

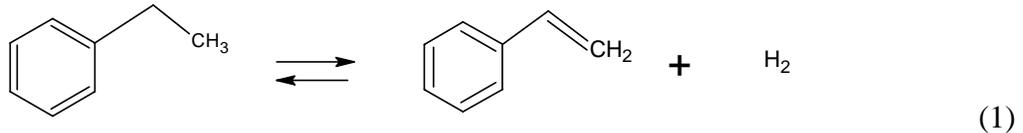
Aspen Plus PFR Reactors Tutorial using Styrene with Equilibrium Considerations

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Section 1:

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:



The conversion of ethylbenzene to styrene is limited by equilibrium. As can be seen in Figure 1, the equilibrium conversion increases with temperature since this is an endothermic reaction. In addition, if an inert species such as steam is added the equilibrium conversion increases. For example at 880 K, the equilibrium conversion is 0.374 and if steam at 10 times the molar flowrate of ethylbenzene is added the conversion increases to 0.725. Why does this happen? How could you have discovered this?

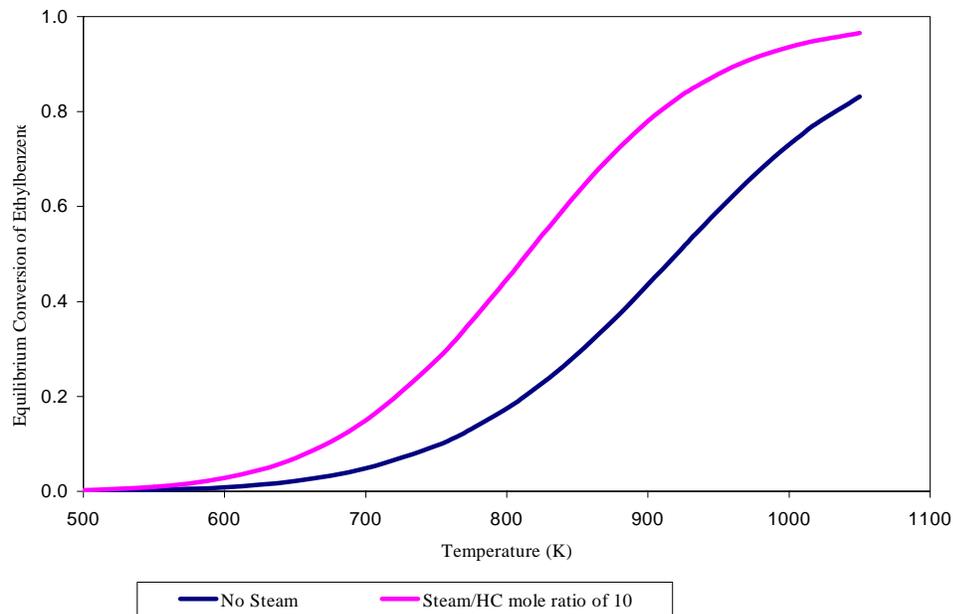


Figure 1: The effect of Temperature and Steam on the Equilibrium Conversion of Ethylbenzene to Styrene. The pressure is 1.36 atm, and the initial flowrate of ethylbenzene is 152.2 mol/s

The reaction rate expression that we will use in this tutorial is from Dittmeyer et al.¹:

$$r_1 = r_{1f} - r_{1r} = -\frac{(k_{1f}P_{EB} - k_{1r}P_{sty}P_{H_2})}{(1 + K_{sty} \cdot p_{sty})} = k_{1f} \frac{\left(P_{EB} - \frac{1}{K_{eq}} P_{sty}P_{H_2} \right)}{(1 + K_{sty} \cdot p_{sty})} \quad (2)$$

Where $k_{1r} = \frac{k_{1f}}{K_p}$. So, $A_{1r} = \frac{A_{1f}}{A_{eq}}$ and $E_{1r} = E_{1f} - E_{eq}$.

$k_{1f} = A_{1f} \exp\left(\frac{-E_{1f}}{R \cdot T}\right)$ where $A_{1f} = 2349.58 \left[\frac{gmol}{kgcat \cdot s \cdot Pa} \right]$ and

$E_{1f} = 158.6 [kJ / gmol]$. The adsorption constant: $K_{sty} = 1.3 \cdot 10^{-4} Pa^{-1}$

Take out a piece of paper and write down the conversion of this **pre-exponential factor for the forward rate constant (A_f)** to SI. This form of the forward rate constant will be used in your simulation.

Hand in this calculation for A_f with your assignment.

For the reverse reaction we will calculate reaction parameters based on the forward rate constant and the equilibrium constant. In the Lab 4 you were provided with equilibrium parameters. In this case we will regress the equilibrium parameters, A_{eq} and E_{eq} , using K_p vs T data. The K_p data is provided in units of atm. First, convert your units of K_p to the SI form [Pa] and plot ($\ln K_p$) vs. $1/T$ (in Kelvins). For this case, use Excel to fit a simple linear expression for ($\ln K_p$) vs $1/T$. So, for

$$\ln K_p = \ln A_{eq} - \frac{E_{eq}}{RT_K} \quad (3)$$

the slope will provide E_{eq}/R , and the intercept will provide $\ln A_{eq}$.

Equilibrium Constant Data:

T (K)	Kp (atm)
500	7.92E-07
550	1.10E-05
600	9.99E-05
650	6.46E-04
700	3.20E-03
750	0.013
775	0.024
800	0.043
810	0.054
820	0.067
830	0.082
840	0.101
850	0.124
860	0.151
870	0.183
880	0.221
890	0.266
900	0.318
910	0.379

¹ Dittmeyer, R., V. Höllein, P. Quicker, G. Emig, G. Hausinger & F. Schmidt., *Chem. Eng. Sci.* **54** (1999) 1432-1439.

920	0.450
930	0.532
950	0.736
970	1.003
990	1.348
1010	1.791
1030	2.351
1050	3.051

Print your Excel graph with parameter fit.

Finally, use the regressed parameters to perform hand calculations (on a piece of paper) for the reverse reaction rate parameters, as illustrated above.

Hand in your calculations with your assignment.

Section 2: Install a Reaction Rate with an Equilibrium Constant – Simple Reaction Rates

We will examine equilibrium reactions in both a plug flow reactor model and an equilibrium reactor model using Aspen Plus. The former permits us to examine how compositions vary axially in the reactor, while the latter provides an indication of where the reaction will go at equilibrium.

1. Start Aspen 13.2.
2. Open a new case by choosing a blank simulation.
3. Choose *Data* from the main menu and click *Setup*. You can enter the title and brief description of the process by choosing the *Description* tab.
4. Select 'SI' units for both input and output results on the Global tab.
5. Under the Report Options, Stream tab, specify Mole and Mass for both the Flow Basis and the Fraction Basis.
6. Choose the *Components* option in the data browser window to start adding chemical components. Install all the chemicals for this reactor: Styrene, ethyl benzene, hydrogen and water.
7. Next, under *Properties, Specifications*, select your base property method. Since these compounds are hydrocarbons, use the Peng-Robinson thermodynamic package.
8. Install RPlug (Kinetic reactor). Using the Model Library, click on *Reactors* and then choose *RPlug*. Click on the *RPlug* icon, then release left mouse button. Move cursor to pfd screen and then press left mouse button only once.
9. Add streams to your reactor in the usual manner.
10. Specify the feed stream with a 10/1 ratio of steam:ethylbenzene. The total molar flow rate of 1674.2 gmol/s (152.2 gmol/s ethylbenzene, 1522 gmol/s water) at initial conditions of 880 K & 1.378 bar.
11. To input the reactor specifications, double click on the reactor block. The reactor Data Browser opens. Specify an isothermal reactor with the length and diameter of the reactor as 7 m and 6.75 m respectively (for 250 m³ reactor). Specify the pressure drop of the reactor as 0 by using the *Pressure* tab.
12. Next, specify the reactions to complete the specification for the PFR. To account for both forward and reverse reactions for the equilibrium reaction (reaction 1), we will enter the reactions for a plug flow reactor as two separate reactions.
 - a. For the reaction set, select reaction type as General. Then for reaction *1f* select type as LHHW.
 - i. Under the *Configuration* tab, specify your stoichiometry.
 - ii. Under the *Kinetic* tab, specify the *phase* as vapor, the *C_i basis* as partial pressure, and the *rate basis* as Cat (wt).

- iii. Specify your pre-exponential factor and activation energy in the *Kinetic Parameter* fields.
- iv. Specify your reaction driving force.
- v. To specify the adsorption term, select Adsorption. Here we need to specify the adsorption terms (in the denominator) as shown here.

- vi. Since styrene has the only concentration driving force for adsorption, it is the only component specified. The first term is 1, so the concentration exponent for the first term is 0, and similarly, for the second term it is 1.
- vii. The adsorption constants are formulated as logarithmic values. Since the first term is 1, $\ln(1) = 0$, so the value specified in the A field is 0. (The additional fields are present to allow for temperature dependence, if applicable).
- viii. Calculated the $\ln K_{sty}$ and specify for Term No. 2.**

b. Specify the next reaction 1r in a similar manner.

13. Run your simulation. You can examine component mole fractions over the reactor length by viewing Results: *Blocks, Profiles* and select *Molar Composition*. Click on the upper left hand corner to copy this Table and paste into an Excel Spreadsheet. EB conversions cannot be calculated directly from the mole fractions, but by creating a stoichiometric table we can see that it can be calculated from mole fraction ratios, say of styrene to EB.

	Moles			Mole Fractions	
	Initial	React/form	Final	Initial	Final
EB	FEB_0	$-FEB_0 \cdot X$	$FEB_0 - FEB_0 \cdot X$	(FEB_0/FT_0)	$(FEB_0 - FEB_0 \cdot X) / (FT_0 + FEB_0 \cdot X)$
Styrene	$FSty_0$	$+ FEB_0 \cdot X$	$FSty_0 + FEB_0 \cdot X$	$(FSty_0/FT_0)$	$(FSty_0 + FEB_0 \cdot X) / (FT_0 + FEB_0 \cdot X)$
H ₂	FH_0	$+ FEB_0 \cdot X$	$FH_0 + FEB_0 \cdot X$	(FH_0/FT_0)	$(FH_0 + FEB_0 \cdot X) / (FT_0 + FEB_0 \cdot X)$
Steam	$FSteam_0$	0	$FSteam_0$	$(FSteam_0/FT_0)$	$(FSteam_0) / (FT_0 + FEB_0 \cdot X)$
Total	FT_0	$+ FEB_0 \cdot X$	$FT_0 + FEB_0 \cdot X$	$(FT_0/FT_0)=1$	$(FT_0 + FEB_0 \cdot X) / (FT_0 + FEB_0 \cdot X)=1$

- 13.1. We will use the mole fractions to back out the ethylbenzene conversion as a function of axial position in the reactor. At any position in the reactor, the ratio of styrene to EB mole fractions can be expressed as:

$$f = \frac{(FSty_0 + FEB_0 \cdot X)}{(FEB_0 - FEB_0 \cdot X)} \quad (9)$$

- 13.2. For $FSty_0 = 0$, this reduces to f as a function of X

$$f = \frac{(FEB_0 \cdot X)}{(FEB_0 - FEB_0 \cdot X)} = \frac{X}{(1 - X)} \quad (9)$$

which can be rearranged to provide X as a function of f :

$$X = \frac{f}{(1 + f)} \quad (9)$$

- 13.3. In your spreadsheet, use the axial mole fraction values from your Aspen data to calculate f and then calculate conversion, X , as a function of axial position.

Plot ethylbenzene as function of axial reactor position z for this 10:1 steam:EB case and hand in with your assignment.

14. Your equilibrium conversion should be around 72.2%. Comparing this to the hand calculated results (done in class today) for a steam to hydrocarbon molar ratio of 10 is 72.3% at 880 and 1.378 bar.

Examine Equilibrium Results at Large Reactor Volumes

15. Next we'll compare this case to one where we don't have the diluent steam. This is a large reactor with 1/11 the total flow, so we'll see that we approach equilibrium quickly in the reactor. Set the feed flowrate of steam to zero (your total flow will be 152.2 gmol.sec) and run the simulation again.
- 15.1. View your results, and copy your Molar Compositions into your spreadsheet.
- 15.2. Calculate a styrene/EB ratio, and resultant X , as a function of axial position z following the procedure outlined earlier.
16. You should get an equilibrium conversion of about 37.1%. This again is close to what we obtained using hand calculations shows for 880K and 137.8 kPa.
17. How do you know that you have reached the equilibrium conversion that is limiting this reaction?
18. Next, let's explore conversion as a function of reactor temperature using a Sensitivity Block.
- 18.1. Create a sensitivity block, and *Define* variables for ethylbenzene flows in your inlet and outlet streams.
- 18.2. *Vary* a block variable for your reactor block for SPEC-TEMP, and identify a location for ID1: as 1.
- 18.3. *Tabulate* your conversion, defined as 1-Ebout/Ebin.
- 18.4. Run your simulation and save it as case 1.

Export your report file (*.rep) for case 1 and hand in with your assignment.

Make a plot of conversion as a function of reactor temperature and hand in with your assignment.

19. Next we'll explore the effect of pressure on your equilibrium conversion. Save you Aspen file with a new name (say, case 2), and modify the sensitivity block to *Vary* reactor pressure (PRES). Aspen is looking for pressure in SI units, or Pa, so vary over the range of 1E5 to 3E5 in steps of 10000.

Make a plot of conversion as a function of reactor pressure and hand in with your assignment.

20. We discovered in our first run that a diluent can affect equilibrium conversion. So, next we explore the the effect of steam flow conversion.
 - 20.1. Save your simulation as case 3, and modify your sensitivity block to vary a *Mole-Flow* variable – the mole flow of steam in your feed stream over the range of 0-10000 gmol/sec (0-10 kmol/sec) in steps of 500 gmol/sec (.5 kmol/sec).
 - 20.2. Create a plot of conversion as a function of steam flow.

Hand in the plot with your assignment.

- 20.3. Notice that conversion goes through a maximum and then decreases. Why do you think this happens?
- 20.4. Save your simulation as case 3.

Equilibrium Reactor Model

21. Now we will install a second reactor that only contains an equilibrium reaction. Create a new simulation following steps 1-7 above.
22. The REquil block requires an inlet stream and two (vapor and liquid) effluent streams, so add them appropriately.
 - 22.1. Examine the first case for a pure ethylbenzene feed of 152.2 gmol/sec EB.
23. To specify the reactor, double click on the icon.
 - 23.1. Specify T=880K and P=1.378 bar under the Specifications tab.
 - 23.2. Create a new Reaction for the dehydrogenation of ethylbenzene to styrene and hydrogen, and enter stoichiometric coefficients.
 - 23.3. Select the Temperature Approach method for the equilibrium calculation and specify 0K above reactor temperature as a place to do the calculation at an Extent estimate of 0 kmol/sec.
 - 23.4. Examine your stream results, record in your spreadsheet and calculate an EB conversion based on inlet and outlet molar flows. How does this compare to the values you obtained in the RPLUG reactor?

Record these values in your spreadsheet and hand in with your assignment.

24. Finally, consider the case where we dilute our feed with steam. Add 1522 gmol/sec steam to your ethylbenzene feed and re-run your simulation.
 - 24.1. Record stream results in your spreadsheet, calculate the EB conversion, and compare with your results obtained from RPLUG. Why are they different?

Record these values in your spreadsheet and hand in with your assignment.