Aspen Plus PFR Reactors Tutorial using Styrene with Multiple Reactions

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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:

$$C_6H_5{-}C_2H_5 \overset{r_{eb1}}{\Leftrightarrow} C_6H_5{-}CH=CH_2 + H_2 \quad (1)$$

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

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

$$C_6H_5 - C_2H_5 + H_2 \overset{r_{eb3}}{\rightarrow} C_6H_5 - CH_3 + CH_4 \quad (3)$$

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 from Hermann[1]:

$$r_{EB1} = r_{EB1_f} - r_{EB1_r} = -(k_1 p_{EB} - k_{-1} p_{sty} p_{H_2}) = k_1 \left(p_{EB} - \frac{1}{K_p} p_{sty} p_{H_2} \right) \quad (4)$$

$$r_{EB1} = -7.491\times10^{-2} \frac{\text{gmol EB}}{\text{g}_{\text{cat}}\ \text{s}\ \text{kPa}} \exp\left[-\frac{21874\ \text{cal/mol}}{\left(1.987 \frac{\text{cal}}{\text{mol K}}\right) T} \right] \left(p_{EB} - \frac{p_{Styrene} p_{H_2}}{K_P} \right) \quad (5)$$

$$r_{EB2} = -1.03\times10^{4} \frac{\text{gmol EB}}{\text{g}_{\text{cat}}\ \text{s}\ \text{kPa}} \exp\left[-\frac{49713.2\ \text{cal/mol}}{1.987 \frac{\text{cal}}{\text{mol K}}} \right] \left((p_{EB}) \right) \quad (6)$$

$$r_{EB3} = -8.52\times10^{-4} \frac{\text{gmol EB}}{\text{g}_{\text{cat}}\ \text{s}\ \text{kPa}^2} \exp\left[-\frac{21869\ \text{cal/mol}}{1.987 \frac{\text{cal}}{\text{mol K}}} \right] \left((p_{EB} * p_{H_2}) \right) \quad (7)$$

ASPEN Reaction rates for this pseudo-homogeneous reactor model must be specified in units of reactor volume. For example, to convert from units per (g_{cat}) to per reactor volume (m^3), you must use catalyst bulk density ρ_{bulk} to convert the rate constant.

[1] [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.

$$r_{cat} \ [=] \ \frac{\text{gmol}}{\text{s gcat}} \tag{8}$$

$$\rho_{bulk} = 1191 \ \text{kg}_{\text{cat}} / \text{m}^3_{\text{reactor}} \tag{9}$$

$$r_{pseudo-\text{hom}ogeneous} = r_{cat} \cdot \rho_{bulk} \ [=] \frac{kmol}{m^3 - s} \tag{10}$$

Since the reaction rate is formulated in terms of partial pressures, this rate constant also includes units of inverse kPa. We've now done this conversion several times, and the forward pre-exponential factor for reaction 1 becomes: $A_f = 0.0892 \ \frac{\text{kmol EB}}{\text{m}^3 - s - Pa}$.

Recall that for the reverse reaction we calculated reaction parameters based on the forward rate constant and the equilibrium constant in Lab # 3. The form of the rate law specified above can be rearranged as:

$$r = k_f \left(p_{EB} - \frac{p_H p_S}{K_p} \right) = k_f p_{EB} - \frac{k_f}{K_p} p_H p_S \tag{11}$$

where $k_r = \frac{k_f}{K_p}$. =Formulating our equilibrium constant in the Arrhenius form,

as $K_{eq} = A_{eq} \exp(-E_{eq} / RT)$, the reverse rate parameters can be found as:

$$A_r = \frac{A_f}{A_{eq}} \text{ and } E_r = E_f - E_{eq} \tag{12}$$

To calculate the equilibrium parameters A_{eq} and E_{eq} we used K_p vs T data to regress parameters. So, for

$$\ln K_p = \ln A_{eq} - \frac{E_{eq}}{RT_K} \tag{13}$$

the slope provided E_{eq}/R, and the intercept provided ln A_{eq}.

Since this has already been done in a previous lab, A_r and E_r will be provided here.
A_r is 2.821×10^{-13} kmol/m^3-s-Pa^2 and E_r is –6923.6 cal/mol/

Calculate the pre-exponential factors for reactions 2 and 3 by adjusting units as described above. (Note that reaction 4 is second order in pressure – indicated by the kPa^2 in the denominator – so make your conversions appropriately).

Hand in these calculations 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.

1. Start Aspen 13.2.
2. Open a new case by choosing a blank simulation. (Do not use the templates for consistent units when specifying your kinetics. We will use SI units for all reactors with kinetics).
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 the chemicals for a reactor: Styrene, ethylbenzene, hydrogen, water, methane, toluene, benzene and ethylene. Use the *Find* button to find the component ID and then add it.
7. Next, under *Properties, Specifications*, select your base property method. Since these compounds are hydrocarbons, use the Peng-Robinson thermodynamic package.
8. Install two RPlug reactors in series with an inter-stage heater between the reactors.
9. Add streams to your reactor in the usual manner.
10. 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.
11. 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.
12. Specify two adiabatic reactors of equal volume, 8 ft in diameter and length.
13. Add pressure drop calculation for both reactors using the ERGUN equation (as done in the last lab) with particle diameter of 4.7 mm and void fraction of 0.445. Remember to specify calculation of pressure drop – not pressure.
14. Next, specify the reactions to complete the specification for the PFR.
    14.1. 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 (as Rxns 1 & 2).
    14.2. Specify the side reactions as reactions 3 & 4. Remember equation 6 is a function of both EB concentration **AND** hydrogen concentration.
15. Next, calculate ethylbenzene conversion values, χ, based on the aspen stream output simulation results and record in your spreadsheet.
16. ***Plot 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.***
17. 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.

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

18. 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.
19. ***Comment on how the styrene selectivity and ethylbenzene conversion varies with steam flow and hand in with your lab.***
20. Export your report file (*.rep) and hand in with your lab.
21. 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). Consider 2 different options, calculate your EB conversion and Styrene selectivity.

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.