CIR310 Phase equilibrium project
Part 2

Submission deadline: 22.05.2017 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.

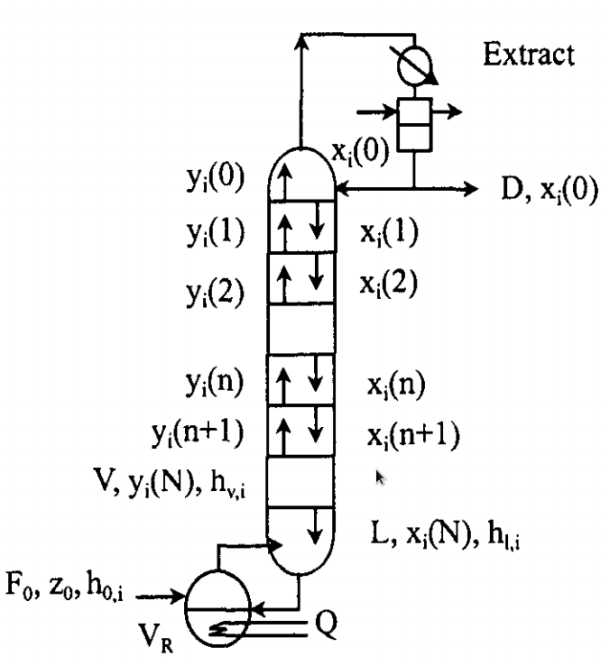

Figure 1: The coupled reactor/column system (adapted from Hu et al. [1]).

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. You and your team have been directed to incorporate a cubic equation of state model with appropriate mixing rule parameters 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 coefficients of a component in a mixture. We can then use the set of equations

$$y_i\hat{\phi}_i^v - x_i\hat{\phi}_i^l = 0$$

for all $i = 1, 2, 3$ to replace the phase equilibrium equations in the system of equations from Table 1 at every equilibrium stage in the column.

3.1 Symbolic computations

The fugacity coefficient of a component i in a mixture can be calculated using Equation 11.60 from Smith, Van Ness and Abbott [2, p. 404]

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

where $\bar{Z}_i = \frac{(\partial nZ)}{\partial n_i}$. Using this equation together with the Van der Waals mixing parameters. [2, p. 561, Equations 14.42 and 14.43])

$$b = \sum_i x_i b_i \tag{2}$$

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{3}$$

where $a_{ij} = \sqrt{a_i a_j}$. Using these three equations derive the following expressions.

1. The van der Waals equation of state is given by

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \tag{4}$$

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

$$\ln\hat{\phi}_i = \ln\left(\frac{v}{v-b}\right) + \frac{b_i}{v-b} - \frac{2\sqrt{a_i}\sum_{j=1}^n x_j\sqrt{a_j}}{vRT} - \ln Z \tag{5}$$

HINT: You can change the variable of integration of Equation 1 with the identity: $\frac{dP}{P} = \frac{dZ}{Z} - \frac{dV}{V}$ *(derive this from* $Z = \frac{PV}{RT}$*).*

(30)

2. The Redlich-Kwong (RK) equation of state is given by

$$P = \frac{RT}{v-b} - \frac{a}{\sqrt{T}v\,(v+b)} \tag{6}$$

Show that the fugacity coefficient of component i in a mixture described by the Redlich-Kwong equation of state is given by

$$\ln\hat{\phi}_i = \ln\left(\frac{v}{v-b}\right) + \frac{b_i}{v-b} - \frac{2\sum_j y_j a_{ji}}{RT^{3/2}b}\ln\left(\frac{v+b}{v}\right) + \frac{ab_i}{RT^{3/2}b^2}\left(\ln\left(\frac{v+b}{v}\right)\frac{b}{v+b}\right) - \ln Z \tag{7}$$

(50)

3. Rewrite the RK-EOS given in Equation 6 in cubic form ($\ldots v^3 + \ldots v^2 + \ldots v + \cdots = 0$) and show how the roots of this equation depend on the composition of the mixture. Describe how you would calculate a liquid and a vapour root.

(20)

Total Marks: (100)

3.2 Numerical computations

Write the functions to work for system consisting of an arbitrary amount of components, but use the compounds and their associated parameters of the ternary system described in this project to test your code. For all these questions you may use the functions you've already developed in subsequent questions. You may assume that the pure component parameters are global parameters (ex. a_i, b_i and R).

1. Write two functions that accepts a vector of compositions as an input and returns the a_{mix} and b_{mix} parameters defined by Equation 3 and Equation 2. Assume that the pure component parameters are global variables in your code. Suggested format:

```
def a_mix(x):
    ...
    return a_mix
```

```
def b_mix(x):
    ...
    return  b_mix
```

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2. Write two functions that accepts as an input the pressure, temperature and compositions states of a mixture calculates a vapour and liquid root of the RK-EOS Equation 6 at the input composition.

```
def V_l(P, T, x):
    ...
    return V_l
```

```
def V_v(P, T, x):
    ...
    return  V_v
```

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3. Write a function that calculates the fugacity coefficient of a component i in in a mixture described by the RK-EOS Equation 7 for an arbitrary phase θ with it's associated volume root v^{θ}.

```
def phi_i_theta(P, T, x, i, v_theta):
    ...
    return  phi_i_theta
```

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4. Remembering that the temperature of the system is a specified input and further assume that P is constant at one atmosphere. Assume that there are only two phases (a liquid and a vapour phase). Write a function that accepts an input a vector of composition variables and outputs the residual of the equations

$$y_i \hat{\phi}_i^v - x_i \hat{\phi}_i^l = 0$$

for all $i = 1, 2, \ldots N$. The function should wrap the previous functions and accept as an input a single vector of dimensions $2 \times N$ containing all compositions (which can be used in a non-linear solver) and output the results of the functions of N

```python
N = 3  # 3 components
def solver(X):  # For N = 3, X is a vector representing
                # X = [x_1, x_2, x_3, y_1, y_2, y_3]
    x = X[0:N]  # A vector of liquid phase compositions
    y = X[N:]   # A vector of vapour phase compositions
    ...
    return F_PHI  # A vector of N outputs of the equations
```

25

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.

[2] Smith, J., Van Ness, H., and Abbott, M. (2005). *Introduction to chemical engineering thermodynamics*. McGraw-Hill chemical engineering series. McGraw-Hill.