

Problem 5.10. Originally in *Introduction to Chemical Engineering Computing*, by Bruce A. Finlayson, Wiley (2006). Copyright, 2006.

Example of process simulation with Excel including phase equilibrium

The next modification you'll try allows phase equilibrium in the separator where most of the ammonia is condensed. For simplicity, though, you should set the conversion per pass in the reactor to 25%. Change the separator so that it is a phase separation. The K values are

nitrogen	4.8
hydrogen	70
ammonia	0.051
carbon dioxide	0.32

(Remember that the symbol K value is used in both chemical reaction equilibria and phase equilibria, but K represents different things in those two cases.) The flow rates of nitrogen and hydrogen into the process are one and three moles per time unit, respectively, but there is also 0.01 moles per time unit of carbon dioxide. Because of the carbon dioxide, you will add a purge stream as one per cent of the recycle stream. Follow the structure of the problem as shown in Fig. 5-10.

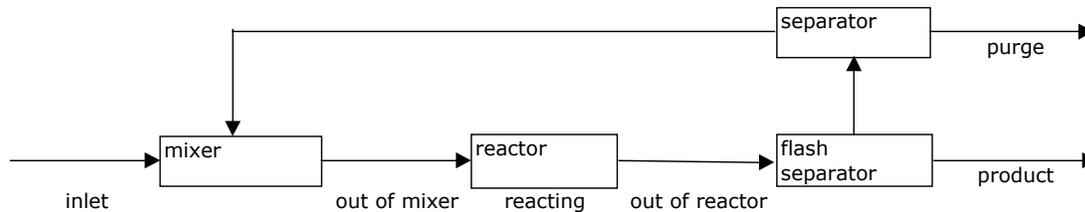


Figure 5-10. Ammonia Process with vapor-liquid equilibria and a purge stream

Now the separator must satisfy the Rachford-Rice equation, Eq. (3.9).

$$\sum_{i=1}^{NCOMP} \frac{(K_i - 1)z_i}{1 + (K_i - 1)v'} = 0 \tag{5.7}$$

Once the value of v' is found that satisfies this equation, the values of mole fraction and molar flow rates are given by Eq. (3.1-3.8).

$$x_i = \frac{z_i}{1 + (K_i - 1)v'}, \quad y_i = K_i x_i \tag{5.8}$$

$$n_i^v = Vy_i = Fv' y_i \tag{5.9}$$

$$n_i^L = Ly_i = F(1 - v')x_i \tag{5.10}$$

In Eq. (5.8-10) z_i is the mole fraction of the i -th species into the flash unit, K_i is the K -value for the i -th species (often the vapor pressure divided by the total pressure), and v' is the fraction of the feed that goes out as vapor (between 0 and 1).

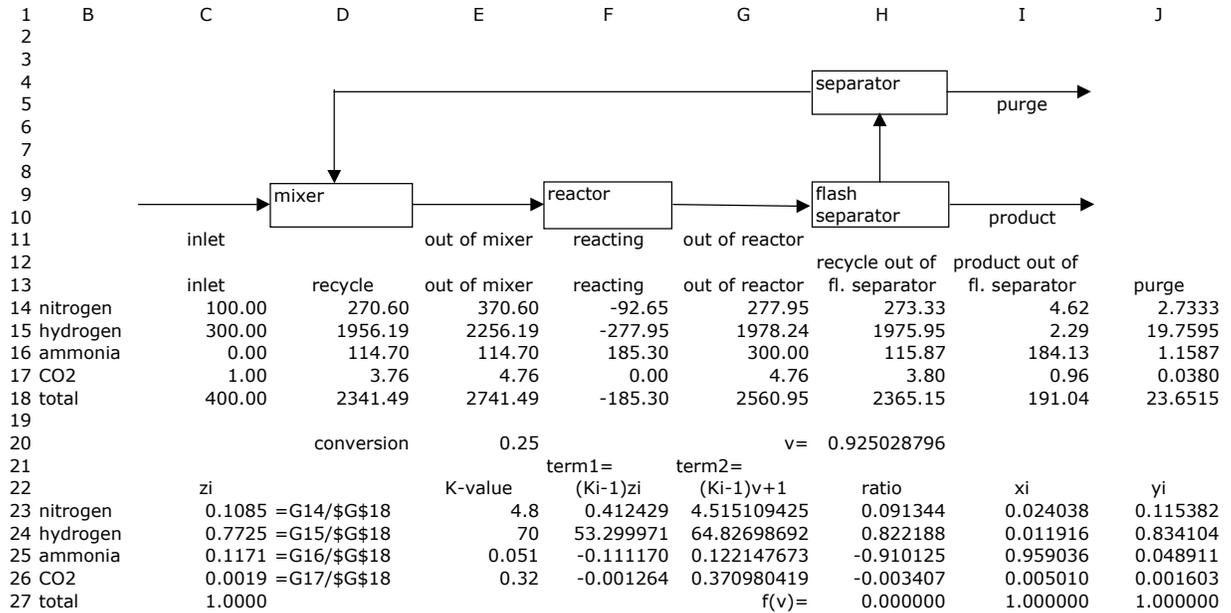


Figure 5-11. Mass balance for ammonia process with vapor-liquid equilibria

Let's use nitrogen to explain the spreadsheet, Fig. 5-11. **Step One.** The recycle stream (cell D14) is obtained by subtracting the purge from the product out of the separator. Set cell D14 to: =H14–J14. **Step Two.** The stream out of the mixer (cell E14) is the sum of the inlet stream and recycle. Set cell E14 to: =C14+D14. **Step Three.** The amount reacting is the conversion times E14. Set cell F14 to: =E14*E20. **Step Four.** The stream out of the reactor is what came in minus what reacted. Set cell G14 to: =E14+F14. **Step Five.** The stream as recycle out of the separator uses Eq. (5.9). Set cell H14 to: = \$H\$20*\$G\$18*J23. **Step Six.** The product stream is the difference. Set cell I14 to: =G14–H14. **Step Seven.** The purge stream is one per cent of the stream. Set cell J14 to: =0.01*H14. These formulas are copied down, except for column F in which the amount of hydrogen reacting and ammonia formed are determined as multiples of the amount of nitrogen reacting. The total row (18) is the sum of the flow rates of the components.

Next, consider how the vapor-liquid equilibrium is solved. **Step Eight.** The mole fractions going into the flash unit are the ones coming out of the reactor. For example, cell C23 uses =G14/\$G\$18. **Step Nine.** The term1 and term2 are calculated as shown, and the ratio is calculated. The sum, cell H27, should be zero. **Step Ten.** The liquid mole fractions, cells I23 to I26, and vapor mole fractions, cells J23 to J26, are calculated using Eq. (5.8). They are summed to check that they add to 1.0. They will add to 1.0 only when the proper vapor fraction is found, i.e. $f(v') = 0$, in cell H27. **Step Eleven.**

You can use 'Solver' to set cell H27 to zero by varying cell H20, the vapor fraction. As Excel changes v' , the values in rows 23-27 change, and these in turn cause changes in the rows 14-18 because they depend upon the vapor mole fractions. Unfortunately, 'Solver' cannot find a solution, but you can vary v' yourself to find the solution.

Did iterations converge? In this example, you have two iterations - one because of the circular reference due to the recycle streams and one because of the non-linear Rachford-Rice equation. Some computer programs cannot handle both of these complications together. Neither Goal Seek nor Solver worked for this example, and you iterated the vapor fraction by hand. **Step One.** In effect you used the spreadsheet to do the molar balances, and you set v' yourself. The spreadsheet shows the value of $f(v')$ for your choice of v' , but it does the molar balance anyway. **Step Two.** If $f(v')$ is not zero, you can change v' and do it again. **Repeat.** You keep this up until $f(v')$ is small enough to satisfy you. Once you are close, 'Solver' should have no problem converging to a tight tolerance. What you are doing is replacing a problem with two iteration loops with a problem in which you supply one of the numbers, and the computer solves the other iteration loop. Then you change your number until the other equation is satisfied.

Extensions. Ideally you would have calculated the equilibrium in the reactor, too. Then you would have three interacting iterations, and it would be the rare problem that Excel could solve. The difficulty is that during the iterations, the values may be physically unrealistic. Then, the equilibrium relation or the Rachford-Rice equation gives even more unrealistic values. Programs such as Aspen Plus can realize this and take precautionary steps to avoid it. As the flow sheet gets more and more complicated, and involves more and more thermodynamics, the power of Aspen Plus is welcome. See Chapters 6 and 7 for examples.