
% 10/8/19
load AmmoniaFullModel.txt -ascii;
load AmmoniaSimplifiedModel.txt -ascii;
vf = AmmoniaFullModel(:,1);
MflowN2f = AmmoniaFullModel(:,2);
MflowH2f = AmmoniaFullModel(:,3);
MflowNH3f = AmmoniaFullModel(:,4);
Pf = AmmoniaFullModel(:,5);
Tf = AmmoniaFullModel(:,6);
Hf = AmmoniaFullModel(:,7);
Convf = AmmoniaFullModel(:,8);
%
vs = AmmoniaSimplifiedModel(:,1);
MflowN2s = AmmoniaSimplifiedModel(:,2);
MflowH2s = AmmoniaSimplifiedModel(:,3);
MflowNH3s = AmmoniaSimplifiedModel(:,4);
Ts = AmmoniaSimplifiedModel(:,5);
Convs = AmmoniaSimplifiedModel(:,6);
```

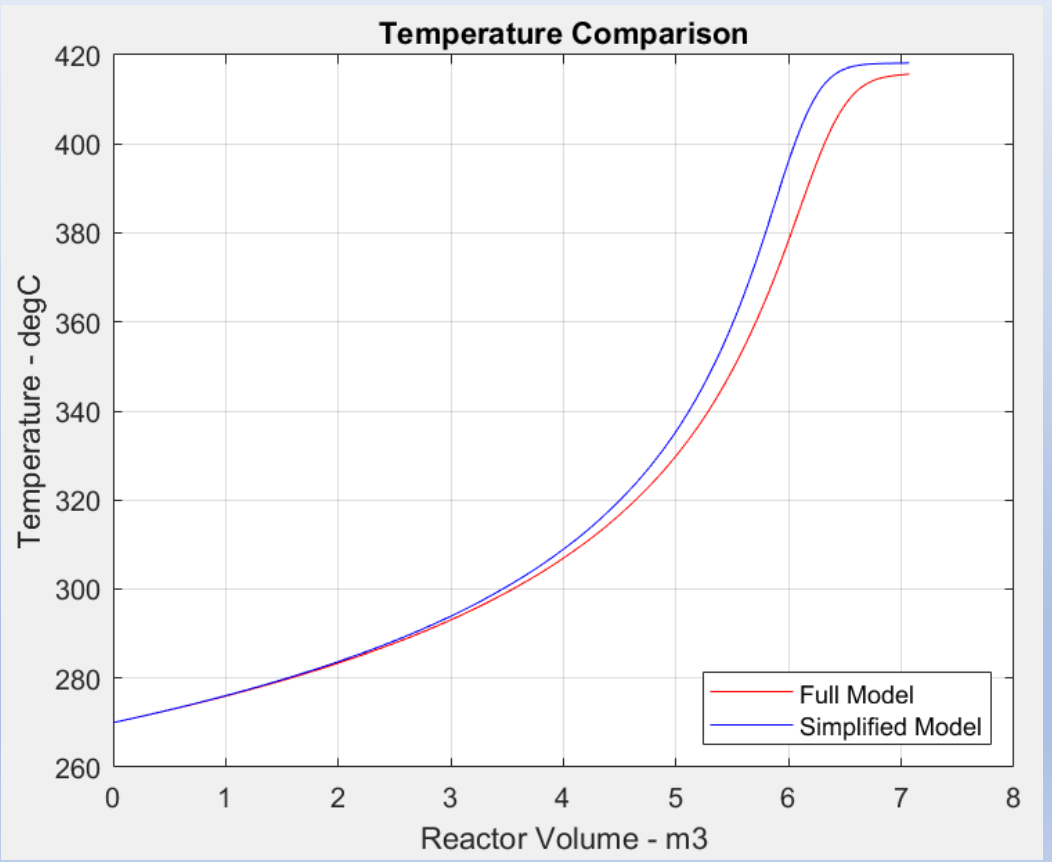
AmmoniaModelComparison.m

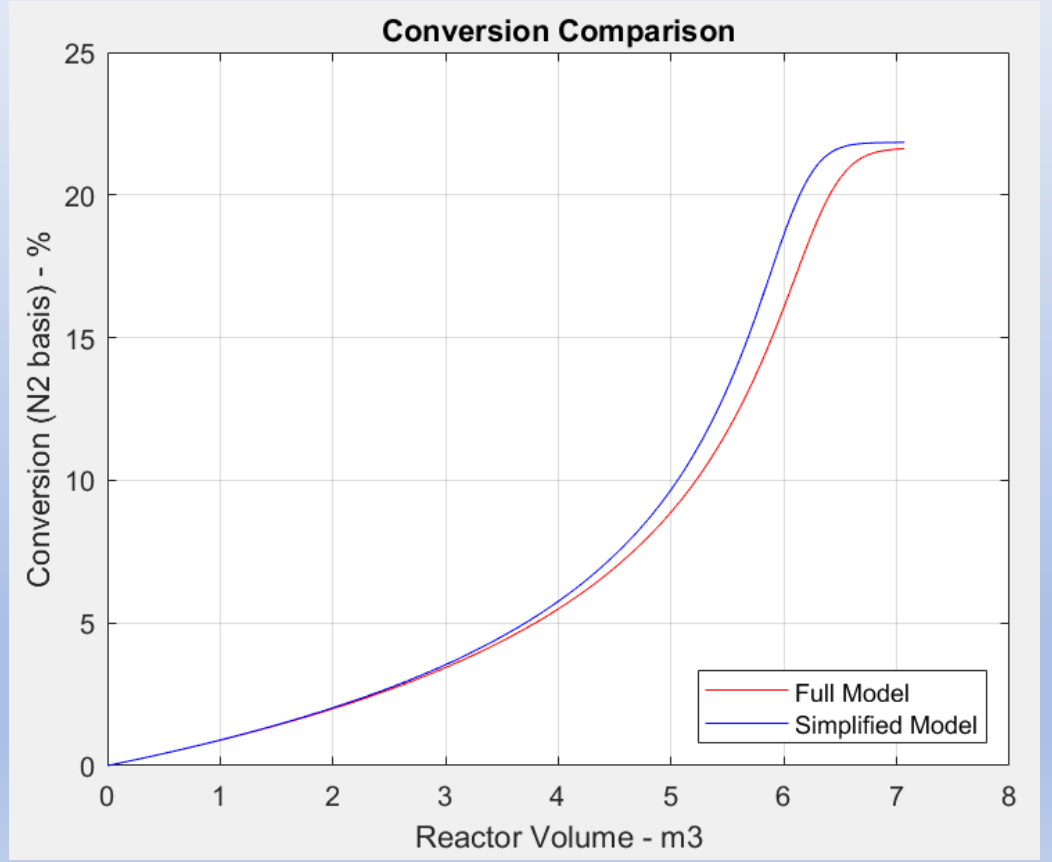
```
%
figure(1)
plot(vf,Tf,'r-',vs,Ts,'b-')
grid
xlabel('Reactor Volume - m3')
ylabel('Temperature - degC')
title('Temperature Comparison')
legend('Full Model','Simplified Model','Location','southeast')
%
figure(2)
plot(vf,Convf,'r-',vs,Convs,'b-')
grid
xlabel('Reactor Volume - m3')
ylabel('Conversion (N2 basis) - %')
title('Conversion Comparison')
legend('Full Model','Simplified Model','Location','southeast')
```

Ordinary Differential Equation Models

Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PBR)

Ammonia Synthesis – Comparison of Models – Matlab Solutions





Case Study 2

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

$$CH_3COCH_3 \Rightarrow CH_2CO + CH_4$$

Feed: 7850 kg/hr
7.85 kg/hr per tube
0.135 kmol/hr

Inlet temperature: 1035 K
Inlet pressure: 162 kPa (1.6 atm)

Counter-current heat transfer
Air: 90 T/hr
Inlet temperature: 1250 K

Reactor: 1000 1" Sch 40 tubes
Total volume: 2 m^3
Tube ID: 26.7 mm
Tube length: 3.57 m

Assume $\Delta P \cong 0$

adapted from
Fogler, H. Scott, **Elements of Chemical Reaction Engineering**, 4th Edition, Prentice-Hall, 2006, p. 504.

Case Study 2

Tubular Reactor with Counter-current Heat Exchange

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Basic data:

$$r_A = -k \cdot C_A \qquad ln(k) = 42.529 - \frac{34222}{T}$$

r_A : reaction rate of acetone, $\frac{kmol}{hr \cdot m^3}$

C_A : concentration of acetone, $\frac{kmol}{m^3}$

k : rate parameter, $1/hr$

T : temperature, K

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Basic data: Heat capacity

Acetone: $C_{PA} = 6.8132 + 278.6 \cdot Tk - 156.28 \cdot Tk^2 + 34.76 \cdot Tk^3$ $\frac{kJ}{kmol \cdot K}$ $Tk = \frac{T[K]}{1000}$

Ketene: $C_{PK} = 18.909 + 143.56 \cdot Tk - 130.23 \cdot Tk^2 + 66.526 \cdot Tk^3 - 14.112 \cdot Tk^4$

Methane: $C_{PM} = -0.7030 + 108.48 \cdot Tk - 42.522 \cdot Tk^2 + 5.8628 \cdot Tk^3 + 0.67857 \cdot \frac{1}{Tk^2}$

$$\bar{C}_{PA}(T) = \frac{\int_{T_{ref}}^{T} C_{PA}(T) \cdot dT}{T - T_{ref}} = 1000 \cdot \frac{\int_{Tk_{ref}}^{Tk} C_{PA}(tk) \cdot d(tk)}{Tk - Tk_{ref}}$$

Heat of reaction

$$\Delta H_{rxn}(T) = \Delta H_{rxn}(25°C) - \Delta H_A(T) + \Delta H_K(T) + \Delta H_M(T)$$

$\Delta H_{rxn}(25°C) = 80{,}770 \frac{kJ}{kmol}$

$$\Delta H_i(T) = 1000 \cdot \int_{Tk_{ref}}^{Tk} C_{Pi}(tk)\, d(tk)$$

endothermic

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Feed concentration:

$$C_{AF} = \frac{n}{V} = \frac{P}{R \cdot T} = \frac{162\left[kPa\right]}{8.314\left[\frac{kPa \cdot m^3}{kmol \cdot K}\right] \cdot 1035\left[K\right]} = 0.018 \ \frac{kmol}{m^3}$$

Reactor balances:

$$\frac{dF_A}{dV} = r_A = -k \cdot C_A \qquad C_A = \frac{F_A}{F_T} \cdot C_{AF} \cdot \frac{T_F}{T}$$

$$F_K = F_M = F_{AF} - F_A \qquad F_T = F_A + F_K + F_M$$

$$\frac{d\dot{H}}{dV} = UA\left(T_a - T\right)$$

$$\dot{H} = \dot{H}_A + \dot{H}_K + \dot{H}_M$$

$$\dot{H}_A = F_A \cdot \left(\bar{C}_{PA}\left(T\right) \cdot \left(T - T_{ref}\right) + H_{fA}\right) \ \ldots$$

Air energy balance:

$$\frac{d\dot{H}_a}{d\left(-V\right)} = UA\left(T - T_a\right)$$

counter-current

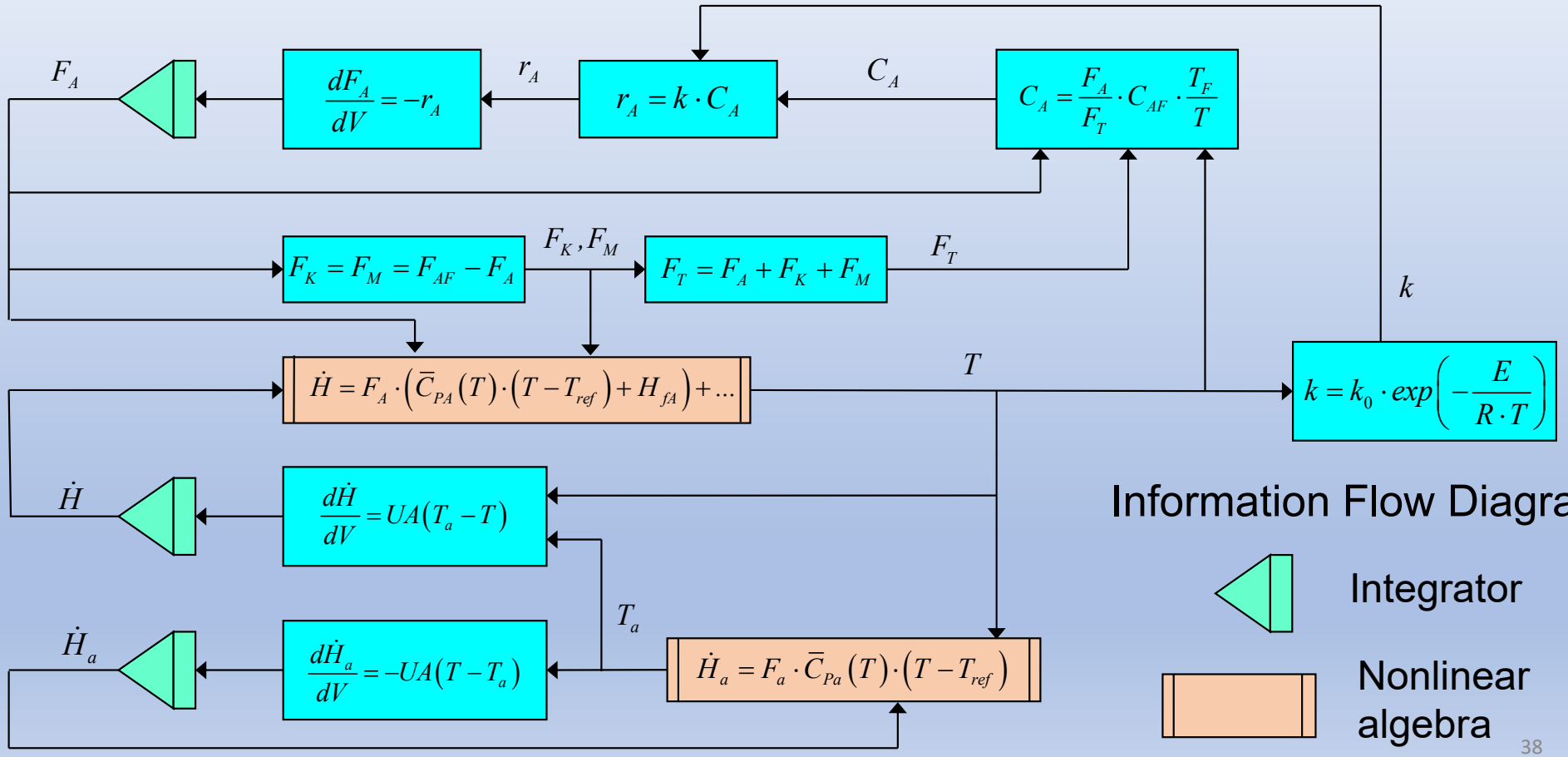
$$\dot{H}_a = F_a \cdot \bar{C}_{Pa}\left(T\right) \cdot \left(T - T_{ref}\right)$$

Note:

$$H_{fa} = 0$$

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene – full model



Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplification of the enthalpy balance

$$\frac{d\dot{H}}{dV} = UA\left(T_a - T\right)$$

$$\frac{d\dot{H}}{dV} = \frac{d\sum\left(F_i H_i\right)}{dV} = \sum \frac{dF_i}{dV} H_i + \sum F_i \frac{dH_i}{dV}$$

$$\frac{dF_i}{dV} = r_i = \nu_i \cdot \left(-r_A\right)$$

$$\frac{dH_i}{dV} = C_{Pi} \frac{dT}{dV} \quad \textit{assuming constant heat capacity}$$

$$\frac{dH_i}{dV} = \left(-r_A\right)\sum \nu_i H_i + \frac{dT}{dV}\sum F_i C_{Pi}$$

$$\sum \nu_i H_i = \Delta H_{rx} \quad \nu_i : \textit{stoichiometric coefficients}$$

$$\frac{dT}{dV} = \frac{r_A \cdot \Delta H_{rx} + UA\left(T_a - T\right)}{\sum F_i C_{Pi}}$$

$$\frac{d\dot{H}_a}{d\left(-V\right)} = UA\left(T - T_a\right)$$

assuming constant heat capacity

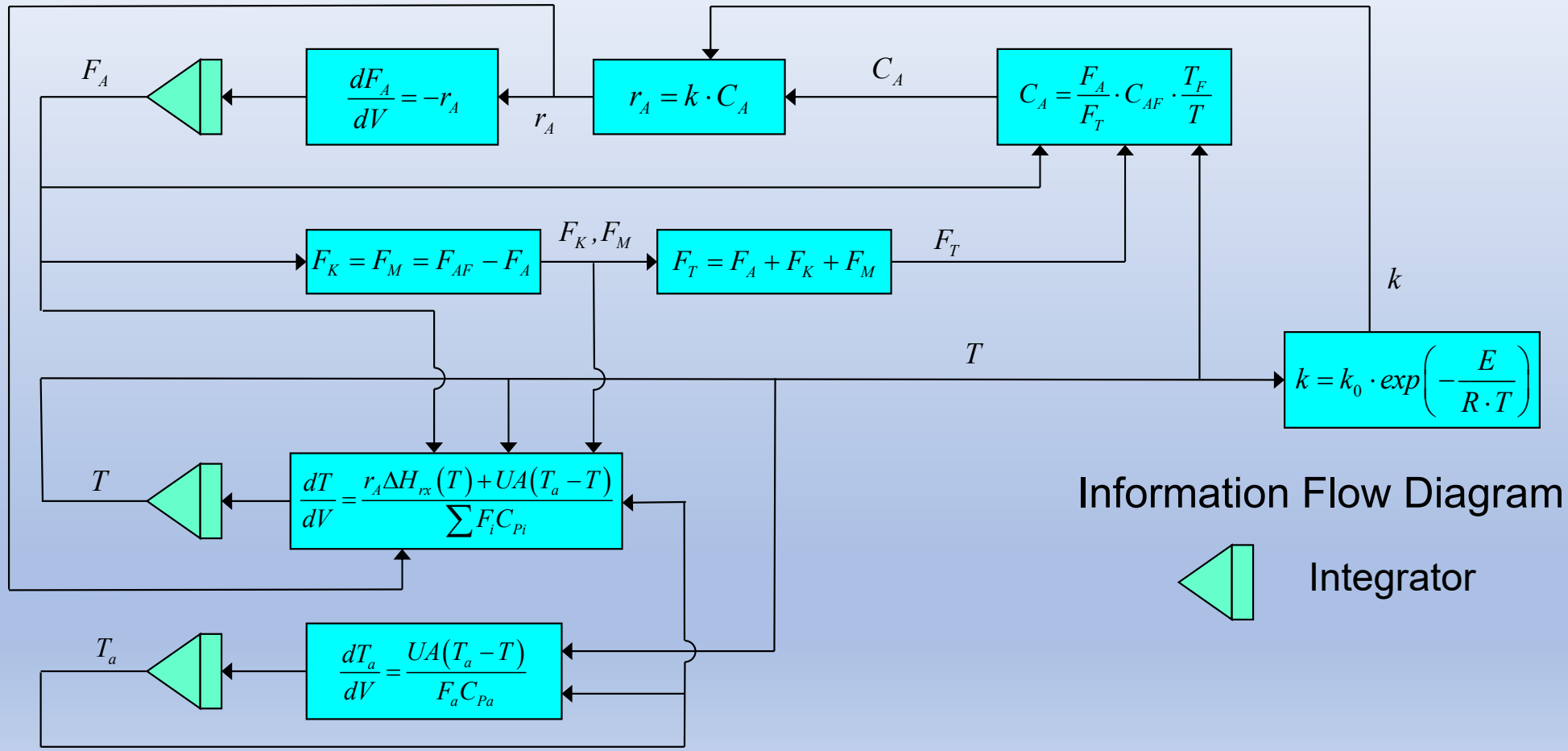
and molar flow rate

$$\frac{d\dot{H}_a}{dV} = F_a \cdot C_{Pa} \cdot \frac{dT}{dV}$$

$$\frac{dT_a}{dV} = \frac{UA\left(T_a - T\right)}{F_a C_{Pa}}$$

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene - simplified model



Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Solution Strategy

Estimate final air temperature at v = 0

→ Solve model from v = 0 to v = Vr

Determine air temperature at v = Vr from solution

If air temperature at v = Vr meets spec → done!

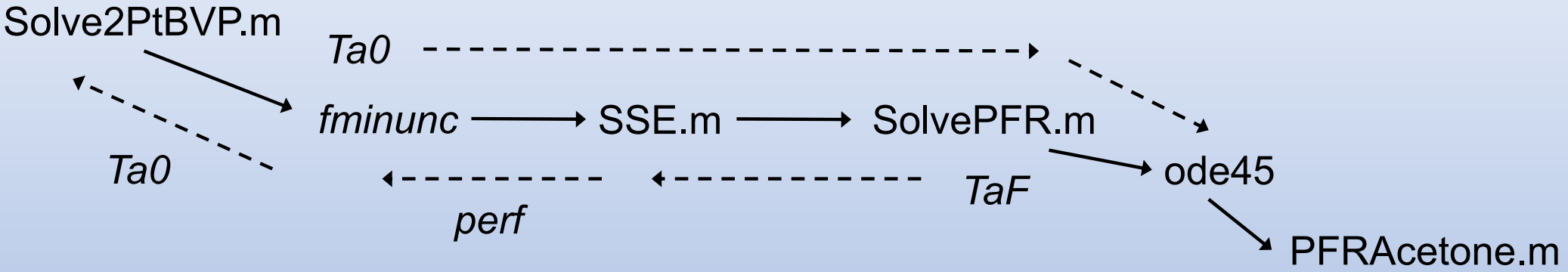
Adjust final air temperature at v = 0

Excel: use Solver
Matlab: use *fminunc*

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Matlab program structure



fminunc : unconstrained minimization function from the Optimization toolbox

Solve2PtBVP.m

```
% Determination of air temperature at v = 0
% to meet the counter-current entry temperature at v = Vr
Ta0 = 1050;  % initial estimate
options = optimoptions(@fminunc,'Algorithm','quasi-newton');
[ Ta0out, SSEval, exitflag, output ] = fminunc(@SSE,Ta0,options);
disp(Ta0out)  % show final result
```

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified model – Matlab solution

```
% Acetone Cracking to Ketene and Methane
% PFR with Counter-current Heat Exchange
% Simplified Model with Constant Heat Capacities
% Example from Fogler, 4th Ed., p. 504.
global R
R = 8.31446; % kJ/kgmol/K  also  m3*kPa/kgmol/K
Tref = 298.15;
% Basic data
MWA = 58.08;
MWAir = 28.96;

% Reactor
NoTubes = 1000;
TotalVolume = 2; % m3
VolPerTube = TotalVolume/NoTubes; % m3
TubeID = 26.7e-3; % m
TubeXC = pi*TubeID^2/4; % m2
TubeLength = VolPerTube/TubeXC; % m

% Heat Transfer
U = 400; % kJ/m2/hr/K
A = 4/TubeID; % m2/m3
```

```
% Acetone Feed
ReactorMassFeed = 7850; % kg/hr
FAM = ReactorMassFeed/NoTubes; % kg/hr per tube
FAF = FAM/MWA; % kgmol/hr
TF = 1035; % K
P = 162; % kPa
CAF = P/R/TF; % kgmol/m3

% Air Feed
AirFeed = 11088*8; % kg/hr
FaM = AirFeed/NoTubes; % kg/hr per tube
Fa = FaM/MWAir; % kgmol/hr
TaF = 1250; % K
Ta0 = 1120; % K -- estimate

% Solution span
vspan = linspace(0,VolPerTube,200);

% Initial conditions

y0 = [ FAF ; TF ; Ta0 ];
```

AcetonePFRSimplified.m

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified model – Matlab solution

```
% anonymous function
PFRanon = @(v,y) PFRAcetoneSimplified(v,y,FAF,CAF,TF,Fa,U,A);

% solve ODEs
[ v, yout ] = ode45(PFRanon,vspan,y0);

% unpack output
FAout = yout(:,1);
FKout = FAF - FAout;
FMout = FAF - FAout;
Tout = yout(:,2);
Taout = yout(:,3);

% conversion
Conv = (FAF - FAout)/FAF;

% plot results
figure(1)
plot(v,FAout,'k-',v,FKout,'g-')
grid
axis([ 0 2e-3 0 0.14 ]);
xlabel('Reactor Volume - m3')
ylabel('Molar Flow Rate - kgmol/hr')
title('Molar Flow Rates')
legend('Acetone','Ketene','Location','northeastoutside')
```

```
figure(2)
plot(v,Tout,'b-',v,Taout,'r-')
grid
xlabel('Reactor Volume - m3')
ylabel('Temperature - K')
title('Temperature Profiles')
legend('Reaction','Air','Location','northwest')

figure(3)
plot(v,Conv,'g-')
grid
axis([ 0 2e-3 0 1 ]);
xlabel('Reactor Volume - m3')
ylabel('Conversion')
title('Conversion Profile')

disp('Air Entry Temperature')
disp(Taout(end))
```

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified model – Matlab solution

PFRAcetoneSimplified.m

```
% Simplified model with constant heat capacities
function derivs = PFRAcetoneSimplified(v,y,FAF,CAF,TF,Fa,U,A)
global R
Cp_A = 163.89;
Cp_K = 84.65;
Cp_M = 71.79;
Cp_Air = 33.44;
lnk0 = 42.529;
k0 = exp(lnk0);  % 1/hr
E = 284522; % kJ/kgmol
FA = y(1);
T = y(2);
Ta = y(3);
FK = FAF - FA;
FM = FAF - FA;
FT = FA + FK + FM;
CA = FA/FT*CAF*TF/T;  % kgmol/m3
rA = k0*exp(-E/R/T)*CA ;
derivs(1) = -rA;
SumFCp = FA*Cp_A + FK*Cp_K + FM*Cp_M;
derivs(2) = (rA*(-HtRxn(T))+U*A*(Ta-T))/SumFCp;
derivs(3) = U*A*(Ta-T)/Fa/Cp_Air;
derivs = derivs';
```

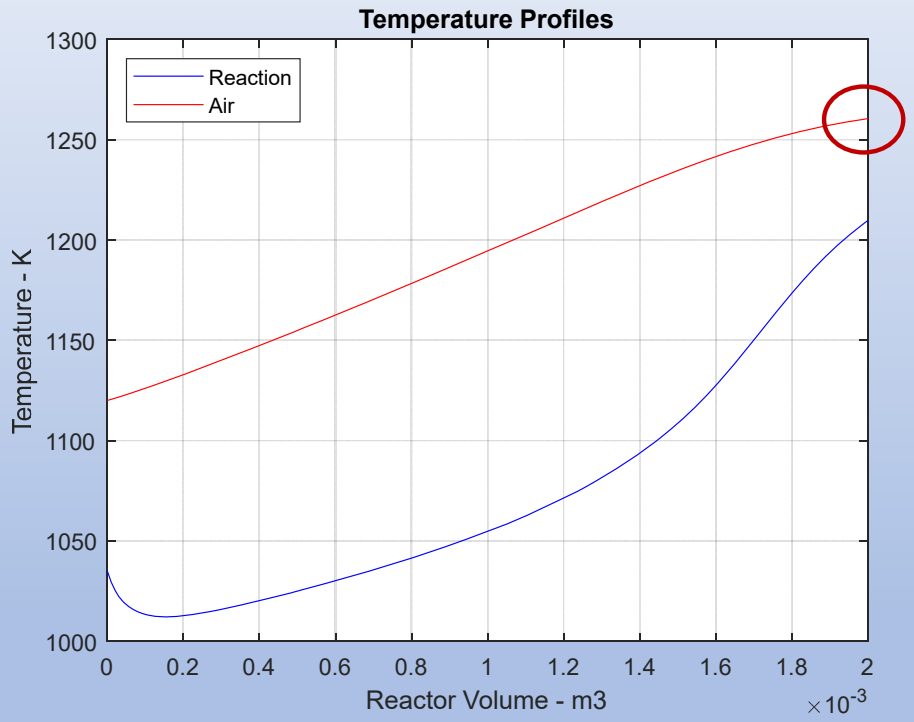
HtRxn.m

```
function hx = HtRxn(T)
Hx0 = 80.77e3; % kJ/kgmol
Tk = T/1000;
Tk0 = (25+273.15)/1000;
% acetone
HA = (6.8132e-3*Tk+0.2786/2*Tk^2-0.15628/3*Tk^3+0.03476/4*Tk^4 ...
    - (6.8132e-3*Tk0+0.2786/2*Tk0^2-0.15628/3*Tk0^3+0.03476/4*Tk0^4))*1000;
% ketene
HK = 18.909*Tk + 143.56/2*Tk^2 - 130.23/3*Tk^3 + 66.526/4*Tk^4 - 14.112/5*Tk^5 ...
    - (18.909*Tk0 + 143.56/2*Tk0^2 - 130.23/3*Tk0^3 + 66.526/4*Tk0^4 - 14.112/5*Tk0^5);
% methane
HM = -0.703028*Tk + 108.4773/2*Tk^2 - 42.52157/3*Tk^3 + 5.862788/4*Tk^4 - 0.678565/Tk ...
    - (-0.703028*Tk0 + 108.4773/2*Tk0^2 - 42.52157/3*Tk0^3 + 5.862788/4*Tk0^4 - 0.678565/Tk0);
hx = Hx0 + ( - HA + HK + HM )*1000;
```

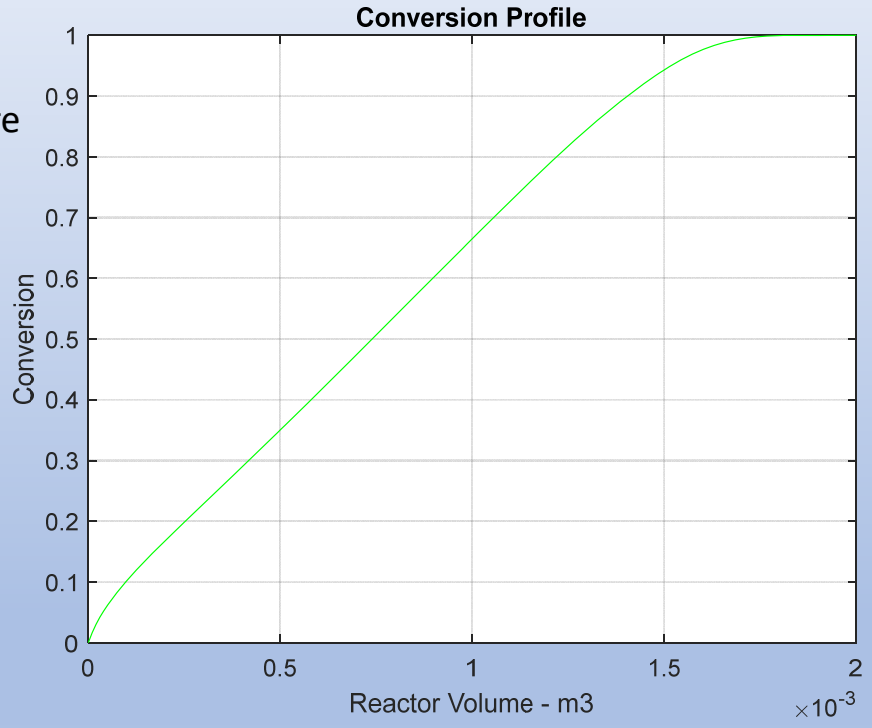
Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified model – Matlab results



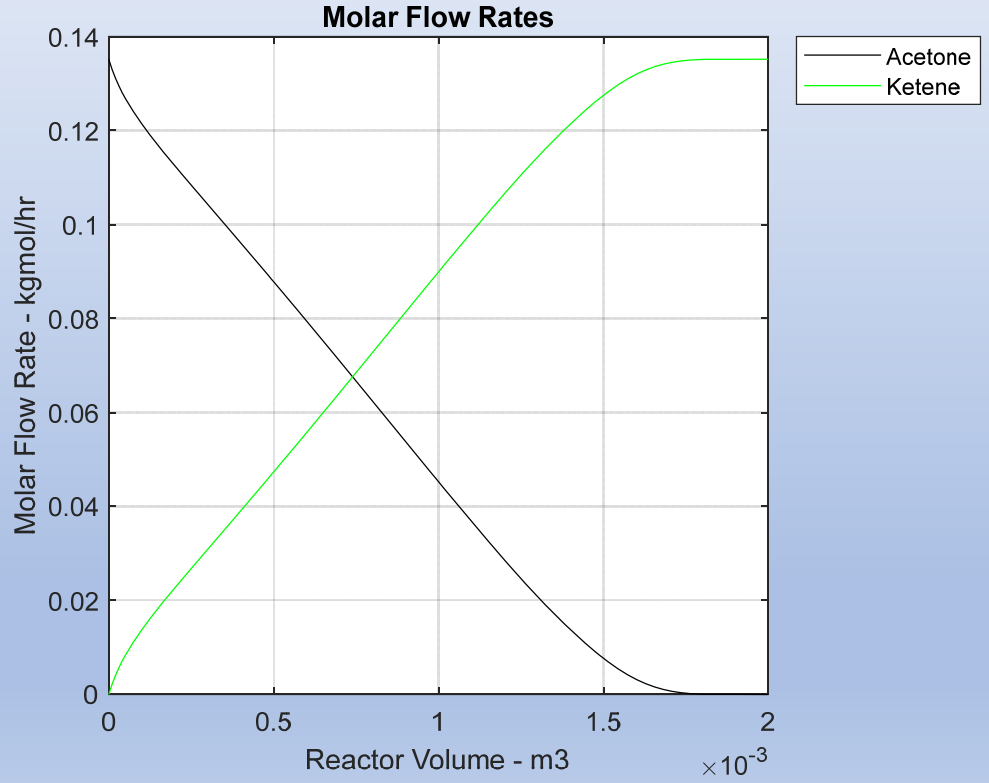
Inlet air temperature of 1250K not met



Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified model – Matlab results



Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified model – Solve two-point boundary value problem

Solve2PtBVP.m

```
% Determination of air temperature at v = 0
% to meet the counter-current entry temperature at v = Vr
Ta0 = 1050;  % initial estimate
options = optimoptions(@fminunc,'Algorithm','quasi-newton');
[ Ta0out, SSEval, exitflag, output ] = fminunc(@SSE,Ta0,options);
disp(Ta0out)  % show final result
```

SSE.m

```
% compute square of error
% between computed air temperature at v = Vr
% and target air entry temperature
function perf = SSE(Ta0)
Taftarget = 1250;
Taf = solvePFRSimplified(Ta0);
perf = (Taf-Taftarget)^2;
```

solvePFRSimplified.m

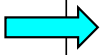
```
% solve PFR for a given air temperature at v = 0
% for simplified model with constant heat capacities
function taf = solvePFRSimplified(Ta0)
global R
R = 8.31446; % kJ/kgmol/K  also  m3*kPa/kgmol/K
Tref = 298.15;

% Basic data
MWA = 58.08;
MWAir = 28.96;

% Reactor
NoTubes = 1000;
TotalVolume = 2; % m3
VolPerTube = TotalVolume/NoTubes; % m3
TubeID = 26.7e-3; % m
TubeXC = pi*TubeID^2/4; % m2
TubeLength = VolPerTube/TubeXC; % m

% Heat Transfer
U = 400; % kJ/m2/hr/K
A = 4/TubeID; % m2/m3
```

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified model – Solve two-point boundary value problem

```
% Acetone Feed
ReactorMassFeed = 7850; % kg/hr
FAM = ReactorMassFeed/NoTubes; % kg/hr per tube
FAF = FAM/MWA; % kgmol/hr
TF = 1035; % K
P = 162; % kPa
CAF = P/R/TF; % kgmol/m3

% Air Feed
AirFeed = 11088*8; % kg/hr
FaM = AirFeed/NoTubes; % kg/hr per tube
Fa = FaM/MWAir; % kgmol/hr

% Solution span
vspan = linspace(0,VolPerTube,200);

% Initial conditions

y0 = [ FAF ; TF ; Ta0  ];
```

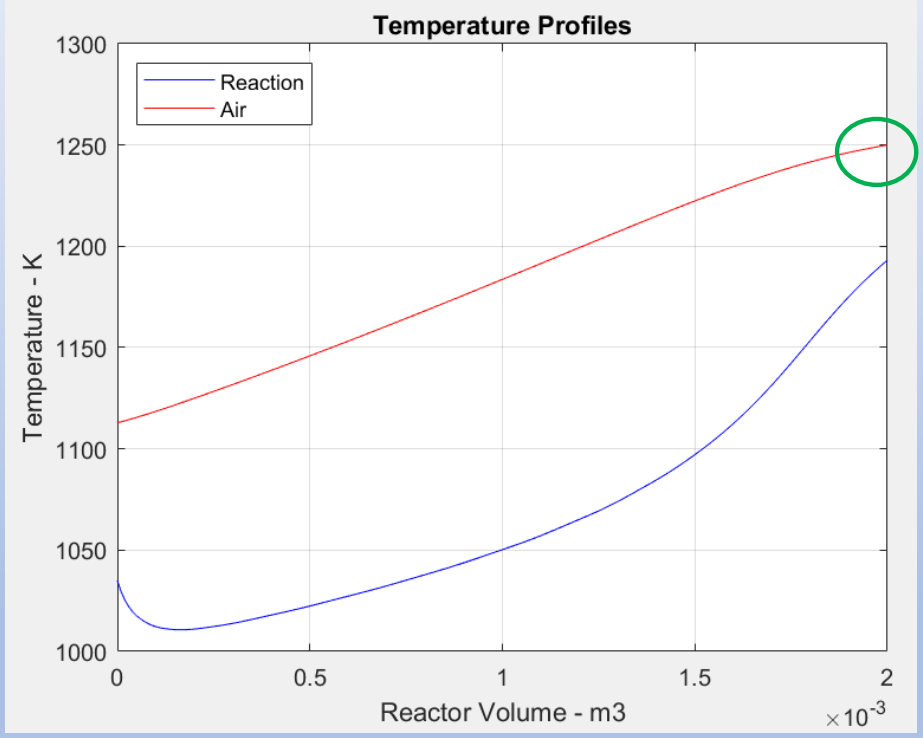


```
% anonymous function
PFRanon = @(v,y) PFRAcetoneSimplified(v,y,FAF,CAF,TF,Fa,U,A);

% solve ODEs
[ v, yout ] = ode45(PFRanon,vspan,y0);

% unpack output
Taout = yout(:,3);
n = length(Taout);
taf = Taout(n);
```

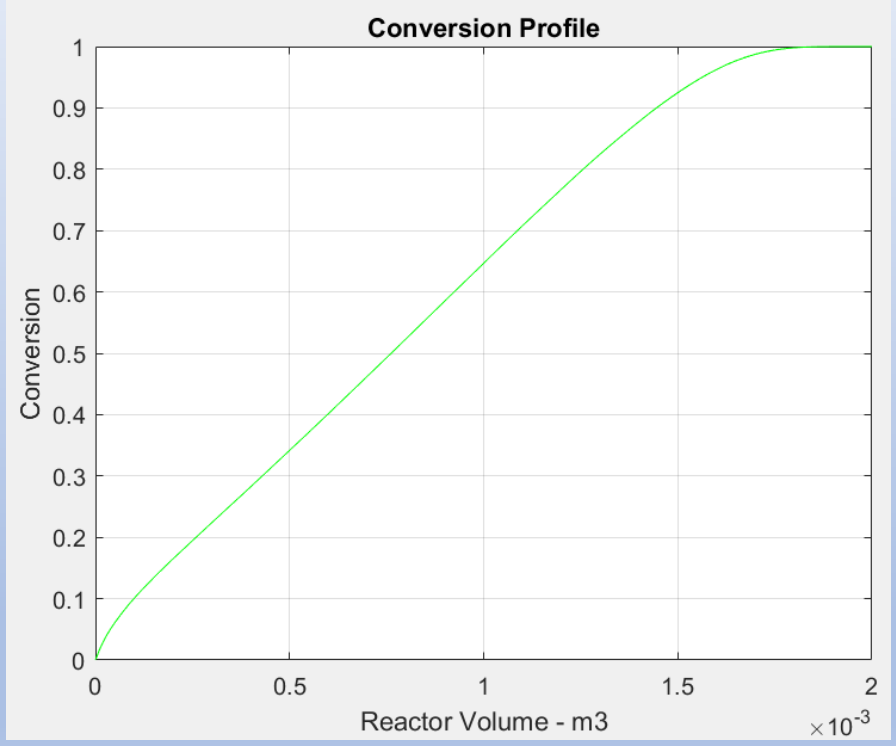
Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified model – Solve two-point boundary value problem - results



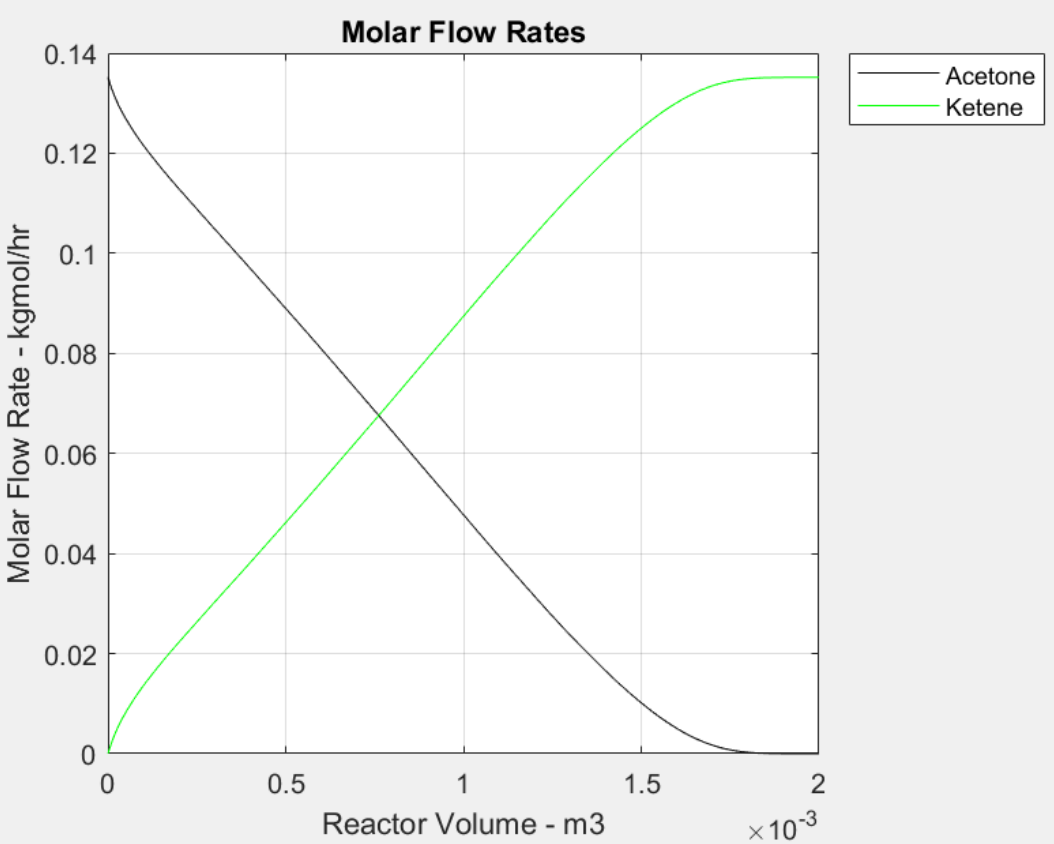
Inlet air temperature of 1250K now met



Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified model – Solve two-point boundary value problem - results



Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

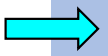
Matlab program structure – Full model

```
% compute square of error
% between computed air temperature at v = Vr
% and target air entry temperature
function perf = SSE(Ta0)
Taftarget = 1250;
Taf = solvePFR(Ta0);
perf = (Taf-Taftarget)^2;
```

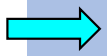
SSE.m

```
% solve PFR for a given air temperature at v = 0
% for simplified model with constant heat capacities
function taf = solvePFR(Ta0)
global R
R = 8.31446; % kJ/kgmol/K  also  m3*kPa/kgmol/K
Tref = 298.15;

% Basic data
MWA = 58.08;
MWAir = 28.96;
```

solvePFR.m



```
% Reactor
NoTubes = 1000;
TotalVolume = 2; % m3
VolPerTube = TotalVolume/NoTubes; % m3
TubeID = 26.7e-3; % m
TubeXC = pi*TubeID^2/4; % m2
TubeLength = VolPerTube/TubeXC; % m

% Heat Transfer
U = 400; % kJ/m2/hr/K
A = 4/TubeID; % m2/m3
```



Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Matlab program structure – Full model

```
% Acetone Feed
ReactorMassFeed = 7850; % kg/hr
FAM = ReactorMassFeed/NoTubes; % kg/hr per tube
FAF = FAM/MWA; % kgmol/hr
TF = 1035; % K
P = 162; % kPa
CAF = P/R/TF; % kgmol/m3

% Air Feed
AirFeed = 11088*8; % kg/hr
FaM = AirFeed/NoTubes; % kg/hr per tube
Fa = FaM/MWAir; % kgmol/hr

% initial conditions
HfA = -216.67*1000  % acetone heat of formation, kJ/kmol
H0 = FAF*(CpAavg(TF)*(TF-Tref)+HfA)
Ha0 = Fa*CpAiravg(Ta0)*(Ta0-Tref)

% Solution span
vspan = linspace(0,VolPerTube,200);

% Initial conditions

y0 = [ FAF ; H0 ; Ha0  ];
```

```
% anonymous function
PFRanon = @(v,y) PFRAcetone(v,y,FAF,CAF,TF,Fa,Ta0,U,A);

% solve ODEs
[ v, yout ] = ode45(PFRanon,vspan,y0);

% unpack output
FAout = yout(:,1);
FKout = FAF - FAout;
FMout = FAF - FAout;

Hout = yout(:,2);
n = length(Hout);
for i = 1:n
    Tout(i) = findT(Hout(i),TF,FAout(i),FKout(i),FMout(i));
end

Haout = yout(:,3);
for i = 1:n
    Taout(i) = findTa(Haout(i),Ta0,Fa);
end

taf = Taout(n);
```

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Matlab program structure - Full model

PFRAcetone.m

```
function derivs = PFRAcetone(v,y,FAF,CAF,TF,Fa,Ta0,U,A)
global R
lnk0 = 42.529;
k0 = exp(lnk0);  % 1/hr
E = 284522; % kJ/kgmol
FA = y(1);
H = y(2);
Ha = y(3);
FK = FAF - FA;
FM = FAF - FA;
FT = FA + FK + FM;
T = findT(H,TF,FA,FK,FM);
CA = FA/FT*CAF*TF/T;  % kgmol/m3
rA = k0*exp(-E/R/T)*CA ;
Ta = findTa(Ha,Ta0,Fa);
derivs(1) = -rA;
derivs(2) = U*A*(Ta-T);
derivs(3) = - U*A*(T-Ta);
derivs = derivs';
```

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Matlab program structure – Full model

findT.m

```
function Tout = findT(H,TF,FA,FK,FM)
T1 = TF;
tol = 1e-6;
while(1)
    T2 = T1 + 0.01;
    Tnew = T1 - 0.01*fH(H,T1,FA,FK,FM)/(fH(H,T2,FA,FK,FM)-fH(H,T1,FA,FK,FM));
    if abs((Tnew-T1)/Tnew) < tol ; break ; end
    T1 = Tnew;
end
Tout = Tnew;
```

fH.m

```
function Hout = fH(H,T,FA,FK,FM)
Tref = 298.15;
HfA = -216.67e3;
HfK = -61.09e3;
HfM = -74.81e3;
HAt = FA*(CpAavg(T)*(T-Tref)+HfA);
HKt = FK*(CpKavg(T)*(T-Tref)+HfK);
HMt = FM*(CpMavg(T)*(T-Tref)+HfM);
Hout = H-(HAt+HKt+HMt);
```

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Matlab program structure – Full model

findTa.m

```
function Taout = findTa(Ha,Ta0,Fa)
Ta1 = Ta0;
tol = 1.e-6;
while(1)
    Ta2 = Ta1 + 0.01;
    Tanew = Ta1 - 0.01*fHa(Ha,Ta1,Fa)/(fHa(Ha,Ta2,Fa)-fHa(Ha,Ta1,Fa));
    if abs((Tanew-Ta1)/Tanew) < tol ; break; end
    Ta1 = Tanew;
end
Taout = Tanew;
```

fHa.m

```
function Haout = fHa(Ha,Ta,Fa)
Tref = 298.15;
Cp = CpAiravg(Ta);
Haout = Ha - Fa*Cp*(Ta-Tref);
```

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Matlab program structure – Full model

CpAavg.m

```
function cpav = CpAavg(T)
a = 6.8132;
b = 278.6;
c = -156.28;
d = 34.76;
Tref = 25+273.15;
Trefk = Tref/1000;
Tk = T/1000;
CpT = a*Tk + b/2*Tk^2 + c/3*Tk^3 + d/4*Tk^4;
CpTref = a*Trefk + b/2*Trefk^2 + c/3*Trefk^3 + d/4*Trefk^4;
cpav = (CpT-CpTref)/(Tk-Trefk);
```

CpMavg.m

```
function cpav = CpMavg(T)
a = -0.703029;
b = 108.4773;
c = -42.52157;
d = 5.862788;
e = 0.678565;
Tref = 25+273.15;
Trefk = Tref/1000;
Tk = T/1000;
CpT = a*Tk + b/2*Tk^2 + c/3*Tk^3 + d/4*Tk^4 - e/Tk;
CpTref = a*Trefk + b/2*Trefk^2 + c/3*Trefk^3 + d/4*Trefk^4 + e/Trefk;
cpav = (CpT-CpTref)/(Tk-Trefk);
```

CpKavg.m

```
function cpav = CpKavg(T)
a = 18.909;
b = 143.56;
c = -130.23;
d = 66.526;
e = -14.112;
Tref = 25+273.15;
Trefk = Tref/1000;
Tk = T/1000;
CpT = a*Tk + b/2*Tk^2 + c/3*Tk^3 + d/4*Tk^4 + e/5*Tk^5;
CpTref = a*Trefk + b/2*Trefk^2 + c/3*Trefk^3 + d/4*Trefk^4 + e/5*Trefk^5;
cpav = (CpT-CpTref)/(Tk-Trefk);
```

CpAiravg.m

```
function cpav = CpAiravg(T)
a = 28.09;
b = 0.001965;
c = 0.000004799;
d = -0.000000001965;
Tref = 25+273.15;
CpT = a*T + b/2*T^2 + c/3*T^3 + d/4*T^4;
CpTref = a*Tref + b/2*Tref^2 + c/3*Tref^3 + d/4*Tref^4;
cpav = (CpT-CpTref)/(T-Tref);
```

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Matlab: solve model with correct air temperature at v = 0

AcetonePFR.m

```
% Acetone Cracking to Ketene and Methane
% PFR with Counter-current Heat Exchange
% Example from Fogler, 4th Ed., p. 504.
global R
R = 8.31446; % kJ/kgmol/K  also  m3*kPa/kgmol/K
Tref = 298.15;
% Basic data
MWA = 58.08;
MWAir = 28.96;

% Reactor
NoTubes = 1000;
TotalVolume = 2; % m3
VolPerTube = TotalVolume/NoTubes; % m3
TubeID = 26.7e-3; % m
TubeXC = pi*TubeID^2/4; % m2
TubeLength = VolPerTube/TubeXC; % m

% Heat Transfer
U = 400; % kJ/m2/hr/K
A = 4/TubeID; % m2/m3
```

```
% Acetone Feed
ReactorMassFeed = 7850; % kg/hr
FAM = ReactorMassFeed/NoTubes; % kg/hr per tube
FAF = FAM/MWA; % kgmol/hr
TF = 1035; % K
P = 162; % kPa
CAF = P/R/TF; % kgmol/m3

% Air Feed
AirFeed = 11088*8; % kg/hr
FaM = AirFeed/NoTubes; % kg/hr per tube
Fa = FaM/MWAir; % kgmol/hr
TaF = 1250; % K
Ta0 = 1117.7; % K -- estimate

% Solution span
vspan = linspace(0,VolPerTube,200);

% Initial conditions
HfA = -216.67*1000; % acetone heat of formation, kJ/kgmol
H0 = FAF*(CpAavg(TF)*(TF-Tref)+HfA) ;
Ha0 = Fa*CpAiravg(Ta0)*(Ta0-Tref) ;
y0 = [ FAF ; H0 ; Ha0 ];
```

Tubular Reactor with Counter-current Heat Exchange

Matlab: solve model with correct air temperature at v = 0

```
% anonymous function
PFRanon = @(v,y) PFRAcetone(v,y,FAF,CAF,TF,Fa,Ta0,U,A);

% solve ODEs
[ v, yout ] = ode45(PFRanon,vspan,y0);

% unpack output
FAout = yout(:,1);
FKout = FAF - FAout;
FMout = FAF - FAout;

Hout = yout(:,2);
n = length(Hout);
for i = 1:n
    Tout(i) = findT(Hout(i),TF,FAout(i),FKout(i),FMout(i));
end

Haout = yout(:,3);
for i = 1:n
    Taout(i) = findTa(Haout(i),Ta0,Fa);
end

% conversion
Conv = (FAF - FAout)/FAF;
```

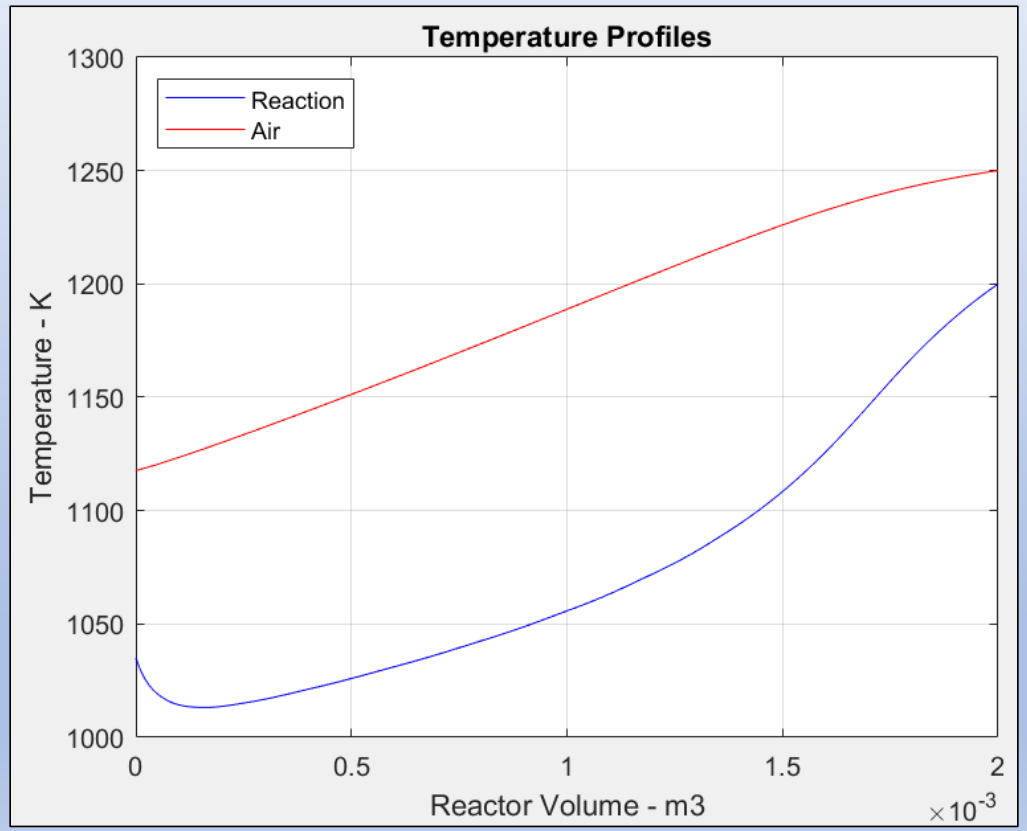
```
% plot results
figure(1)
plot(v,FAout,'k-',v,FKout,'g-')
grid
axis([ 0 2e-3 0 0.14 ]);
xlabel('Reactor Volume - m3')
ylabel('Molar Flow Rate - kgmol/hr')
title('Molar Flow Rates')
legend('Acetone','Ketene','Location','northeastoutside')

figure(2)
plot(v,Tout,'b-',v,Taout,'r-')
grid
xlabel('Reactor Volume - m3')
ylabel('Temperature - K')
title('Temperature Profiles')
legend('Reaction','Air','Location','northwest')

figure(3)
plot(v,Conv,'g-')
grid
axis([ 0 2e-3 0 1 ]);
xlabel('Reactor Volume - m3')
ylabel('Conversion')
title('Conversion Profile')
```

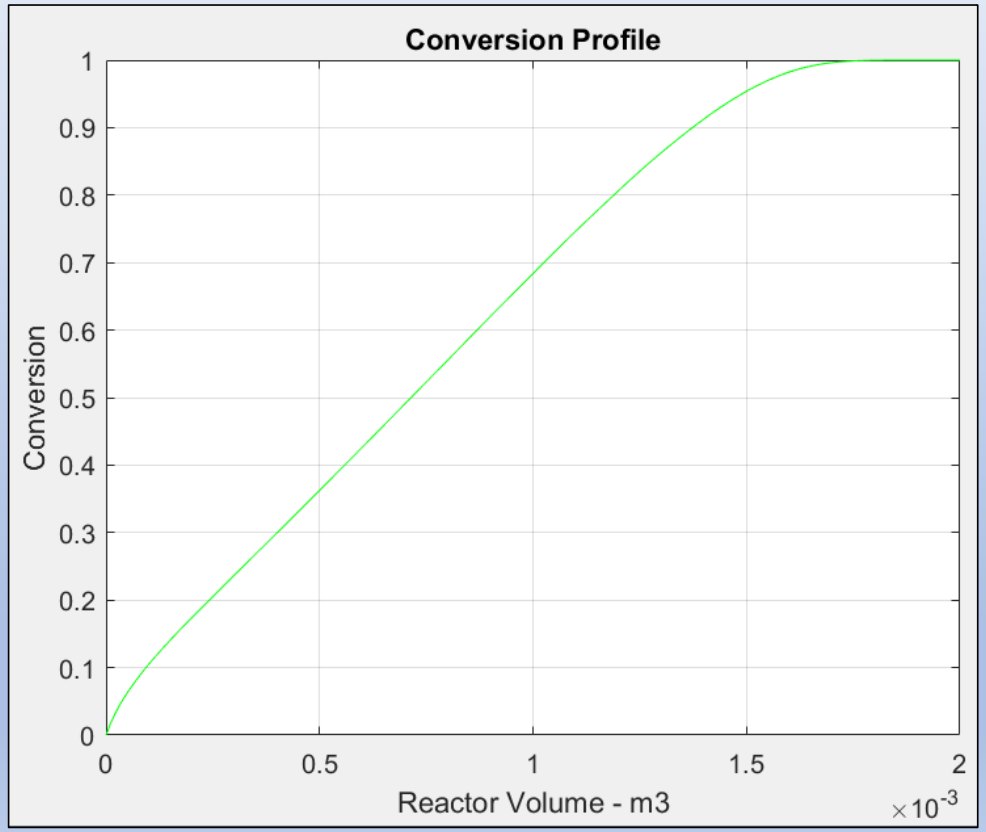
```
disp('Air Entry Temperature')
disp(Taout(n))
```

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Matlab results – Full model

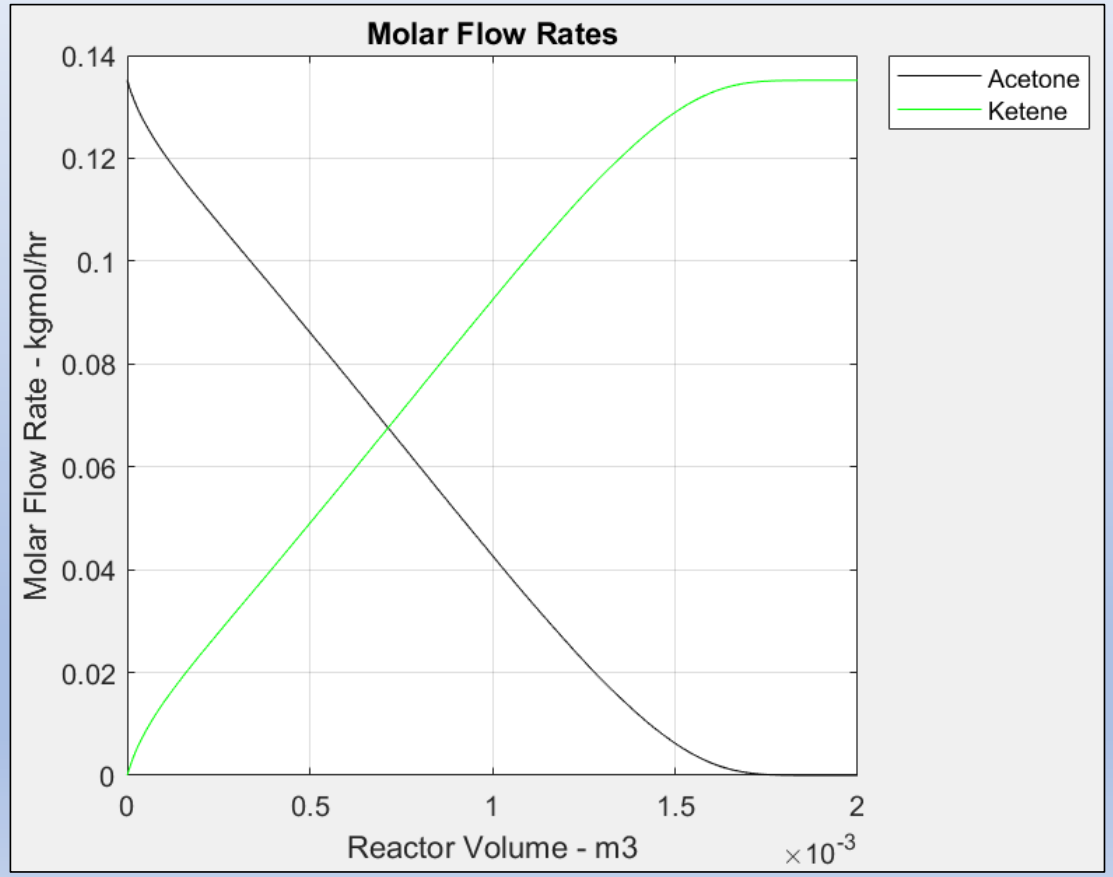




Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Matlab results – Full model



Matlab Bootcamps 1, 2 and 3

- ✓ 1: Getting up to speed with MATLAB
- ✓ 2: Learning to use MATLAB to solve typical problem scenarios
- ✓ 3: Detailed modeling of packed-bed and plug-flow reactors

References:

Elements of Chemical Reaction Engineering, 4th Edition
Fogler, H. Scott,, Prentice-Hall, 2006.

Applied Numerical Methods with MATLAB for Engineers and Scientists,
Steven C. Chapra, 5th Edition, McGraw-Hill, 2022.

Contact **David.Clough@Colorado.edu** for follow-up assistance.

"Prof. Clough, may I be excused? My brain is full."