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:

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

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

$$C_{6}H_{5}-C_{2}H_{5} \xleftarrow{r_{EB2}}{} C_{6}H_{6}+CH_{2}=CH_{2}$$

$$\tag{2}$$

$$C_{6}H_{5}-C_{2}H_{5}+H_{2} \xleftarrow{r_{EB3}}{} C_{6}H_{5}CH_{3}+CH_{4}$$
(3)

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

Pressure	Bar
Flow	gmole/s
Component flow	gmole/s
Temperature	Κ
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.

& Component	List View				
Add Component	Selected Components		-Components Availa	able in the Component Library	
Components	E-Benzene Styrene		Match		View Filters
Electrolyte Hypothetical	H2O Benzene		Sim Name	C Full Name / Synonym	C Formula
- Other	Toluene Ethylene	<add pure<="" th=""><th>Ethane Propane</th><th>C2 C3 FC4</th><th>C2H6</th></add>	Ethane Propane	C2 C3 FC4	C2H6
	meurare	<-Substitute->	n-Butane i-Pentane	n-C4 i-C5	C4H10 C5H12
		Remove>	n-Pentane n-Hexane n-Hentane	n-C5 C6 C7	C5H12 C6H14 C7H16
		Sort List	n-Octane n-Nonane	C8 C9	C8H18 C9H20 C10H22
		View Component	n-C11 n-C12	C11 C12	C11H24 C12H26
		view component	n-C13		C13H28
			I≝ Silow Syllonyin		
Selected Compon	ent by Type				
Delete		Name Basis-1	Component List		

The reaction rates are from Hermann¹

$$r_{EB1} = -7.491 \times 10^{-2} \frac{\text{mol EB}}{g_{cat} \text{s kPa}} \exp\left[-\frac{21874 \text{ cal/mol}}{\left(1.987 \frac{\text{cal}}{\text{mol K}}\right)T}\right] \left(p_{EB} - \frac{p_{Styrene} p_{H_2}}{K_P}\right)$$
(4)

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

$$\ln(K) = A + B/T + C\ln(T) + DT$$
(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

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

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

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

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

$$r_{EB2} = -9.924 \times 10^{12} \frac{\text{kmol EB}}{\text{m}_{\text{gas}}^3 \text{ hr bar}} \exp \left[-\frac{208,000 \text{ J/mol}}{\left(8.314 \frac{\text{J}}{\text{mol K}}\right)T} \right] (p_{EB})$$
(11)

$$r_{EB3} = -8.209 \times 10^{7} \frac{\text{kmol EB}}{\text{m}_{\text{gas}}^{3} \text{ hr bar}^{2}} \exp\left[-\frac{91,500 \text{ J/mol}}{\left(8.314 \frac{\text{J}}{\text{mol K}}\right)T}\right] \left(p_{EB} p_{H_{2}}\right)$$
(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.

Simple Rate Reaction: EB-StyHermann 🛛 🔣 🗵						
Basis						
Basis	Partial Pres					
Base Component	E-Benzene 👘					
Rxn Phase	VapourPhase 👘					
Min Temperature	0.0000 K					
Max Temperature	3273 K					
B <u>a</u> sis Units 🛛	oar 💌					
<u>R</u> ate Units	kgmole/m3-h 💌					
	Basis Parameters					
Delete	Name EB-StyHermann	Ready				

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

Simp	le Rate: I	EB-Sty⊦	lerm	ann	1				
			ST	оісні	OMETRY				
Сотроле	nt			Moleci	ular Weight		Stoichi	ometric Co	efficient
componer	E-Benz	ene		110100		106.2	2	00	-1 *
	Styr	rene				104.2	2		1 *
	Hydro	oqen				2.016	3		1 *
Balance	Error: 0.0000					Reaction	Heat (25 C): 1.176e+0)05 kJ/kam	ole
				BA	sis				
Basis	Base Com	ponent		Rxn F	Phase		Min. Temp	Ν	Max. Temp
Partial Pres		E-Benzene			VapourPhase		0.0000		3273
			P	ARAN	METERS				
Fo	rward Reactior	I					Reverse Reaction	on	
	A: 7.217e+00	7		×			A': -5.476		*
	E: 9.132e+004	4		*			B': -1.341e+	004	*
							<u>C': 3.152</u>		*
							D': -2.3/Ue-	JU3	
	Kinet	ic: rxn	2EB_	to_	benzene	_herr	nann		
Compor	ant	Molocula	ar Moight	SI		Υ off	Ecoward Order		Bayaraa Ordar
Compor	E-Benzene	Molecula	ar vvelgrit 1	06.2	SLUICH CU	-1	* Forward Order	1 000	
	Benzene		. 7	8.11		1	* 0	.0000	1.00
	Ethylene		2	8.05		1	* 0	.0000	1.00
	<u> </u>								1.4 1
	Balarice Error . 0.1	000			BASIS	Re	action Heat (25 C) . 1.0	556+005 K	Jrkgmule
Basis	Ba	ise Component			R×n Phase	Rxn Phase Min. Temp Max. Tem (C) (C)			Max. Temp (C)
Parti	al Pres	E-Ber	nzene		VapourPl	hase	-27	3.1	300
				P	ARAMETERS				
	Forward Re	eaction					Reverse Re	action	
	A: 9.	924e+012			*		A':		
	E: 2.	080e+005			*		E':		
	Kinetic: ı	xn3_E	3_to	_tol	uene-hei	man	n		
			ST	OICH	IOMETRY				
Component -	M	olecular Weight	t		Stoich Coeff	4.1	Forward Order	_	Reverse Order
<u> </u>			106.2			-1 *	1.000	_	0.0000
F	Toluene		2.016			-1	1.000	_	4.000
	Methane		16.04			1 *	0.0000		1.000
						·	0.0000		
Balance	Error : 0.0000					Reaction	Heat (25 C) : -5.468e+	004 kJ/kqm	nole
				BA	SIS				
Basis	Base Comp	onent		Rxn P	Phase		Min. Temp (K)		Max. Temp (K)
Partial Pres		E-Benzene			VapourPhase		0.0000		3273
			Р	ARAN	METERS				
F	Forward Reaction						Reverse Reaction		
	A: 8.209e+00	7					<u>A':</u>		
	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 m³ 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) [gmd	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 **
Name Temperature [K]	PFR 2 inlet 880.0	PFR 2 outlet 850.7	PFR 3 inlet 880.0	PFR 3 Outlet 871.2	** New **
Name Temperature [K] Comp Molar Flow (E-Benzene) [g	PFR 2 inlet 880.0 116.8021	PFR 2 outlet 850.7 67.6646	PFR 3 inlet 880.0 67.6646	PFR 3 Outlet 871.2 47.5322	** New **
Name Temperature [K] Comp Molar Flow (E-Benzene) [g Comp Molar Flow (Styrene) [gmol	PFR 2 inlet 880.0 116.8021 96.2281	PFR 2 outlet 850.7 67.6646 138.5859	PFR 3 inlet 880.0 67.6646 138.5859	PFR 3 Outlet 871.2 47.5322 152.5834	×* New **
Name Temperature [K] Comp Molar Flow (E-Benzene) [g Comp Molar Flow (Styrene) [gmol Comp Molar Flow (Hydrogen) [gm	PFR 2 inlet 880.0 116.8021 96.2281 92.6791	PFR 2 outlet 850.7 67.6646 138.5859 129.3247	PFR 3 inlet 880.0 67.6646 138.5859 129.3247	PFR 3 Outlet 871.2 47.5322 152.5834 138.2601	** New **
Name Temperature [K] Comp Molar Flow (E-Benzene) [g Comp Molar Flow (Styrene) [gmol Comp Molar Flow (Hydrogen) [gm Comp Molar Flow (H2O) [gmole/s	PFR 2 inlet 880.0 116.8021 96.2281 92.6791 2610.0000	PFR 2 outlet 850.7 67.6646 138.5859 129.3247 2610.0000	PFR 3 inlet 880.0 67.6646 138.5859 129.3247 2610.0000	PFR 3 Outlet 871.2 47.5322 152.5834 138.2601 2610.0000	** New **
Name Temperature [K] Comp Molar Flow (E-Benzene) [g Comp Molar Flow (Styrene) [gmol Comp Molar Flow (Hydrogen) [gm Comp Molar Flow (H2O) [gmole/s Comp Molar Flow (Benzene) [gmole/s	PFR 2 inlet 880.0 116.8021 96.2281 92.6791 2610.0000 0.9210	PFR 2 outlet 850.7 67.6646 138.5859 129.3247 2610.0000 1.9885	PFR 3 inlet 880.0 67.6646 138.5859 129.3247 2610.0000 1.9885	PFR 3 Outlet 871.2 47.5322 152.5834 138.2601 2610.0000 3.0613	** New **
Name Temperature [K] Comp Molar Flow (E-Benzene) [g Comp Molar Flow (Styrene) [gmol Comp Molar Flow (Hydrogen) [gm Comp Molar Flow (H2D) [gmole/s Comp Molar Flow (Benzene) [gm	PFR 2 inlet 880.0 116.8021 96.2281 92.6791 2610.0000 0.9210 3.5491	PFR 2 outlet 850.7 67.6646 138.5859 129.3247 2610.0000 1.9885 9.2613	PFR 3 inlet 880.0 67.6646 138.5859 129.3247 2610.0000 1.9885 9.2613	PFR 3 Outlet 871.2 47.5322 152.5834 138.2601 2610.0000 3.0613 14.3233	** New **
Name Temperature [K] Comp Molar Flow (E-Benzene) [g Comp Molar Flow (Styrene) [gmol Comp Molar Flow (Hydrogen) [gm Comp Molar Flow (H2O) [gmole/s Comp Molar Flow (Benzene) [gmo Comp Molar Flow (Toluene) [gmo Comp Molar Flow (Ethylene) [gmo	PFR 2 inlet 880.0 116.8021 96.2281 92.6791 2610.0000 0.9210 3.5491 0.9210	PFR 2 outlet 850.7 67.6646 138.5859 129.3247 2610.0000 1.9885 9.2613 1.9885	PFR 3 inlet 880.0 67.6646 138.5859 129.3247 2610.0000 1.9885 9.2613 1.9885	PFR 3 Outlet 871.2 47.5322 152.5834 138.2601 2610.0000 3.0613 14.3233 3.0613	** New **

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

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

	SPRDS	HT-1					-* 🔀	3		
-0	Current Ce									
				E	<u>x</u> portab	ole				
	A1	Variable:		A	ngles ir	n 🗌				
		,			_	,	_			
		A	В	С		D				
1		Xoverall	0.7815	i total Volu	me	31	00.0 m3			
2		Feed EB	217.5000 gmole/	s volum	e1	10	00.0 m3			
3		outlet EB	47.5322 gmole/	s volum	e 2	11	00.0 m3			
4	07	erall Selectivity	0.8144	l volum	e 3	1	00.0 m3			
5		Benzene	3.0613 gmole/	s Hea	at 1	2.663e+0	08 kJ/h			
6		I oluene	14.3233 gmole/	s Hea	at 2	4.233e+U	07 kJ/h			
6		Ethylene	3.0613 gmole/	s Hea	10.3	1.778e+0 2.264++0	07 KJ7h			
		Sturene	14.3233 gmole/	s total neat d	uty old	3.264e+0	06 KJ/N 0 9977			
臣		Stylene	152.5654 gmole/	s	ciu		0.0377			
~	Connec	tions Parame	eters Formulas	Spreadsheet Ca	alculatio	on Order	riables 🛛	-		
				<u> </u>						
-	SPRDS	HT-1			Onl <u>y</u>		🔲 Ignored			
	Ed- C									
Γ.	For <u>m</u> ula S	ummary			SPR	RDSHT-1				
	Cell	Fe	ormula	Result						
	B1		=(b2-b3)/b2	0.7815		eadsheet Pag	ameters		Dynamic Execu	tion
	B4	=b9/(b	5+b6+b7+b8+b9j	0.8144		umber of Colu umber of Bow	imns <u>I</u>	4	After Pressure	Flow Step 1
	D1		=d2+d3+d4	300.0 m3	Ur	nits Set	styre	ne1 👘	Each Compos	sition Step
	08		=d5+d6+d7	3.264e+008 kJ/h					Alway Update	e Exports
	03		=037(02-03)	0.0377	-Expo	rtable Cells A	/isible in Spreads	heet's Var	iable List)	
						ell	Visible Name		Variable Name	Variable T
					B1	I E	1: Overall Conve	ersion	Overall Convers	ion
					B4	1	B4: Overall Selec	stivity	Overall Selectiv	vity Viel
					DE	3	D1: Total Heat	Duty	Total Heat D	utv En
					DS	3	D9: Overall	Yield	Overall Yi	eld
Ľ										
-	Connec	tions Doctor	tora Formulas	Sprandshoot L.C.		onnections	Parameters	Formulas	Spreadsheet	Calculation Order
	Connec		rormulas			Delete	Eurotio	n Heln	Spreads	neet Only
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_	Delet		<u>shotorrrop</u>							

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Variable Type

Volume Energy

es

🔲 Ignore

anditions	Length	E-Bonzono	Sturenc	Hudrogen	H20	Banzana	Tolueno	Ethulano	Mathany
	Lengun [m]	E-Derizene	Styrene [amolo/o]	Inyurugen Iamala/al	famala (al	female /al	Toluene	Euriyiene Iamolo (al	I amela /a
WS	0.017	[gmole7s] 202.725	[gmole/s]		2610.000		0.112		[gmole/s 0.11
n Rates	0.017	190 629	26.261	25 979	2610.000	0.134	0.113	0.134	0.11
aanat	0.032	180.020	36.104	35.628	2610.000	0.330	0.202	0.330	0.20
ispon	0.007	171 870	44 443	43 762	2610.000	0.423	0.470	0.423	0.47
npositions	0.122	164 451	51 593	50 704	2610.000	0.567	0.001	0.567	0.00
	0.192	158,008	57 779	56,682	2610.000	0.616	1.097	0.616	1.0
	0.102	152.373	63 169	61 868	2610.000	0.657	1.301	0.657	1.3
	0.262	147 417	67,890	66,390	2610.000	0.693	1.500	0.693	1.5
	0.297	143.037	72.045	70.351	2610.000	0.723	1.695	0.723	1.6
	0.332	139 151	75 715	73,831	2610.000	0.750	1 884	0.750	1.8
	0.367	135,690	78,968	76.899	2610.000	0.774	2.069	0.774	2.0
	0.402	132,599	81.858	79.609	2610.000	0.795	2.248	0.795	2.2
	0.437	129.831	84.430	82.007	2610.000	0.815	2.423	0.815	2.4
	0.472	127.348	86.725	84.130	2610.000	0.833	2.594	0.833	2.5
	0.507	125.115	88.774	86.012	2610.000	0.850	2.762	0.850	2.7
	0.542	123.102	90.607	87.682	2610.000	0.866	2.925	0.866	2.9
	0.577	121.286	92.249	89.163	2610.000	0.881	3.085	0.881	3.0
	0.612	119.641	93.721	90.479	2610.000	0.895	3.243	0.895	3.2
	0.647	118.153	95.042	91.645	2610.000	0.908	3.397	0.908	3.3
	0.682	116.802	96.228	92.679	2610.000	0.921	3.549	0.921	3.5
	,								

You should now have the following result:

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?

Select Comps-

E-Benzene Styrene Hydrogen Toluene

- 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)

 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:

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.



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 <i>Optimizer</i> SpreadSheet, which possesses the full capabilities of the <i>Main Flowsheet</i> 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.gA*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.</k).

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).