

Catalytic Rates & Pressure Drop in PFR Reactors: HYSYS 3.0

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Objectives:

1. In this session you will learn how to convert a first order catalytic reaction rate for use in the PFR.
2. In addition you will use the Ergun Equation to simulate the pressure drop within a PFR. (The reverse reaction or equilibrium will be ignored in this tutorial.)

The references for this section are taken from the 2 HYSYS manuals:

Simulation Basis: Chapter 5 Reactions

Operations Guide: Chapter 9 Reactors

Reactor Types in HYSYS

1) CSTR model reactors – Well Mixed Tank-Type

HYSYS Reactor Name	Reaction Types (See above)
Conversion Reactor	Conversion ($X\% = C_0 + C_1T + C_2T^2$)
CSTR	Simple Rate, Heterogeneous Catalytic, Kinetic
Equilibrium Reactor	$K_{eq} = f(T)$; equilibrium based on reaction stoichiometry. K_{eq} predicted from Gibbs Free Energy K_{eq} specified as a constant or from a table of values
Gibbs	minimization of Gibbs free energy of all specified components, option 1) no the reaction stoichiometry is required option 2) reaction stoichiometry is given

2) Plug Flow Reactor: Simple Rate, Heterogeneous Catalytic, Kinetic

Taken from: 9.3 Plug Flow Reactor (PFR)

The PFR (Plug Flow Reactor, or Tubular Reactor) generally consists of a bank of cylindrical pipes or tubes. The flow field is modeled as plug flow, implying that the stream is radially isotropic (without mass or energy gradients). This also implies that axial mixing is negligible.

As the reactants flow the length of the reactor, they are continually consumed, hence, there will be an axial variation in concentration. Since reaction rate is a function of concentration, the reaction rate will also vary axially (except for zero-order reactions).

To obtain the solution for the PFR (axial profiles of compositions, temperature, etc.), the reactor is divided into several subvolumes. Within each subvolume, the reaction rate is considered to be spatially uniform.

You may add a Reaction Set to the PFR on the Reactions tab. ***Note that only Kinetic, Heterogeneous Catalytic and Simple Rate reactions are allowed in the PFR.***

Reaction Sets (portions from Simulation Basis: Chapter 5 Reactions)

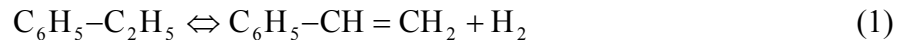
Reactions within HYSYS are defined inside the Reaction Manager. The Reaction Manager, which is located on the Reactions tab of the Simulation Basis Manager, provides a location from which you can define an unlimited number of Reactions and attach combinations of these Reactions in Reaction Sets. The Reaction Sets are then attached to Unit Operations in the Flowsheet.

Summary of Reactions in HYSYS

Reaction Type	Description:
Conversion	Conversion% ($X\% = C_0 + C_1T + C_2T^2$)
Equilibrium	$K_{eq} = f(T)$; equilibrium based on reaction stoichiometry. K_{eq} predicted or specified
Gibbs	minimization of Gibbs free energy of all components
Kinetic	$r_A = -k_f C_A^\alpha C_B^\beta + k_{rev} C_R^\phi C_S^\gamma$ where the reverse rate parameters must be thermodynamically consistent and rate constants are given for both the forward and reverse rate constant by $k = AT^n \exp(-E/RT)$
Heterogeneous Catalytic	Yang and Hougen form: $-r_A = \frac{k \left(C_A^a C_B^b - \frac{C_R^r C_S^s}{K} \right)}{1 + \sum K_i C_i^{\gamma_i}}$ <p>This form includes Langmuir-Hinshelwood, Eley-Rideal and Mars-van Krevelen <i>etc.</i></p>
Simple Rate	$r_A = -k_f \left(C_A^\alpha C_B^\beta - \frac{C_R^\phi C_S^\gamma}{K_{eq}} \right)$ in which K_{eq} is predicted from equilibrium data. K_{eq} must be given as a Table of data or in the form of $\ln(K) = A + B/T + C \ln(T) + DT$

HYSYS PFR Reactors using kinetic rates– Tutorial using Styrene

Styrene is a monomer used in the production of many plastics. It has the fourth highest production rate behind the monomers of ethylene, vinyl chloride and propylene. Styrene is made from the dehydrogenation of ethylbenzene:



In this reactor we will neglect the aspect that reaction 1 is an equilibrium reaction and model this system using a power law expression. In HYSYS this is called a **Kinetic Rate** expression. The reaction rate expression that we will use in this tutorial is from Hermann¹ and has been modified by removing the reverse reaction rate:

$$r_{EB} = -7.491 \times 10^{-2} \frac{\text{mol EB}}{\text{g}_{\text{cat}} \text{ s kPa}} p_{EB} \exp \left[- \frac{21874 \text{ cal/mol}}{\left(1.987 \frac{\text{cal}}{\text{mol K}} \right) T} \right] \quad (2)$$

Notice that the reaction rate has units in terms of the mass of catalyst and that the concentration term is partial pressure with units of kPa.

HYSYS Reaction rates must be given in units of volume of gas phase. For example, to convert from units of kgcat given in equation 3 to the units required by HYSYS given in equation 4, you must use equation 5.

$$r \quad [=] \frac{\text{mol}}{\text{s kgcat}} \quad (3)$$

$$r_{\text{HYSYS}} [=] \frac{\text{mol}}{\text{s m}_{\text{gas}}^3} \quad (4)$$

$$r_{\text{HYSYS}} = r \rho_c \frac{(1-\phi)}{\phi} \quad (5)$$

From the source of the original reaction rate studies¹ the properties of the catalyst and reactor are given as:

$$\phi = 0.445 \quad (6)$$

$$\rho_{\text{cat}} = 2146 \text{ kg}_{\text{cat}}/\text{m}_{\text{cat}}^3 \quad (7)$$

$$D_p = 4.7 \text{ mm} \quad (8)$$

In many of the rates in your reaction engineering text the units of mol/(L_{reactor} s) are used. Take out a piece of paper and write down the conversion from gcat given in Equation 2 to HYSYS units.

$$A_{EB\text{new}} = -7.491 \times 10^{-2} \frac{\text{mol EB}}{\text{g}_{\text{cat}} \text{ s kPa}} \left(\frac{(\quad)}{(\quad)} \right) \quad (9)$$

$$A_{EB\text{new}} =$$

Verify with your neighbor that you have the correct reaction rate constant.

Please note that if you change the void fraction in your simulation you will need to also change the reaction rate that is based on your void fraction.

In this simulation the pressure drop will be calculated by using the Ergun Equation given in the Steady-State Simulation manual Section 9.4.1 and is identical to that given by Fogler as equation 4-22 in a slightly modified form

$$\frac{dP}{dz} = -\frac{G}{\rho D_p} \left(\frac{1-\phi}{\phi^3} \right) \left[\frac{150(1-\phi)\mu}{D_p} + 1.75G \right] \quad (10)$$

where G [=] superficial mass velocity, kg/(m²s)
 ρ and μ are fluid density and viscosity

Procedure to Install a Kinetic Reaction Rate:

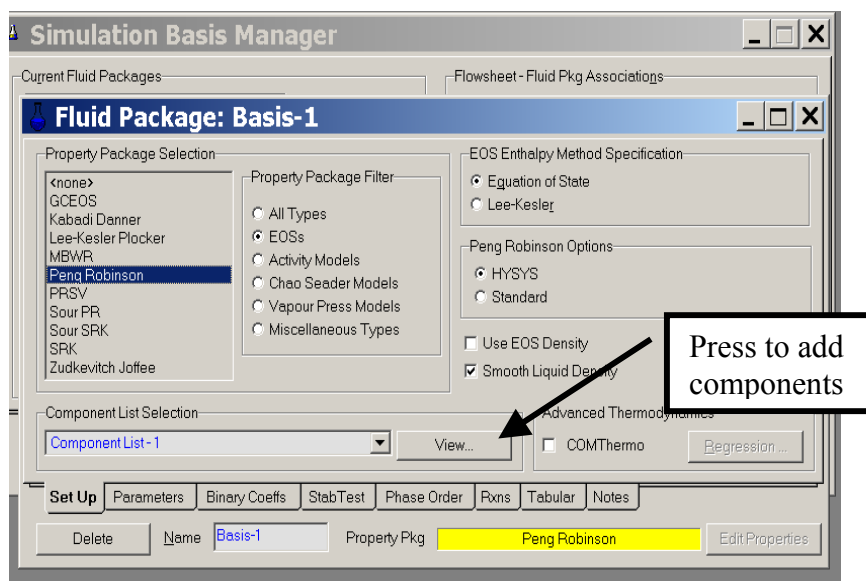
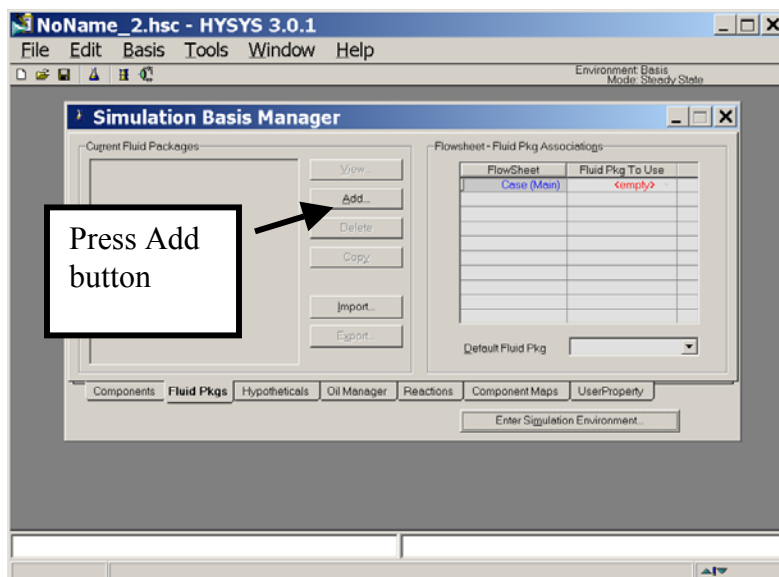
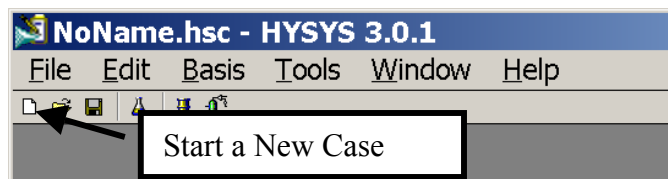
1. Start HYSYS
2. Open a new case by clicking on the blank white page OR use the commands *File New*.
3. Since these compounds are hydrocarbons, use the Peng-Robinson thermodynamic package.

(Additional information on HYSYS thermodynamics packages can be found in the *Simulation Basis Manual Appendix A: Property Methods and Calculations*. Note an alternative package for this system is the PRSV)

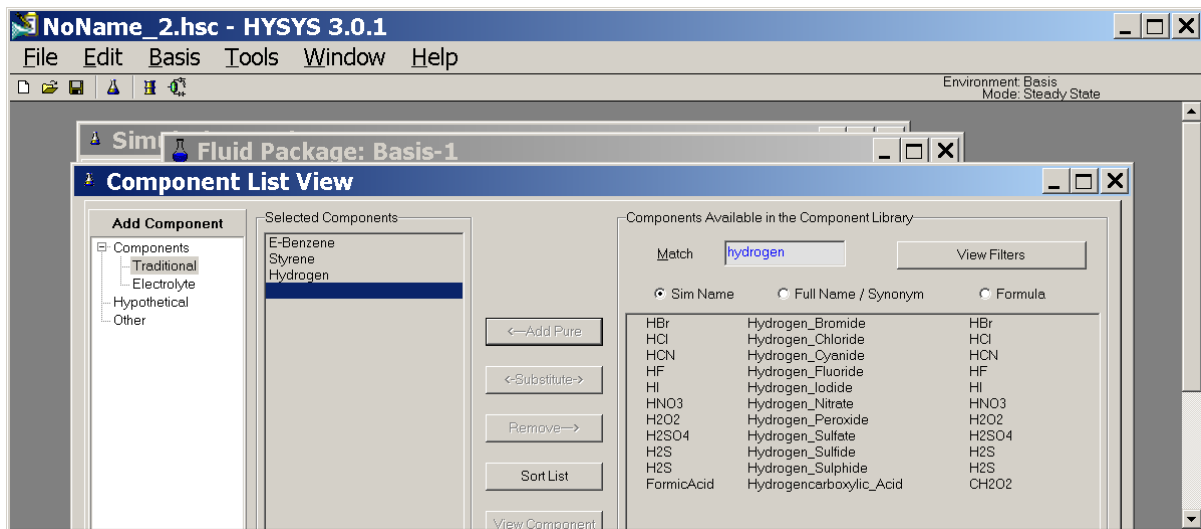
- 3.1. Select the Fluid Pkgs menu tab and Press the Add button
- 3.2. Select the EOS filter radio button to see only Equations of State (EOS)
- 3.3. Then select the Peng Robinson Equation of State.

- 3.4. Notice that you have a choice in calculating the enthalpies. You can either use the equation of state – This will be discussed in thermodynamics or you can use a prediction method called the Lee-Kesler Method which is an extension of the Pitzer method. For this tutorial we will use the equation of state method.

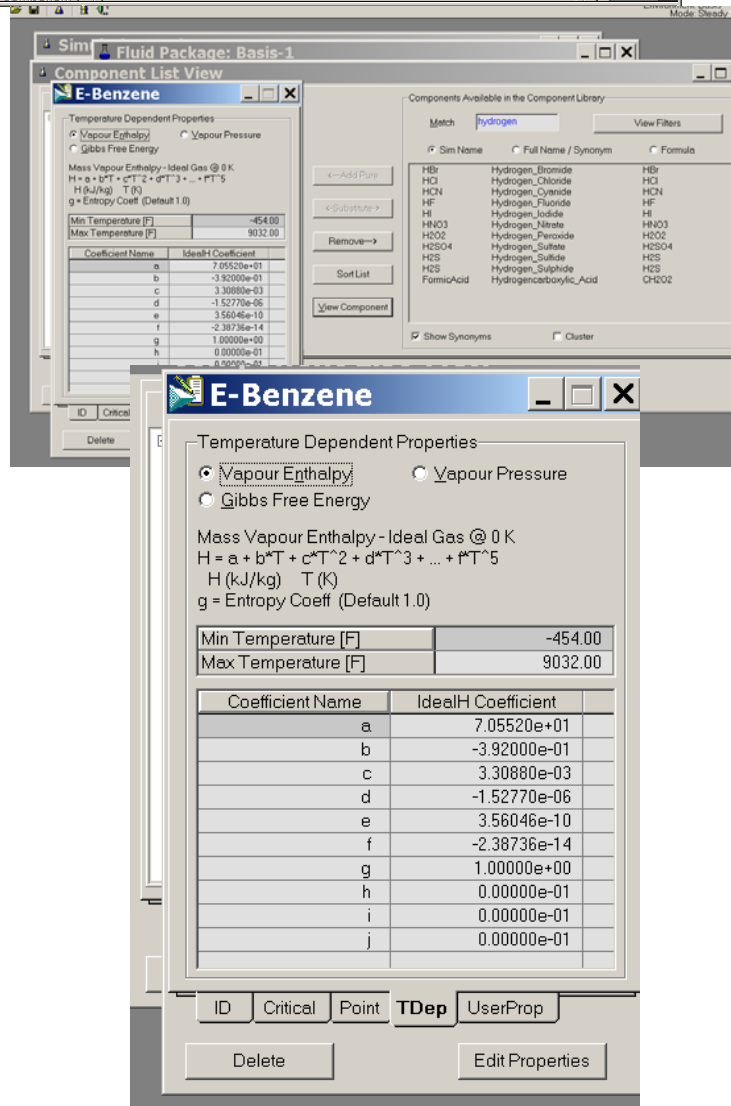
- 3.5. Press the View button to start adding chemical compounds



4. Install the chemicals for a styrene reactor: ethylbenzene, styrene, and hydrogen. If they are not in the order given below then use the Sort List... button feature.



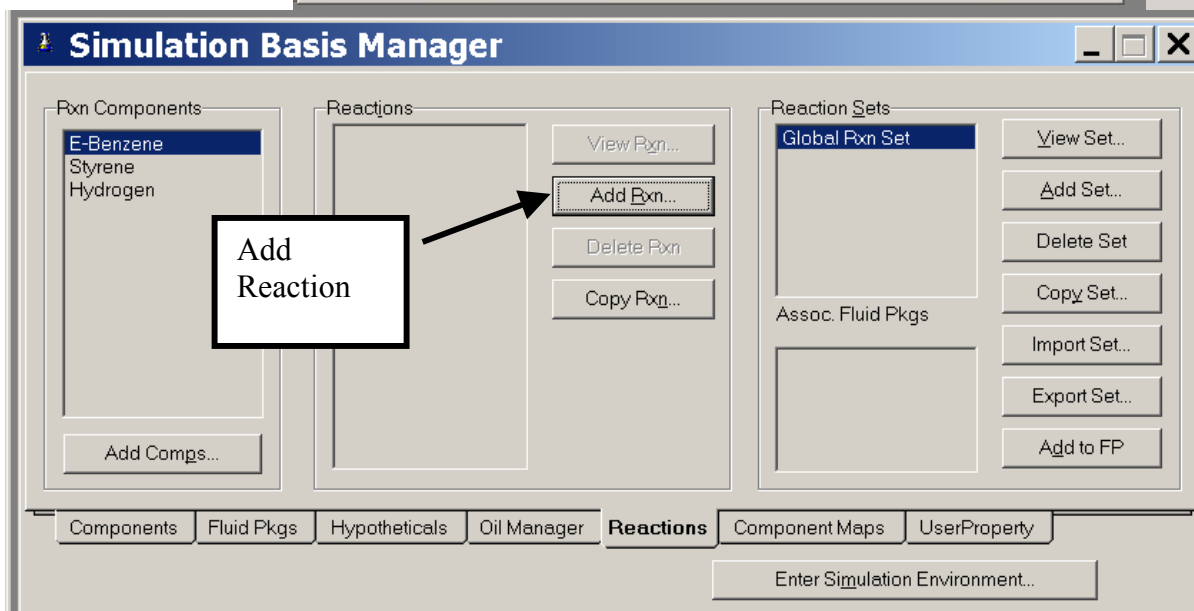
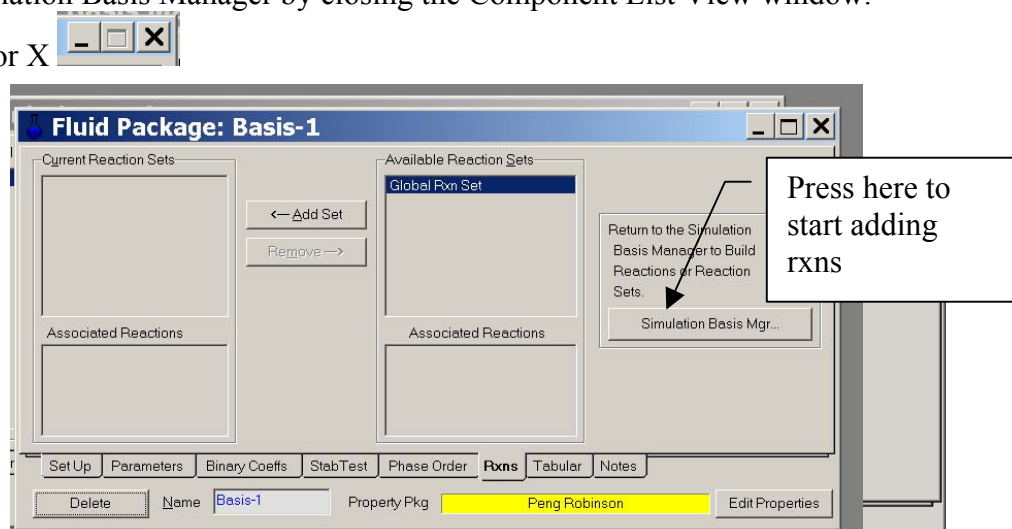
5. Let's look at one of the components and see some of the physical properties that it is using.
 - 5.1. Select Ethyl benzene
 - 5.2. Click on the View Component button
 - 5.3. Examine the temperature dependent properties given on the Tdep page
 - 5.4. Notice that the ideal gas enthalpy has been correlated using a 5th order polynomial.



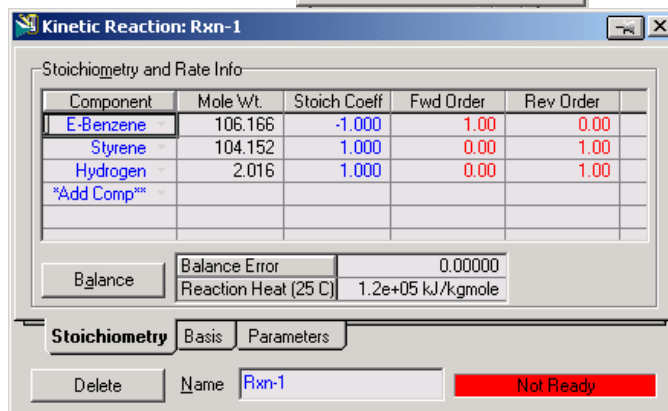
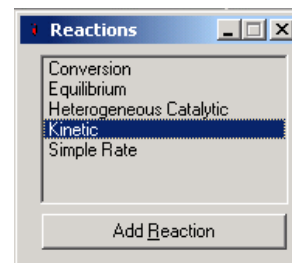
6. Now return to the Simulation Basis Manager by closing the Component List View window.

Press the *Close* button or X

7. Select the Rxns tab and then press the Simulation Basis Mgr... button.
8. The Reaction Component Selection view will appear.
9. Press the Add Rxn button
10. To install a reaction, press the *Add Rxn* button.



11. From the Reactions view, highlight the Kinetic reaction type and press the Add Reaction button. Refer to Section 5 of the Simulation Basis Manual for information concerning reaction types and the addition of reactions.
12. On the Stoichiometry tab select the first row of the Component column in Stoichiometry Info matrix. Select **ethylbenzene** from the drop down list in the Edit Bar. The Mole Weight column should automatically provide the molar weight of ethylbenzene. In the Stoich Coeff field enter -1 (i.e. 1 moles of ethylbenzene will be consumed).
13. Now define the rest of the Stoichiometry tab as shown in the adjacent figure.



14. Go to Basis tab and set the Basis as partial pressure, the base component as ethylbenzene and have the reaction take place only in the vapor phase.

15. From your previous hand calculation given by equation 9 you should have converted the reaction rate given in equation 2 by using the following:

$$A = 7.491 \times 10^{-2} \left(\frac{\text{mol}}{\text{gcat s kPa}} \right) \frac{10^3 \text{ g}_{\text{cat}}}{\text{kg}_{\text{cat}}} \left(\frac{2146 \text{ kg}_{\text{cat}}}{\text{m}_{\text{cat}}^3} \right) \frac{(1 - 0.445) \text{ m}_{\text{cat}}^3}{\text{m}_{\text{R}}^3} \left(\frac{\text{m}_{\text{R}}^3}{0.445 \text{ m}_{\text{gas}}^3} \right) \frac{1 \text{ m}_{\text{gas}}^3}{10^3 \text{ L}_{\text{gas}}} \quad (11)$$

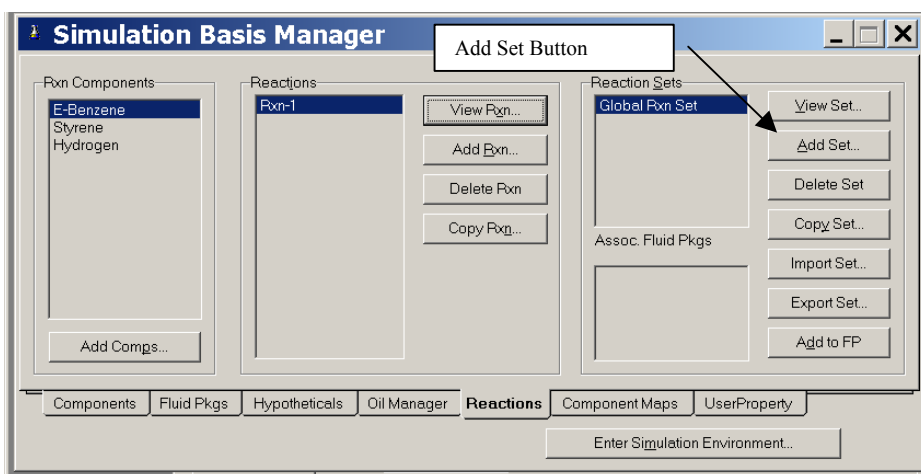
$$= 200.48 \frac{\text{mol}}{\text{L}_{\text{gas}} \text{ s kPa}}$$

The new reaction rate expression is then given by Equation 12 which should agree with the calculation:

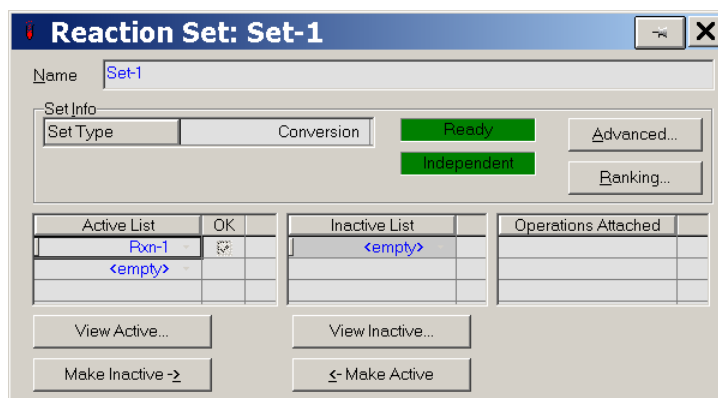
$$r_{EB} = -200.48 \frac{\text{mol EB}}{\text{L}_{\text{gas}} \text{ s kPa}} p_{EB} \exp \left[- \frac{21874 \text{ cal/mol}}{\left(1.987 \frac{\text{cal}}{\text{mol K}} \right) T} \right] \quad (12)$$

16. The pressure basis units should be kPa and the units of the reaction rate given by equation 12 is mol/(L s). Since the status bar at the bottom of the property view shows **Not Ready**, then go to the Parameters tab.
17. Add the pre-exponential which is assumed to give the units given in the basis tab. Then enter the activation energy – with units of cal/mol (which is transformed to kJ/kmol after entry.) Leave β blank or place a zero in the cell. Notice that you don't enter the negative sign with the pre-exponential.
18. Close the Kinetic Reaction Window

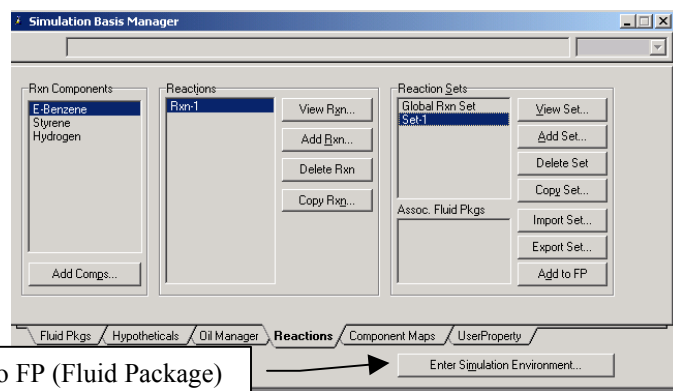
19. By default, the Global Rxn Set is present within the Reaction Sets group when you first display the Reaction Manager. However, for this procedure, a new Reaction Set will be created. Press the Add Set button. HYSYS provides the name Set-1 and opens the Reaction Set property view.



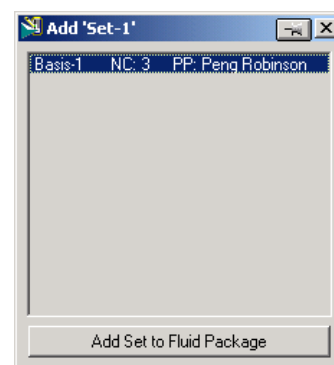
20. Open the drop down list in the Edit Bar and select the name of the Reaction. **Rxn-1** The Set Type will correspond to the type of Reaction which you have added to the Reaction Set. The status message will now display Ready. (Refer to Section 5.4 – Reaction Sets for details concerning Reactions Sets.)



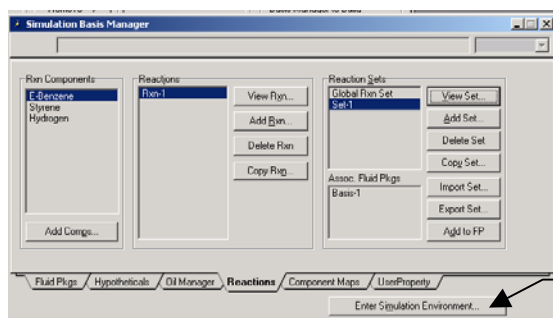
21. Press the Close button to return to the Reaction Manager.
22. To attach the reaction set to the Fluid Package (your peng robinson thermodynamics), highlight Set-1 in the Reaction Sets group and press the Add to FP button. When a Reaction Set is attached to a Fluid Package, it becomes available to unit operations within the Flowsheet using that particular Fluid Package.
23. The Add 'Set-1' view appears, from which you highlight a Fluid Package and press the Add Set to Fluid Package button.



24. Press the Close button. Notice that the name of the Fluid Package (Basis-1) appears in the Assoc. Fluid Pkgs group when the Reaction Set is highlighted in the Reaction Sets group.

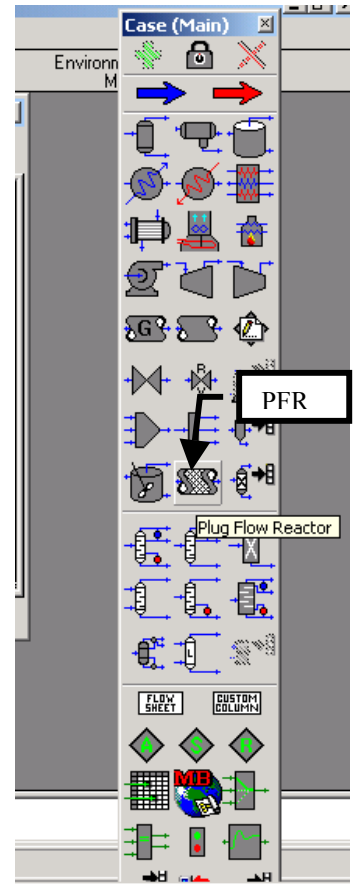
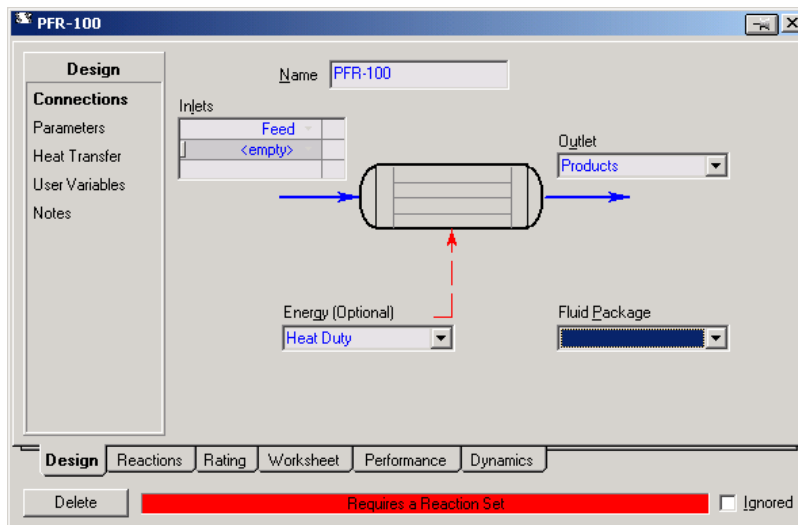


25. Now Enter the Simulation Environment by pressing the button in the lower right hand portion

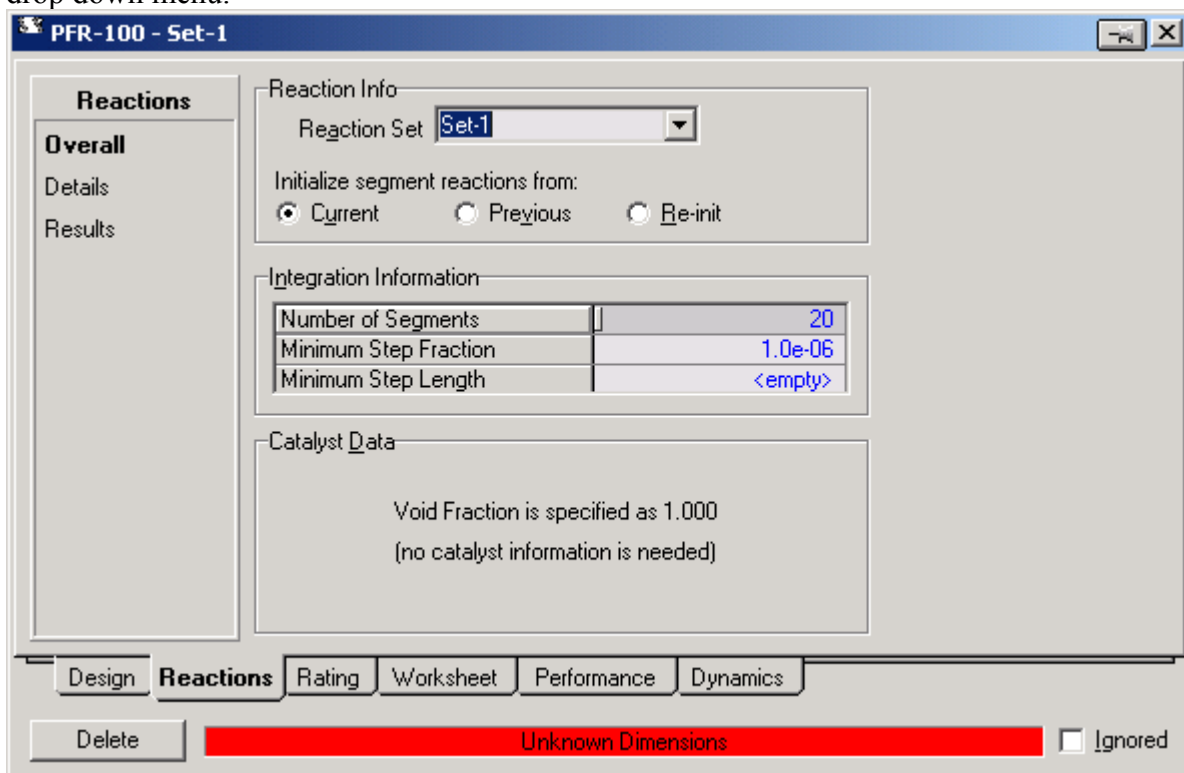


Enter Simulation Environment

26. Install a PFR reactor. Either through the
 - 26.1. Flowsheet, Add operation
 - 26.2. f12
 - 26.3. or icon pad. Click on PFR, then release left mouse button. Move cursor to pfd screen and press left mouse button. Double click on the reactor to open.
27. Add stream names as shown.



28. Next add the reaction set by selecting the reactions tab and choosing Reaction Set from the drop down menu.



29. Go to the Ratings Tab. Remember in the case of distillation columns, in which you had to specify the number of stages? Similarly with PFR's you have to specify the volume. In this case add the volume as 160 m^3 , 3 m length, and a void fraction of 0.445 as shown in the figure. Notice that the volume of gas in the reactor or void volume has been calculated.

The screenshot shows the 'Rating' tab of the 'PFR-100 - Set-1' window. On the left, under the 'Rating' section, the 'Sizing' sub-tab is selected. The main area contains two tables for inputting reactor dimensions and packing parameters.

Total Volume	160.000 m ³
Length	3.000 m
Diameter	8.2405 m
Number of Tubes	1
Wall Thickness	0.0050 m

Void Fraction	0.445
Void Volume	71.200 m ³

At the bottom, there are tabs for 'Design', 'Reactions', 'Rating' (which is active), 'Worksheet', 'Performance', and 'Dynamics'. Below these tabs is a 'Delete' button and a status bar showing 'Unknown Duty' in a yellow box, with an 'Ignored' checkbox to its right.

30. Return to the Reactions tab. Notice that additional data must be entered since you specified a void fraction. Add the particle size and density of catalyst from equations 7 and 8. Notice that the bulk density of the catalyst is calculated for you. This has units mass of catalyst per volume of reactor.

The screenshot shows the 'Reactions' tab of the 'PFR-100 - Set-1' window. On the left, under the 'Reactions' section, the 'Overall' sub-tab is selected. The main area contains three sections for reaction setup.

Reaction Info

Reaction Set: Set-1 (dropdown menu)

Initialize segment reactions from:

☒ Current ☐ Previous ☐ Re-init

Integration Information

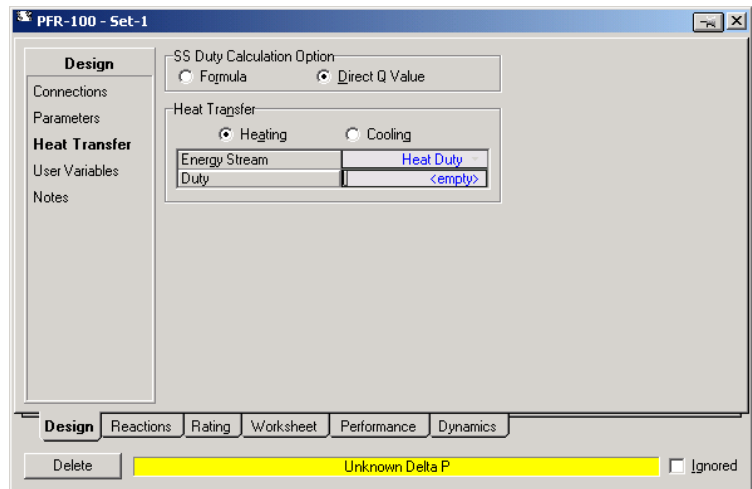
Number of Segments	20
Minimum Step Fraction	1.0e-06
Minimum Step Length	3.0e-06 m

Catalyst Data

Particle Diameter	0.00470 m
Particle Sphericity	1.000
Solid Density	2146.0 kg/m ³
Bulk Density	1191.0 kg/m ³
Solid Heat Capacity	250.000 kJ/kg-C

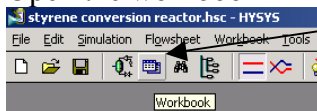
At the bottom, there are tabs for 'Design', 'Reactions' (which is active), 'Rating', 'Worksheet', 'Performance', and 'Dynamics'. Below these tabs is a 'Delete' button and a status bar showing 'Unknown Duty' in a yellow box, with an 'Ignored' checkbox to its right.

31. Go to the Design Tab and select heat transfer. To make this reactor adiabatic you need to set the heat duty to zero. For this tutorial we will have an isothermal reactor so leave this unspecified. The yellow note at the bottom is a warning and is letting you know that the pressure drop has not been specified. We will add this later.



32. Close the PFR Reactor

33. Open the workbook



Workbook

34. Isn't it strange that you can't see the molar flowrate in the composition window? Let's add the molar flowrates to the workbook windows. Go to Workbook setup.

35. Press the Add button on the right side

36. Select Component Molar Flow and then press the All radio button.

37. To change the units of the variables go to Tools, preferences

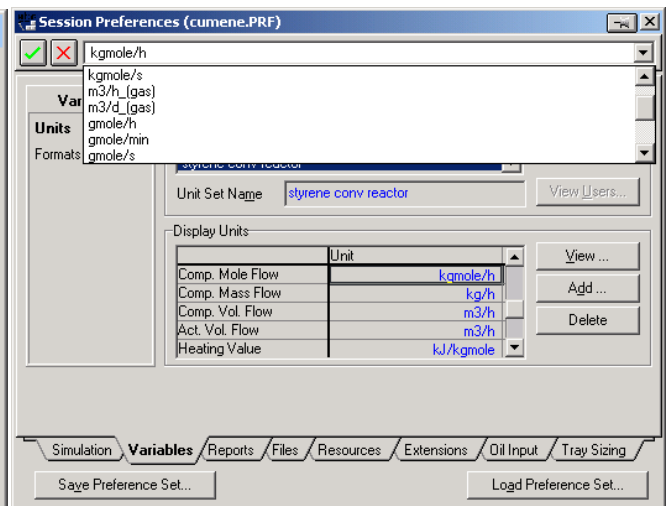
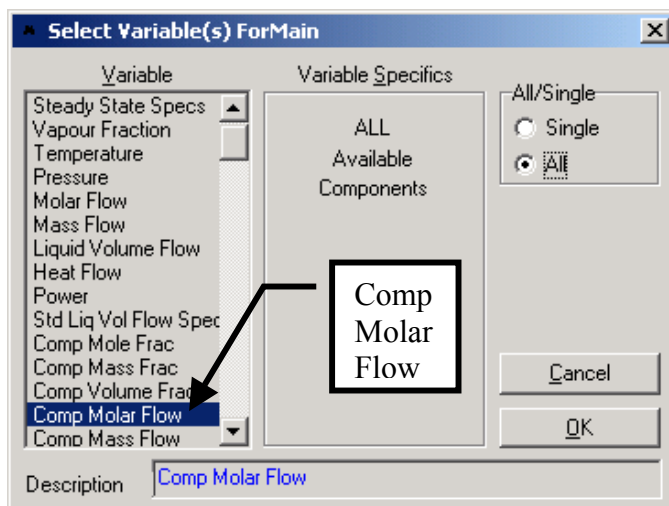
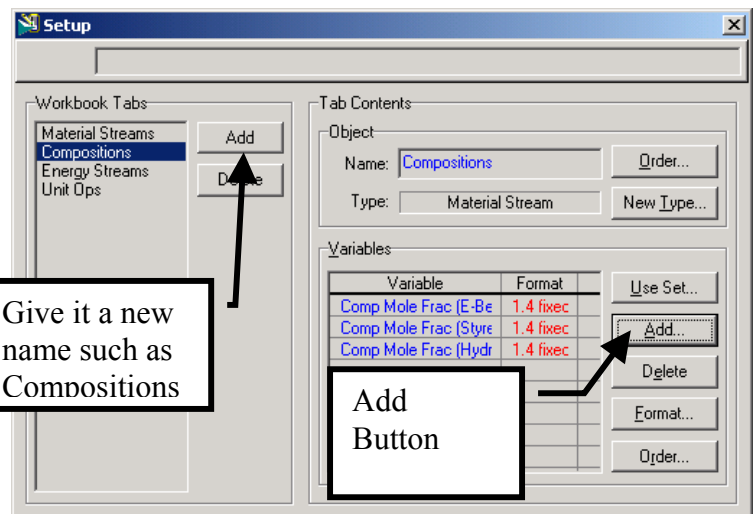
38. Then either bring in a previously named preference set or go to the variables tab and clone the SI set and give this new set a name.

39. Change the component molar flowrate units from kmol/hr to gmol/s.

40. Change the Flow units from kmol/hr to gmol/s

41. Next change the Energy from kJ/hr to kJ/s.

42. Save preference set as well as the case. Remember that you need to open this preference set every time you use this case.



43. Now add a feed composition of pure ethylbenzene at 217.5 gmol/s, 2610 gmol/s of water, 880 K, and 1.378 bar. Whoops! We forgot to add the water. Water is used in this reaction to drive the conversion to higher values. You will see the utility of adding water after you complete the equilibrium tutorial.

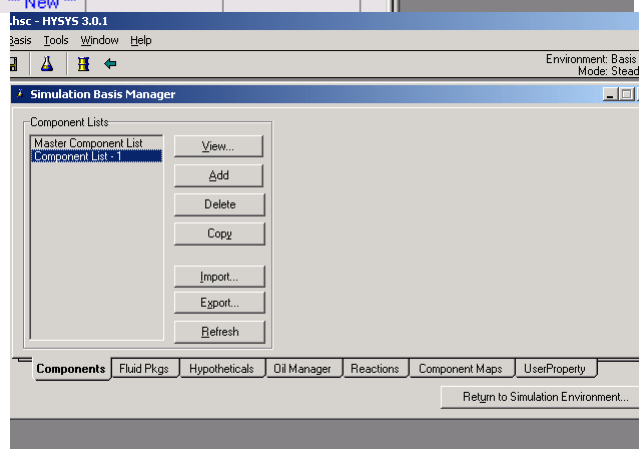
43.1. Go back to the fluid Property package by clicking on the Erlenmeyer flask or selecting Simulation, Enter Basis Environment.



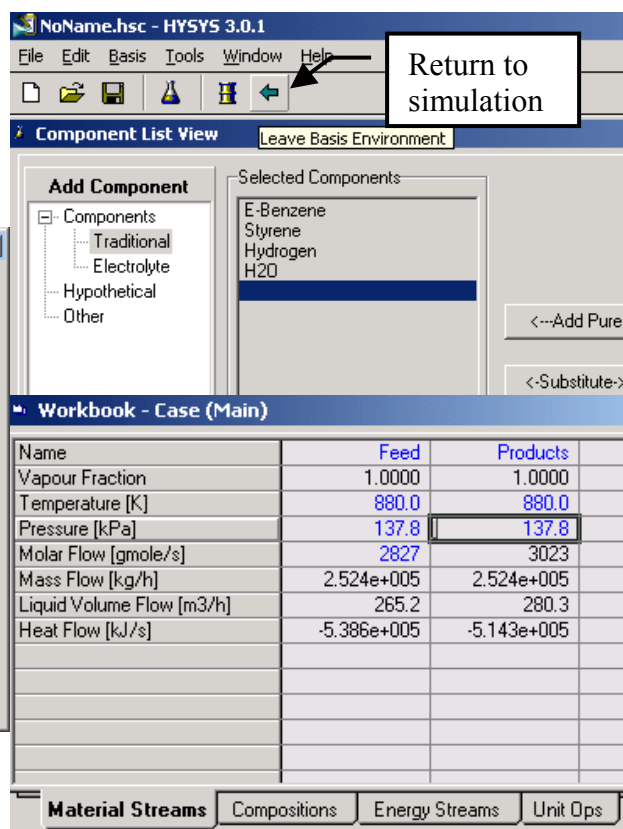
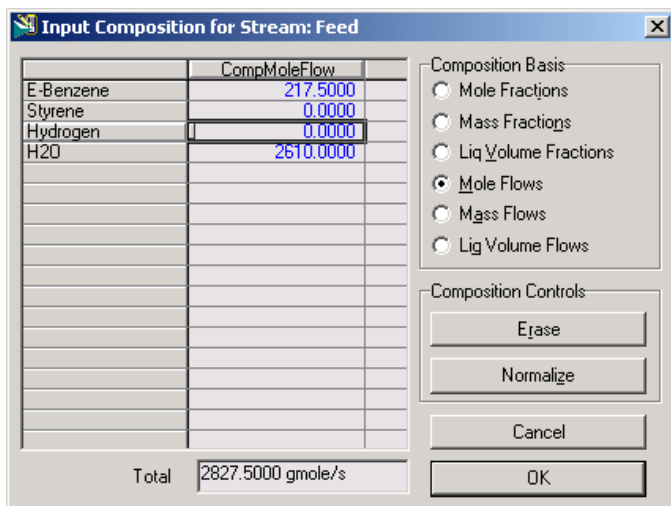
43.2. Go and view Component List-1

43.3. Add water and then return to the simulation environment by pressing on the green arrow.

43.4. It will put you in “holding mode” which stops all calculations. If you answer yes, then press the Green light to return to the automatic calculation mode. Be careful that you have added water to the correct list. You should be able to see water in the workbook component list.



44. Next set the outlet reactor temperature to 880K and the outlet reactor pressure to 1.378 bar to obtain an isothermal and isobaric reactor. Remember you can type the variable and then press the space bar and type or select the units.



Polymath hand calculations

$$r_{EB} = -k p_{EB}$$

$$k = -7.491 \times 10^{-2} \frac{\text{mol EB}}{\text{g cat s Pa}} \exp \left[-\frac{21874 \frac{\text{cal/mol}}{\text{mol K}}}{T} \right]$$

$$\phi = 0.445 \text{ m}^3 \text{ gas} / \text{m}^3 \text{ Reactor}$$

$$\rho_{\text{cat}} = 2146 \text{ kg cat} / \text{m}^3 \text{ Reactor}$$

mole Balance on EB, S, H₂ & W

$$\frac{dF_{EB}}{dV} = r'_{EB}$$

$$\frac{dF_S}{dV} = r'_S = -r'_{EB}$$

$$\frac{dF_{H_2}}{dV} = r'_{H_2} = -r'_{EB}$$

$$F_{W_0} = F_W$$

$$r'_{EB} = r_{EB} \frac{10^3 \text{ g cat}}{1 \text{ kg cat}} \left(2146 \frac{\text{kg cat}}{\text{m}^3 \text{ cat}} \right) (1 - 0.445) \frac{\text{m}^3 \text{ cat}}{\text{m}^3 \text{ Reactor}}$$

$$p_{EB_0} = y_{EB_0} P_0 = \frac{F_{EB_0} P_0}{F_T}$$

$$F_T = F_{EB} + F_{H_2} + F_W + F_S$$

Initial value for P_{EB_0}

$$P_{EB_0} = \frac{217.5 \text{ mol/s}}{(2610 + 217.5) \text{ mol/s}} (137.8 \text{ kPa}) = 10.6 \text{ kPa}$$

$$r_{EB} \Big|_{\text{at initial conditions}} = -7.491 \times 10^{-2} \frac{\text{mol EB}}{\text{g cat s kPa}} \exp \left[\frac{-21874 \text{ cal/mol}}{1.987 \frac{\text{cal}}{\text{mol K}} 880 \text{ K}} \right] 10.6 \text{ kPa}$$

$$r_{EB_0} = -2.93 \times 10^{-6} \frac{\text{mol EB}}{\text{g cat s}}$$

$$r_{EB_0} = -2.93 \times 10^{-6} \frac{\text{mol EB}}{\text{g cat s}} \frac{10^3 \text{ g cat}}{\text{kg cat}} 2146 \frac{\text{kg cat}}{\text{m}^3 \text{ cat}} (1 - 0.445) \frac{\text{m}^3 \text{ cat}}{\text{m}^3 \text{ reactn}}$$

$$\text{or } r_{EB_0} = -3.49 \frac{\text{mol EB}}{\text{m}^3 \text{ s}} \text{ or } -3.49 \times 10^{-3} \frac{\text{mol EB}}{\text{L R s}}$$

If the rate were constant and $V = 160 \text{ m}^3$

$$dF_{EB} = dV r_{EB_0}$$

$$F_{EB} - F_{EB_0} = (160 \text{ m}^3) \left(-3.49 \frac{\text{mol}}{\text{m}^3 \text{ s}} \right) = -1006 \text{ mol/s}$$

↑
all reacts!

Initial Reaction rate for comparison to Hysys

$$r_{EB_0} = -3.49 \times 10^{-3} \left(\frac{\text{mol EB}}{\text{L R s}} \right) \left(\frac{\text{L R}}{0.445 \text{ L}_{\text{gas}}} \right) = -7.842 \times 10^{-3} \frac{\text{mol EB}}{\text{L}_{\text{gas}} \text{ s}}$$

$$\text{or at } L = 0.075 \text{ m } F_{EB} = 192.922 \text{ mol/s } F_T = 2852$$

$$r_{EB} \Big|_{L=0.075 \text{ m}} = -7.842 \times 10^{-3} \frac{192.922}{2852} \frac{2827}{217.5} = -6.895 \times 10^{-3} \frac{\text{mol EB}}{\text{L}_{\text{gas}} \text{ s}}$$

Polymath Solution to Isothermal & Isobaric Reactor

POLYMATH Results

Styrene irreversible rate - volume reactor 2003 02-20-2003, Rev5.1.230

Calculated values of the DEQ variables

<u>Variable</u>	<u>initial value</u>	<u>minimal value</u>	<u>maximal value</u>	<u>final value</u>
VR	0	0	160	160
FEB	217.5	18.779137	217.5	18.779137
FS	0	0	198.72086	198.72086
FH	0	0	198.72086	198.72086
FW	2610	2610	2610	2610
P	137.8	137.8	137.8	137.8
rho_cat	2146	2146	2146	2146
T	880	880	880	880
FT	2827.5	2827.5	3026.2209	3026.2209
pEB	10.6	0.8551144	10.6	0.8551144
void_frac	0.445	0.445	0.445	0.445
k	0.3292753	0.3292753	0.3292753	0.3292753
rEB	-3.4903181	-3.4903181	-0.281568	-0.281568
XEB	0	0	0.9136591	0.9136591

ODE Report (RK45)

Differential equations as entered by the user

- [1] $d(\text{FEB})/d(\text{VR}) = r_{\text{EB}}$
- [2] $d(\text{FS})/d(\text{VR}) = -r_{\text{EB}}$
- [3] $d(\text{FH})/d(\text{VR}) = -r_{\text{EB}}$

Explicit equations as entered by the user

- [1] $\text{FW} = 2610$
- [2] $\text{P} = 137.8$
- [3] $\text{rho_cat} = 2146$
- [4] $\text{T} = 880$
- [5] $\text{FT} = \text{FEB} + \text{FS} + \text{FH} + \text{FW}$
- [6] $\text{pEB} = \text{FEB} / \text{FT} * \text{P}$
- [7] $\text{void_frac} = 0.445$
- [8] $k = 7.491e-2 * \text{rho_cat} * (1 - \text{void_frac}) * \exp(-21874 / 1.987 / \text{T}) * 1000$
- [9] $r_{\text{EB}} = -k * \text{pEB}$
- [10] $\text{XEB} = (217.5 - \text{FEB}) / 217.5$

Comments

- [1] $d(\text{FEB})/d(\text{VR}) = r_{\text{EB}}$
V in L of reactor and P in kPa
- [6] $k = 7.491e-2 * \text{rho_cat} * (1 - \text{void_frac}) * \exp(-21874 / 1.987 / \text{T}) * 1000$
mol/(s kPa m³ reactor)
- [9] $\text{P} = 137.8$
kPa

Independent variable

variable name : VR
initial value : 0
final value : 160

Precision

Step size guess. h = 0.000001
Truncation error tolerance. eps = 0.000001

46. Comparision to POLYMATH Solution:

46.1. Actual Conversion from HYSYS is 90.09% whereas the POLYMATH solution gives 91.36%.

[illegible]

46.2. Compare the reaction rates from the hand calculation to that in HYSYS. HYSYS does not give the initial reaction rate. Instead it gives the reaction rate at the first iteration of Length. With the default conditions this is at 0.075 m in length. The last line of the hand calculations given on the previous page was adjusted using the ethylbenzene molar flowrate at 0.075 m of 192.922 mol/s and the total flowrate at 2852 mol/s. These results are found in the performance tab. The hand calculation gives $6.895 \times 10^{-3} \text{ mol}/(\text{L}_{\text{gas}} \text{ s})$ compared to $6.904 \times 10^{-3} \text{ mol}/(\text{L}_{\text{gas}} \text{ s})$ given by HYSYS below.

Performance		Basis: Molar Flows			
Conditions					
Flows					
Rxn Rates					
Transport					
Compositions					
	Length [m]	E-Benzene [gmole/s]	Styrene [gmole/s]	Hydrogen [gmole/s]	
	0.075	192.922	24.579	24.	
	0.225	171.267	46.234	46.	
	0.375	152.155	65.346	65.	
	0.525	135.264	82.237	82.	
	0.675	120.316	97.185	97.	
	0.825	107.073	110.428	110.	
	0.975	95.330	122.171	122.	
	1.125	84.907	132.594	132.	
	1.275	75.650	141.851	141.	
	1.425	67.422	150.079	150.	
	1.575	60.105	157.396	157.	
	1.725	53.595	163.906	163.	

PFR-100 - Set-1

Performance

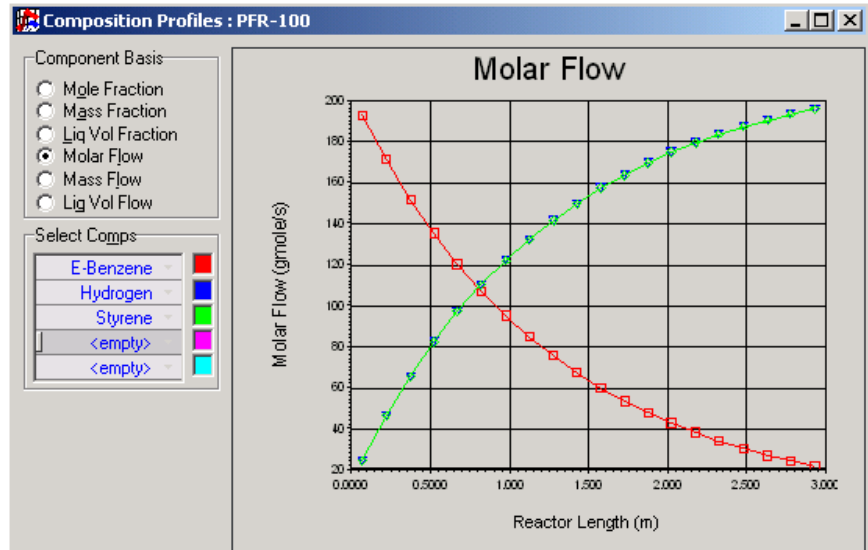
Conditions
Flows
Rxn Rates
Transport
Compositions

Length [m]	Rxn-1 [gmole/L-s]
7.500e-02	6.904e-03
2.250e-01	6.083e-03
3.750e-01	5.368e-03
5.250e-01	4.745e-03
6.750e-01	4.199e-03
8.250e-01	3.720e-03
9.750e-01	3.299e-03
1.125e+00	2.928e-03
1.275e+00	2.600e-03
1.425e+00	2.311e-03
1.575e+00	2.055e-03
1.725e+00	1.829e-03
1.875e+00	1.628e-03

Design Reactions Rating Worksheet **Performance**

Delete OK

48. To improve the performance of HYSYS you need to increase the number of steps used to solve the differential equations. Increase the number of steps to 40 segments. This results in an actual conversion of



90.74% compared to 91.36% from POLYMATH. Believe it or not POLYMATH is a more powerful ordinary differential equation solver than the default used by HYSYS. Increasing to 200 segments gives a HYSYS conversion of 91.28%. If your simulation is very complex this number of segments could slow the computer down considerably. You should always examine reactor behavior at low segment values and then increase the number to check your solution.

The screenshot displays two overlapping windows from the ChemCAD software interface.

Main Window - Reactions Panel:

- Reactions**: Overall, Details, Results.
- Reaction Info**:
 - Reaction Set: **Set-1**
 - Initialize segment reactions from:
 - ☒ Current
 - ☐ Previous
 - ☐ Re-init
- Integration Information**:
- Catalyst Data**:

Integration Information	
Number of Segments	200
Minimum Step Fraction	1.0e-06
Minimum Step Length	3.0e-06 m

Catalyst Data	
Particle Diameter	0.00470 m
Particle Sphericity	1.000
Solid Density	2146.0 kg/m³
Bulk Density	1191.0 kg/m³
Solid Heat Capacity	250.000 kJ/kg-C

Navigation tabs at the bottom: Design | **Reactions** | Rating | Worksheet | Performance | Dynamics.

Secondary Window - Reaction Balance:

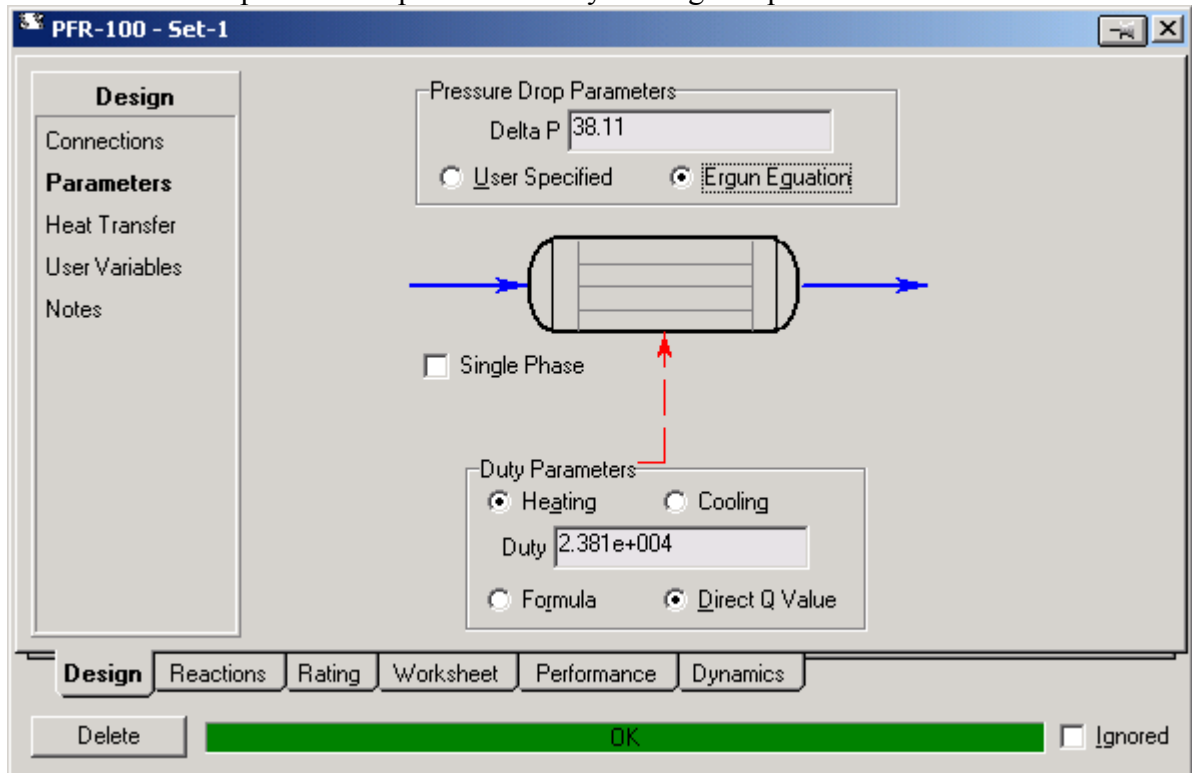
Reaction Balance options: ☒ Reaction Extents | ☐ Reaction Rate

	Act. % Conv.	Base Co
Rxn-1	91.28	E-Ber

Navigation tabs at the bottom: Design | **Reactions** | Rating | Worksheet | Performance | Dynamics.

49. Now let's add the pressure drop equation.

- 49.1. Change the number of segments back to 20.
- 49.2. Delete the outlet reactor pressure in the worksheet or workbook
- 49.3. Next go to the Parameters portion of the Design window. Click on the radio button next to the pressure drop calculation by the Ergun equation. Voila!



50. The rule of thumb for reactors is that the inlet pressure drop should be less than 10% of the inlet pressure. If the pressure drop is higher than this value then you should do something to decrease the pressure drop.

$$\Delta P \leq 0.1P_0 \quad (13)$$

Write the ways that you can decrease the pressure drop given by equation 10:

50.1. _____

50.2. _____

50.3. _____

The answers are: G , D_p and z or reactor length.

Making the reactor shorter will decrease the pressure drop.

Decreasing the superficial mass velocity, G , will decrease the pressure drop, but if you have a production rate that is based on your reactant flowrate how do you decrease G ?

Remember that $G = \frac{v_0 \rho_0}{A_c}$. If you have found a volume of reactor that gives a desired

conversion then you need to increase A_c and decrease L (length of reactor) such that the volume remains constant $V = A_c L$. HYSYS does this automatically! Try this. The

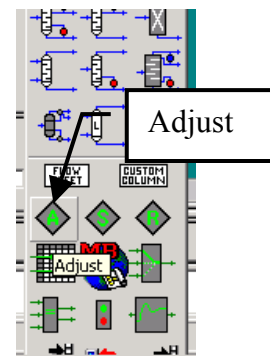
inlet pressure is 137.8 kPa. A 10% loss in pressure would give an outlet pressure of 124.02 or a $\Delta P = 13.8$ kPa. If you get tired of switching back and forth then you could try the adjust function.

51. Add the adjust function. (F4 or Flowsheet palette).

51.1. Select the adjusted variable of reactor tube length and the target variable (the variable you would like to find) product pressure.

51.2. Go to the Parameters page and change the step size to 0.2 m and set the minimum to 0.5 m and the maximum to 3 m. Why did you pick these values? You know that 3 m is gives too large a pressure drop! If you give a really large value of reactor length HYSYS will yell at you and do strange things! To fix this turn the adjust off by clicking the ignored box on the connections page. Then go back to the PFR reator and reset the value of the reactor tube length. Then find out what you did wrong!

51.3. Now you may need to increase your volume to obtain the 90% conversion.



ADJ-1

Adjust Name: ADJ-1

Adjusted Variable

Object: PFR-100 Select Var...

Variable: Tube Length

Target Variable

Object: Products Select Var...

Variable: Pressure

Target Value

Source

☒ User Supplied ☐ Another Object

Specified Target Value: 124.0 kPa

Connections

Notes

Connections

Parameters

Monitor

User Variables

124.0 kPa

1.240 bar

17.99 psia

Unknown Maximum

Delete Start Ignored

Solving Parameters

☐ Simultaneous Solution

Method	Secant
Tolerance	0.10000 kPa
Step Size	0.20000 m
Minimum (Optional)	0.50000 m
Maximum (Optional)	3.0000 m
Maximum Iterations	10

☐ Optimizer Controlled

Sim Adj Manager...

Connections Parameters Monitor User Variables

OK

52. Changing the particle diameter D_p is dangerous (well you just need to be careful)!

If you change the particle size then you will also change the void fraction of catalyst. Figure 5-70 of the 5th Edition of the Chemical Engineers Handbook shows the relation between particle diameter and void fraction for various types of particles.

In Figure 1 shown below is the curve that I have digitized for spherical particles. The x-axis is the ratio of the particle size to the tube or reactor diameter. This equation can be entered into a HYSYS spreadsheet so that the void fraction is automatically calculated when the particle diameter or reactor diameter change. Notice that you must also include the void fraction in your reaction rate term!

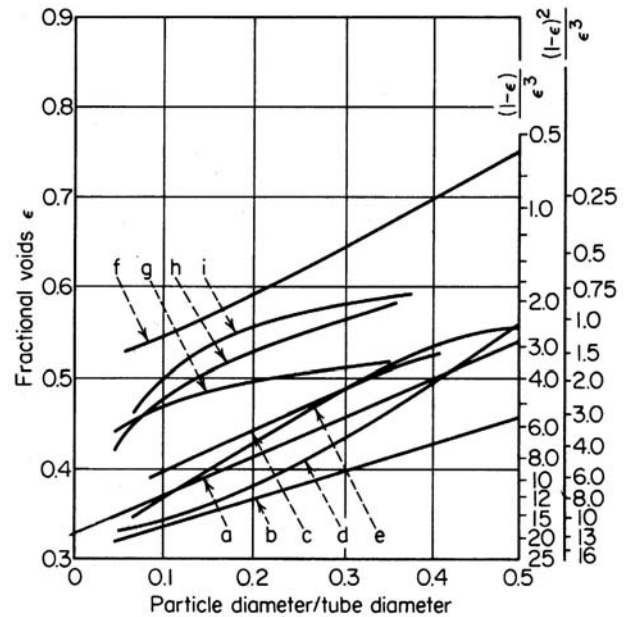


Fig. 5-70. Voidage in packed beds. Spherical: *a*, smooth, uniform; *b*, smooth, mixed; *c*, clay. Cylindrical: *d*, smooth, uniform; *e*, alundum, uniform; *f*, clay Raschig rings. Granules: *g*, fused magnetite (synthetic ammonia catalyst); *h*, fused alundum; *i*, Aloxite. (Leva, "Fluidization," p. 54, McGraw-Hill, New York, 1959.)

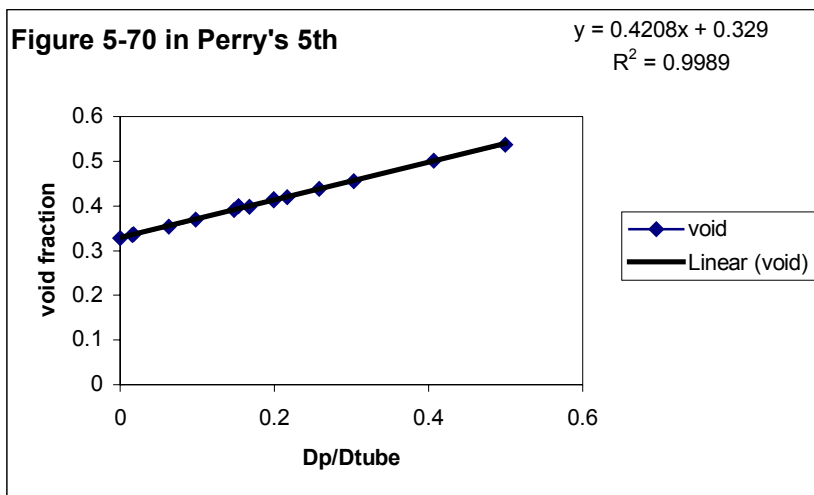


Figure 1: Void Fraction for Spherical Particles

POLYMATH and Hand Calculations

53. Now we will look at verifying what is going on in HYSYS. Notice that HYSYS is a black box calculation. You can't see what it is doing. Reading the help files will give an indication on how it is integrating the reactor. To fully understand the PFR let's go to some hand calculations given on the following page.

53.1. For the comparison with POLYMATH reset the size of the reactor to the following a volume of 163 m³ and a length of 2.190 m. You could also add a spreadsheet for ease in examining variables. Remember that to quickly add variables you can right click on the variable that you want and drag it to the spreadsheet.

The screenshot displays the HYSYS software interface with several windows open:

- Reactions** (Left Panel): Shows the overall reaction details.
- Reaction Balance** (Top Window): Displays the reaction extent for Rxn-1.

Rxn	Act. % Cnv.	Base Comp	Rxn Extent
Rxn-1	89.36	E-Benzene	194.4
- PFR-100 - Set-1** (Middle Window): Shows the reactor rating and design parameters.
 - Rating** (Sizing):

Tube Dimensions	
Total Volume	163.000 m ³
Length	2.190 m
Diameter	9.7348 m
Number of Tubes	1
Wall Thickness	0.0050 m

Tube Packing	
Void Fraction	0.445
Void Volume	72.535 m ³
 - Design** (Bottom):
 - Pressure Drop Parameters: Delta P = 13.79, Ergun Equation selected.
 - Duty Parameters: Heating selected, Duty = 2.414e+004, Direct Q Value selected.
- SPRDSHT-1** (Right Window): A spreadsheet showing the current cell calculation.

	A	B
1	Inlet Pressure	137.8 kPa
2	Outlet Pressure	123.9 kPa
3	Percent of Inlet	10.06
4	Actual % conversion	90.58
5	EB Product flow	20.4836 gmole/s
6		
7		
8		
- Reaction Balance** (Bottom Right Window): Shows the reaction balance for E-Benzene, Styrene, Hydrogen, and H2O.

	Total In	Total Rxn	Total Out
E-Benzene	217.5	-194.4	23.15
Styrene	0.0000	194.4	194.4
Hydrogen	0.0000	194.4	194.4
H2O	2610	3.109e-012	2610

Sample Calculations

Pressure Drop Calculation

- Properties based on 92% water -

J.P. Holman Heat Transfer 5th Ed. 1981

$$\left. \begin{array}{l} V = 163 \text{ m}^3 \\ D = 9.73 \text{ m} \\ L = 2.19 \text{ m} \end{array} \right\} \text{From Hysys}$$

$$\mu|_{\text{Steam}} = 29.69 \times 10^{-6} \frac{\text{kg}}{\text{m s}} \\ T = 850 \text{ K}$$

$$\overline{MW} = 18 \times 0.92 \text{ mol} + 0.08(106)$$

$$\bar{P}_0 = \frac{P}{RT} \overline{MW} = \frac{1.378 \times 10^5 \text{ Pa}}{8.314 \frac{\text{Pa m}^3}{\text{mol K}} (880 \text{ K})} \frac{25 \text{ g}}{\text{mol}} \frac{\text{kg}}{10^3 \text{ g}}$$

$$\rho_0 = 0.467 \text{ kg/m}^3$$

$$\overline{MW} = \frac{18 \text{ g}}{\text{mol}} \frac{0.92 \text{ mol}}{\text{mol Tot}} + \frac{106 \text{ g}}{\text{mol EB}} \frac{0.08 \text{ mol}}{\text{mol Tot}} \\ = 25 \text{ g/mol}$$

$$\frac{dP}{dW} = - \frac{\beta_0}{A_c (1-\phi) \rho_c} \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

4-27

$$\beta_0 = \frac{G (1-\phi)}{\rho_0 D_p \phi^3} \left[\frac{150 (1-\phi) \mu}{D_p} + 1.75 G \right]$$

$$A_c G = F_{EB} MW_{EB} + F_W MW_W = \left[217.5 \left(\frac{106.17 \text{ g}}{\text{mol}} \right) + 2610 \left(\frac{18 \text{ g}}{\text{mol}} \right) \right] \frac{\text{kg}}{1000 \text{ g}} \\ A_c G = 70.07 \text{ kg/s}$$

$$V_0 = \frac{F_{T0} RT}{P_0} = \frac{(217.5 + 2610) \text{ mol/s} \cdot 8.314 \frac{\text{Pa m}^3}{\text{mol K}} \cdot 880 \text{ K}}{1.378 \times 10^5 \text{ Pa}}$$

$$V_0 = 150 \text{ m}^3/\text{s}$$

$$\frac{G}{A_c} = \frac{70.07 \text{ kg/s}}{\pi/4 (9.73 \text{ m})^2}$$

$$D = 4.37 \text{ Reactor} \quad L = 0.1 \text{ m} \quad V = 1.5 \text{ m}^3$$

$$\frac{G}{A_c} = 0.941 \frac{\text{kg}}{\text{m}^2 \text{ s}}$$

$$\beta_0 = \frac{(0.941 \frac{\text{kg}}{\text{m}^2 \text{ s}})(1-0.445)}{(0.467 \frac{\text{kg}}{\text{m}^3})(4.7 \times 10^{-3} \text{ m})(0.445)^3} \left[\frac{150(1-0.445)}{4.7 \times 10^{-3} \text{ m}} 3 \times 10^{-5} \frac{\text{kg}}{\text{m s}} + 1.75 \cdot 18.6 \frac{\text{kg}}{\text{m}^2 \text{ s}} \right] \\ = 2701 \cdot \frac{1}{5} \left[0.531 \frac{\text{kg}}{\text{m}^2 \text{ s}} + 1.65 \right] = 5886 \frac{\text{kg}}{\text{m}^2 \text{ s}^2}$$

$$\frac{\beta_0}{A_c(1-\phi)\rho_c} = \frac{5886 \frac{\text{kg}}{\text{m}^2 \text{s}^2}}{\pi/4 (9.73 \text{ m})^2 (1-0.445) (2146.3 \text{ kg/m}^3)} = 0.0166 \frac{\text{Pa}}{\text{kg}}$$

$$P_a = \frac{N}{m^2} = \frac{\text{kg m/s}^2}{m^2}$$

$$\frac{\text{kg m}^3}{\text{m}^2 \text{s}^2 \text{ m}^2 \text{ kg}} = \frac{\text{Pa}}{\text{kg}}$$

$$\frac{dP}{dW} = -6.64 \times 10^{-2} \frac{\text{Pa}}{\text{kg}} \quad \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}} \frac{1 \text{ kg}}{1000 \text{ g}} = -6.64 \times 10^{-5} \frac{\text{Pa}}{\text{g}} \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

Now for mole Balances:

$$\frac{dF_{EB}}{dW} = r'_{EB}$$

$$\frac{dF_S}{dW} = +r_S = -r'_{EB}$$

$$\frac{dF_H}{dW} = r_H = -r'_{EB}$$

$$F_T = F_{W_0} + F_{EB} + F_S + F_H$$

$$P_{EB} = \frac{F_{EB}}{F_T} P = \left(\frac{217.5}{2827.5} \right) 1.378 \times 10^5 \text{ Pa} \frac{1 \text{ kPa}}{1000 \text{ Pa}} = 10.6 \text{ kPa}$$

$$P_0 = 1.378 \times 10^5 \text{ Pa} = 137.8 \text{ kPa}$$

Expected catalyst weight from HYSYS

$$V = 163 \text{ m}^3$$

$$W = 163 \text{ m}^3 \left(\frac{(1-0.445) \text{ m}^3}{\text{m}^3_R} \right) \frac{2146 \text{ kg}_c}{\text{m}^3_c} = 194,138 \text{ kg} = 1.94 \times 10^8 \text{ g}$$

$$X = 90\%$$

$$\text{Isothermal} = 880 \text{ K}$$

Check on pressure drop

$$\frac{dP}{dw} \approx -6.64 \times 10^{-5} \frac{\text{Pa}}{\text{g}}$$

$$\Delta P \approx -6.64 \times 10^{-5} \frac{\text{Pa}}{\text{g}} (1.94 \times 10^8 \text{g}) = 12,881 \text{ Pa}$$

$$\left(\frac{12,816 \text{ Pa}}{1.378 \times 10^5 \text{ Pa}} \right) 100 = (0.0934) 100 = 9.3\%$$

you should always do this calculation
to check your Polymath Program.

check on Conversion

$$\frac{dF_{EB}}{dw} = -F_{EB} \frac{dX_{EB}}{dw} \approx 7.491 \times 10^{-2} \exp \left[\frac{-21874 \frac{\text{cal/mol}}{\text{mol K}}}{1.987 \frac{\text{cal}}{\text{mol K}}} \right] \frac{\text{mol}}{\text{g s kPa}} 10.6 \text{ kPa}$$

Again using the highest possible rate at $w=0$ and $P_{EB}|_{\text{max}} = 10.6 \text{ kPa}$

$$k = 2.764 \times 10^{-7} \frac{\text{mol}}{\text{g s kPa}}$$

$$r = 2.764 \times 10^{-7} \frac{\text{mol}}{\text{g s kPa}} 10.6 \text{ kPa}$$

$$r = 2.93 \times 10^{-6} \frac{\text{mol}}{\text{g s}}$$

$$X_{EB} \approx \frac{(2.764 \times 10^{-7} \frac{\text{mol}}{\text{g s kPa}}) (1.94 \times 10^8 \text{g}) 10.6 \text{ kPa}}{217 \text{ mol/s}}$$

↑
this number
is in Polymath
output

$$= \frac{548}{217} = 2.6 \text{ — this is OK since the average } P_{EB} \text{ will be less than } 10.6 \text{ kPa}$$

Construct a POLYMATH program to give the following:

POLYMATH Results

Pressure Drop in Isothermal Styrene Reactor

Calculated values of the DEQ variables

<u>Variable</u>	<u>initial value</u>	<u>minimal value</u>	<u>maximal value</u>	<u>final value</u>
W	0	0	1.941E+08	1.941E+08
FEB	217.5	20.299645	217.5	20.299645
FS	0	0	197.20036	197.20036
FH	0	0	197.20036	197.20036
P	1.378E+05	1.236E+05	1.378E+05	1.236E+05
FW	2610	2610	2610	2610
T	880	880	880	880
k	2.765E-07	2.765E-07	2.765E-07	2.765E-07
FT	2827.5	2827.5	3024.7004	3024.7004
P0	1.378E+05	1.378E+05	1.378E+05	1.378E+05
pEB	10.6	0.8291809	10.6	0.8291809
rEB	-2.931E-06	-2.931E-06	-2.292E-07	-2.292E-07
FT0	2827.5	2827.5	2827.5	2827.5
Betacat	6.639E-05	6.639E-05	6.639E-05	6.639E-05
X	0	0	0.9066683	0.9066683

ODE Report (RK45)

Differential equations as entered by the user

- [1] $d(\text{FEB})/d(W) = r\text{EB}$
- [2] $d(\text{FS})/d(W) = -r\text{EB}$
- [3] $d(\text{FH})/d(W) = -r\text{EB}$
- [4] $d(P)/d(W) = -\text{Betacat} \cdot P0/P \cdot \text{FT}/\text{FT0}$

Explicit equations as entered by the user

- [1] $\text{FW} = 2610$
- [2] $\text{T} = 880$
- [3] $k = 7.491\text{e-}2 \cdot \exp(-21874/1.987/\text{T})$
- [4] $\text{FT} = \text{FEB} + \text{FS} + \text{FH} + \text{FW}$
- [5] $P0 = 1.378\text{e}5$
- [6] $p\text{EB} = \text{FEB}/\text{FT} \cdot P/1000$
- [7] $r\text{EB} = -k \cdot p\text{EB}$
- [8] $\text{FT0} = 217.5 + 2610$
- [9] $\text{Betacat} = 6.639\text{E-}05$
- [10] $X = (217.5 - \text{FEB})/217.5$

Comments

- [6] $k = 7.491\text{e-}2 \cdot \exp(-21874/1.987/\text{T})$
mol/(gcat s kPa)
- [8] $p\text{EB} = \text{FEB}/\text{FT} \cdot P/1000$
kPa
- [13] $\text{Betacat} = 6.639\text{E-}05$
Pa/g

Independent variable

variable name : W

initial value : 0

final value : 194137890

Precision

Step size guess. h = 0.000001

Truncation error tolerance. eps = 0.000001

54. Now let's compare the solution of POLYMATH with that given in HYSYS.

Volume **163 m³**

Catalyst Weight **1.941E+08 kg**

Length **2.19 m**

	HYSYS	HYSYS	HYSYS	HYSYS	HYSYS	POLYMATH
Number of Segments	20	200	300	400	500	
$\Delta P/P_0$ (%)	10.01	10.06	10.06	10.07	10.07	10.30
Conversion (%)	89.36	90.58	90.63	90.657	90.66	90.66
Ethylbenzene Product Flow (mol/s)	23.15	20.48	20.38	20.33	20.30	20.30

The above values show that HYSYS is using the same equations as those that you entered in POLYMATH. The 2 differences are in the calculation of pressure drop and the manner in which the ordinary differential equations are integrated. The difference of 2% in the percent pressure drop is attributed to the value of viscosity that was used. I assumed that the gases were all steam with a viscosity of 2.969e-5 kg/(m s). HYSYS uses a value of 2.63E-05 kg/(m s). Plugging the HYSYS value of viscosity into a spreadsheet to eliminate any round-off errors in the hand calculation and then placing the new pressure drop value of Betacat = 6.4428E-05 results in a pressure drop ratio to inlet pressure of 10.01! The method of integration of ODE's requires an adjustment of the number of segments to between 400 and 500 to have an precision equal to that of POLYMATH. We will find in later calculations that a setting of number of segments this high will cause the HYSYS program to solve very slowly. .

At the end of this exercise submit 4 printouts (5 pages total).

- 1) From a word document printout the following (2 pages): (Paste all of your results into one word document.) Make the following plots from your Conversion reactor simulation:
 - a) The effect of reactor length on pressure drop for a constant volume of 163 m³. Notice that diameter will vary. You may have already done this above by trial and error for a fixed amount of catalyst to determine the pressure drop at 10% of the inlet pressure. Before you begin find the limits on the pressure drop – Find out when HYSYS says that the pressure drop is too big!
 - b) The effect of reactor diameter on pressure drop for a constant volume of 160 m³. Notice that length will vary.
 - c) The effect of changing the particle diameter from 1.2 mm to 0.2 m (really big particles!) on the pressure drop given that the void fraction from Figure 5-70 in Perry's 5th edition for spherical particles is

$$\phi_{\text{spherical}} = 0.4208 \frac{D_p}{D_{\text{tube}}} + 0.329 \quad (14)$$

Notice that that the void fraction will be nearly constant for this problem and it will be much less than 0.445! This means that this catalyst was not spherical! To solve this problem just change the void fraction to the new value. If you needed to change the void fraction as a function of particle diameter then you would need to do the following:

- i) Create a spreadsheet that you can import the particle diameter and the tube diameter. Then calculate the void fraction and export it to the reactor.
 - ii) Now you must adjust the reaction rate pre-exponential!
 - iii) Again make a calculation in the spreadsheet based on equation 5 and then export it the pre-exponential within the reactor.
 - iv) To find the pre-exponential term you need to go to the reactor, select the reactions menu, and view the reaction. See figures on this page for help.
- 2) On a separate sheet printout the Reaction Summary Printout (See Below for instructions)
 - 3) On a separate sheet printout the Reactor Summary Printout

SPRDSHT-1

Current Cell: Imported From: PFR-100 Exportable: ☐
 D7 Variable: Tube Length Angles in:

	A	B	C	D
1	Pressure Drop	8.195 kPa	catalyst density	2146 kg/m3
2	P0	1.378 bar	Pre-exp for gcat	7.491e-002
3	% of P0	5.947	Pre-exp for HYSYS	107.7
4				
5	conversion	62.16		
6	FEB	82.2931 gmole/s		
7	Diameter of Tube	9.735 m	Reactor Length	2.190 m
8	catalyst Dp	1.905e-002 m		
9	Dp/Dtube	1.957e-003		
10	calc void frac	0.3298		

Connections Parameters Formulas **Spreadsheet** Calculation Order Variables

Delete Function Help... Spreadsheet Only... ☐ Ignored

SPRDSHT-1

Formula Summary

Cell	Formula	Result
B3	+b1/b2	1.914
B9	+b8/b7	1.993e-003
B10	+0.4208*b9+0.329	0.3298
D3	+d2*d1*(1-b10)	107.7

Connections Parameters **Formulas** Spreadsheet Calculation Order Variables

Delete Function Help... Spreadsheet Only... ☐ Ignored

Reaction Summary

1. Go back to the simulation Basis Manager by clicking on the Erlenmeyer flask.
2. View the reaction
3. Remove the pushpin
4. Select File Print and use the preview feature to see the following:
5. Print

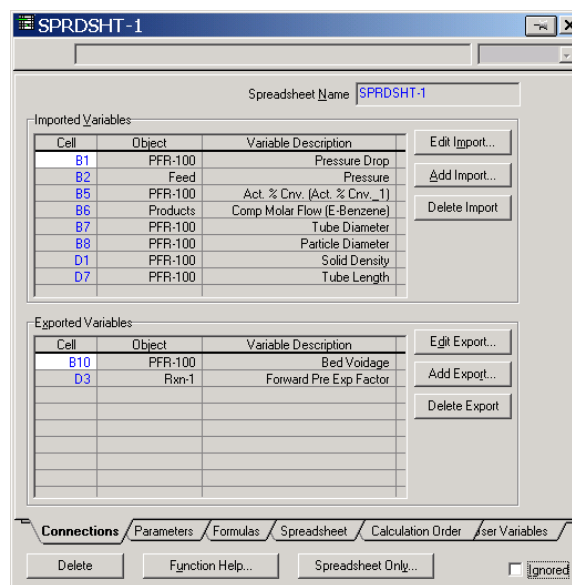
Reactor Summary:

Double click on reactor

Undo pushpin

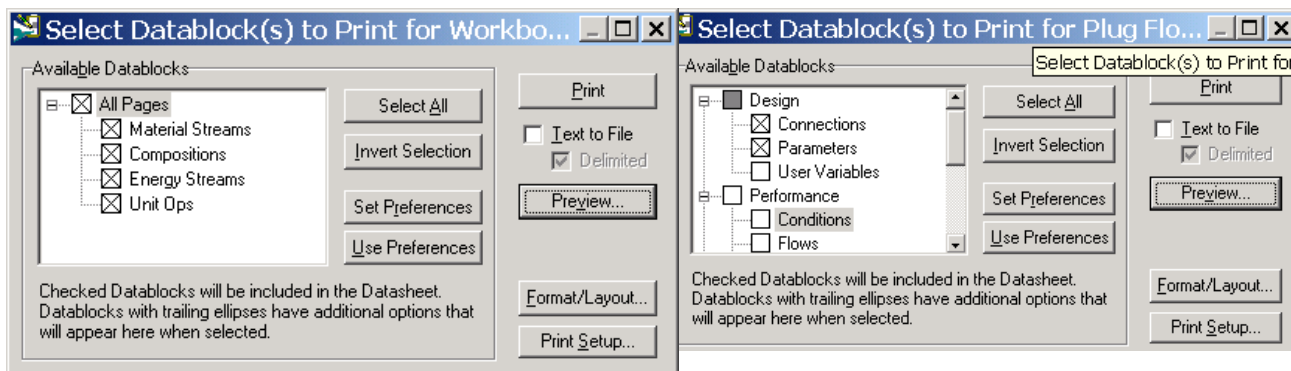
Select Print from main menu

Then select the Datablock(s) shown in the Select Datablock(s) to Print for PFR figure:

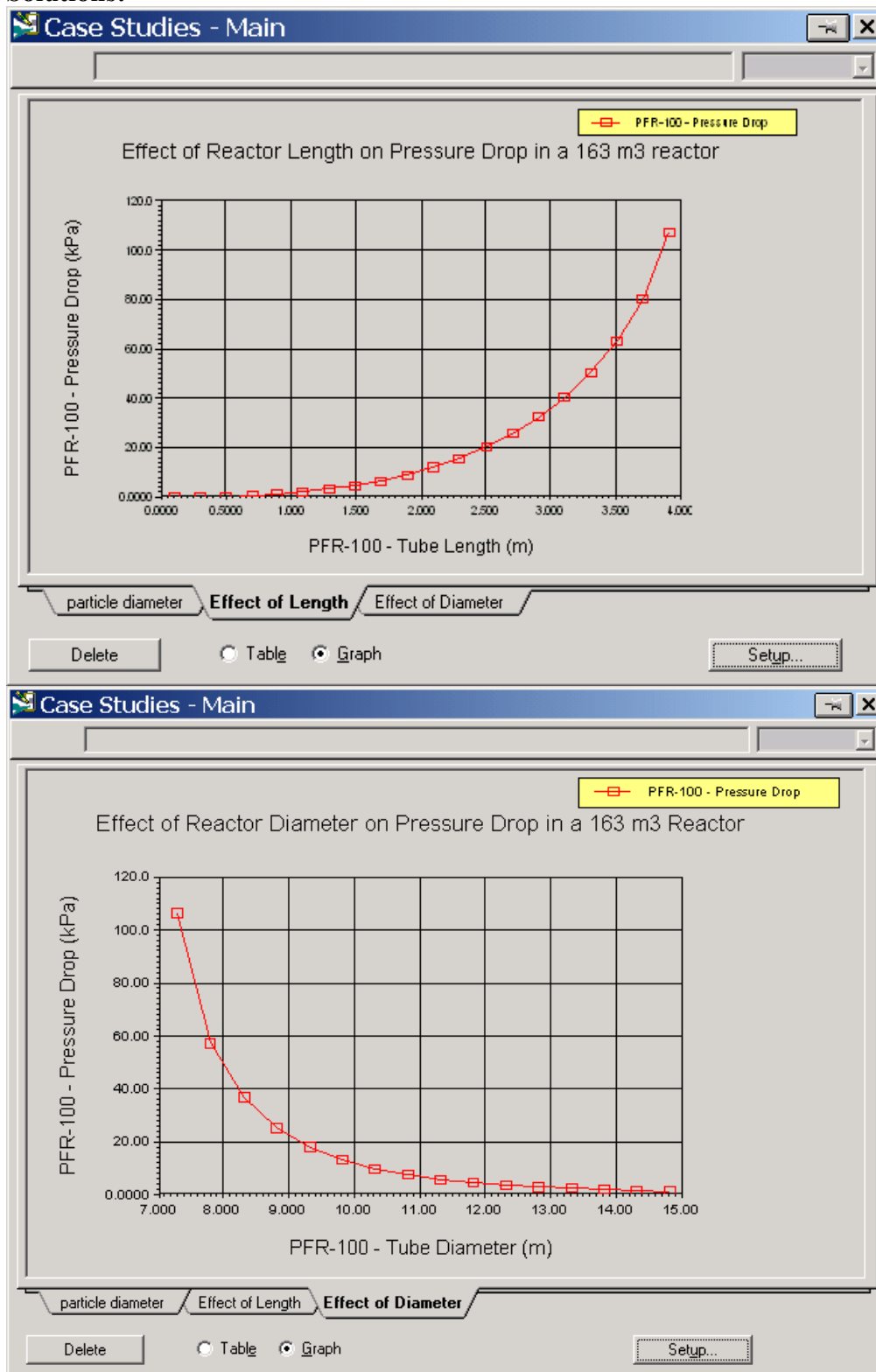


Workbook

Select workbook and print.



Solutions:



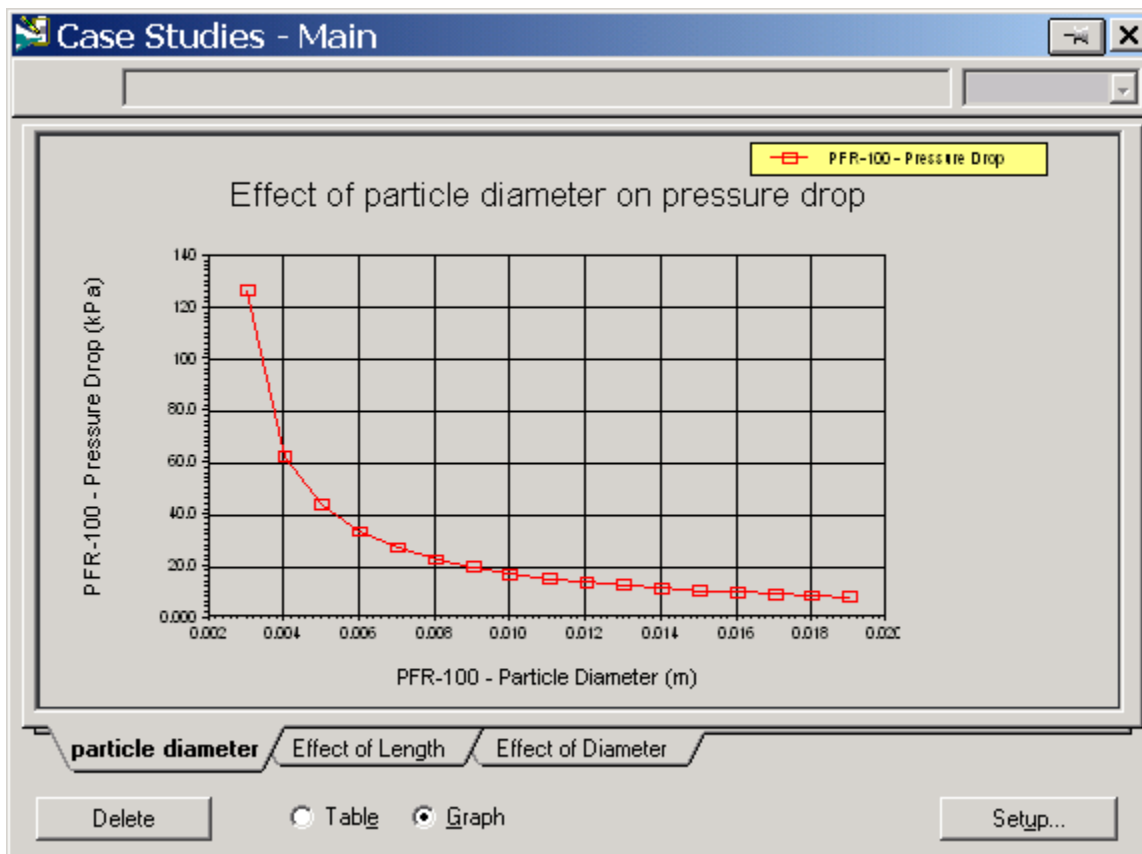


Figure 2: Effect of Particle Diameter on Pressure Drop for a reactor with spherical particles and a void fraction of 0.33, volume of 163 m³, length of 2.19 m, diameter 9.73 m and pre-exponential in the rate expression of 107.8 mol/(L_{gas} s kPa).

Reference:

¹ Hermann, Ch.; Quicker, P.; Dittmeyer, R., "Mathematical simulation of catalytic dehydrogenation of ethylbenzene to styrene in a composite palladium membrane reactor." J. Membr. Sci. (1997), 136(1-2), 161-172.