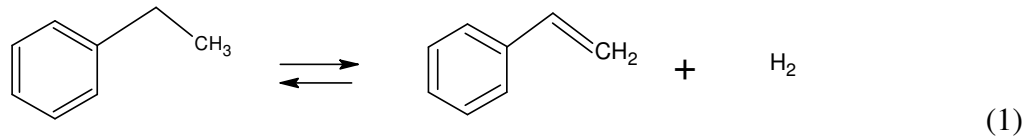


Aspen Plus PFR Reactors Tutorial using Styrene with Multiple Reactions with Langmuir-Hinshelwood-Hougen-Watson Kinetics

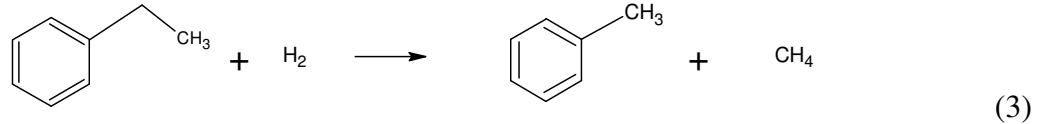
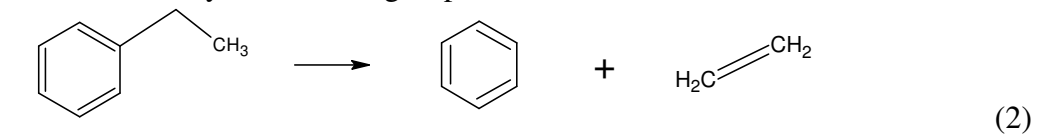
Spring 2008

Section 1:

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



This reaction mechanism includes several undesired side reactions that produce benzene, ethylene, toluene and methane, by the following steps.



The conversion of ethylbenzene to styrene given by reaction (1) is limited by equilibrium. The reaction rate expressions that we will use in this tutorial are derived from Dittmeyer et al.¹ The primary catalytic reaction is described as forward and reverse rates:

$$r_1 = r_{1f} - r_{1r} = -\frac{(k_{1f} p_{EB} - k_{1r} p_{sty} p_{H_2})}{(1 + K_{sty} \cdot p_{sty})} = k_{1f} \frac{\left(p_{EB} - \frac{1}{K_{eq}} p_{sty} p_{H_2} \right)}{(1 + K_{sty} \cdot p_{sty})} \quad (4)$$

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

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

$$E_{1f} = 158.6 \text{ [kJ / gmol]}$$

$$\ln A_{eq} = 27.161 \text{ [Pa]} \text{ and } E_{eq} = 124.261 \text{ kJ / gmol, and } K_{sty} = 1.3 \cdot 10^{-4} \text{ Pa}^{-1}.$$

To use these rates in Aspen, you will need to separate them out as forward and reverse rates.

1. Write down the rate expression for step 1 as two separate steps.
2. Calculate the pre-exponential factor and activation energy for the forward and reverse reactions in SI units.

The secondary reactions to byproducts are described by first order expressions:

$$r_3 = k_3 p_{EB} \text{ for } A_3 = 1.37606 \cdot 10^{-3} \text{ gmol / kgcat} \cdot \text{s} \cdot \text{Pa} \text{ and } E_3 = 114.2 \text{ kJ / gmol} \quad (5)$$

$$r_4 = k_4 p_{EB} \text{ for } A_4 = 47410.7 \text{ gmol / kgcat} \cdot \text{s} \cdot \text{Pa} \text{ and } E_4 = 208. \text{ kJ / gmol} \quad (6)$$

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

3. ASPEN Reaction rates for this LHHW kinetics model must be specified in SI units. Convert all rate parameters to SI Units and hand in these conversions with your lab.

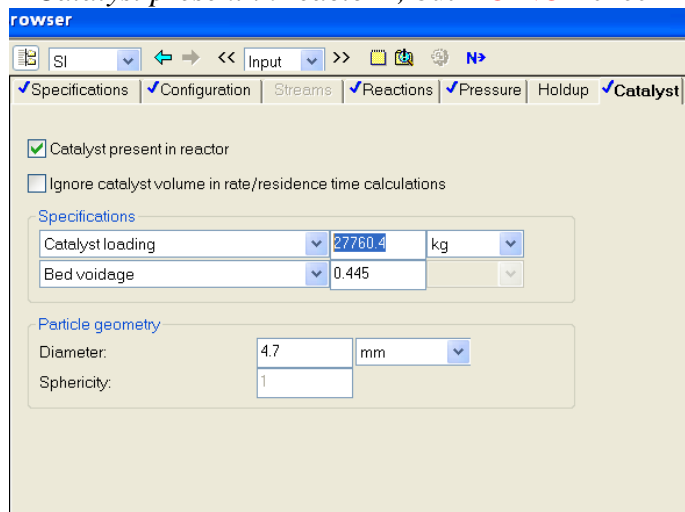
Hand in steps 1 – 3 with your lab.

Install an Aspen Model with Multiple Reaction Rates

Section 2:

We will examine multiple reactions in a two-reactor, plug flow reactor train using Aspen Plus.

4. Start Aspen 2006. Open a new case by choosing a blank simulation.
5. 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.
6. Select 'SI' units for both input and output results on the Global tab.
7. Under the Report Options, Stream tab, specify Mole and Mass for both the Flow Basis and the Fraction Basis.
8. Choose the *Components* option in the data browser window to start adding chemical components. Select the chemicals for a reaction system: ethylbenzene, styrene, hydrogen, water, methane, toluene, benzene and ethylene.
9. Next, under *Properties, Specifications*, select your base property method. Since these compounds are hydrocarbons, use the Peng-Robinson thermodynamic package.
10. Install two RPlug reactors in series with an inter-stage heater between the reactors.
11. Add streams to your reactor in the usual manner.
12. Specify the feed stream starting with a 10/1 ratio of steam:ethylbenzene. (15.22 gmol/s ethylbenzene, 152.2 gmol/s water) at initial conditions of 880 K & 1.378 bar.
13. Specify the heater to set the initial temperature before the second reactor to also be 880K. You'll need to specify a second parameter for your heater. Choose to select a nearly negligible pressure drop by specifying the pressure as -1 N/sqm.
14. Specify two adiabatic reactors of equal volume, 8 ft in diameter and length.
15. Add pressure drop calculation for both reactors using the ERGUN equation (as done in lab 3) with particle diameter of 4.7 mm and void fraction of 0.445. Specify catalyst weight as 27760.4 kg, check "*Catalyst present in reactor*", but **DO NOT** check "*Ignore cat vol ...*".



16. Next, specify the reactions to complete the specification for the PFR.

- a. 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.
 - i. For the reaction set, select reaction type as General. Then for reaction 1f select type as LHHW.
 1. Under the *Configuration* tab, specify your stoichiometry.
 2. Under the *Kinetic* tab, specify the *phase* as vapor, the C_i basis as partial pressure, and the *rate basis* as Cat (wt).
 3. Specify your pre-exponential factor and activation energy in the *Kinetic Parameter* fields.
 4. Specify your reaction driving force.
 5. To specify the adsorption term, select Adsorption. Here we need to specify the adsorption terms (in the denominator) as shown here.

Reacting phase: Vapor

[C] basis: Partial pressure

Adsorption expression: 1

Component	Term no. 1	Term no. 2	Term no. 3
STYRE-01	0	1	
*			

Adsorption constants

Term No.: 1

A: 0 B: 0 C: 0 D: 0

OK Close

Lets you enter/select the term number. See Help.

6. 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.
7. 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).
- 8. Calculated the $\ln K_{sty}$ and specify for Term No. 2.**
 - ii. Specify the next reaction 1r in a similar manner.
- b. Specify the side reactions as reactions 3 & 4.**
- 17.** Run your simulations and copy stream results from each reactor into a spreadsheet.
- 18.** Next, calculate ethylbenzene conversion values, χ , based on the aspen stream output simulation results and record in your spreadsheet.
- 19.** Record the reactor profiles for both reactors, and plot the ethylbenzene, toluene and benzene mole fractions as function of axial reactor position z for this 10:1 steam:EB case and hand in with your lab.
- 20.** Next, calculate the overall selectivity for the reaction for Styrene based on your stream flowrates, and record in your spreadsheet. This can be found by using equation 13 below.

$$S_{styrene} = \frac{F_{styrene}}{F_{benzene} + F_{ethylene} + F_{toluene} + F_{methane}} \quad (14)$$

21. Next, examine the effect of steam flow (from 0—500 gmol/s) on the conversion of ethylbenzene and selectivity of styrene using a sensitivity block or using sequential runs. Be sure to calculate both χ and S_{sty} for each case considered if you do the latter, and record in your spreadsheet.
22. Comment on how the styrene selectivity and ethylbenzene conversion varies with steam flow and hand in with your lab.
23. Export your report file (*.rep) and hand in with your lab.
24. Finally, explore varying the relative sizes of the two reactors (keeping inlet temperature to both set at 880K, and keeping a fixed total volume of the two reactors, and back to the 10:1 steam to EB case). The easiest way to do this is to keep reactor diameter constant, and vary the 2 reactor length for rx1 and rx2. Consider 2 different options, calculate your EB conversion and Styrene selectivity.
25. *Compare these values with what you obtained originally, comment on the difference and why that might be the case, and hand in with your lab.*