CIR310 Phase equilibrium project
Part 2

Submission deadline: 24.04.2017 before 13:30

1 System description

A coupled reactor/column system is used for trioxane synthesis from formaldehyde to trioxane. The reversible liquid phase chemical reaction is given by the trimerization reaction:

$$3\,CH_2O \overset{[H^+]}{\rightleftharpoons} C_3H_6O_3$$

The equilibrium concentration of trioxane is very low in this reaction. A common design solution to increase overall conversion of the process is by using azeotropic distillation with water. A simplified model of this process was developed by Hu et al. [1]. Figure 1 demonstrates this process.

The feed stream of the reactor contains an aqueous solution of formaldehyde and water. The goal of the process is to maximise the overall conversion of formaldehyde to trioxane.

2 Model

The following assumptions have been made for the process.

1. The entire reactor/column system operates at a continuous steady state equilibrium.
2. The reactor is controlled at a set temperature and the heat transfer dynamics is negligible.
3. The system is adiabatic so that no heat is lost to the environment.
4. The catalytic reaction occurs in the liquid phase of the reactor only. No reaction occurs in the column equilibrium stages.
5. Side reactions and intermediate products are negligible so that the system is a tertiary formaldyhyde-trioxane-water system.

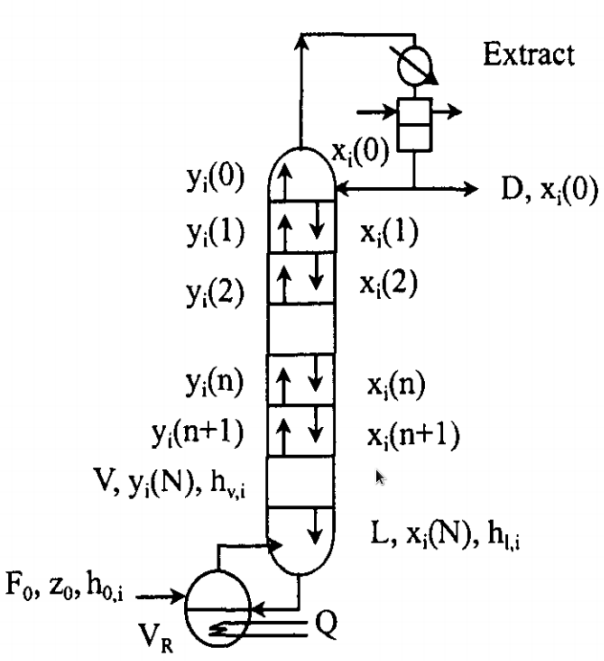

Figure 1: The coupled reactor/column system (adapted from Hu et al. [1]).

6. A constant relatively volatility is assumed at all stages of the reaction.

The system equations as developed by Hu et al. [1] are shown in Table 1.

Table 1: System equations. Here i is the chemical component index where $i = 1$ is formaldehyde, $i = 2$ is trioxane and $i = 3$ is water. n represents an equilibrium stage $n = 0, 1, 2, \ldots N$, the stage $n = N$ is the reactor stage.

	Equation	Parameters	Inputs	Outputs
	Reactor mass balance			
1	$Fz_i + Lx_{i,N} - Vy_{i,N} + \upsilon_i r = 0$	υ_i	$F\ z_i$	$x_{i,N}\ y_{i,N}\ L\ V\ r$
	Column mass balance			
2	$Vy_{i,n} - (L + w_i D)x_{i,n} = 0$	w_i	D	$x_{i,n}\ y_{i,n}$
3	$L = RD$		R	
	Component continuity			
4	$\sum_i^3 z_i = 1$			
5	$\sum_i^3 x_{i,n} = 1$			
6	$\sum_i^3 y_{i,n} = 1$			
	Phase equilibrium			
7	$\alpha_i = \frac{y_{i,n}/y_{1,n}}{x_{i,n+1}/x_{1,n+1}}$			α_i
	Reaction rate equation			
8	$r = V_r\left(k_1 C_1^2 - k_2 C_2\right)$	$k_1\ k_2$		r
	Energy balance			
9	$\sum_i^3 \left[Fz_i h_{F,i} + Lx_{i,N} h_{l,i} - Vy_{i,N} h_{v,i}\right] + Q = 0$		$h_{F,i}\ h_{l,i}\ h_{v,i}\ Q$	
	Total: 21 =	4	+8	+9

3 Instructions

Based on your findings from the initial investigation into the process model it was decided that a more sophisticated thermodynamic model would be required to accurately simulate this system. It was decided to incorporate a cubic equation of state into the model. To calculate the fugacities from the mechanical equation of state (a PVT relation) we will need to find expressions for the fugacity coefficient of a component in a mixture.

The van der Waals equation of state is given by

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

The fugacity coefficient of a component i in a mixture can be calculated using Equation 11.60 from Smith, Van Ness and Abbott (SvA) p. 404

$$\ln \hat{\phi}_i = \int_0^P (\bar{Z}_i - 1)\frac{dP}{P}$$

where $\bar{Z}_i = \frac{(\partial nZ)}{\partial n_i}$. Using this equation together with the van der Waals mixing parameters. (SvA Equations 14.42 and 14.43 p. 561)

$$b = \sum_i x_i b_i$$

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

where $a_{ij} = \sqrt{a_i a_j}$

Show that the fugacity coefficient of component i in a mixture described by the Van der Waals equation of state is given by

$$\ln \hat{\phi}_i = \ln\left(\frac{v}{v-b}\right) + \frac{b_i}{v-b} - \frac{2\sqrt{a_i}\sum_{i=1}^{n} x_i\sqrt{a_i}}{vRT} - \ln Z$$

Total Marks: 100

References

[1] Hu, M., Zhou, X.-G., and Yuan, W.-K. (1999). Simulation and optimization of a coupled reactor/column system for trioxane synthesis. *Chemical Engineering Science*, 54(10):1353 – 1358.