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Design of Optimal Reactive Distillation Processes for ETBE Production using Rigorous Thermodynamic Models

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Abstract

In this work we propose a model for the design of a reactive distillation unit for ETBE synthesis from ethanol and isobutene, with both rigorous thermodynamic models (UNIFAC and SRK) and hydraulic constraints, in an equation oriented environment within GAMS. The objective is to minimize total annual cost. The main contribution of this paper is the estimation of binary interaction parameters yet unavailable for the system being considered, using experimental data taken from literature, within a reactive distillation column optimization environment.

Keywords: Reactive Distillation, Process Intensification, Thermodynamics.

1. Introduction

Most successful commercial process intensification applications at industrial scale include reactive distillation, microreactors, rotating packed bed systems, simulating moving bed reactors, thus the importance of developing reliable methods for the optimal design of such systems. In particular, reactive distillation (RD) is a simultaneous implementation of sequential reaction and distillation in a countercurrent column. The industrial application of these processes is motivated by significant reductions in capital and operating costs, as compared to the equivalent conventional reaction-separation processes. Reactive distillation has also significant advantages when chemical equilibrium limits the conversion, the reason being that continuous removal of products enhances overall conversion. Other benefits include reduced downstream processing and higher energy efficiency due to the utilization of the reaction heat for evaporation of the liquid phase when reaction is exothermic.

ETBE (ethyl tert-butyl ether) is an octane enhancer additive used in gasoline as a replacement for MTBE (methyl tert-butyl ether), which showed some drawbacks as contamination of ground water reservoirs nearby the petrol stations due to leakage from small fractures of the containing underground vessels, and its use was discontinued since 2006. ETBE synthesis can be efficiently carried out through reactive distillation to achieve high conversion and low capital and operating costs. The conventional process for ETBE synthesis basically consists of pretreatment of the C_4 hydrocarbon feed flow, reaction, purification, and recovery of non-reacted products (Domingues et al., 2012), which renders high capital and operating costs. The design of RD for ETBE synthesis, requiring good kinetic models integrated to reliable thermodynamic predictions still requires further analysis and it was not thoroughly explored in literature yet. A review on the evolution of ETBE and its future prospects is presented by Yee et al. (2013).

2. General description of the model

The RD unit model formulation is based on MESH equations. Special attention is given to the thermodynamic model. The model includes an activity coefficient approach for the liquid phase, UNIFAC, and a cubic equation of state for the vapor phase, SRK with quadratic mixing rules with a k_{ij} on a and l_{ij} on b. To the best of our knowledge, there are not SRK binary interaction parameters for all the components in the RD unit studied. Thus, k_{ik} and l_{ik} had to be estimated using parameter estimation techniques with experimental data taken from literature. Sources for the data are shown in Table 1. Having PTxy data for each binary set and proposing the desired thermodynamic model it is possible to find the adjusted k_{ik} and l_{ik}. The parameters were checked predicting the V-L equilibria with GPEC (Cismondi et al., 2008). All three binary mixtures with ethanol present azeotropic compositions.

3. Thermodynamic model

3.1 UNIFAC

$$\ln \gamma_{s,i} = \ln \gamma^{C}_{s,i} + \ln \gamma^{R}_{s,i} \tag{1}$$

$$ln\ \gamma^{R}_{s,i} = \sum_j \upsilon^{i}_{j} \cdot (ln\ \Gamma_{s,j} - ln\ \Gamma^{i}_{s,j}) \tag{2}$$

$$\ln \gamma^{C}_{s,i} = \ln(\phi_{s,i}/x_{s,i}) + z/2 \cdot q_i \cdot \ln(\theta_{s,i}/\phi_{s,i}) + l_i - (\phi_{s,i}/x_{s,i}) \cdot \sum_k x_{s,k} \cdot l_k \tag{3}$$

$$ln\ \Gamma_{s,j} = Q_j \cdot [\ 1 - ln\ (\sum_m \Theta_{s,m} \cdot \Psi_{s,m,j}) - (\sum_m (\Theta_{s,m} \cdot \Psi_{s,m,j} / \sum_n \Theta_{s,n} \cdot \Psi_{s,n,m}))] \tag{4}$$

$$\Theta_{s,m} = Q_m \cdot X_{s,m} / \sum_n Q_n \cdot X_{s,n} \tag{5}$$

$$\phi_{s,i} = r_i \cdot x_{s,i} / \sum_k r_k \cdot x_{s,k} \tag{6}$$

$$\theta_{s,i} = q_i \cdot x_{s,i} / \sum_k q_k \cdot x_{s,k} \tag{7}$$

$$X_{s,m} = \sum_k \upsilon^{k}_{m} \cdot x_{s,k} / \sum_k \sum_n \upsilon^{k}_{n} \cdot x_{s,k} \tag{8}$$

$$\Psi_{s,n,m} = exp(-\ a_{n,m} / T_s) \tag{9}$$

$$r_i = \sum_j \upsilon^{i}_{j} \cdot R_j \tag{10}$$

$$q_i = \sum_j \upsilon^{i}_{j} \cdot Q_j \tag{11}$$

$$l_i = z/2 \cdot (\ r_i - q_i) - (\ r_i - 1\ ) \tag{12}$$

Where z=10. R_j and Q_j are group surface area and volume contributions, respectively, and $a_{m,n}$ is a group interaction parameter (Pretel, 1997). υ^{i}_{j} is the number of ocurrences of group j in molecule i. Eq. (4) is also valid for $\ln \Gamma^{i}_{s,j}$.

3.2 SRK

$$z_{mix_s}^{3} - z_{mix_s}^{2} + (A_s - B_s - B_s^{2}) \cdot z_{mix_s} - A_s \cdot B_s = 0 \tag{13}$$

$$A_s = P \cdot (\sum_i \sum_k y_{s,i} \cdot y_{s,k} \cdot \alpha_{s,i,k}) / (T_s \cdot R)^2 \tag{14}$$

$$B_s = P \cdot (\sum_i \sum_k y_{s,i} \cdot y_{s,k} \cdot \beta_{i,k}) / (T_s \cdot R) \quad (15)$$

$$\alpha_{s,i,k} = [(a_c \cdot \alpha)_{s,i} \cdot (a_c \cdot \alpha)_{s,k}]^{1/2} \cdot (1 - k_{ik}) \quad (16)$$

$$[\alpha_{s,i}]^{1/2} = 1 + m_{ci} \cdot (1 - [T_s/T_{ci}]^{1/2}) \quad (17)$$

$$a_{ci} = 0.42747 \cdot (R \cdot T_{ci})^2 / P_{ci} \quad (18)$$

$$b_{ci} = 0.08664 \cdot R \cdot T_{ci} / P_{ci} \quad (19)$$

$$m_{ci} = 0.48 + 1.574 \cdot w_i - 0.176 \cdot w_i^2 \quad (20)$$

$$\beta_{i,k} = (b_{ci} + b_{ck})/2 \cdot (1 - l_{ik}) \quad (21)$$

$$\ln \varphi_{s,i} = b_{ci}/(\sum_i \sum_k y_{s,i} \cdot y_{s,k} \cdot \beta_{i,k}) \cdot (z_{mix_s} - 1) - \ln (z_{mix_s} - B_s) + A_s/B_s \cdot [b_{ci}/(\sum_i \sum_k y_{s,i} \cdot y_{s,k} \cdot \beta_{i,k}) - 2 \cdot \sum_k (y_{s,k} \cdot \alpha_{s,i,k})/(\sum_i \sum_k y_{s,i} \cdot y_{s,k} \cdot \alpha_{s,i,k})] \cdot \ln (1 + B_s/z_{mix_s}) \quad (22)$$

UNIFAC and SRK are related in the equilibrium calculations in each stage of the column. Discrimination of cubic roots is not a trivial task. A methodology to find the vapor root is implemented within the model, taking into account that in Eq. (13) $f(z_{mix_s})=0$ can be differentiated to yield the desired roots at the values where $f'(z_{mix_s})>0$.

4. Column model

For the model of the column, blocks for condenser, reboiler and stages (either reactive or non-reactive) are written as MESH equations using molar compositions and mole flow rates. In particular,

$$F_{L_s} \cdot x_{F_i} + L_{s-1} \cdot x_{s-1,i} + v_{s+1} \cdot y_{s+1,i} - L_s \cdot x_{s,i} - V_s \cdot y_{s,i} + F_{V_{s+1}} \cdot y_{F_i} + r_{s,i} = 0 \quad (23)$$

Where $r_{s,I}$ is the generation or consumption due to reaction rate. For the reactive stages, the value of the term $r_{s,i}$ depends on the existence of catalyst in the stage. Within the optimization, the catalyst amount M_{cat_s} (mass in [g]) is defined for each reactive stage as shown in the following section.

4.1 Reaction kinetics (Al-Arfaj and Luyben, 2002)

$$r_{s,i} = k_{rate_s} \cdot g_s \cdot M_{cat_s} \quad (24)$$

$$k_{rate_s} = 7.418E12 \cdot \exp(-60.4E3/(R \cdot T_s)) \quad Y \quad (25)$$

$$g_s = act_{s-1,Ethanol} \cdot (act_{s-1,Isobutene} - act_{s-1,ETBE}/K_{ETBE_s})/(1 + K_{A_s} \cdot act_{s-1,Ethanol})^3 \quad (26)$$

$$K_{ETBE_s} = 10.4 + 4060/T_s - 2.9 \ln T_s - 0.02 T_s + 5.3E\text{-}5 T_s^2 - 5.3E\text{-}8 T^3 \quad (27)$$

$$K_{A_s} = \exp(-1.0707 + 1323.1/T_s) \quad (28)$$

$$act_{s,i} = \gamma_{s,i} \cdot x_{s,i} \quad (29)$$

4.2 Hydraulic constraints

$$\rho_g = P \cdot MW_g / (R \cdot Tsf) \quad (30)$$

$$u_g = F^{1/2} / \rho_g^{1/2} \quad (31)$$

$$V_g = V_{sf} * MW_g / \rho_g \quad (32)$$

$$A_{COL} = V_g / u_g \quad (33)$$

$$D_{COL} = (4 \cdot A_{COL} / \pi)^{1/2} \quad (34)$$

$$Psi = 0.000265 \cdot (1/D_{COL})^2 - 0.018827 \cdot (1/D_{COL}) + 0.559770 \quad (35)$$

$$V_l = l_{sf} \cdot MW_l / \rho_l \quad (36)$$

$$u_l = V_l / A_{COL} \quad (37)$$

$$u_l < u_{lmax} \quad (38)$$

$$CAT_{LIM} = \tfrac{1}{4} \cdot \pi \cdot D_{COL}^2 \cdot \Delta Z \cdot Psi \cdot (1 - 0.3) \cdot \rho_{CAT} \quad (39)$$

$$M_{CAT} < CAT_{LIM} \quad (40)$$

5. Numerical results

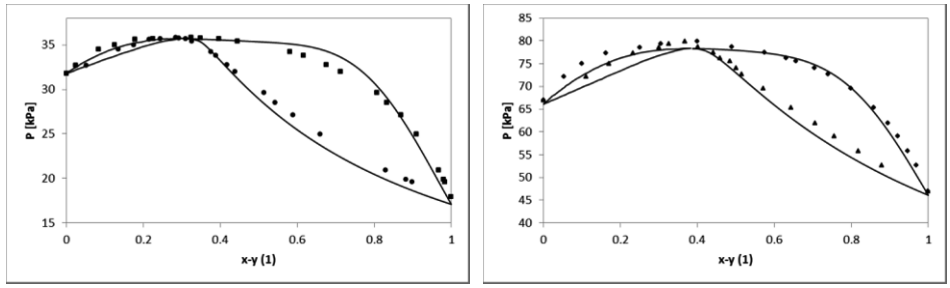
Estimation of binary interaction parameters for the system is important for the correct simulation of the process, due to the binary azeotropes present. Data taken from literature were used to estimate the values of k_{ij} and l_{ij}, thus obtaining reliable VLE predictions for all the components present in the system. A parameter estimation problem was posed in order to find such binary data.

There is good agreement between experimental and predicted data. Table 1 shows the interaction parameters estimated for the system. Using the same binary interaction coefficients for iC4-EtOH and nC4-EtOH yields a good prediction of VLE.

Plots showing the agreement between the proposed thermodynamic model and experimental data are shown for the systems containing ETBE in Figures 1 and 2. They are not shown for the other binary sets due to lack of space, but they also show good agreement with experimental data.

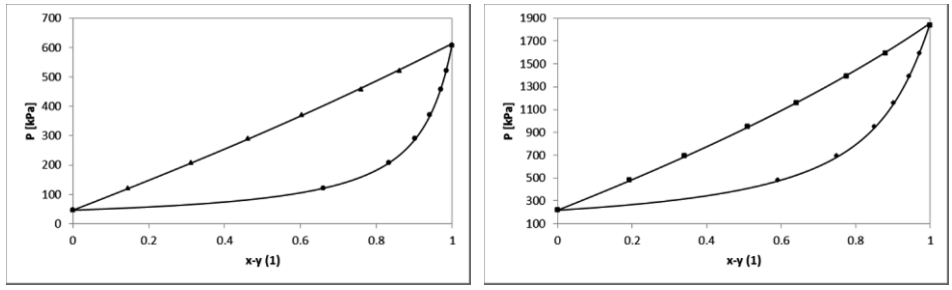
Table 1. Estimated binary interaction parameters k_{ij} and l_{ij}

		k_{ij}	l_{ij}	Experimental data from:
ETBE	Ethanol	0.3728	0.4006	Kammerer et al. (1999)
	i-butene	-0.0068	-0.005	Leu et al. (1999)
	n-butene	-0.0068	-0.005	Id.
Ethanol	i-butene	0.1826	0.1254	Ouni et al. (2005)
	n-butene	0.1724	0.1203	Laakkonen et al. (2003)
Isobutene	n-butene	0	0	--



(a) (b)

Figure 1. Ethanol (1) – ETBE (2) equilibrium at (a) 313.15K and (b) 333.15K. ▪ and ● equilibrium data for liquid and vapor phase, respectively (Kammerer et al. 1999). ─ Prediction.



(a) (b)

Figure 2. Isobutene (1) – ETBE (2) equilibrium at (a) 323.15K and (b) 373.15. ▲ and ● equilibrium data for liquid and vapor phase, respectively (Leu et al. 1999). ─ Prediction.

Optimization of the reactive distillation system is carried out using GAMS, for minimizing the total annualized cost (See Appendix) with constraints on purity of ETBE in the bottom stream (>95 % mole basis) and an isobutene conversion (> 90 %). The cost of the process is reduced by roughly 30 % compared to the traditional ETBE process scaled to match for this column capacity (Sneesby, 1998).

6. Conclusions

In this work, optimization of a reactive distillation column is carried out. The model is implemented in GAMS, including rigorous thermodynamic model and hydraulic constraints. Parameters required for simulating this system were unavailable in literature, thus they were estimated from experimental data taken from different sources. The fact of using a cubic equation of state within an equation oriented modelling environment made necessary to discriminate correct roots. This task was performed with an algorithm embedded in the optimization environment that evaluates derivatives of the function in order to find the correct roots.

Reactive distillation poses a challenge for process control (Nikacevic et al, 2011) which will be addressed in future work, within a dynamic optimization environment.

7. Appendix: Column Costs

$$ATC = 0.2\,(C_{COL} + C_{REB} + C_{COND} + C_{CAT}) + C_{STEAM} + C_{WATER} + \quad (41)$$

$C_{C4} + C_{ETHANOL} - C_{PRODUCT}$

$C_{COL} = 17640D^{1.066}L^{0.802}$ [$, D and L in m] (Sharifzadeh, 2013) (42)

$C_{REB} = 7296\ A_{REB}^{0.65}$ [$, A in m^2] (Sharifzadeh, 2013) (43)

$C_{COND} = 7296\ A_{COND}^{0.65}$ [$, A in m^2] (Sharifzadeh, 2013) (44)

$C_{STEAM} = 0.0019$ ($/kg) (P=9.4bar, T=451.7K) (45)

$C_{WATER} = 0.0414$ ($/kg) (P=7bar, T_{supply}=451.7K) (46)

$C_{C4} = 29.65$ ($/kmol) (47)

$C_{ETHANOL} = 39.67$ ($/kmol) (48)

$C_{ETBE} = 118.25$ ($/kmol) (49)

$C_{CAT} = 10.16$ ($/kg, Amberlyst 15) (50)

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