Excel Bootcamps 1, 2, 3 and 4

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

Bootcamp 4 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 (PFR)

Ammonia Synthesis

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

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

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

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

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

Ordinary Differential Equation Models

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

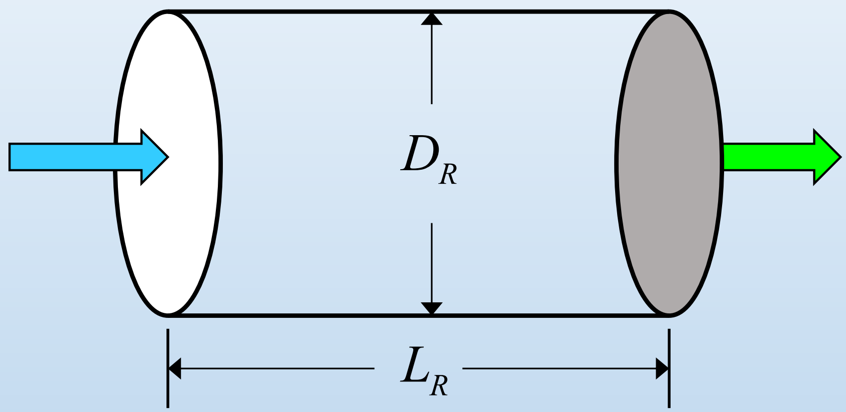
Ammonia Synthesis

Reactor Feed

$FeedN_2$

$FeedH_2$

(kmol/h)



$FlowN_2(V_r)$

$FlowH_2(V_r)$

$FlowNH_3(V_r)$

(kmol/h)

Reactor Outlet

Differential Mole Balance on N_2

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

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

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

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

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 (PFR)

Ammonia Synthesis

Energy Balance

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

with constant heat capacity approximation

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

pressure effect on enthalpy

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

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

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

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 (PFR)

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*

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

Differential form:

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

Ordinary Differential Equation Models

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

Ammonia Synthesis

Pressure Drop – the Ergun equation for packed beds

Fluid Density

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

$\tilde{V}$ 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 (PFR)

Ammonia Synthesis

Peng-Robinson EOS Mixture Coefficients

Coefficients for individual components

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

$$a_i = 0.45724\frac{R^2T_c^2}{P_c}\left(1+m_i\left(1-\sqrt{\frac{T}{T_c}}\right)\right)^2$$

$$m_i = 0.37464 + 1.54226\,\omega_i - 0.26992\,\omega_i^2$$

$$b_i = 0.07780\frac{RT_c}{P_c}$$

k_{ij} : binary interactor factors

ω_i : acentric factor for component i

$\mathbf{x}$: mole fractions

Mixture coefficients

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

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

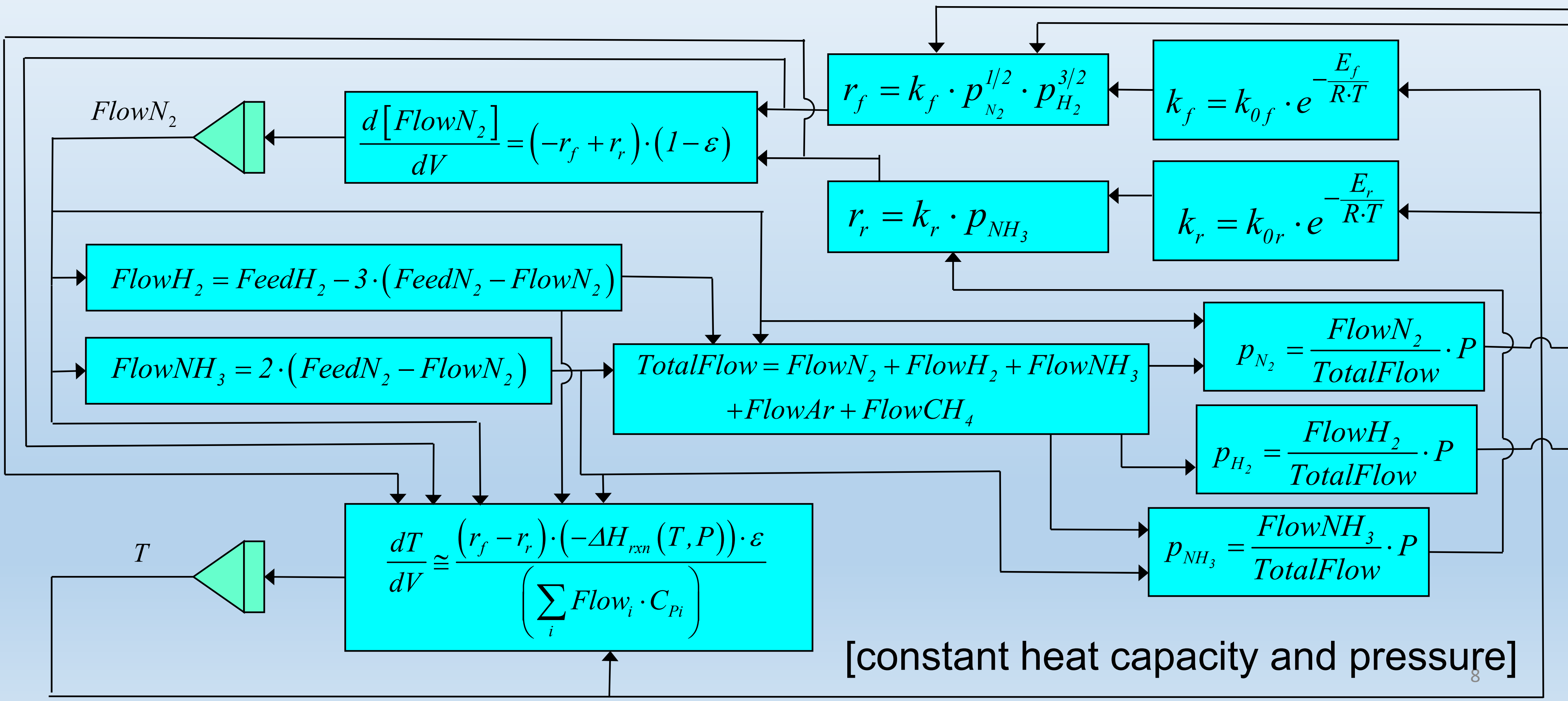
$$b_m = \mathbf{x}'\cdot\mathbf{b} = \sum_{i=1}^{n} x_i\cdot b_i$$

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

Ordinary Differential Equation Models

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

Ammonia Synthesis – Simplified Model Information Diagram



[constant heat capacity and pressure]

Ordinary Differential Equation Models

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

Ammonia Synthesis – Simplified Model – Spreadsheet Solution

AmmoniaSimulationSimplifiedModel.xlsm

Ammonia PFR Simulation

Simplified Model

				Rgas	8.314	kJ/kmol/K			
Feed Conditions							Kinetics		
N2	12348	kmol/h	Pressure	150	atm		Forward		
H2	37044		Temperature	270	degC		k0f	1.00E+04	kmol/m3/s/atm^2
Ar	12391		Heat of Reaction	-107816	kJ/kmol			3.60E+07	kmol/m3/h/atm^2
CH4	5652						Ef	9.10E+04	kJ/kmol
							Reverse		
Void Fraction	0.4						k0r	1.30E+10	kmol/m3/s/atm
Particle Diameter	1.00E-03	m						4.68E+13	kmol/m3/h/atm
Reactor Diameter	3	m	ReactorX-sect Area	7.069	m2		Er	1.41E+05	kJ/kmol
Reactor Length	1	m	Reactor Volume	7.069	m3				

from Hysys molar enthalpies

Heat of Reaction	
aa	-1.931E+05
bb	4.840E+05
cc	-9.944E+05
dd	8.805E+05
ee	-2.908E+05

Heat Capacities at Tavg

Tavg	350
N2	31.98
H2	29.91
NH3	54.65
Ar	22.09
CH4	56.05

Heat Capacity - coefficients for kJ/mol/K Fit of Hysys properties at 150 atm

	a	b	c	d	e
N2	4.04E+01	-3.53E+01	4.69E+01	-1.94E+01	0.00E+00
H2	2.88E+01	1.86E+00	0.00E+00	0.00E+00	0.00E+00
NH3	1.09E+03	-5.69E+03	1.18E+04	-1.09E+04	3.80E+03
Ar	3.68E+01	-5.30E+01	6.40E+01	-2.70E+01	0.00E+00
CH4	2.47E+01	5.03E+01	0.00E+00	0.00E+00	0.00E+00

Ordinary Differential Equation Models

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

Ammonia Synthesis – Simplified Model – Spreadsheet Solution

Pitzer Correlation for Pressure Correction of Heat of Reaction

	Tc (K)	Pc (atm)	Pc (kPa)	Ω
NH3	405.6	112.5	11399	0.25
N2	126.2	33.5	3394.4	0.04
H2	33.2	12.8	1297.0	0.00

Pitzer Acentric Factor

N2	0.039
H2	-0.216
NH3	0.25
Ar	0.001
CH4	0.011

Binary Interaction Matrix

	N2	H2	NH3	Ar	CH4
N2	0	-0.036	0.222	0	0.036
H2	-0.036	0	0	0	0.202
NH3	0.222	0	0	0	0
Ar	0	0	0	0	0.023
CH4	0.036	0.202	0	0.023	0

Critical Temperature K	Critical Pressure kPa
126.2	3394
33.19	1297
405.65	11277
150.86	4870
190.564	4641

Ordinary Differential Equation Models

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

Ammonia Synthesis – Simplified Model – Spreadsheet Solution

	Molar Flow Rates - kmol/h								Partial Pressure - atm					Reaction Rates - kmol/m3/h			Energy Balance	
Volume (m3)	N2	H2	NH3	Ar	CH4	Total	Temp-erature (degC)	N2	H2	NH3	Ar	CH4	Forward	Reverse	dFN2/dV	Heat of Reaction (kJ/kmol)	dT/dV	Conversion (N2 Basis)
0.0000	12348.0	37044	0	12391	5652	67435	270.0	27.466	82.399	0.000	27.562	12.572	249.931	0.000	-99.972	-114646	5.475E+00	0.0%
0.0010	12347.9	37044	0.20	12391	5652	67435	270.0	27.466	82.399	0.000	27.562	12.572	249.979	0.001	-99.991	-114646	5.476E+00	0.0%
0.0020	12347.8	37043	0.40	12391	5652	67435	270.0	27.466	82.399	0.001	27.562	12.572	250.027	0.001	-100.010	-114646	5.477E+00	0.0%
0.0030	12347.7	37043	0.60	12391	5652	67434	270.0	27.466	82.398	0.001	27.562	12.572	250.075	0.002	-100.029	-114646	5.478E+00	0.0%
0.0040	12347.6	37043	0.80	12391	5652	67434	270.0	27.466	82.398	0.002	27.562	12.572	250.123	0.002	-100.048	-114646	5.479E+00	0.0%
•	•	•	•	•	•	•												
7.0640	9650.6	28952	5394.83	12391	5652	62040	418.2	23.333	69.999	13.044	29.959	13.665	13544.783	13532.486	-4.919	-113946	2.721E-01	21.8%
7.0650	9650.6	28952	5394.84	12391	5652	62040	418.2	23.333	69.999	13.044	29.959	13.665	13544.858	13532.644	-4.886	-113946	2.703E-01	21.8%
7.0660	9650.6	28952	5394.85	12391	5652	62040	418.2	23.333	69.999	13.044	29.959	13.665	13544.933	13532.800	-4.853	-113946	2.685E-01	21.8%
7.0670	9650.6	28952	5394.86	12391	5652	62040	418.2	23.333	69.999	13.044	29.959	13.665	13545.007	13532.956	-4.820	-113946	2.666E-01	21.8%
7.0680	9650.6	28952	5394.87	12391	5652	62040	418.2	23.333	69.999	13.044	29.959	13.665	13545.080	13533.110	-4.788	-113946	2.649E-01	21.8%
7.0690	9650.6	28952	5394.88	12391	5652	62040	418.2	23.333	69.999	13.044	29.959	13.665	13545.153	13533.263	-4.756	-113946	2.631E-01	21.8%

Ordinary Differential Equation Models

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

Ammonia Synthesis – Simplified Model – Spreadsheet Solution

Euler method for N2

	A	B	C
15		Volume (m3)	N2
16		0.0000	12348.0
17	=C16+Q16*(B17-B16)		

Stoichiometry for H2 and NH3

	A	B	C	D
15		Volume (m3)	N2	H2
16		0.0000	12348.0	37044
17		=FeedH2-3*(FeedN2-C17)		

	B	C	D	E
15	Volume (m3)	N2	H2	NH3
16	0.0000	12348.0	37044	0
17	0.0010	12347.9	=2*(FeedN2-C17)	

Forward reaction rate

	I	J	K	L	M	N	O
15	Temp-erature (degC)	N2	H2	NH3	Ar	CH4	Forward
16	270.0	=k0f*EXP(-Ef/Rgas/(I16+273.15))*J16 ^ 0.5 * K16 ^ 1.5					

Rate of change of N2

	O	P	Q
15	Forward	Reverse	dFN2/dV
16	249.931	=-eps*(O16-P16)	

Heat of reaction

	P	Q	R
15	Reverse	dFN2/dV	Heat of Reaction (kJ/kmol)
16	=@HtRxnP(I16,FeedP)		

Euler method for temperature

	G	H	I
15	CH4	Total	Temp-erature (degC)
16	5652	67435	270.0
17	=I16+S16*(B17-B16)		

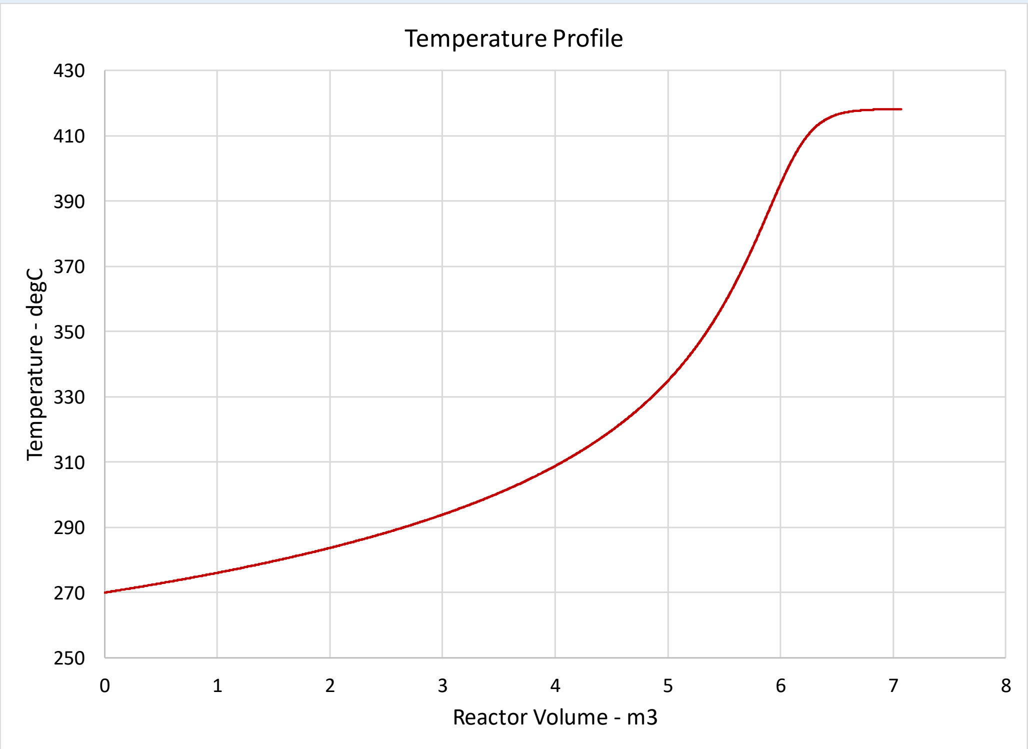
Rate of change of temperature

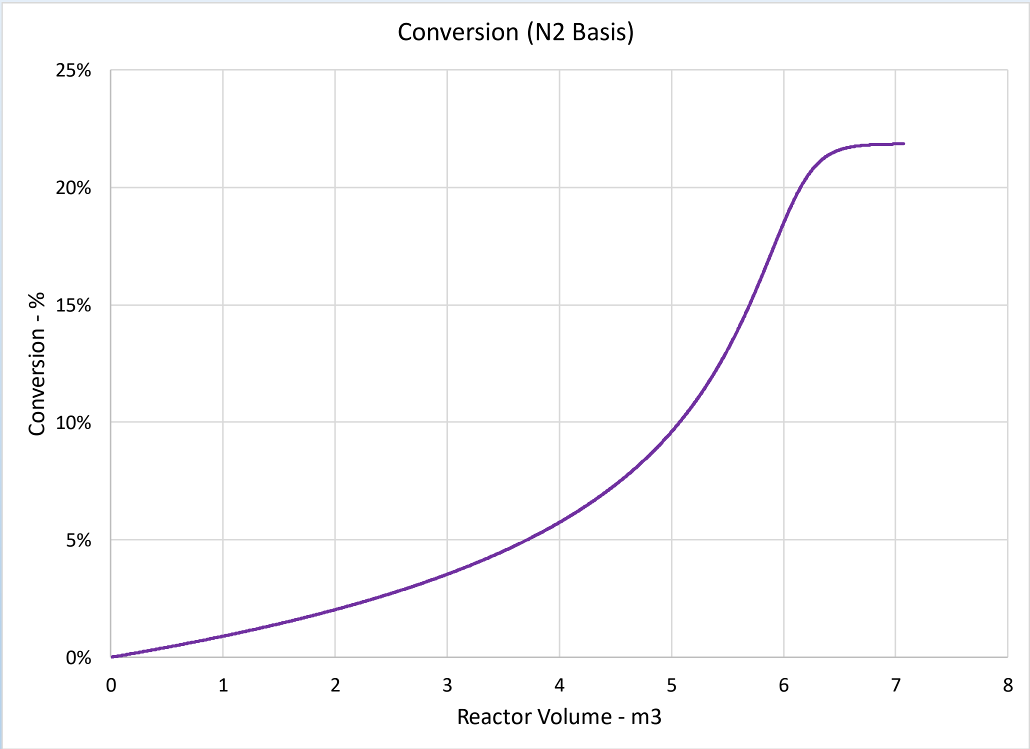
	G	H	I	J	K	L	M	N	O	P	Q	R	S
15	CH4	Total	Temp-erature (degC)	N2	H2	NH3	Ar	CH4	Forward	Reverse	dFN2/dV	Heat of Reaction (kJ/kmol)	dT/dV
16	5652	67435	270.0	27.466	82.399	=(O16-P16)*(-R16)*eps/(C16*Cp_N2+D16*Cp_H2+E16*Cp_NH3+F16*Cp_Ar+G16*Cp_CH4)							
17	5652	67435	270.0	27.466	82.399	0.000	27.562	12.572	249.979	0.001	-99.991	-114646	5.476E+00

Ordinary Differential Equation Models

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

Ammonia Synthesis – Simplified Model – Spreadsheet Solution

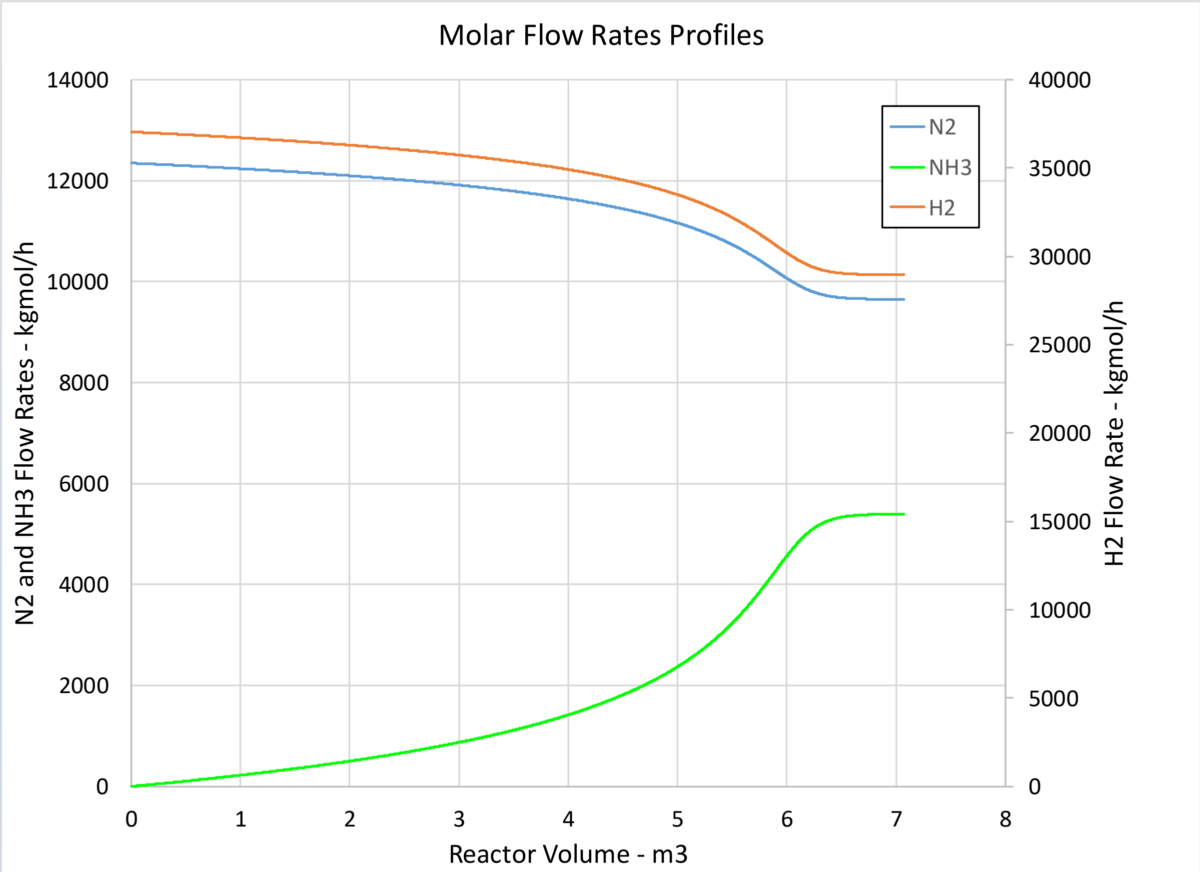




Ordinary Differential Equation Models

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

Ammonia Synthesis – Simplified Model – Spreadsheet Solution



Ordinary Differential Equation Models

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

Ammonia Synthesis – Simplified Model – Spreadsheet Solution

Heat capacity function

```
Function HtCap(component As String, T)
Dim a, b, c, d, e, Tk, Tk1
a = Application.WorksheetFunction.VLookup(component, Range("HtCapTable"), 2, False)
b = Application.WorksheetFunction.VLookup(component, Range("HtCapTable"), 3, False)
c = Application.WorksheetFunction.VLookup(component, Range("HtCapTable"), 4, False)
d = Application.WorksheetFunction.VLookup(component, Range("HtCapTable"), 5, False)
e = Application.WorksheetFunction.VLookup(component, Range("HtCapTable"), 6, False)
   Tk = T + 273.15
   Tk1 = Tk / 1000
   HtCap = a + b * Tk1 + c * Tk1 ^ 2 + d * Tk1 ^ 3 + e * Tk1 ^ 4
End Function
```

Heat of reaction temperature-based function

```
Function HtRxn(T)
Dim a, b, c, d, e, Tk1
a = Range("aa")
b = Range("bb")
c = Range("cc")
d = Range("dd")
e = Range("ee")
Tk1 = (T + 273.15) / 1000
HtRxn = a + b * Tk1 + c * Tk1 ^ 2 + d * Tk1 ^ 3 + e * Tk1 ^ 4
End Function
```

Ordinary Differential Equation Models

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

Ammonia Synthesis – Simplified Model – Spreadsheet Solution

Heat of reaction temperature- and pressure-based function

```
Function HtRxnP(T, P)
' Heat of reaction with Pitzer correction for pressure
Dim a, b, c, d, e, Tk1, HtRxnT, R, Pk, Tk
Dim TcNH3, TcN2, TcH2, PcNH3, PcN2, PcH2
Dim OmegaNH3, OmegaN2, OmegaH2, TrNH3, TrN2, TrH2
Dim B0_NH3, B0_N2, B0_H2, B1_NH3, B1_N2, B1_H2
Dim dB0_NH3, dB0_N2, dB0_H2, dB1_NH3, dB1_N2, dB1_H2
Dim H_NH3, H_N2, H_H2
R = 8.31446  ' kJ/kgmol/K
a = Range("aa")
b = Range("bb")
c = Range("cc")
d = Range("dd")
e = Range("ee")
Tk = T + 273.15  ' K
Tk1 = Tk / 1000
Pk = P * 101.325  ' kPa
HtRxnT = a + b * Tk1 + c * Tk1 ^ 2 + d * Tk1 ^ 3 + e * Tk1 ^ 4
```

Ammonia Synthesis – Simplified Model – Spreadsheet Solution

Heat of reaction temperature- and pressure-based function

```
TcNH3 = Application.WorksheetFunction.VLookup("NH3", Range("PitzerTable"), 2, False)
TcN2 = Application.WorksheetFunction.VLookup("N2", Range("PitzerTable"), 2, False)
TcH2 = Application.WorksheetFunction.VLookup("H2", Range("PitzerTable"), 2, False)
PcNH3 = Application.WorksheetFunction.VLookup("NH3", Range("PitzerTable"), 4, False)
PcN2 = Application.WorksheetFunction.VLookup("N2", Range("PitzerTable"), 4, False)
PcH2 = Application.WorksheetFunction.VLookup("H2", Range("PitzerTable"), 4, False)
OmegaNH3 = Application.WorksheetFunction.VLookup("NH3", Range("PitzerTable"), 5, False)
OmegaN2 = Application.WorksheetFunction.VLookup("N2", Range("PitzerTable"), 5, False)
OmegaH2 = Application.WorksheetFunction.VLookup("H2", Range("PitzerTable"), 5, False)
TrNH3 = Tk / TcNH3
TrN2 = Tk / TcN2
TrH2 = Tk / TcH2
```

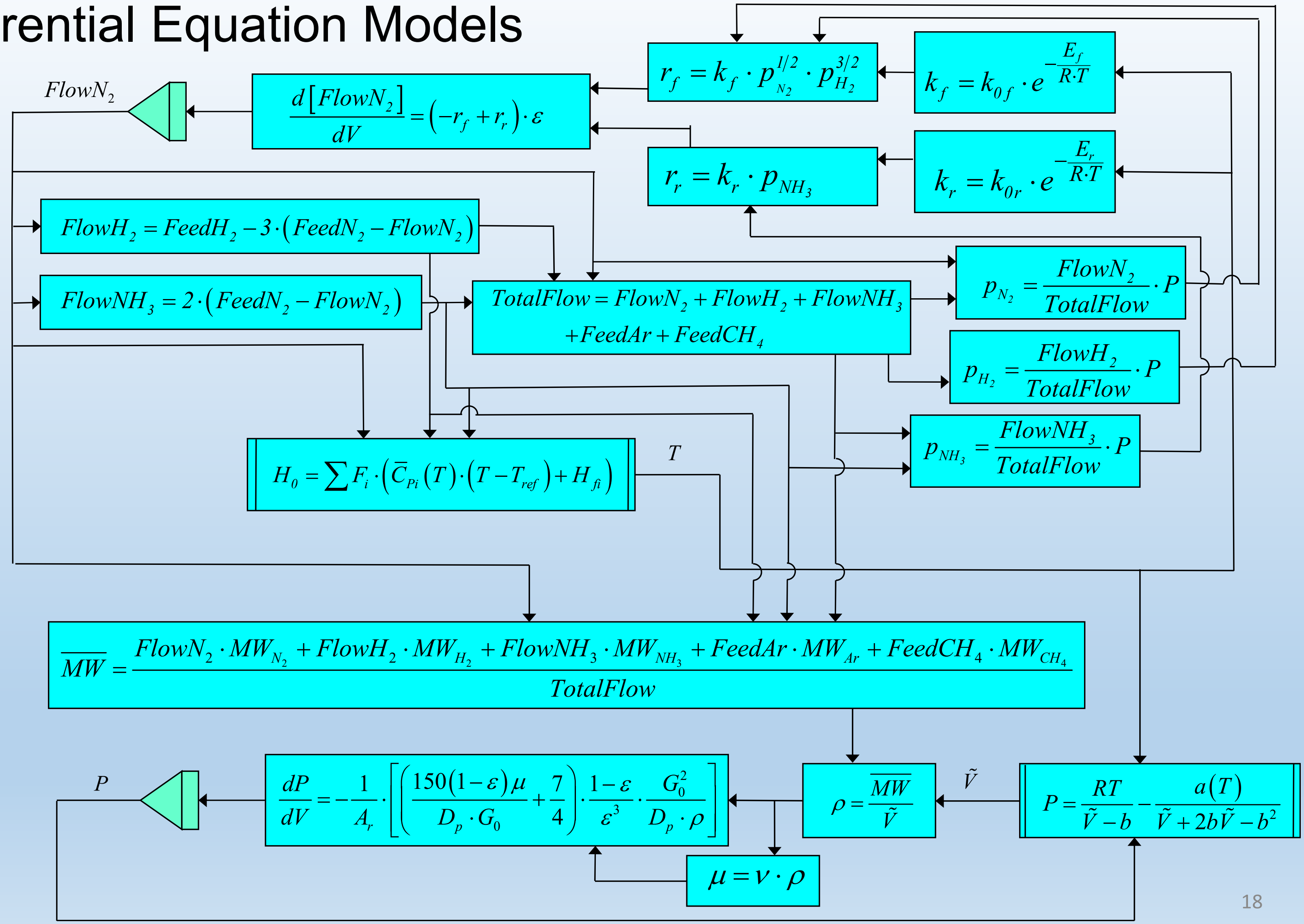
```
B0_NH3 = 0.1445 - 0.33 / TrNH3 - 0.1385 / TrNH3 ^ 2 - 0.0121 / TrNH3 ^ 3
B0_N2 = 0.1445 - 0.33 / TrN2 - 0.1385 / TrN2 ^ 2 - 0.0121 / TrN2 ^ 3
B0_H2 = 0.1445 - 0.33 / TrH2 - 0.1385 / TrH2 ^ 2 - 0.0121 / TrH2 ^ 3
B1_NH3 = 0.073 + 0.46 / TrNH3 - 0.5 / TrNH3 ^ 2 - 0.097 / TrNH3 ^ 3 - 0.0073 / TrNH3 ^ 8
B1_N2 = 0.073 + 0.46 / TrN2 - 0.5 / TrN2 ^ 2 - 0.097 / TrN2 ^ 3 - 0.0073 / TrN2 ^ 8
B1_H2 = 0.073 + 0.46 / TrH2 - 0.5 / TrH2 ^ 2 - 0.097 / TrH2 ^ 3 - 0.0073 / TrH2 ^ 8
dB0_NH3 = 0.33 / TrNH3 ^ 2 + 0.277 / TrNH3 ^ 3 + 0.0363 / TrNH3 ^ 4
dB0_N2 = 0.33 / TrN2 ^ 2 + 0.277 / TrN2 ^ 3 + 0.0363 / TrN2 ^ 4
dB0_H2 = 0.33 / TrH2 ^ 2 + 0.277 / TrH2 ^ 3 + 0.0363 / TrH2 ^ 4
dB1_NH3 = -0.46 / TrNH3 ^ 2 + 1 / TrNH3 ^ 3 + 0.291 / TrNH3 ^ 4 + 0.0584 / TrNH3 ^ 9
dB1_N2 = -0.46 / TrN2 ^ 2 + 1 / TrN2 ^ 3 + 0.291 / TrN2 ^ 4 + 0.0584 / TrN2 ^ 9
dB1_H2 = -0.46 / TrH2 ^ 2 + 1 / TrH2 ^ 3 + 0.291 / TrH2 ^ 4 + 0.0584 / TrH2 ^ 9
H_NH3 = R * Tk * (1 - Pk) / PcNH3 * ((dB0_NH3 - B0_NH3 / TrNH3) + OmegaNH3 * (dB1_NH3 - B1_NH3 / TrNH3))
H_N2 = R * Tk * (1 - Pk) / PcN2 * ((dB0_N2 - B0_N2 / TrN2) + OmegaN2 * (dB1_N2 - B1_N2 / TrN2))
H_H2 = R * Tk * (1 - Pk) / PcH2 * ((dB0_H2 - B0_H2 / TrH2) + OmegaH2 * (dB1_H2 - B1_H2 / TrH2))
HtRxnP = HtRxnT - H_N2 - 3 * H_H2 + 2 * H_NH3
End Function
```

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 (PFR)

Ammonia Synthesis – Full Model – Spreadsheet Solution

Ammonia PFR Simulation					Rgas	8.314	kJ/kmol/K				
					Rgas2	0.082057	atm*m3/kmol/K				
Feed Conditions								Kinetics			
N2	12348	kmol/h		Pressure	150	atm		Forward			
H2	37044			Temperature	270	degC			k0f	1.00E+04	kmol/m3/s/atm^2
Ar	12391			Heat of Reaction	-107816	kJ/kmol				3.60E+07	kmol/m3/h/atm^2
CH4	5652								Ef	9.10E+04	kJ/kmol
								Reverse			
Void Fraction	0.4								k0r	1.30E+10	kmol/m3/s/atm
Particle Diameter	1.00E-03	m								4.68E+13	kmol/m3/h/atm
Reactor Diameter	3	m		ReactorX-sect Area	7.069	m2			Er	1.41E+05	kJ/kmol
Reactor Length	1	m		Reactor Volume	7.069	m3					

AmmoniaSimulationFullModel.xlsm

Ordinary Differential Equation Models

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

Ammonia Synthesis – Full Model – Spreadsheet Solution

from Hysys molar enthalpies

Heat of Reaction	
aa	-1.931E+05
bb	4.840E+05
cc	-9.944E+05
dd	8.805E+05
ee	-2.908E+05

Molecular Weights		Feed Mass Flow Rates	
N2	28.0134	345909.5	kg/h
H2	2.016	74680.7	
NH3	17.02	0	
Ar	39.948	494995.7	
CH4	16.043	90675.04	
		1006261	
	Mass Flux	39.54	kg/s/m2

Kinematic viscosity	0.5075	cSt
	0.005075	St
	5.075E-07	m2/s
stoke	1.00E-04	m2/s

Heat Capacity - coefficients for kJ/mol/K Fit of Hysys properties at 150 atm

	a	b	c	d	e
N2	4.04E+01	-3.53E+01	4.69E+01	-1.94E+01	0.00E+00
H2	2.88E+01	1.86E+00	0.00E+00	0.00E+00	0.00E+00
NH3	1.09E+03	-5.69E+03	1.18E+04	-1.09E+04	3.80E+03
Ar	3.68E+01	-5.30E+01	6.40E+01	-2.70E+01	0.00E+00
CH4	2.47E+01	5.03E+01	0.00E+00	0.00E+00	0.00E+00

Final Temperature	415.7
Final Comversion	21.6%

Pitzer Correlation for Pressure Correction of Heat of Reaction

	Tc (K)	Pc (atm)	Pc (kPa)	Ω
NH3	405.6	112.5	11399	0.25
N2	126.2	33.5	3394.4	0.04
H2	33.2	12.8	1297.0	0.00

Pitzer Acentric Factor

N2	0.039
H2	-0.216
NH3	0.25
Ar	0.001
CH4	0.011

Binary Interaction Matrix

	N2	H2	NH3	Ar	CH4
N2	0	-0.036	0.222	0	0.036
H2	-0.036	0	0	0	0.202
NH3	0.222	0	0	0	0
Ar	0	0	0	0	0.023
CH4	0.036	0.202	0	0.023	0

Critical Temperature K	Critical Pressure kPa
126.2	3394
33.19	1297
405.65	11277
150.86	4870
190.564	4641

Ordinary Differential Equation Models

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

Ammonia Synthesis – Full Model – Spreadsheet Solution

	Molar Flow Rates - kgmol/h								Partial Pressure - atm				
Volume (m3)	N2	H2	NH3	Ar	CH4	Total	Pressure (atm)	Temp-erature (degC)	N2	H2	NH3	Ar	CH4
0.0000	12348.0	37044	0	12391	5652	67435	150	270.0	27.466	82.399	0.000	27.562	12.572
0.0010	12347.9	37044	0.20	12391	5652	67435	150.00	270.0	27.466	82.399	0.000	27.562	12.572
0.0020	12347.8	37043	0.40	12391	5652	67435	150.00	270.0	27.466	82.398	0.001	27.562	12.572
0.0030	12347.7	37043	0.60	12391	5652	67434	150.00	270.0	27.466	82.397	0.001	27.562	12.572
0.0040	12347.6	37043	0.80	12391	5652	67434	150.00	270.0	27.465	82.396	0.002	27.562	12.572
0.0050	12347.5	37042	1.00	12391	5652	67434	150.00	270.0	27.465	82.395	0.002	27.562	12.572

Reaction Rates - kmol/m3/h		N2 derivative	Ergun Equation for Pressure Drop					Energy Balance				
Forward	Reverse	dFN2/dV	MW avg	Density (kg/m3)	Viscosity (Pa*s)	dP/dz (Pa/m)	dP/dV (Pa/m3)	dP/dV (atm/m3)	Heat of Reaction (kJ/kmol)	dH/dV	H	FindT	Conversion (N2 Basis)
249.931	0.000	-99.972	14.922	48.124	2.44E-05	-550016	-77811	-0.768	-114646	1.1461E+07	5.5929E+08	270.00	0.0%
249.976	0.001	-99.990	14.922	48.124	2.44E-05	-550022	-77812	-0.768	-114646	1.1463E+07	5.5930E+08	270.01	0.0%
250.021	0.001	-100.008	14.922	48.123	2.44E-05	-550028	-77813	-0.768	-114646	1.1465E+07	5.5931E+08	270.01	0.0%
250.066	0.002	-100.026	14.922	48.123	2.44E-05	-550034	-77814	-0.768	-114646	1.1468E+07	5.5932E+08	270.02	0.0%
250.111	0.002	-100.043	14.922	48.122	2.44E-05	-550040	-77815	-0.768	-114646	1.1470E+07	5.5933E+08	270.02	0.0%

Ordinary Differential Equation Models

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

Ammonia Synthesis – Full Model – Spreadsheet Solution

Euler method for N2

	A	B	C
15		Volume (m3)	N2
16		0.0000	12348.0
17	=C16+R16*(B17-B16)		

Stoichiometry for H2 and NH3

	B	C	D	E
15	Volume (m3)	N2	H2	NH3
16	0.0000	12348.0	37044	0
17	0.0010	12347.9	=FeedH2-3*(FeedN2-C17)	

	B	C	D	E	F
15	Volume (m3)	N2	H2	NH3	A
16	0.0000	12348.0	37044	0	
17	0.0010	12347.9	37044	=2*(FeedN2-C17)	
18	0.0020	12347.8	37043	0.40	

Euler method for P

	I	J
15	Pressure (atm)	Temp-erature (degC)
16	150	270.0
17	=I16+X16*(B17-B16)	

dP/dz

	T	U	V	W	X	Y	
15	Density (kg/m3)	Viscosity (Pa*s)	dP/dz (Pa/m)	dP/dV (Pa/m3)	dP/dV (atm/m3)	Heat of Reaction (kJ/kmol)	dH
16	48.124	2.44E-05	=-(150*(1-eps)/Dp/G0*U16+7/4)*(1-eps)/eps^3/Dp/T16*G0^2				

then converted to dP/dV in atm/m3

Euler method for H

	Z	AA
15	dH/dV	H
16	1.1461E+07	5.5929E+08
17	=AA16+Z16*(B17-B16)	

dH/dV

	Y	Z
15	Heat of Reaction (kJ/kmol)	dH/dV
16	-114646	1.1461E+07
17	=(P17-Q17)*(-Y17)*eps	

	Y	Z	AA	AB
15	Heat of Reaction (kJ/kmol)	dH/dV	H	FindT
16	-114646	1.1461E+07	5.5929E+08	270.00
17	=FindT(AA17,AB16,C17,D17,E17,F17,G17)			

Solve for temperature from H

Ordinary Differential Equation Models
Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PFR)
Ammonia Synthesis – Full Model – Spreadsheet Solution

Functions FindT and fH to solve for temperature given enthalpy

```
Function FindT(H, Tg, FlowN2, FlowH2, FlowNH3, FlowAr, FlowCH4)
Dim Tg1, tol, TgNew
tol = 0.0000001
Do
   Tg1 = Tg + 0.1
   TgNew = Tg - 0.1 * fH(H, Tg, FlowN2, FlowH2, FlowNH3, FlowAr, FlowCH4) / _
      (fH(H, Tg1, FlowN2, FlowH2, FlowNH3, FlowAr, FlowCH4) - fH(H, Tg, FlowN2, FlowH2, FlowNH3, FlowAr, FlowCH4))
   If Abs((TgNew - Tg) / TgNew) < tol Then Exit Do
   Tg = TgNew
Loop
FindT = TgNew
End Function
```

```
Function fH(H, T, FlowN2, FlowH2, FlowNH3, FlowAr, FlowCH4)
fH = H - (FlowN2 * HtCap("N2", T) + FlowH2 * HtCap("H2", T) + FlowNH3 * HtCap("NH3", T) + _
   FlowAr * HtCap("Ar", T) + FlowCH4 * HtCap("CH4", T)) * T
End Function
```

Ordinary Differential Equation Models
Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PFR)
Ammonia Synthesis – Full Model – Spreadsheet Solution

Function SpecVol to solve
Peng-Robinson equation of state
for the specific volume

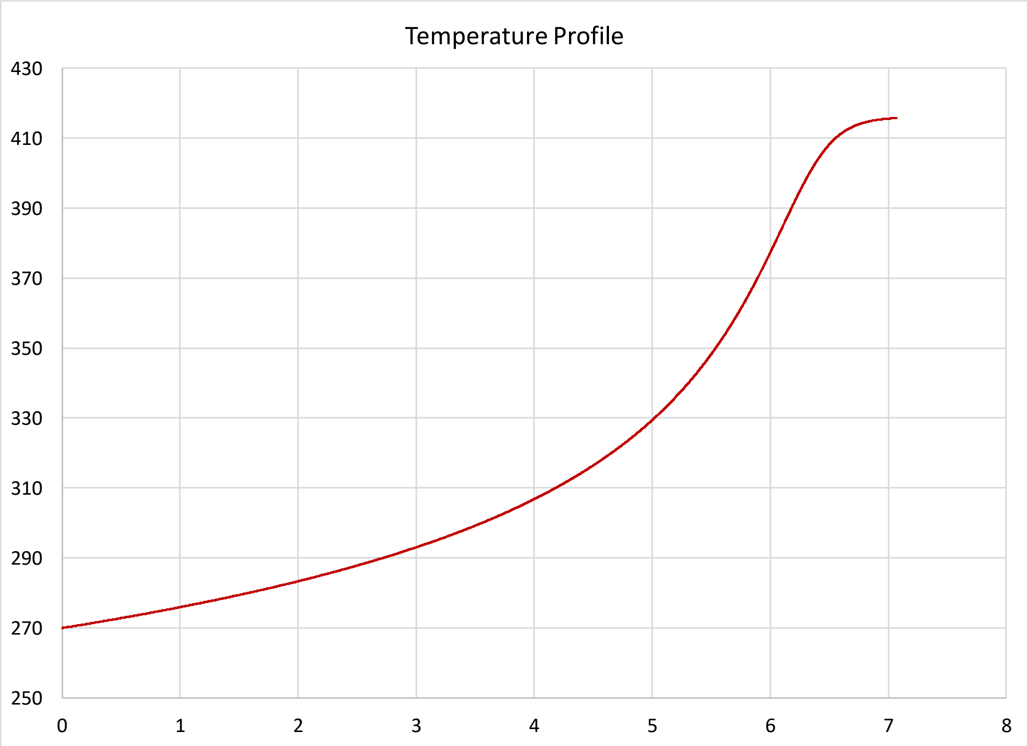
```
Option Explicit
Option Base 1
Function SpecVol(Tf, Patm, F, w, Tc, Pc, K)
' find specific volume based on Peng-Robinson equation of state
Dim n As Integer, i As Integer, j As Integer
Dim z(), m(), a(), b(), Q(), Rgas, am, bm, V1, V2, Vnew, tol, z1(), FT, T, P
Rgas = 8.314
T = Tf + 273.15
P = Patm * 101.325
n = F.Count
ReDim z(n), m(n), a(n), b(n), Q(n, n), z1(n)
```

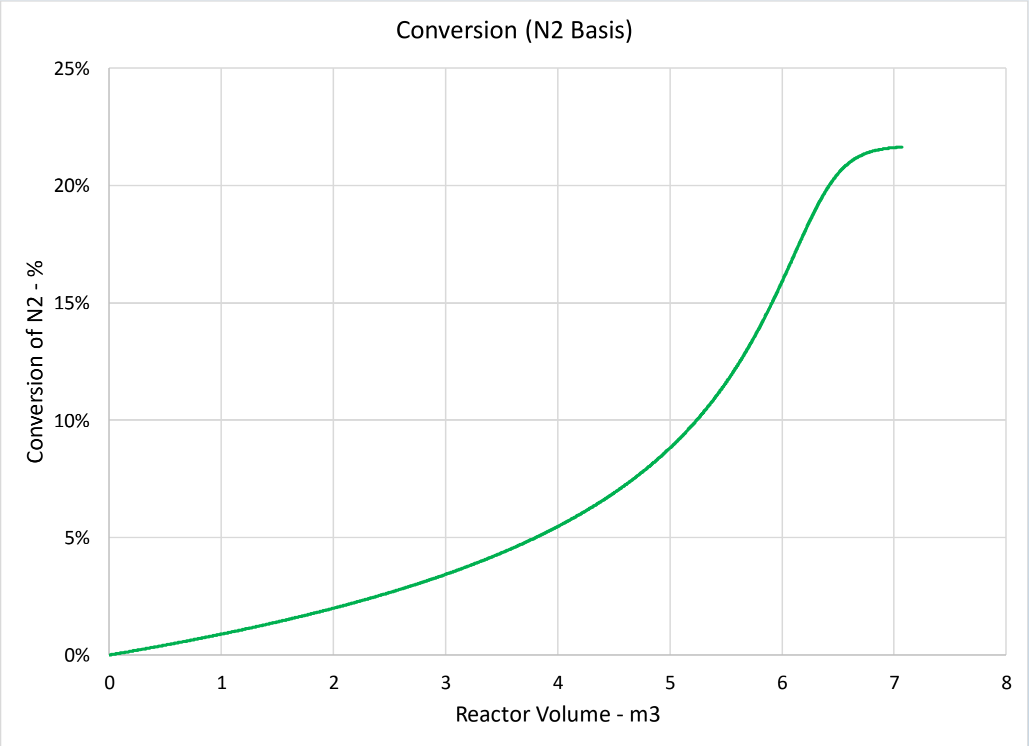
```
' compute mixture coefficients am and bm
FT = WorksheetFunction.Sum(F)
For i = 1 To n
   z(i) = F(i) / FT
Next i
For i = 1 To n
   m(i) = 0.37464 + 1.54226 * w(i) - 0.26992 * w(i) ^ 2
   a(i) = 0.45724 * Rgas ^ 2 * Tc(i) ^ 2 / Pc(i) * (1 + m(i) * (1 - Sqr(T / Tc(i)))) ^ 2
   b(i) = 0.0788 * Rgas * Tc(i) / Pc(i)
Next i
For i = 1 To n
   For j = 1 To n
      Q(i, j) = Sqr(a(i) * a(j)) * (1 - K(i, j))
   Next j
Next i
For i = 1 To n
   For j = 1 To n
      z1(i) = z1(i) + Q(i, j) * z(j)
   Next j
Next i
For i = 1 To n
   am = am + z(i) * z1(i)
Next i
For i = 1 To n
   bm = bm + z(i) * b(i)
Next i
```

Ordinary Differential Equation Models
Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PFR)
Ammonia Synthesis – Full Model – Spreadsheet Solution

```
' now solve the Peng-Robinson equation of state for V
' initial estimate for V from ideal gas law
V1 = Rgas * T / P
tol = 0.000001
Do
   V2 = V1 + 0.001
   Vnew = V1 - 0.001 * PR(V1, T, P, am, bm) / (PR(V2, T, P, am, bm) - PR(V1, T, P, am, bm))
   If Abs((Vnew - V1) / Vnew) < tol Then Exit Do
   V1 = Vnew
Loop
SpecVol = Vnew
End Function
Function PR(V, T, P, a, b)
Dim Rgas
Rgas = 8.314
PR = P - (Rgas * T / (V - b) - a / (V ^ 2 + 2 * b * V - b ^ 2))
End Function
```

Ordinary Differential Equation Models
Modeling and Simulation of a Plug-flow, Packed-bed Reactor (PFR)
Ammonia Synthesis – Full Model – Spreadsheet Solution

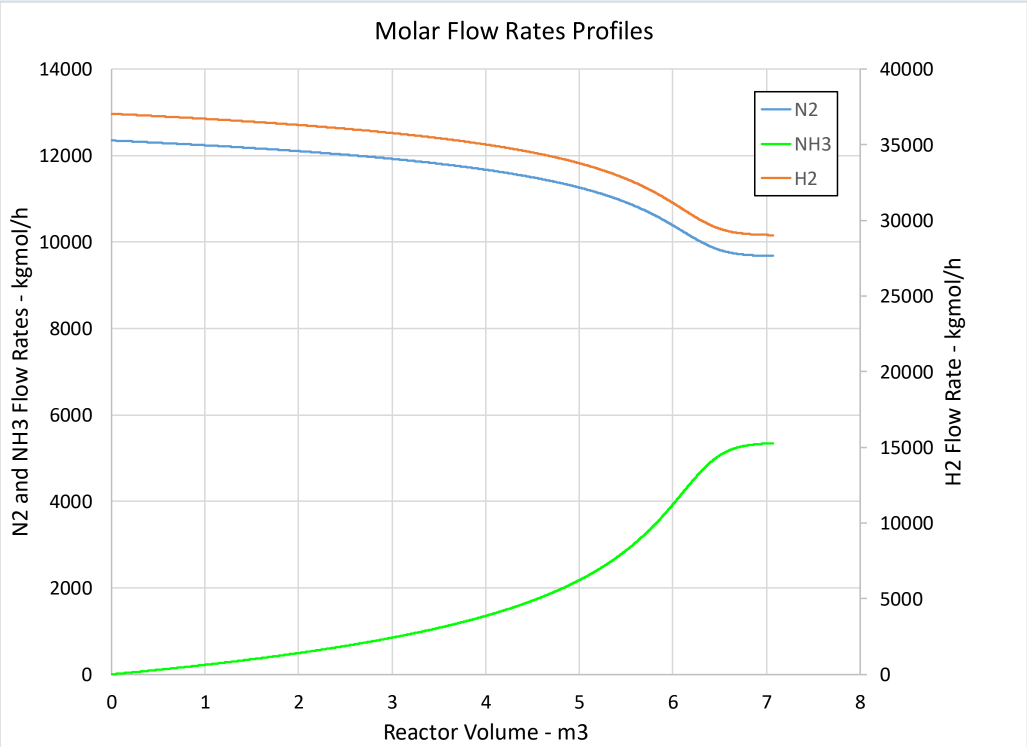


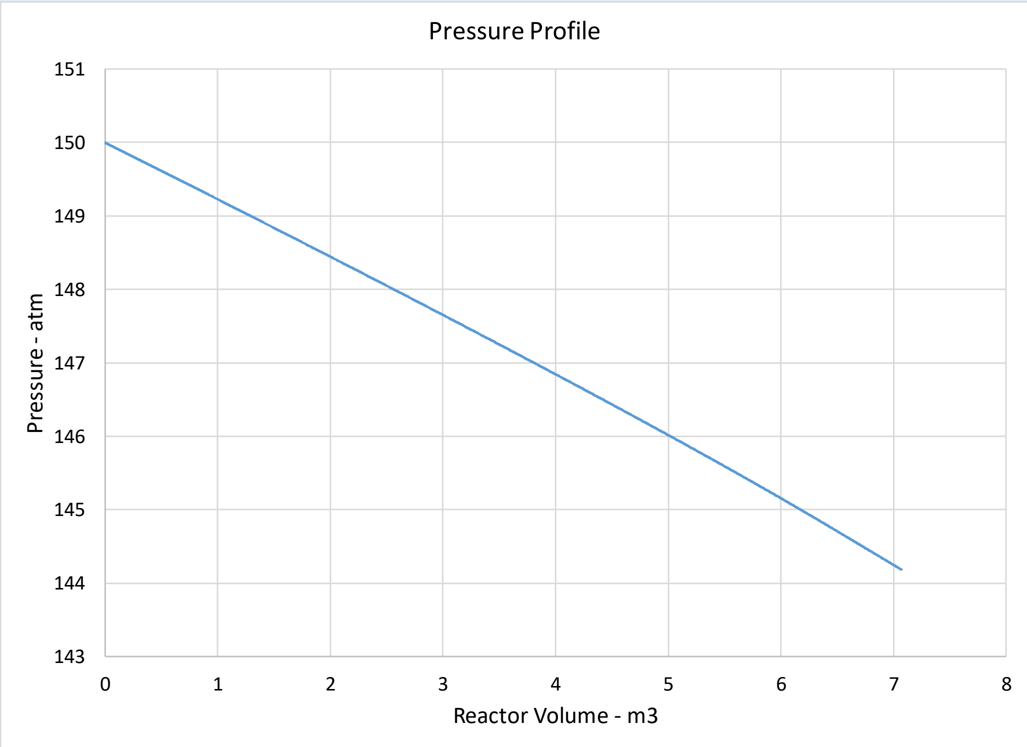


Ordinary Differential Equation Models

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

Ammonia Synthesis – Full Model – Spreadsheet Solution





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.

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

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

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

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

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

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

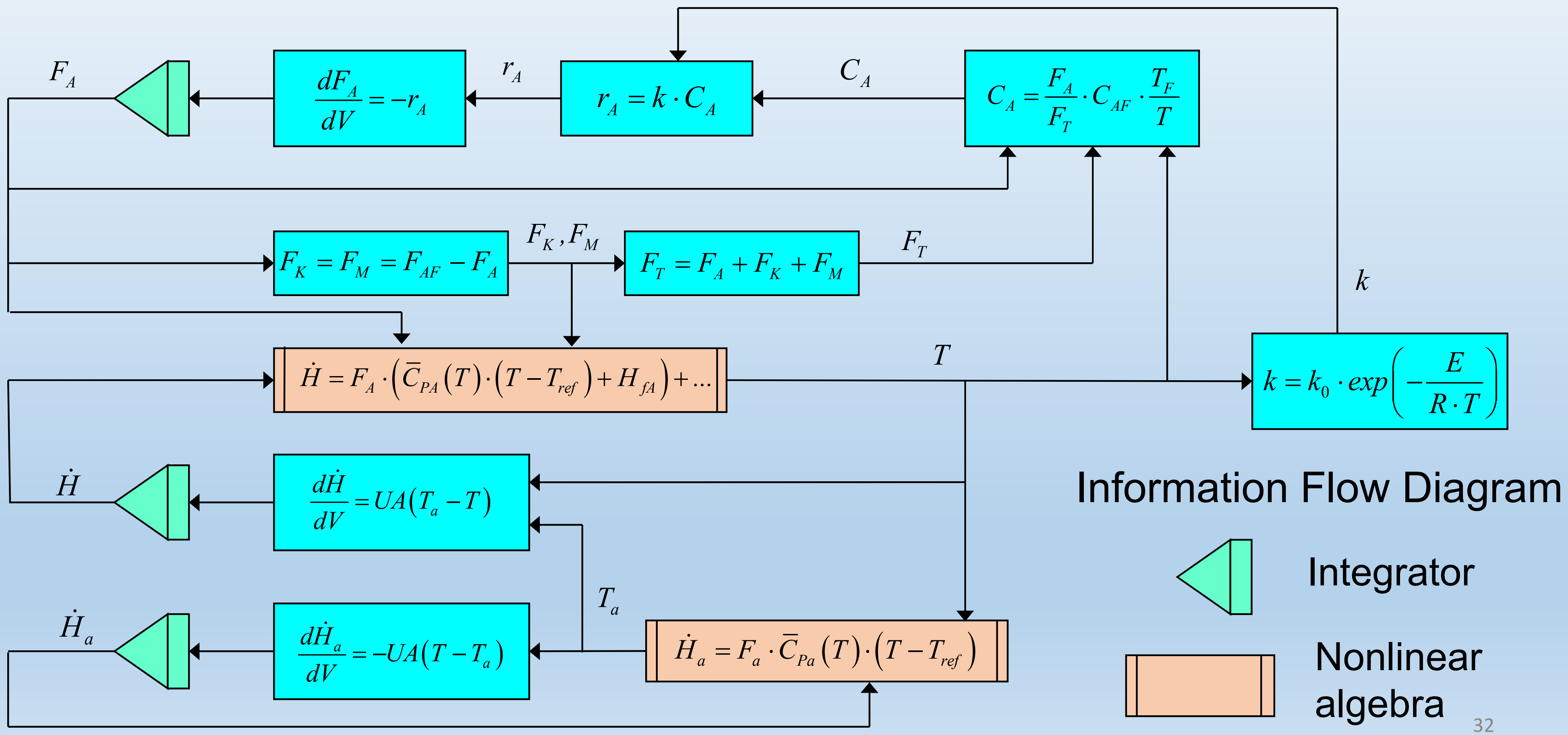
$$\dot{H}_a = F_a \cdot \bar{C}_{Pa}\left(T\right) \cdot \left(T - T_{ref}\right)$$

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

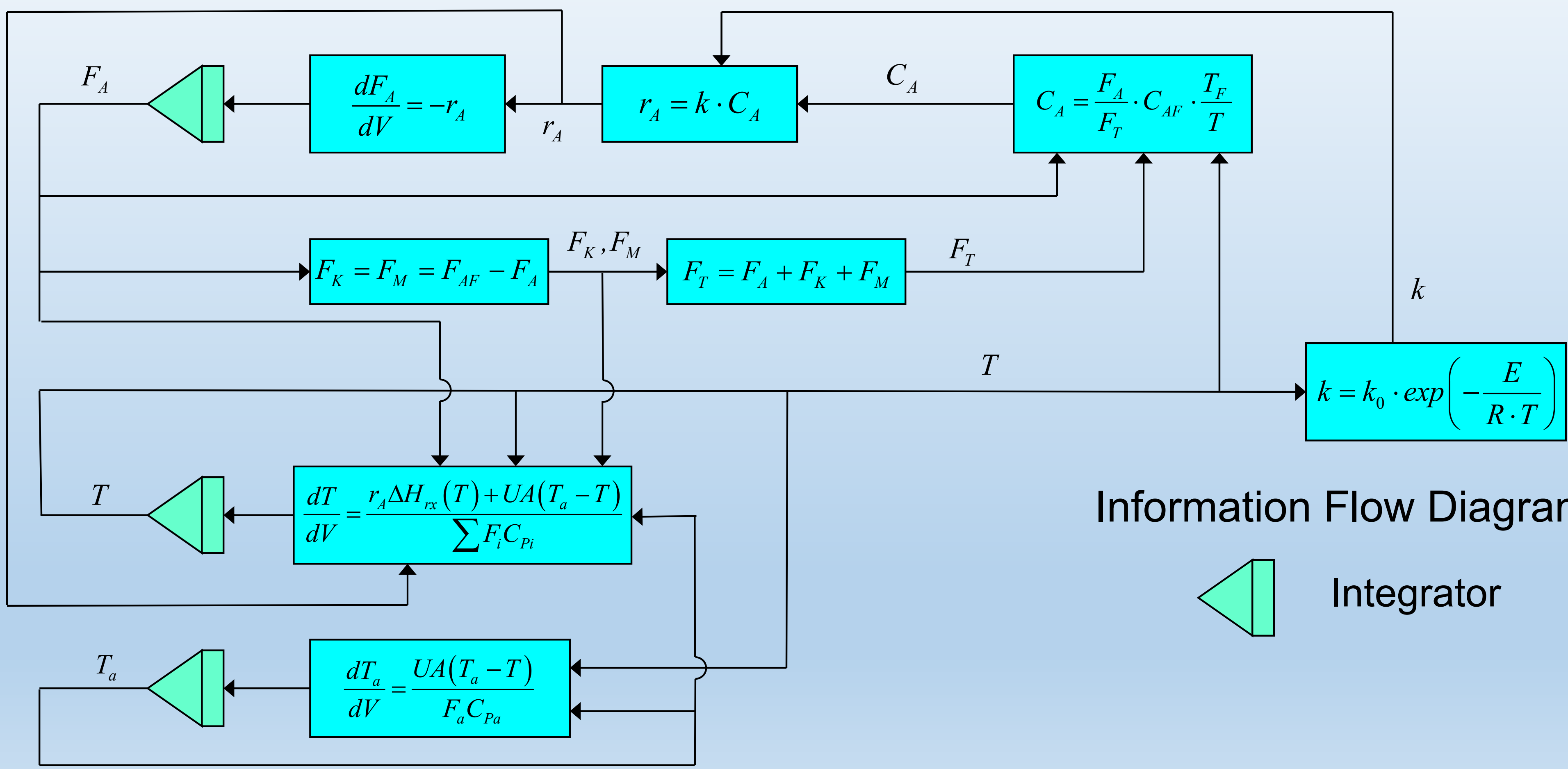
and molar flow rate

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

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

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 (loop back to "Solve model")

Excel: use Solver

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified Model

AcetonePFRSimplifiedModel.xlsm

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	**Acetone Cracking PFR with Counter-current Heat Exchange**						Rgas	8.314	kJ/kgmol/K	NoSteps	200		TAirError	0.0	
2	9/26/2019		*Simplified Model*				MWA	58.08	kg/kgmol	dV	1.00E-06		*Use Solver to drive this to zero*		
3	Reactor Specifications			Heat Transfer			MWAir	28.96	kg/kgmol						
4	NoTubes	1000		A	149.8	m2/m3				Air Feed			Reaction Kinetics		
5	TotalVolume	2	m3	U	400	kJ/m2/hr/K	Acetone Feed			MassFeedAir	88704	kg/hr	lnk0	42.529	
6	VolPerTube	0.002	m3				MassFeedA	7850	kg/hr	FAirM	88.70	kg/hr per tube	k0	2.95E+18	1/hr
7	TubeID	2.67E-02	m3	Feed Conditions			FAM	7.85	kg/hr per tube	FAir	3.06	kgmol/hr	E	284522	kJ/kgmol
8	TubeXC	5.60E-04	m2	TF	1035	K	FAF	0.135	kgmol/hr	TAirF	1250	K			
9	TubeLength	3.572	m	PF	162	kPa	CAF	0.0188	kgmol/m3	Tair0	1112.9	K - estimate	Tref	298.15	K
10															
11	Reactor Volume (m3)	FA (kgmol/hr)	FK (kgmol/hr)	FM (kgmol/hr)	FT (kgmol/hr)	T (K)	TAir (K)	CA (kgmol/m3)	rA (kgmol/m3/hr)	dFA/dV (kgmol/m3/hr)	dT/dV (K/m3)	dTa/dV (K/m3)	Conversion		
12	0.000E+00	0.13516	0.00000	0.00000	0.00000	1035.0	1112.9	0.01883	242.68	-242.68	-6.566E+05	4.557E+04	0.00000		
13	1.000E-06	0.13492	0.00024	0.00024	0.13540	1034.3	1112.9	0.01877	236.93	-236.93	-6.343E+05	4.598E+04	0.00180		
14	2.000E-06	0.13468	0.00048	0.00048	0.13564	1033.7	1113.0	0.01872	231.50	-231.50	-6.132E+05	4.638E+04	0.00355		
15	3.000E-06	0.13445	0.00071	0.00071	0.13587	1033.1	1113.0	0.01866	226.36	-226.36	-5.931E+05	4.676E+04	0.00526		
16	4.000E-06	0.13422	0.00094	0.00094	0.13610	1032.5	1113.1	0.01861	221.47	-221.47	-5.740E+05	4.714E+04	0.00694		
17	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		

● ● ● ● ● ● ● ●

	A	B	C	D	E	F	G	H	I	J	K	L	M
2004	1.992E-03	0.00000	0.13516	0.13516	0.27032	1191.9	1249.7	0.00000	0.01	-0.01	1.640E+05	3.385E+04	1.00000
2005	1.993E-03	0.00000	0.13516	0.13516	0.27032	1192.0	1249.8	0.00000	0.01	-0.01	1.636E+05	3.377E+04	1.00000
2006	1.994E-03	0.00000	0.13516	0.13516	0.27032	1192.2	1249.8	0.00000	0.00	0.00	1.632E+05	3.370E+04	1.00000
2007	1.995E-03	0.00000	0.13516	0.13516	0.27032	1192.4	1249.8	0.00000	0.00	0.00	1.629E+05	3.362E+04	1.00000
2008	1.996E-03	0.00000	0.13516	0.13516	0.27032	1192.5	1249.9	0.00000	0.00	0.00	1.625E+05	3.355E+04	1.00000
2009	1.997E-03	0.00000	0.13516	0.13516	0.27032	1192.7	1249.9	0.00000	0.00	0.00	1.621E+05	3.347E+04	1.00000
2010	1.998E-03	0.00000	0.13516	0.13516	0.27032	1192.8	1249.9	0.00000	0.00	0.00	1.618E+05	3.340E+04	1.00000
2011	1.999E-03	0.00000	0.13516	0.13516	0.27032	1193.0	1250.0	0.00000	0.00	0.00	1.614E+05	3.332E+04	1.00000
2012	2.000E-03	0.00000	0.13516	0.13516	0.27032	1193.2	1250.0	0.00000	0.00	0.00	1.610E+05	3.325E+04	1.00000
2013													

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified Model

Euler method for FA

	A	B
11	Reactor Volume (m3)	FA (kmol/hr)
12	0.000E+00	0.13516
13	=B12+J12*dV	

	A	B	C
11	Reactor Volume (m3)	FA (kmol/hr)	FK (kmol/hr)
12	0.000E+00	0.13516	0.00000
13	1.000E-06	=FAF-B13	

	B	C	D
11	FA (kmol/hr)	FK (kmol/hr)	FM (kmol/hr)
12	0.13516	0.00000	0.00000
13	0.13492	=FAF-B13	

Stoichiometry for FK and FM

CA

	F	G	H
11	T (K)	TAir (K)	CA (kmol/m3)
12	1035.0	1112.9	0.01883
13	1034.3	=B13/E13*CAF*TF/F13	

rA

	F	G	H	I
11	T (K)	TAir (K)	CA (kmol/m3)	rA (kmol/m3/hr)
12	1035.0	1112.9	0.01883	242.68
13	1034.3	1112.9	=k0*EXP(-E/Rgas/F13)*H13	

dFA/dV

	I	J
11	rA (kmol/m3/hr)	dFA/dV (kmol/m3/hr)
12	242.68	-242.68
13	236.93	=-I13

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified Model

Euler method for T

	E	F
11	FT (kmol/hr)	T (K)
12	0.00000	1035.0
13	=F12+K12*dV	

dT/dV

	E	F	G	H	I	J
11	FT (kmol/hr)	T (K)	TAir (K)	CA (kmol/m3)	rA (kmol/m3/hr)	dFA/dV (kmol/m3/hr)
12	0.00000	1035.0	1112.9	0.01883	242.68	-242.68
13	0.13540	=(I13*(-HtRxn(F13))+U*A*(G13-F13))/(B13*Cp_A+C13*Cp_K+D13*Cp_M)				

Euler method for TAir

	F	G
11	T (K)	TAir (K)
12	1035.0	1112.9
13	=G12+L12*dV	

dTAir/dV

	G	H	I	J	K	L
11	TAir (K)	CA (kmol/m3)	rA (kmol/m3/hr)	dFA/dV (kmol/m3/hr)	dT/dV (K/m3)	dTa/dV (K/m3)
12	1112.9	0.01883	242.68	-242.68	-6.566E+05	4.557E+04
13	1112.9	0.01877	236.93	=-U*A*(F13-G13)/FAir/Cp_Air		

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified Model – VBA code

```vba
Option Explicit
Function CpA(T)
'heat capacity of acetone gas, kJ/kgmol/K
'from Felder & Rousseau, 3rd Ed., p. 635
Dim Tk, Cp
Tk = T / 1000
Cp = 0.0068132 + 0.2786 * Tk - 0.15628 * Tk ^ 2 + 0.03476 * Tk ^ 3  'kJ/mol/K
CpA = Cp * 1000  ' kJ/kgmol/K
End Function
Function CpK(T)
'heat capacity of ketene
'from regression of data from NIST Webbook
Dim Tk
Tk = T / 1000
CpK = 18.909 + 143.56 * Tk - 130.23 * Tk ^ 2 + 66.526 * Tk ^ 3 - 14.112 * Tk ^ 4
End Function
Function CpM(T)
'heat capacity of methane
'Shomate equation from NIST Webbook
Dim Tk
Tk = T / 1000
CpM = -0.703029 + 108.4773 * Tk - 42.52157 * Tk ^ 2 + 5.862788 * Tk ^ 3 + 0.678565 / Tk ^ 2
End Function
Function CpAir(T)
'heat capacity of air
'from Felder & Rousseau, 3rd Ed., p. 635
Dim Cp
Cp = 0.02809 + 0.000001965 * T + 0.000000004799 * T ^ 2 - 0.000000000001965 * T ^ 3 ' kJ/mol/K
CpAir = Cp * 1000 'kJ/kgmol/K
End Function
```

```vba
Function HtRxn(T)
Dim Hx0, Tk, Tk0, Ha, HK, HM
Hx0 = 80770#   ' kJ/kgmol
Tk = T / 1000
Tk0 = (25 + 273.15) / 1000
'acetone
Ha = (0.0068132 * Tk + 0.2786 / 2 * Tk ^ 2 - 0.15628 / 3 * Tk ^ 3 + 0.03476 / 4 * Tk ^ 4 _
   - (0.0068132 * 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)
'
HtRxn = Hx0 + (-Ha + HK + HM) * 1000
End Function
```

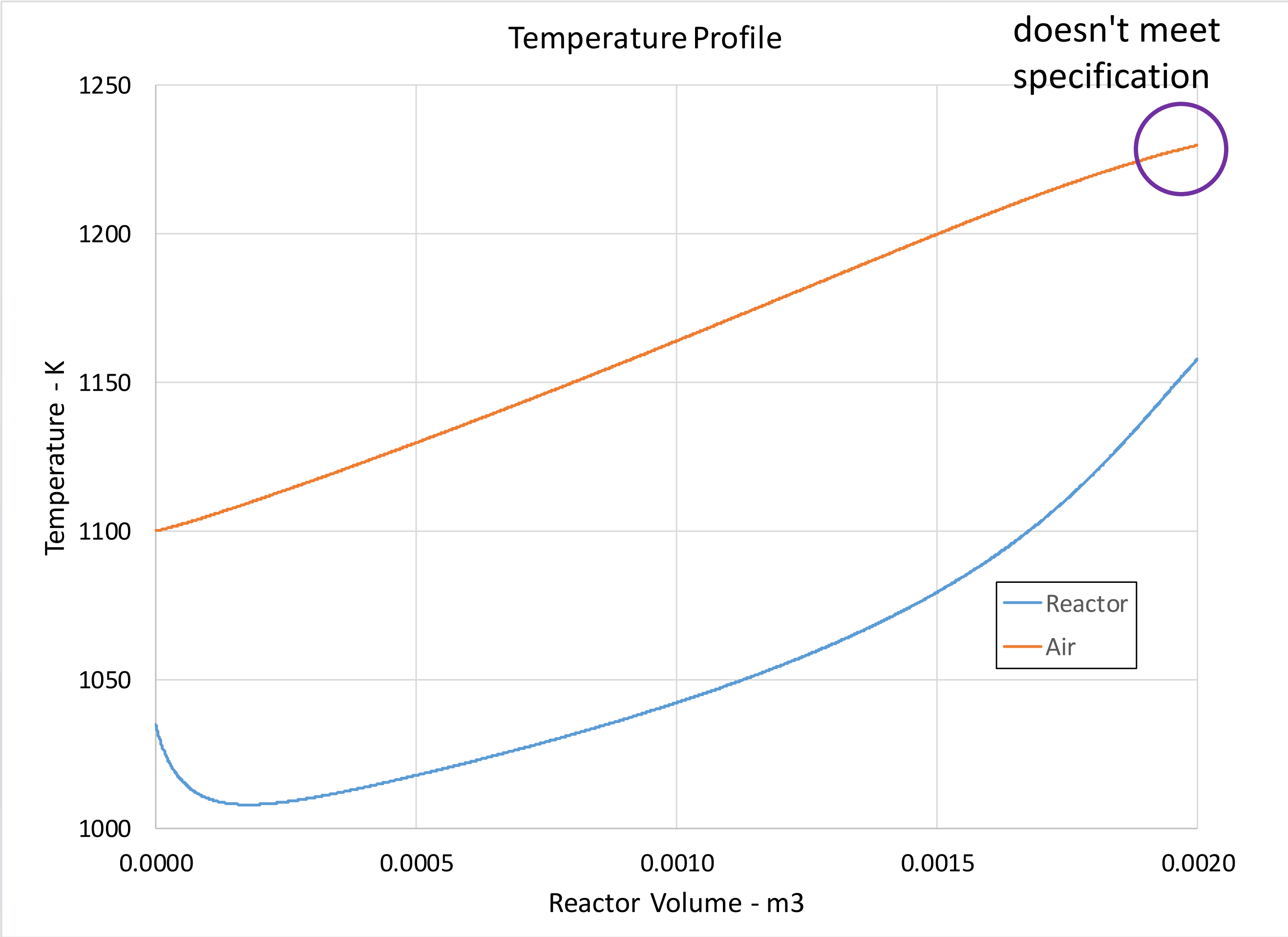
Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Simplified Model

Initial Estimate of
Air Temperature
at V = 0

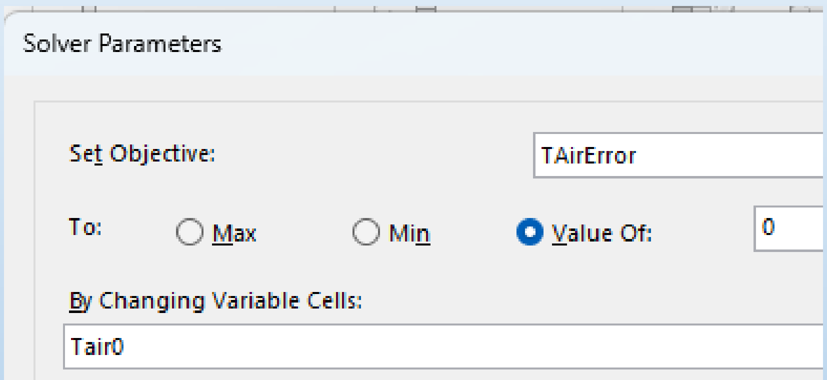
TAirF	1250	K
Tair0	1100.0	K - estimate



Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Excel Solver setup



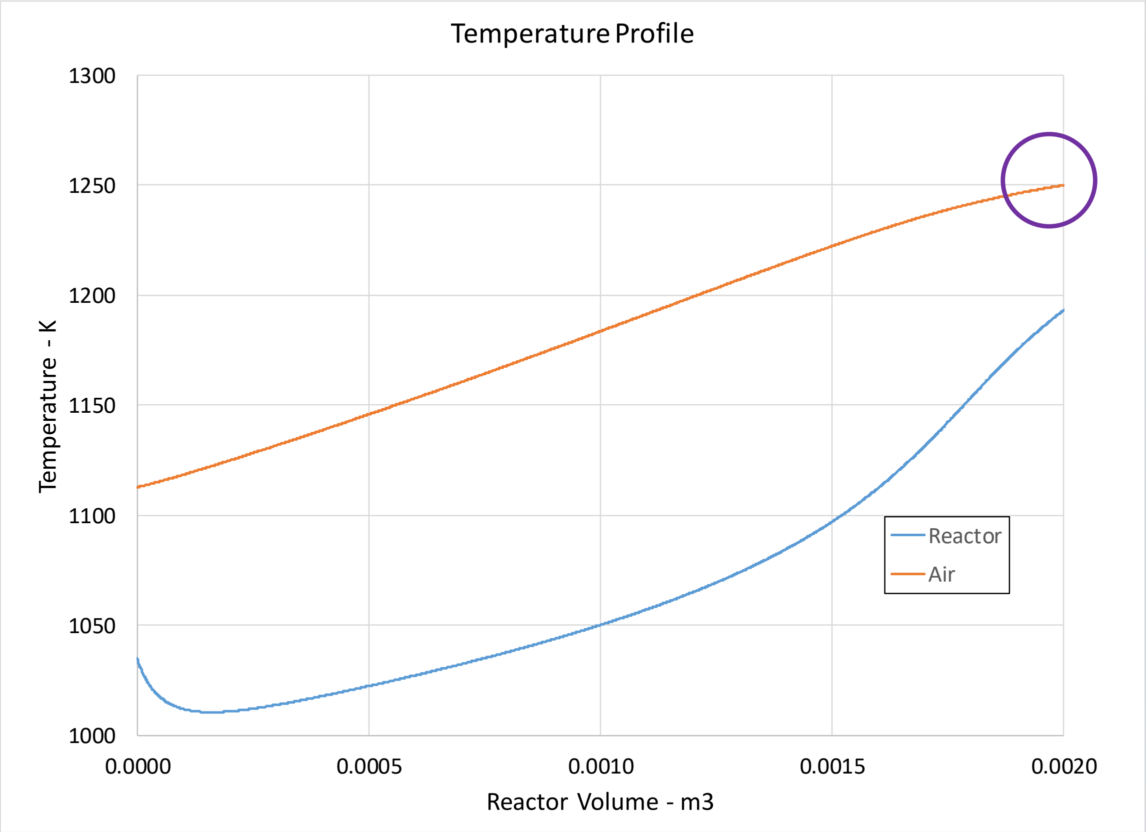
Solution

J	K	L	M	N	
NoSteps	200		TAirError	0.0	
dV	1.00E-06		*Use Solver to drive this to zero*		
Air Feed			Reaction Kinetics		
MassFeedAir	88704	kg/hr	lnk0	42.529	
FAirM	88.70	kg/hr per tube	k0	2.95E+18	1/hr
FAir	3.06	kmol/hr	E	284522	kJ/kg
TAirF	1250	K			
Tair0	1112.9	K - estimate	Tref	298.15	K

Tubular Reactor with Counter-current Heat Exchange

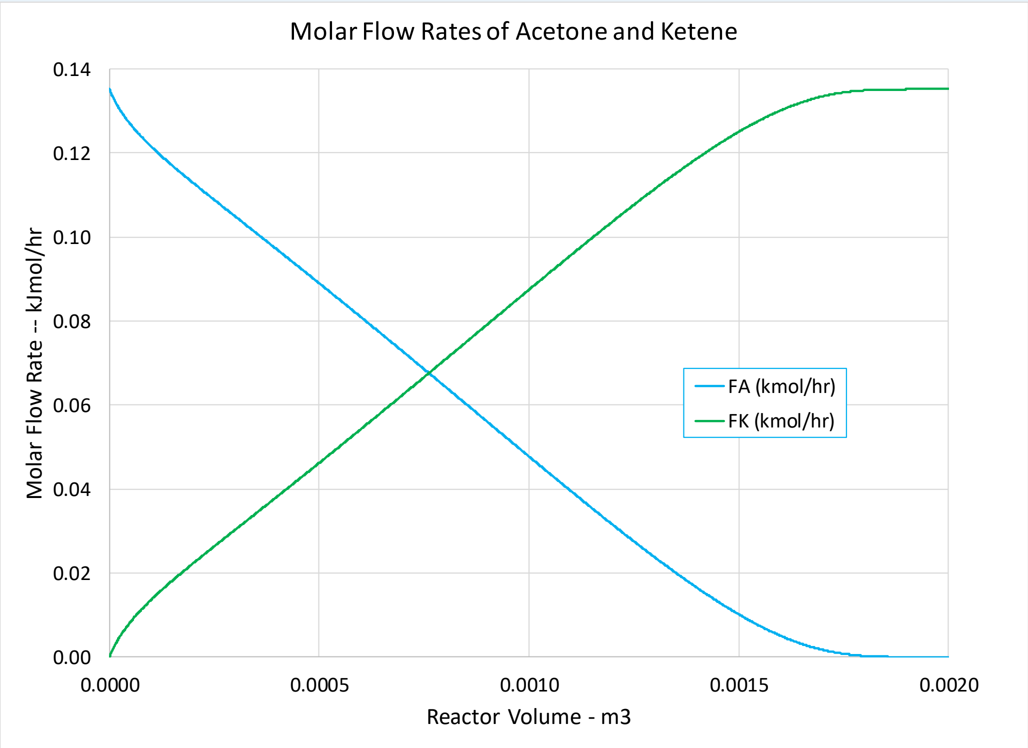
Example: Vapor-phase cracking of acetone to ketene

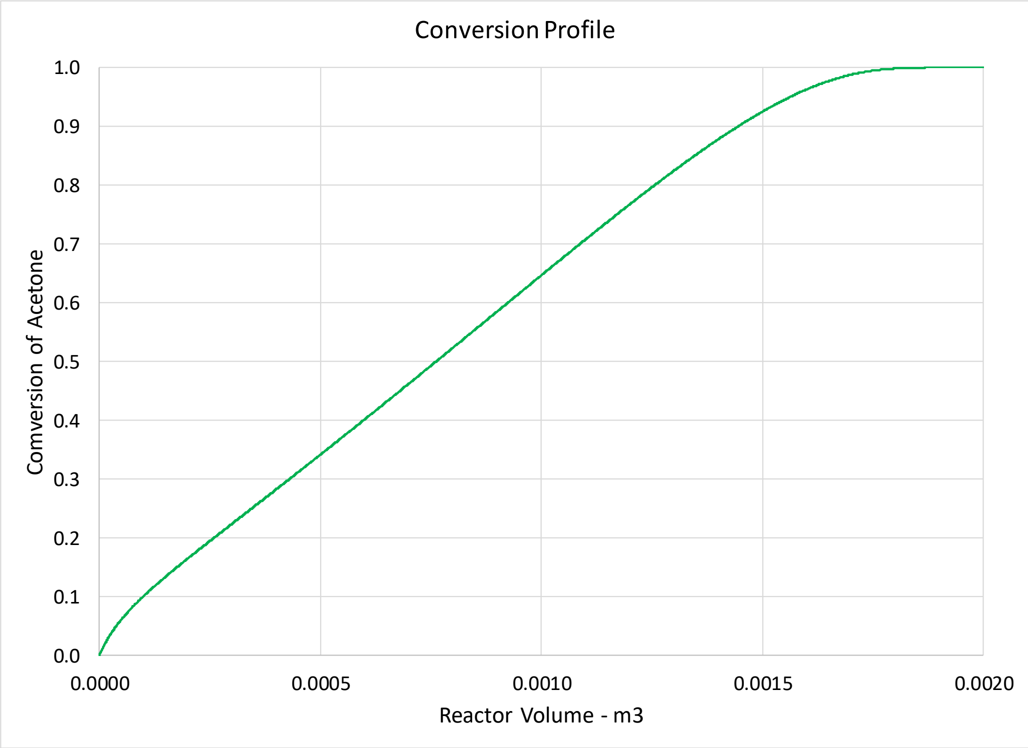
Converged temperature profile



Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene





Tubular Reactor with Counter-current Heat Exchange

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

Acetone Cracking PFR with Counter-current Heat Exchange

Reactor Specifications		
NoTubes	1000	
TotalVolume	2	m3
VolPerTube	0.002	m3
TubeID	2.67E-02	m3
TubeXC	5.60E-04	m2
TubeLength	3.572	m

Heat Transfer		
A	149.8	m2/m3
U	400	kJ/m2/hr/K

Feed Conditions		
TF	1035	K
PF	162	kPa

Rgas	8.314	kJ/kmol/K
MWA	58.08	kg/kmol
MWAir	28.96	kg/kmol

Acetone Feed		
MassFeedA	7850	kg/hr
FAM	7.85	kg/hr per tube
FAF	0.135	kmol/hr
CAF	0.0188	kmol/m3

NoSteps	200	
dV	1.00E-06	

Air Feed		
MassFeedAir	88704	kg/hr
FAirM	88.70	kg/hr per tube
FAir	3.06	kmol/hr
TAirF	1250	K
Tair0	1100.0	K - estimate

TAirError	24.0

Use Solver to drive this to zero

Reaction Kinetics		
lnk0	42.529	
k0	2.95E+18	1/hr
E	284522	kJ/kmol
Tref	298.15	K

Reactor Volume (m3)	FA (kmol/hr)	FK (kmol/hr)	FM (kmol/hr)	FT (kmol/hr)	H (kJ/m3)	T (K)	HAir (kJ/m3)	TAir (K)	CA (kmol/m3)	rA (kmol/m3/hr)	dFA (kmol/m3/hr)	dH (kJ/m3/hr)	dHAir (kJ/m3/hr)	Conversion
0.000E+00	0.13516	0.00000	0.00000	0.00000	-1.639E+04	1035.0	7.656E+04	1100.0	0.01883	242.68	-242.68	3.895E+06	3.895E+06	0.00000
1.000E-06	0.13492	0.00024	0.00024	0.13540	-1.639E+04	1034.3	7.657E+04	1100.0	0.01877	236.93	-236.93	3.937E+06	3.937E+06	0.00180
2.000E-06	0.13468	0.00048	0.00048	0.13564	-1.638E+04	1033.7	7.657E+04	1100.1	0.01872	231.49	-231.49	3.977E+06	3.977E+06	0.00355
3.000E-06	0.13445	0.00071	0.00071	0.13587	-1.638E+04	1033.1	7.658E+04	1100.1	0.01866	226.32	-226.32	4.016E+06	4.016E+06	0.00526
4.000E-06	0.13422	0.00094	0.00094	0.13610	-1.638E+04	1032.5	7.658E+04	1100.2	0.01861	221.42	-221.42	4.055E+06	4.055E+06	0.00694

• • • • • • • •

Reactor Volume (m3)	FA (kmol/hr)	FK (kmol/hr)	FM (kmol/hr)	FT (kmol/hr)	H (kJ/m3)	T (K)	HAir (kJ/m3)	TAir (K)	CA (kmol/m3)	rA (kmol/m3/hr)	dFA (kmol/m3/hr)	dH (kJ/m3/hr)	dHAir (kJ/m3/hr)	Conversion
1.994E-03	0.00011	0.13505	0.13505	0.27021	-3.380E+03	1154.8	8.958E+04	1225.8	0.00001	2.73	-2.73	4.256E+06	4.256E+06	0.99919
1.995E-03	0.00011	0.13505	0.13505	0.27021	-3.375E+03	1155.0	8.958E+04	1225.8	0.00001	2.68	-2.68	4.247E+06	4.247E+06	0.99921
1.996E-03	0.00010	0.13505	0.13505	0.27021	-3.371E+03	1155.1	8.959E+04	1225.9	0.00001	2.62	-2.62	4.239E+06	4.239E+06	0.99923
1.997E-03	0.00010	0.13506	0.13506	0.27021	-3.367E+03	1155.3	8.959E+04	1225.9	0.00001	2.57	-2.57	4.231E+06	4.231E+06	0.99925
1.998E-03	0.00010	0.13506	0.13506	0.27022	-3.363E+03	1155.5	8.959E+04	1226.0	0.00001	2.52	-2.52	4.222E+06	4.222E+06	0.99926
1.999E-03	0.00010	0.13506	0.13506	0.27022	-3.358E+03	1155.7	8.960E+04	1226.0	0.00001	2.46	-2.46	4.214E+06	4.214E+06	0.99928
2.000E-03	0.00009	0.13506	0.13506	0.27022	-3.354E+03	1155.9	8.960E+04	1226.0	0.00001	2.41	-2.41	4.206E+06	4.206E+06	0.99930

AcetonePFRFullModel.xlsm

Tubular Reactor with Counter-current Heat Exchange

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

Euler method for FA

Reactor Volume (m3)	FA (kmol/hr)
0.000E+00	0.13516
=B12+L12*dV	

rA

CA (kmol/m3)	rA (kmol/m3/hr)
=k0*EXP(-E/Rgas/TF)*J12	

Euler method for H

FT (kmol/hr)	H (kJ/m3)
0.00000	-1.639E+04
=F12+M12*dV	

dH/dV

dFA (kmol/m3/hr)	dH (kJ/m3/hr)
=U*A*(I12-G12)	

similar for Hair

Solve for T given H

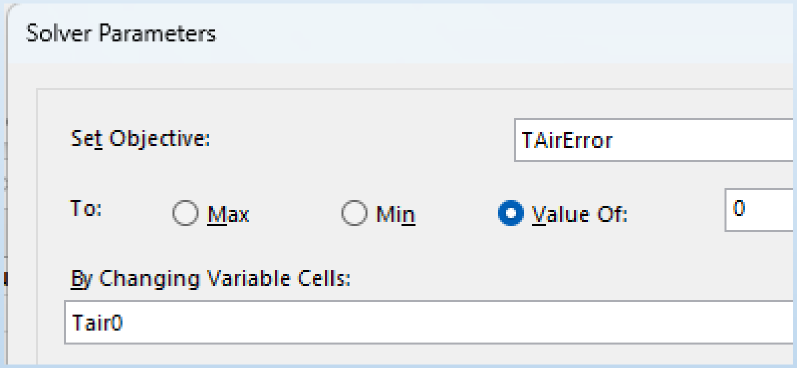
	B	C	D	E	F	G
11	FA (kmol/hr)	FK (kmol/hr)	FM (kmol/hr)	FT (kmol/hr)	H (kJ/m3)	T (K)
12	0.13516	0.00000	0.00000	0.00000	-1.639E+04	1035.0
13	0.13492	0.00024	0.00024	=findT(F13,G12,B13,C13,D13)		

similar for Tair

Tubular Reactor with Counter-current Heat Exchange

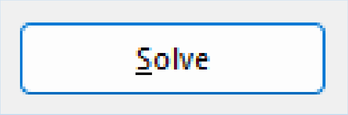
Example: Vapor-phase cracking of acetone to ketene – full model

Excel Solver setup



TAirF	1250	K
Tair0	1100.0	K - estimate

	N	O
	TAirError	24.0
	Use Solver to drive this to zero	



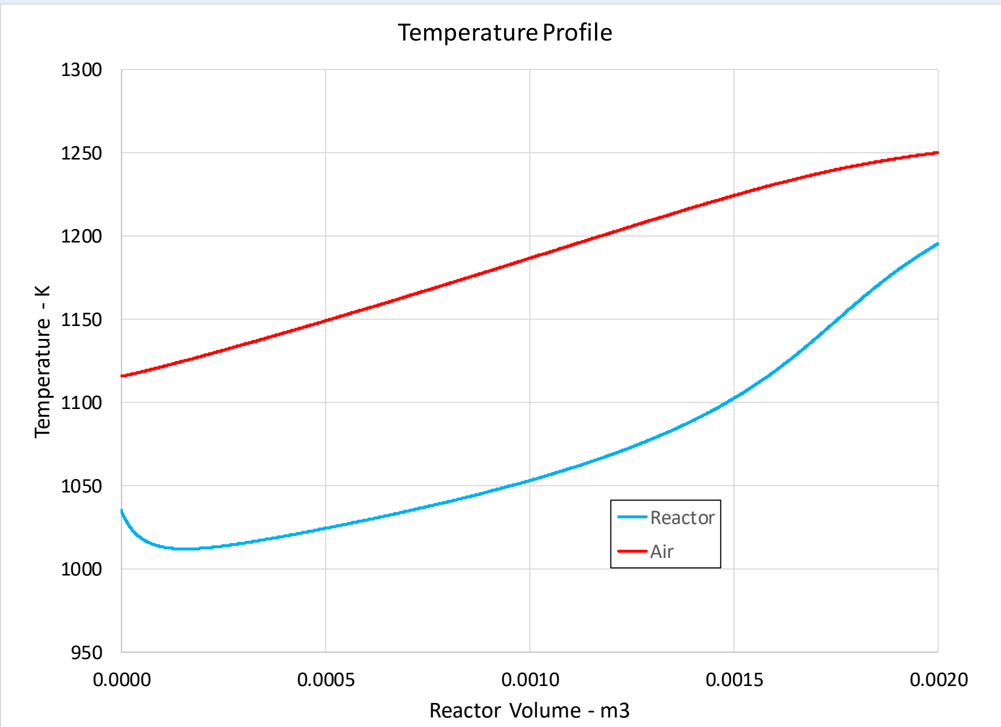
TAirF	1250	K
Tair0	1115.7	K - estimate

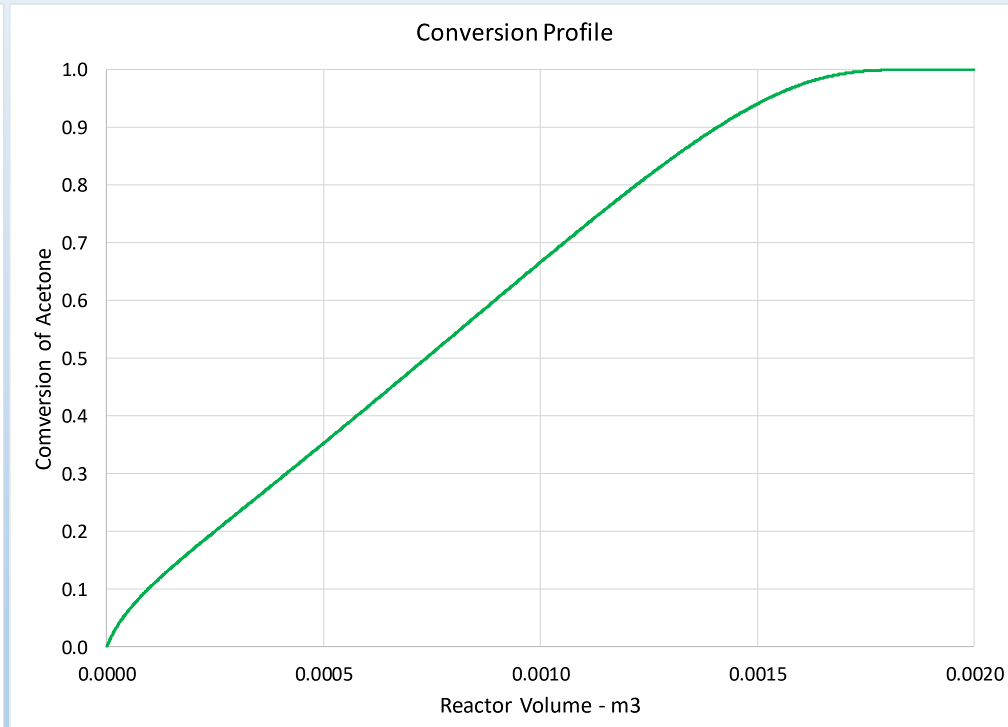
	N	O
	TAirError	0.0
	Use Solver to drive this to zero	

Tubular Reactor with Counter-current Heat Exchange

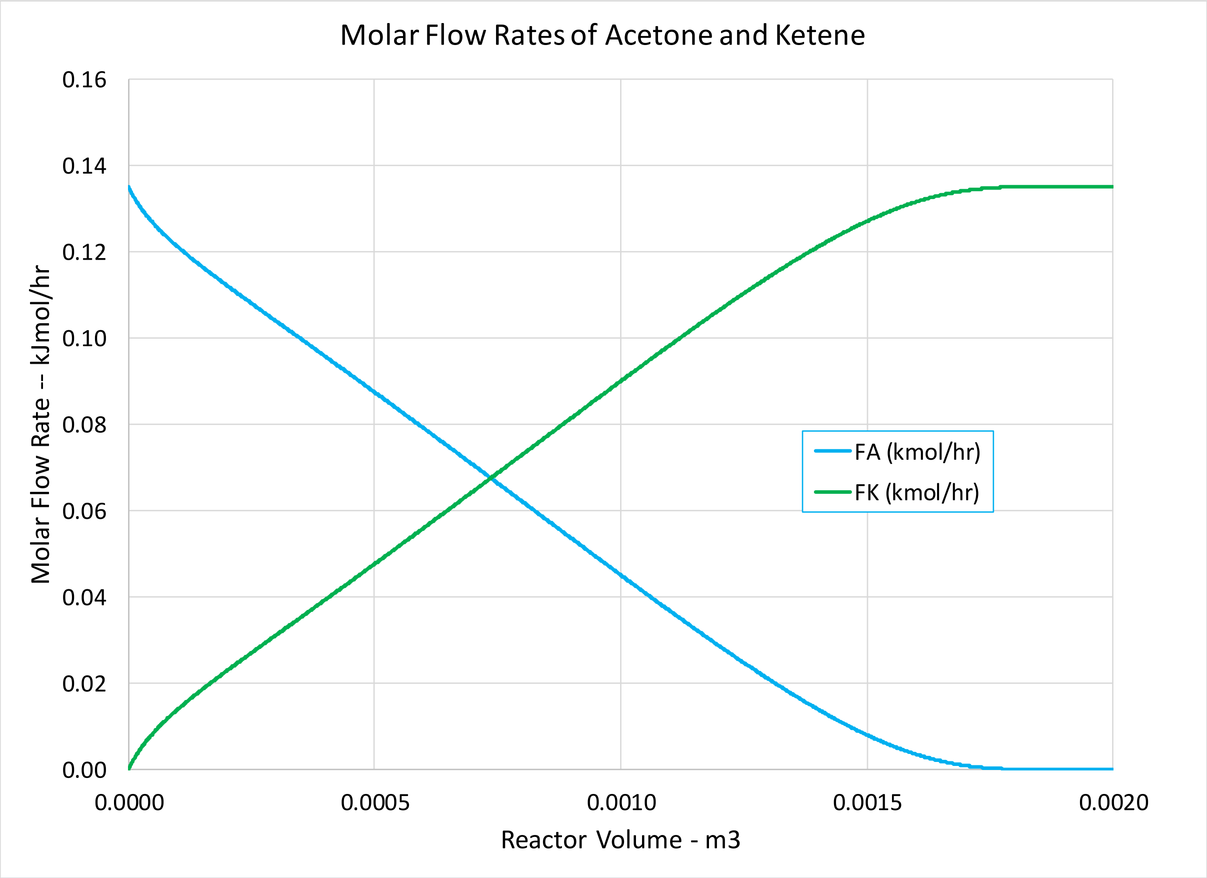
Example: Vapor-phase cracking of acetone to ketene

Excel solution





Tubular Reactor with Counter-current Heat Exchange
Example: Vapor-phase cracking of acetone to ketene
Excel solution



Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Excel VBA Code

```
Option Explicit
Function findT(H, TF, FA, FK, FM)
'solve nonlinear algebraic equation to find T
'using the secant method
Dim T1, tol, T2, Tnew
T1 = TF
tol = 0.000001
Do
    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 Then Exit Do
    T1 = Tnew
Loop
findT = Tnew
End Function
Function fH(H, T, FA, FK, FM)
'computes difference between given enthalpy rate
'and enthalpy rate computed from a value of T
Dim HAt, HKt, HMt, HfA, HfK, HfM, Tref
Tref = 298.15
HfA = -216.67 * 1000
HfK = -61.09 * 1000
HfM = -74.81 * 1000
HAt = FA * (CpAavg(T) * (T - Tref) + HfA)
HKt = FK * (CpKavg(T) * (T - Tref) + HfK)
HMt = FM * (CpMavg(T) * (T - Tref) + HfM)
fH = H - (HAt + HKt + HMt)
End Function
```

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Excel VBA Code

```
Function findTAir(Ha, Ta0, FA)
'solve nonlinear algebraic equation to find Tair
'using the secant method
Dim Ta1, tol, Ta2, Tanew
Ta1 = Ta0
tol = 0.000001
Do
   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 Then Exit Do
   Ta1 = Tanew
Loop
findTAir = Tanew
End Function
```

```
Function fHa(Ha, Ta, FA)
'computes difference between given enthalpy rate
'and enthalpy rate computed from a value of T
Dim Cp, Tref
Tref = 298.15
Cp = CpAiravg(Ta)
fHa = Ha - FA * Cp * (Ta - Tref)
End Function
```

Tubular Reactor with Counter-current Heat Exchange

Example: Vapor-phase cracking of acetone to ketene

Excel VBA Code – functions for average heat capacity

```
Function CpAavg(T)
Dim a, b, c, d, Tref, Trefk, Tk, CpT, CpTref
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
CpAavg = (CpT - CpTref) / (Tk - Trefk)
End Function
```

```
Function CpMavg(T)
Dim a, b, c, d, e, Tref, Trefk, Tk, CpT, CpTref
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 / Tref
CpMavg = (CpT - CpTref) / (Tk - Trefk)
End Function
```

```
Function CpKavg(T)
Dim a, b, c, d, e, Tref, Trefk, Tk, CpT, CpTref
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
CpKavg = (CpT - CpTref) / (Tk - Trefk)
End Function
```

```
Function CpAiravg(T)
Dim a, b, c, d, Tref, CpT, CpTref
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
CpAiravg = (CpT - CpTref) / (T - Tref)
End Function
```

References:

Spreadsheet Problem Solving and Programming for Engineers and Scientists,
David E. Clough and Steven C. Chapra,
CRC Press - Taylor & Francis Group, 2024.

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

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

Excel Bootcamps 1, 2, 3 and 4

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