HYSYS – Multiple Reactions - Styrene
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Styrene Reactor System

You have been studying how to use HYSYS using the example of a Styrene reactor system. In this session you will use multiple reactions, rates and reactors to model this system. Styrene is made from the dehydrogenation of ethylbenzene:

$$C_6H_5{-}C_2H_5 \xleftrightarrow{r_{EB1}} C_6H_5{-}CH{=}CH_2 + H_2 \quad (1)$$

This reaction mechanism includes several undesired side reactions that produce toluene and benzene:

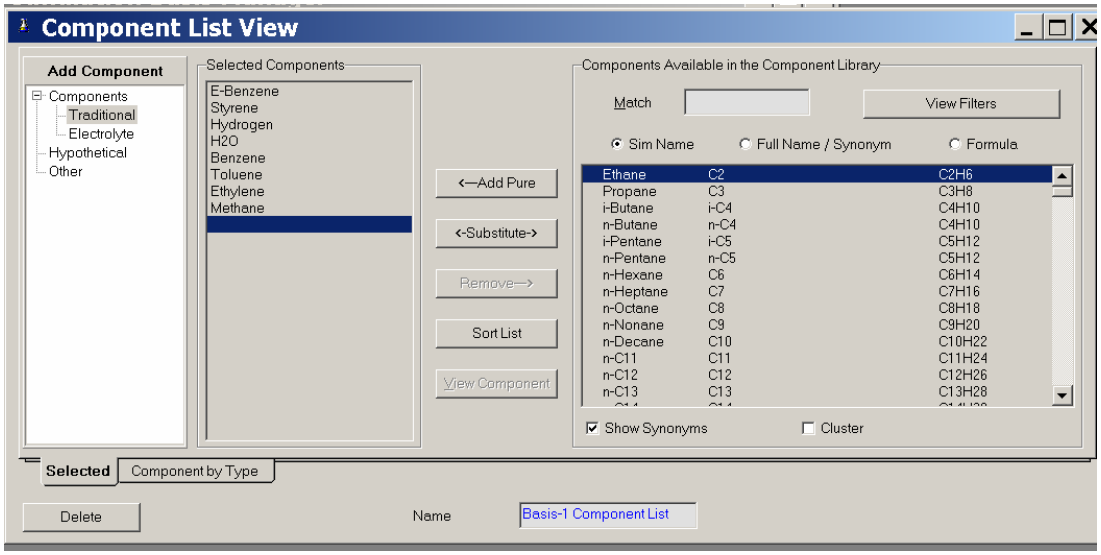
$$C_6H_5{-}C_2H_5 \xleftrightarrow{r_{EB2}} C_6H_6 + CH_2{=}CH_2 \quad (2)$$

$$C_6H_5{-}C_2H_5 + H_2 \xleftrightarrow{r_{EB3}} C_6H_5CH_3 + CH_4 \quad (3)$$

First set your units using Tools, Preferences for the workbook to the following

Pressure	Bar
Flow	gmole/s
Component flow	gmole/s
Temperature	K
Heat flow	KJ/s

Add the required chemical species based on the reactions above and use the Peng-Robinson Equation of State. Ethylbenzene, styrene, hydrogen, benzene, ethane, toluene, methane and steam.



The reaction rates are from Hermann[1]

$$r_{EB1} = -7.491\times10^{-2}\,\frac{\text{mol EB}}{\text{g}_{\text{cat}}\text{s kPa}}\exp\left[-\frac{21874\ \text{cal/mol}}{\left(1.987\,\frac{\text{cal}}{\text{mol K}}\right)T}\right]\left(p_{EB} - \frac{p_{Styrene}\,p_{H_2}}{K_P}\right) \quad (4)$$

In the simple rate reaction type the equilibrium constant is given as

$$\ln(K) = A + B/T + C\ln(T) + DT \tag{5}$$

The above reaction rate is converted again to the HYSYS requirement of a basis of gas volume within reactor:

$$r_{HYSYS} = r\rho_c \frac{(1-\phi)}{\phi} \tag{6}$$

The properties of the catalyst are

$$\phi = 0.445 \tag{7}$$

$$\rho_{cat} = 2146\ \mathrm{kg_{cat}}/\mathrm{m^3_{cat}} \tag{8}$$

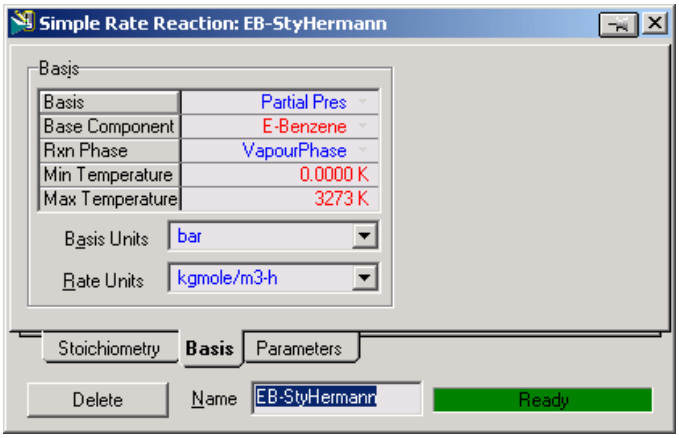
$$D_p = 3\ \mathrm{mm} \tag{9}$$

$$r_{EB1} = -7.217\times10^{7}\ \frac{\mathrm{kmol\ EB}}{\mathrm{m^3_{gas}\ hr\ bar}} \exp\left[-\frac{91{,}320\ \mathrm{J/mol}}{\left(8.314\ \frac{\mathrm{J}}{\mathrm{mol\ K}}\right)T}\right]\left(p_{EB} - \frac{p_{Styrene}\,p_{H_2}}{K_P}\right) \tag{10}$$

$$r_{EB2} = -9.924\times10^{12}\ \frac{\mathrm{kmol\ EB}}{\mathrm{m^3_{gas}\ hr\ bar}} \exp\left[-\frac{208{,}000\ \mathrm{J/mol}}{\left(8.314\ \frac{\mathrm{J}}{\mathrm{mol\ K}}\right)T}\right]\left(p_{EB}\right) \tag{11}$$

$$r_{EB3} = -8.209\times10^{7}\ \frac{\mathrm{kmol\ EB}}{\mathrm{m^3_{gas}\ hr\ bar^2}} \exp\left[-\frac{91{,}500\ \mathrm{J/mol}}{\left(8.314\ \frac{\mathrm{J}}{\mathrm{mol\ K}}\right)T}\right]\left(p_{EB}\,p_{H_2}\right) \tag{12}$$

Remember these above rates are only for a void fraction of 0.445.
The units for the 3 reaction rates are kgmole/m^3-hr as given in the adjacent figure. The activation energies have units kJ/kgmole. Reaction 10 is a HYSYS *simple rate* and reactions 11 and 12 are HYSYS *kinetic reaction* types.



Install these 3 reactions into a new reaction set using the following information that was given in equations 10 through 12.

Simple Rate: EB-StyHermann

STOICHIOMETRY

Component	Molecular Weight	Stoichiometric Coefficient
E-Benzene	106.2	-1 *
Styrene	104.2	1 *
Hydrogen	2.016	1 *

Balance Error : 0.0000 — Reaction Heat (25 C) : 1.176e+005 kJ/kgmole

BASIS

Basis	Base Component	Rxn Phase	Min. Temp (K)	Max. Temp (K)
Partial Pres	E-Benzene	VapourPhase	0.0000	3273

PARAMETERS

Forward Reaction		Reverse Reaction	
A : 7.217e+007	*	A' : -5.476	*
E : 9.132e+004	*	B' : -1.341e+004	*
		C' : 3.152	*
		D' : -2.370e-003	*

Date/Time: Mon Mar 07 14:11:07 2005

Kinetic: rxn2EB_to_benzene_hermann

STOICHIOMETRY

Component	Molecular Weight	Stoich Coeff	Forward Order	Reverse Order
E-Benzene	106.2	-1 *	1.000	0.0000
Benzene	78.11	1 *	0.0000	1.000
Ethylene	28.05	1 *	0.0000	1.000

Balance Error : 0.0000 — Reaction Heat (25 C) : 1.055e+005 kJ/kgmole

BASIS

Basis	Base Component	Rxn Phase	Min. Temp (C)	Max. Temp (C)
Partial Pres	E-Benzene	VapourPhase	-273.1	3000

PARAMETERS

Forward Reaction		Reverse Reaction
A : 9.924e+012	*	A' : ---
E : 2.080e+005	*	E' : ---

Kinetic: rxn3_EB_to_toluene-hermann

STOICHIOMETRY

Component	Molecular Weight	Stoich Coeff	Forward Order	Reverse Order
E-Benzene	106.2	-1 *	1.000	0.0000
Hydrogen	2.016	-1 *	1.000	0.0000
Toluene	92.14	1 *	0.0000	1.000
Methane	16.04	1 *	0.0000	1.000

Balance Error : 0.0000 — Reaction Heat (25 C) : -5.468e+004 kJ/kgmole

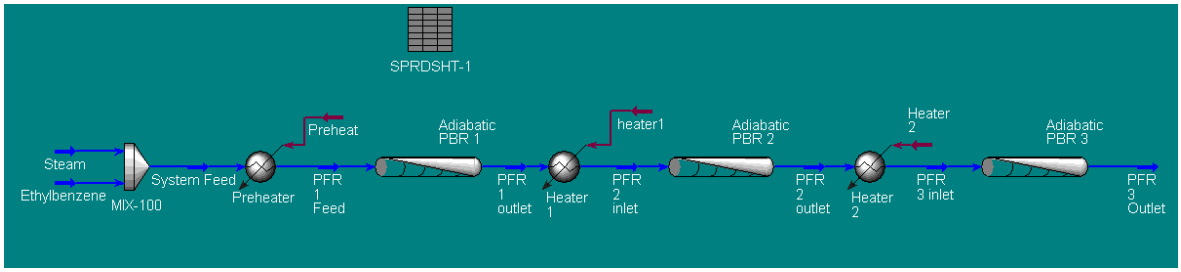
BASIS

Basis	Base Component	Rxn Phase	Min. Temp (K)	Max. Temp (K)
Partial Pres	E-Benzene	VapourPhase	0.0000	3273

PARAMETERS

Forward Reaction		Reverse Reaction
A : 8.209e+007	*	A' : ---
E : 9.150e+004	*	E' : ---

Next add 3 adiabatic PBR reactors, mixer and 3 heaters as shown in the pdf below.



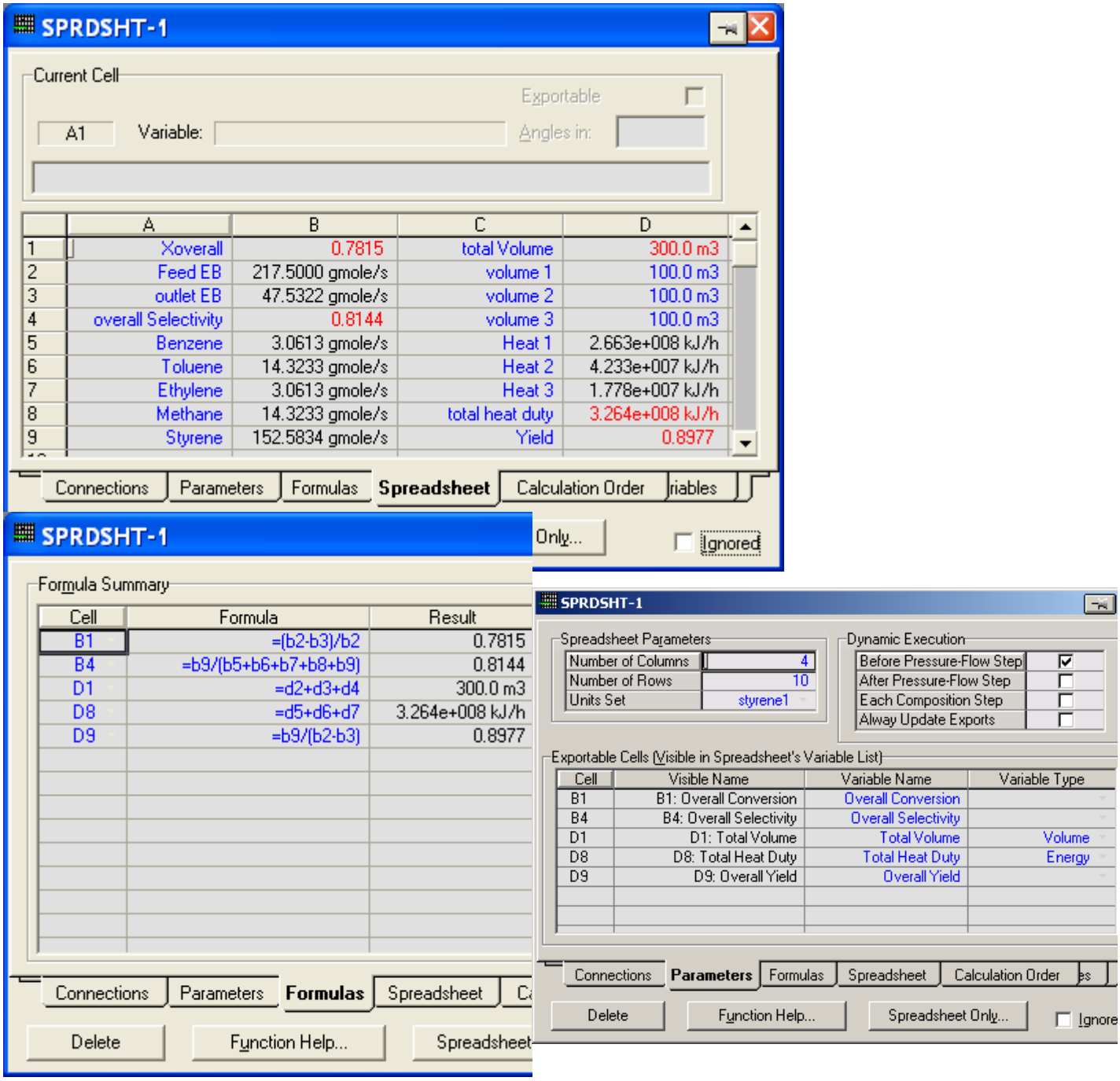
The system feed is from an ethylbenzene plant. To simplify this analysis we will assume that the steam is mixed with pure ethylbenzene in the mixer and then is heated from a temperature of 110°C to 880 K. The pressure of these streams is 1.4 bar. Assume for this simulation that the heat exchangers have no pressure drop. The flowrate of ethylbenzene is 217.5 gmole/s. The steam stream should be input with a mole fraction of 1 for steam and 2610 gmole/s for the Flow of the steam stream. This is done so that you can manipulate the steam flowrate using the databook and/or optimizer. HYSYS can not change the single values of mole fractions with external sources (e.g. spreadsheet, databook) (See Workbook printout below for help).
I would suggest starting with equal volume reactors with 100 m^3 each with a length of 0.7 m each. Set the inlet temperature to each reactor to 880 K. Turn on the Ergun Equation to calculate pressure drop.

Name	Steam	Ethylbenzene	System Feed	PFR 1 Feed	PFR 1 outlet
Vapour Fraction	1.0000	0.0000	1.0000	1.0000	1.0000
Temperature [K]	471.7	383.1	383.1	880.0	809.5
Pressure [bar]	1.400	1.400	1.400	1.400	1.377
Molar Flow [gmole/s]	2610	217.5	2827	2827	2925
Mass Flow [kg/h]	1.693e+005	8.313e+004	2.524e+005	2.524e+005	2.524e+005
Liquid Volume Flow [m3/h]	169.6	95.55	265.2	265.2	272.8
Heat Flow [kJ/s]	-6.137e+005	1112	-6.126e+005	-5.386e+005	-5.386e+005
Name	PFR 2 inlet	PFR 2 outlet	PFR 3 inlet	PFR 3 Outlet	** New **
Vapour Fraction	1.0000	1.0000	1.0000	1.0000	
Temperature [K]	880.0	850.7	880.0	871.2	
Pressure [bar]	1.377	1.352	1.352	1.325	
Molar Flow [gmole/s]	2925	2968	2968	2983	
Mass Flow [kg/h]	2.524e+005	2.524e+005	2.524e+005	2.524e+005	
Liquid Volume Flow [m3/h]	272.8	276.4	276.4	277.8	
Heat Flow [kJ/s]	-5.268e+005	-5.267e+005	-5.218e+005	-5.218e+005	

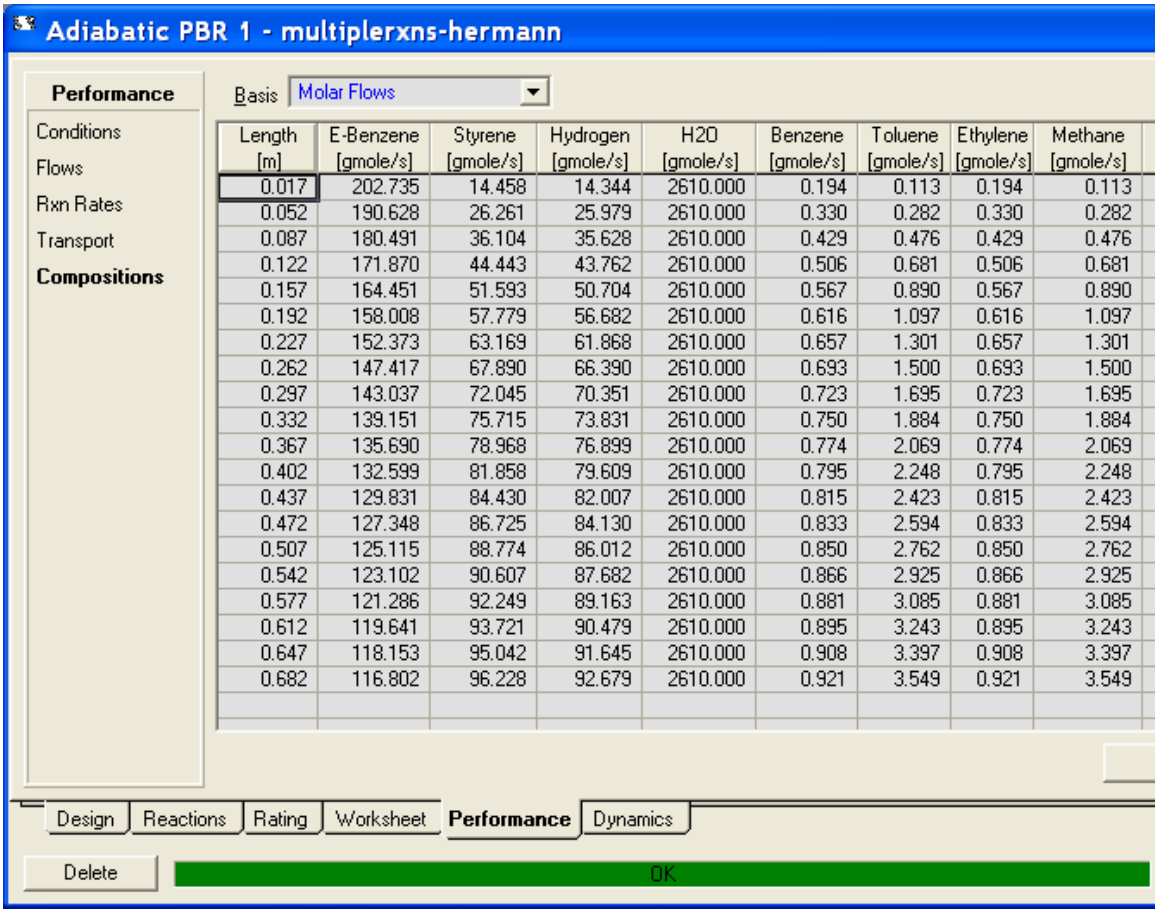
Name	Steam	Ethylbenzene	System Feed	PFR 1 Feed	PFR 1 outlet
Temperature [K]	471.6	383.1	383.1	880.0	809.5
Comp Molar Flow (E-Benzene) [g	0.0000	217.5000	217.5000	217.5000	116.8021
Comp Molar Flow (Styrene) [gmol	0.0000	0.0000	0.0000	0.0000	96.2281
Comp Molar Flow (Hydrogen) [gm	0.0000	0.0000	0.0000	0.0000	92.6791
Comp Molar Flow (H2O) [gmole/s	2610.0000	0.0000	2610.0000	2610.0000	2610.0000
Comp Molar Flow (Benzene) [gm	0.0000	0.0000	0.0000	0.0000	0.9210
Comp Molar Flow (Toluene) [gmo	0.0000	0.0000	0.0000	0.0000	3.5491
Comp Molar Flow (Ethylene) [gm	0.0000	0.0000	0.0000	0.0000	0.9210
Comp Molar Flow (Methane) [gm	0.0000	0.0000	0.0000	0.0000	3.5491
Name	PFR 2 inlet	PFR 2 outlet	PFR 3 inlet	PFR 3 Outlet	** New **
Temperature [K]	880.0	850.7	880.0	871.2	
Comp Molar Flow (E-Benzene) [g	116.8021	67.6646	67.6646	47.5322	
Comp Molar Flow (Styrene) [gmol	96.2281	138.5859	138.5859	152.5834	
Comp Molar Flow (Hydrogen) [gm	92.6791	129.3247	129.3247	138.2601	
Comp Molar Flow (H2O) [gmole/s	2610.0000	2610.0000	2610.0000	2610.0000	
Comp Molar Flow (Benzene) [gm	0.9210	1.9885	1.9885	3.0613	
Comp Molar Flow (Toluene) [gmo	3.5491	9.2613	9.2613	14.3233	
Comp Molar Flow (Ethylene) [gm	0.9210	1.9885	1.9885	3.0613	
Comp Molar Flow (Methane) [gm	3.5491	9.2613	9.2613	14.3233	

Next I would suggest that you put in the overall conversion, heat duty, total volume, overall yield and selectivity into a spreadsheet.
For this tutorial we will define the overall selectivity as

$$S_{overall} = \frac{F_{styrene}}{F_{Benzene} + F_{Ethylene} + F_{Toluene} + F_{Methane}} \tag{13}$$

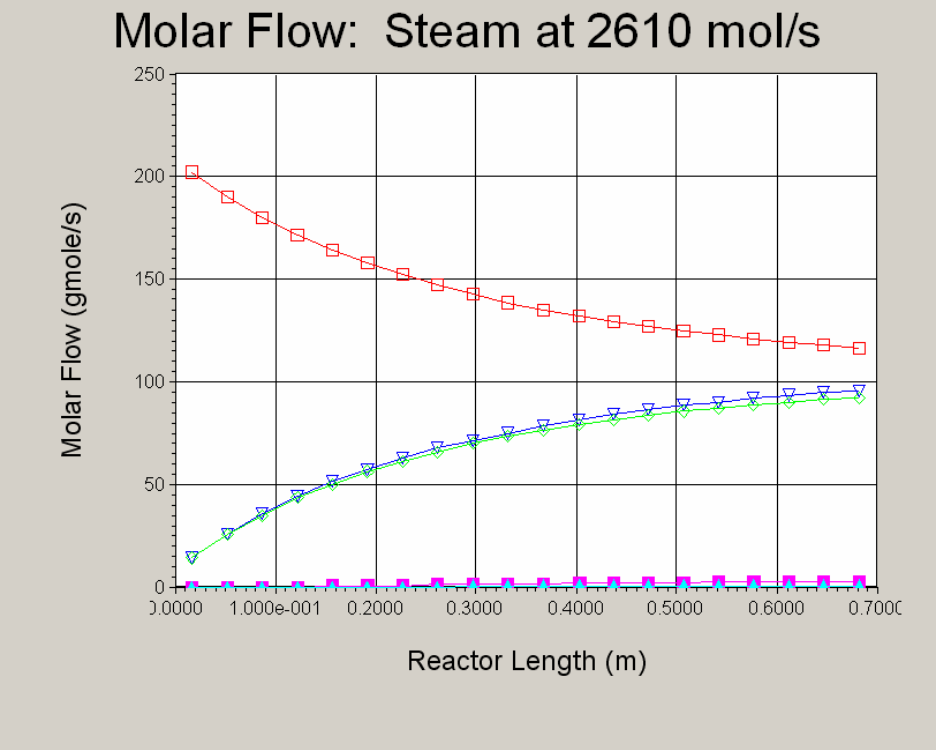


You should now have the following result:



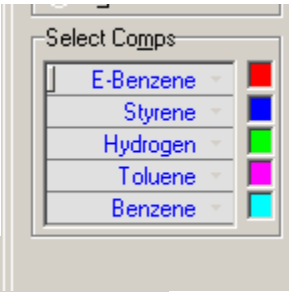
Length [m]	E-Benzene [gmole/s]	Styrene [gmole/s]	Hydrogen [gmole/s]	H2O [gmole/s]	Benzene [gmole/s]	Toluene [gmole/s]	Ethylene [gmole/s]	Methane [gmole/s]
0.017	202.735	14.458	14.344	2610.000	0.194	0.113	0.194	0.113
0.052	190.628	26.261	25.979	2610.000	0.330	0.282	0.330	0.282
0.087	180.491	36.104	35.628	2610.000	0.429	0.476	0.429	0.476
0.122	171.870	44.443	43.762	2610.000	0.506	0.681	0.506	0.681
0.157	164.451	51.593	50.704	2610.000	0.567	0.890	0.567	0.890
0.192	158.008	57.779	56.682	2610.000	0.616	1.097	0.616	1.097
0.227	152.373	63.169	61.868	2610.000	0.657	1.301	0.657	1.301
0.262	147.417	67.890	66.390	2610.000	0.693	1.500	0.693	1.500
0.297	143.037	72.045	70.351	2610.000	0.723	1.695	0.723	1.695
0.332	139.151	75.715	73.831	2610.000	0.750	1.884	0.750	1.884
0.367	135.690	78.968	76.899	2610.000	0.774	2.069	0.774	2.069
0.402	132.599	81.858	79.609	2610.000	0.795	2.248	0.795	2.248
0.437	129.831	84.430	82.007	2610.000	0.815	2.423	0.815	2.423
0.472	127.348	86.725	84.130	2610.000	0.833	2.594	0.833	2.594
0.507	125.115	88.774	86.012	2610.000	0.850	2.762	0.850	2.762
0.542	123.102	90.607	87.682	2610.000	0.866	2.925	0.866	2.925
0.577	121.286	92.249	89.163	2610.000	0.881	3.085	0.881	3.085
0.612	119.641	93.721	90.479	2610.000	0.895	3.243	0.895	3.243
0.647	118.153	95.042	91.645	2610.000	0.908	3.397	0.908	3.397
0.682	116.802	96.228	92.679	2610.000	0.921	3.549	0.921	3.549

Examine the effect of steam on the conversion ethylbenzene and selectivity styrene over byproducts. Open the first reactor and bring up the plots of composition of chemical species as shown below:

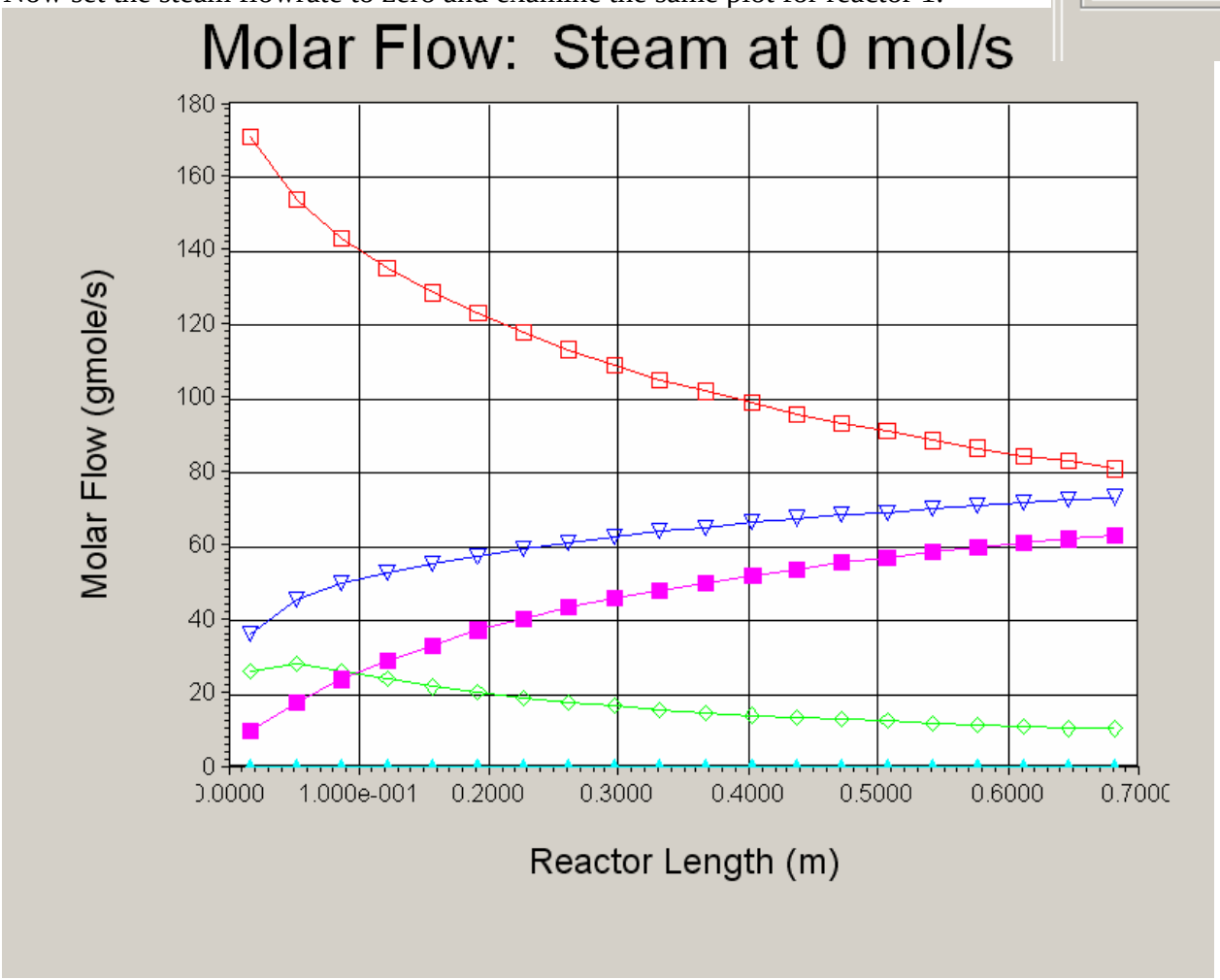


Make a plot of the molar flowrates as a function of reactor length by pressing the Plot button and plotting all of the species. (Right click on

plot to change titles and copy plot)



Now set the steam flowrate to zero and examine the same plot for reactor 1.

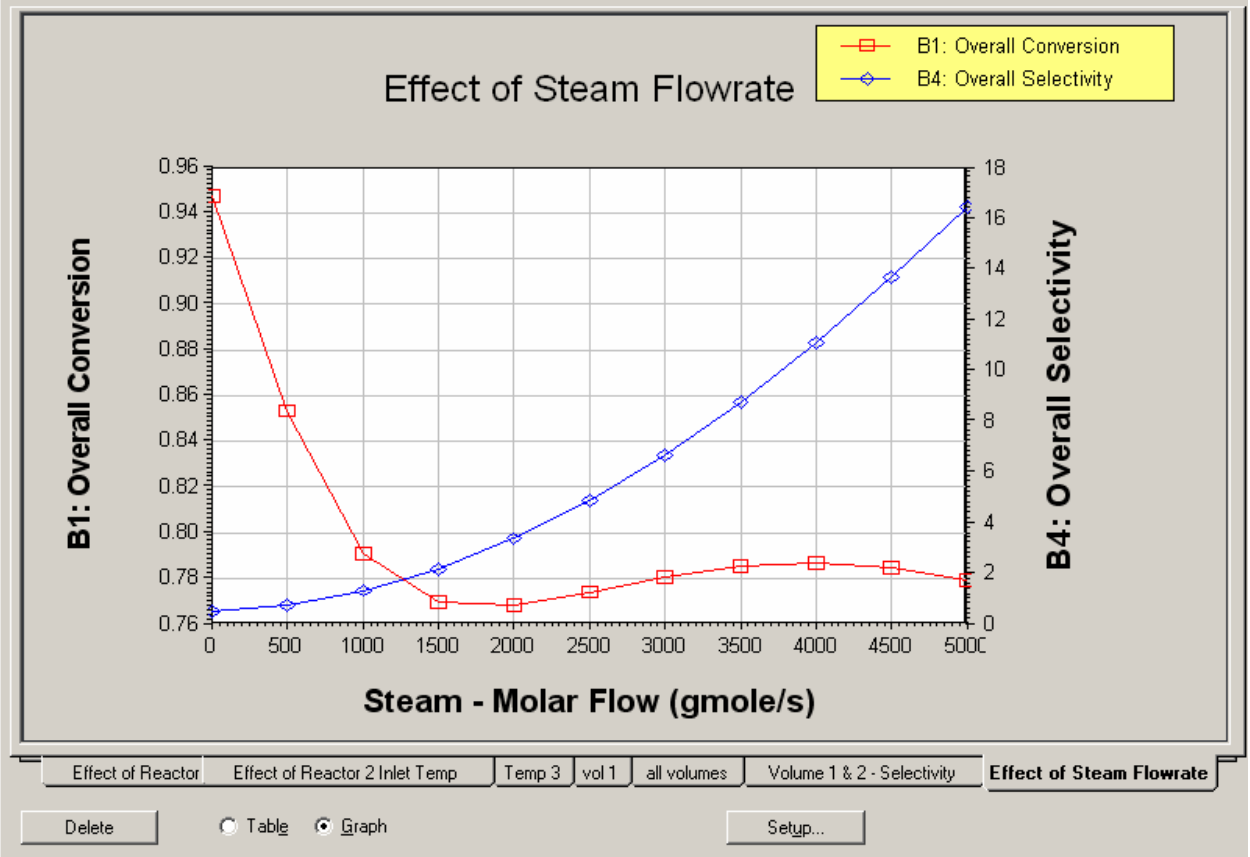


Notice that the production of styrene exiting reactor 1 has dropped from 96 to 72 mol/s. Also notice that the amount of the byproduct (undesired) toluene exiting reactor 1 has increased dramatically from 3.55 to 62 mol/s. This shows one of the effects of steam; it dilutes concentration of all species and lowers the byproduct reaction rates.

Now Open the Databook and examine the following: **(Remember that after each databook run the parameters that you are changing are left at the ending value. For example if you are changing the temperature from 600 to 1000 K, then at the end of the databook run the temperature will be left at 1000 K)**

1. Examine the effect of varying the steam flow to the reactor system on the overall conversions and selectivity of the reactor system. What effect would it have on reactor pressure drop if you had a smaller diameter reactor?

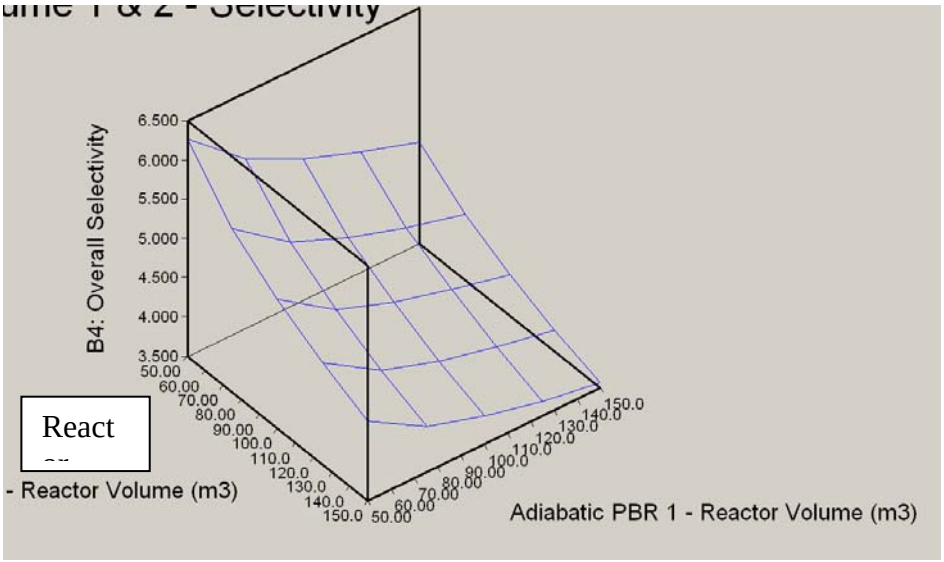
a. Vary the steam Flow from 0 to 5000.
b. Make a plot of Conversion and Selectivity as a function of Steam Flow.



Notice that the overall conversion drops with flowrate. This drop in conversion is caused by a decrease in byproduct formation. Remember conversion is only telling you that your reactants reacted, but it does not tell you what the reactants formed. Your selectivity indicates the ratio of desired products to undesired products. Now reset the value of the Steam Flow to 2610 mol/s.

2. After you have reset the value of the steam flow to 2610 mol/s, then examine the effect of at least 2 other parameters such as reactor volumes, inlet temperature to the reactors on the overall conversion, yield and selectivity. If you vary 2 parameters at one time HYSYS will produce a 3-D plot of your results (See next page)

3. Write a summary of your findings. Provide graphs to explain your trends.



Optional For Experts:
Now if you dare, examine the reactor using the optimizer. This feature is described in the Operations Guide Manual in Chapter 13.
The following terms are used in the manual and optimizer:

Terms	Definition
Primary Variables	These are the variables imported from the Flowsheet whose values are manipulated in order to minimize (or maximize) the objective function. You set the upper and lower bounds for all of the primary variables, which are used to set the search range, as well as for normalization.
Objective Function	This is the function which is to be minimized or maximized. There is a great deal of flexibility in describing the Objective Function; primary variables may be imported and functions defined within the *Optimizer* SpreadSheet, which possesses the full capabilities of the *Main Flowsheet* SpreadSheet.
Constraint Functions	*Inequality and Equality* Constraint functions may be defined in the Optimizer SpreadSheet. An example of a constraint is the product of two variables satisfying an inequality (e.g. -A*B<K). The *Box*, *Mixed* and *Sequential Quadratic Programming* (SQP) methods are available for constrained minimization with *inequality* constraints. Only the SQP method can handle equality constraints. The *Fletcher-Reeves* and *Quasi-Newton* methods are available for unconstrained optimization problems.

For our first objective function let's maximize the yield of styrene by changing the reactor inlet temperatures. You must put in some constraints such as having the overall conversion greater than 0.6.

To start the optimizer use simulation, optimizer or press F5.

[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. **136**(1-2) 161-172 (1997).