

Finding Rigorous Thermodynamic Model parameters for the Simulation of a Reactive Distillation Column: Case of ETBE Production

Gisela N. Durruty, M. Soledad Diaz, Patricia M. Hoch*

Universidad Nacional del Sur, Chemical Engineering Department, Planta Piloto de Ingeniería Química, 8000 Bahía Blanca, ARGENTINA

{gdurruty, sdiaz, p.hoch}@plapiqui.edu.ar

Abstract.

A model for a reactive distillation column for ETBE production was developed using both a rigorous thermodynamic model (UNIFAC) and hydraulic constrains. The thermodynamic model included an activity coefficient approach for the liquid phase, UNIFAC, and ideal gas approximation for the vapor phase. The binary interaction parameters of UNIFAC were improved to better predict the equilibrium in the column. The binary interaction parameters were estimated using experimental data taken from literature.

Keywords: Reactive distillation, ETBE, thermodynamics.

1 Introduction

Reactive distillation (RD) is an example of process intensification. Instead of performing the reaction step in a reactor and the separation in a distillation column, the proposed RD-device consists basically of a section where the reaction takes place and a rectifying and/or a stripping section above/below the reactive section. There are a number of benefits related to this scheme, for example that products are constantly removed from the reaction section, increasing the conversion of reactants because the products are constantly extracted, and also because products are constantly withdrawn, avoids reaching azeotropic concentrations where applicable. Energy integration is also achieved, especially in cases in which the reaction is exothermic, using the reaction energy to evaporate the liquid phase. Thus, RD reduces capital investment and operational costs [1, 2].

ETBE has been considered to replace MTBE as a fuel oxygenate because of the former's superior qualities as an octane enhancer. Because ETBE is less soluble in water than MTBE, its use as fuel additive also minimizes groundwater contamination due to leakage of containing underground fuel vessels. Besides, ETBE can be produced from renewable sources, such as bio-ethanol, cellulose, biomass or other farm products [3]. 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 pre-treatment of the C₄ hydrocarbon feed flow, reaction, purification, and recovery of non-reacted products [4], 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.

In this paper, the main objective is to devise adequate thermodynamic models for better predicting the behavior of the mixtures ETBE-ethanol-isobutene-butane, with the final purpose of optimizing the operation of the reactive distillation column.

2 Model Description

The RD unit is modeled with MESH equations (Mass, Equilibrium, Summation, Enthalpy) with a rigorous thermodynamic activity model for the liquid phase (UNIFAC) and an ideal gas approximation for the vapor phase. With data taken from literature, the binary interaction parameters of UNIFAC, a_{mm} , were adjusted to better predict the equilibrium. The predictions were made within GAMS [5] and results were compared with data and with results obtained from tabulated parameters [6], as shown in the Numerical Results section.

3 Thermodynamic Model

3.1 UNIFAC

$$\ln \gamma_{ne,d,i} = \ln \gamma_{ne,d,i}^C + \ln \gamma_{ne,d,i}^R \quad (1)$$

$$\ln \gamma_{ne,d,i}^R = \sum_j v_j^i \cdot (\ln \Gamma_{ne,d,j} - \ln \Gamma_{ne,d,j}^i) \quad (2)$$

$$\ln \gamma_{ne,d,i}^C = \ln \frac{\phi_{ne,d,i}}{x_{ne,d,i}} + \frac{z}{2} \cdot q_i \cdot \ln \frac{\theta_{ne,d,i}}{\phi_{ne,d,i}} + l_i - \frac{\phi_{ne,d,i}}{x_{ne,d,i}} \cdot \sum_k x_{ne,d,k} \cdot l_k \quad (3)$$

$$\ln \Gamma_{ne,d,j} = Q_j \cdot \ln \left(1 - \sum_m \theta_{ne,d,m} \cdot \Psi_{ne,m,j} - \sum_m \frac{\theta_{ne,d,m} \cdot \Psi_{ne,m,j}}{\sum_n \theta_{ne,d,n} \cdot \Psi_{ne,n,m}} \right) \quad (4)$$

$$\theta_{ne,d,m} = \frac{Q_m \cdot X_{ne,d,m}}{\sum_n Q_n \cdot X_{ne,d,n}} \quad (5)$$

$$\phi_{ne,d,i} = \frac{r_i \cdot x_{ne,d,i}}{\sum_k r_k \cdot x_{ne,d,k}} \quad (6)$$

$$\theta_{ne,d,i} = \frac{q_i \cdot x_{ne,d,i}}{\sum_k q_k \cdot x_{ne,d,k}} \quad (7)$$

$$X_{ne,d,m} = \frac{\sum_k v_m^k \cdot x_{ne,d,k}}{\sum_k v_n^k \cdot x_{ne,d,k}} \quad (8)$$

$$\Psi_{ne,n,m} = \exp \left(-\frac{a_{n,m}}{T_{ne}} \right) \quad (9)$$

$$r_i = \sum_j v_j^i \cdot R_j \quad (10)$$

$$q_i = \sum_j v_j^i \cdot Q_j \quad (11)$$

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

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 [6]. v_j^i is the number of occurrences of group j in molecule i . Eq. (4) is also valid for $\ln \Gamma_{ne,d,j}^i$.

UNIFAC and the ideal gas approximation are related to each other in the equilibrium calculations in each stage of the column.

3.1.1 Parameters estimation

The parameter estimation was performed within GAMS.

In the equilibrium, the isofugacity criteria between the two phases must be satisfied, then

$$y_{ne,d,i} \cdot P_{ne,d}^{CALC} = P_{ne,i}^V \cdot x_{ne,d,i} \cdot \gamma_{ne,d,i} \quad (13)$$

Eq. (13) is calculated for each pair of experimental data x - y taken at each P^{EXP} . The objective function is then

$$OF = \text{Min} \sum_{ne} \sum_d \frac{(P_{ne,d}^{CALC} - P_{ne,d}^{EXP})^2}{P_{ne,d}^{EXP}} \quad (14)$$

After parameters are estimated, bubble point calculations are performed to predict the equilibrium. These calculations are also made with tabulated parameters. Then, standard percent relative deviation in pressure P , σ_P (Eq. (15)), and standard percent deviation in mole fraction y_1 , σ_y (Eq. (16)), are calculated to compare results.

$$\sigma_P = 100 \cdot \frac{\left(\frac{P_{ne,d}^{CALC} - P_{ne,d}^{EXP}}{P_{ne,d}^{EXP}} \right)^2}{N_{ne}}^{0.5} \quad (15)$$

$$\sigma_y = 100 \cdot \frac{\left(y_{ne,d,1}^{EXP} - y_{ne,d,1}^{CALC} \right)^2}{N_{ne}}^{0.5} \quad (16)$$

4 Numerical Results

In order to perform an optimization of the system, a correct simulation of the process is required. For the system under study, estimation of binary interaction parameters is important due to the binary azeotropes present. Data taken from literature were used to estimate and improve a_{nm} , thus obtaining reliable VLE predictions for all the components present in the system. In order to find such binary data a parameter estimation problem was posed.

Table 1 shows the interaction parameters estimated for the system. All the parameters were obtained adjusting the experimental data available. Then, with these parameters, bubble point calculations are made to predict P-y. These predictions are also made with tabulated interaction parameters to compare. The objective function in the calculations for pressure and composition is the same as for the parameters estimation.

Table 1. a_{nm} UNIFAC interaction parameters for all groups present in the RD unit.

	CH_3	CH_2	C	CCH_2	OCH_2	OH	CH_2CH
CH_3	0	0	0	417.71	14506.1	972.26	-439.86
CH_2	0	0	0	417.71	14506.1	972.26	-439.86
C	0	0	0	417.71	14506.1	972.26	-439.86
CCH_2	-238.62	-238.62	-238.62	0	407.72	791.61	0
OCH_2	-327.78	-327.78	-327.78	-33.512	0	131.362	-33.512
OH	7440.8	7440.8	7440.8	851480	379.09	0	851480
CH_2CH	17181.6	17181.6	17181.6	0	407.72	791.61	0

Table 2. Standard percent relative deviation in pressure P, for each set of experimental data, calculated with results obtained from calculations with both tabulated and estimated parameters

ne	σ_P	
	Tabulated parameters	Estimated parameters
1	1.786	1.092
2	1.873	0.793
3	2.48	0.714
4	5.234	3.444
5	7.736	0.763
6	5.618	1.089
7	3.789	0.957

Standard percent relative deviation in pressure P and standard percent deviation in mole fraction y_1 were calculated with results obtained with both predicted and tabu-

lated parameters to compare. Table 2 and 3 show that in each experience but number 6, in σ_y , deviations are lower (results obtained with estimated parameters).

Table 3. Standard percent deviation in mole fraction y_1 , for each set of experimental data, calculated with results obtained from calculations with both tabulated and estimated parameters

ne.i	σ_y	
	Tabulated parameters	Estimated parameters
1.Ethanol	6.474	5.128
2.Ethanol	8.511	4.619
3.Ethanol	11.457	7.269
4.Isobutene	4.889	2.103
5.Isobutene	11.416	8.2
6.n-butene	3.697	4.016
7.Isobutene	3.736	2.955

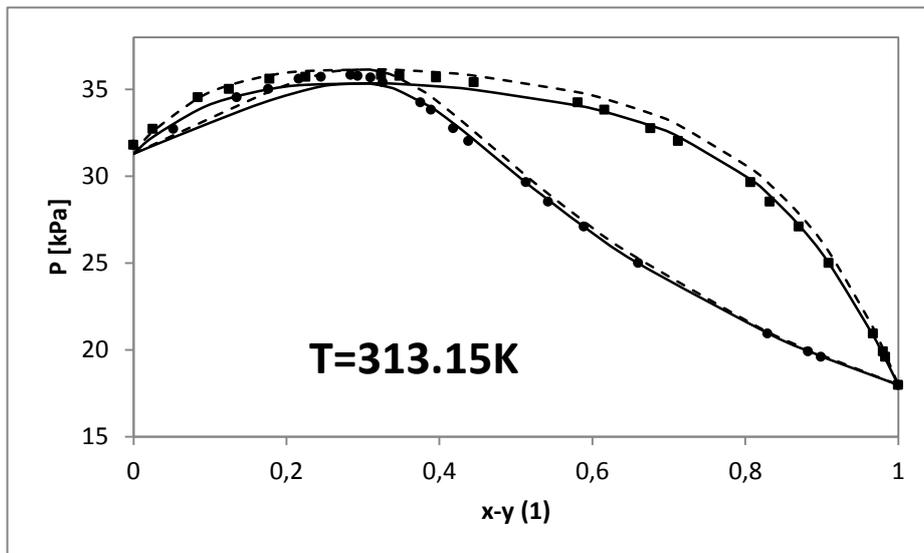


Figure 1. Ethanol (1) and ETBE (2) equilibrium. \blacksquare and \bullet equilibrium data for liquid and vapor phase, respectively [8]. — Prediction with calculated parameters. - - - Prediction with tabulated parameters.

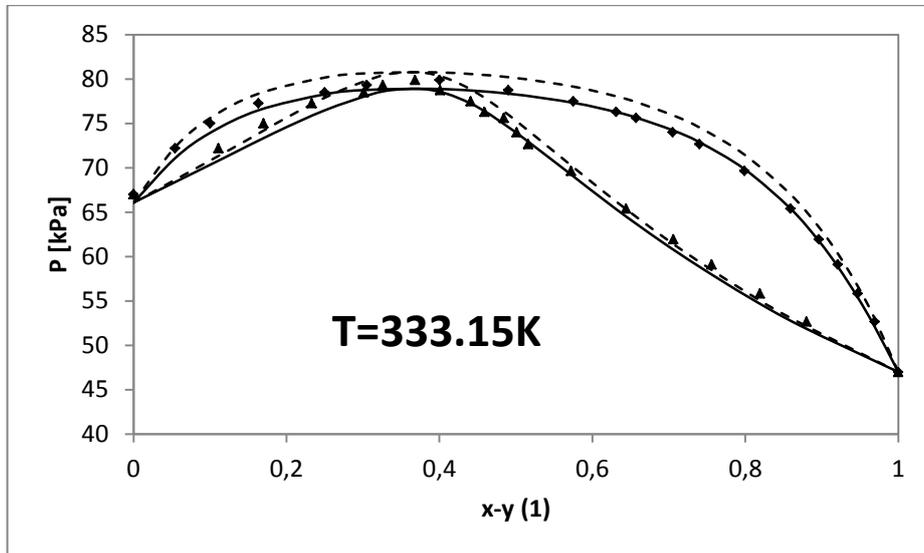


Figure 2. Ethanol (1) and ETBE (2) equilibrium. \blacklozenge and \blacktriangle equilibrium data for liquid and vapor phase, respectively [8]. — Prediction with calculated parameters. - - - Prediction with tabulated parameters.

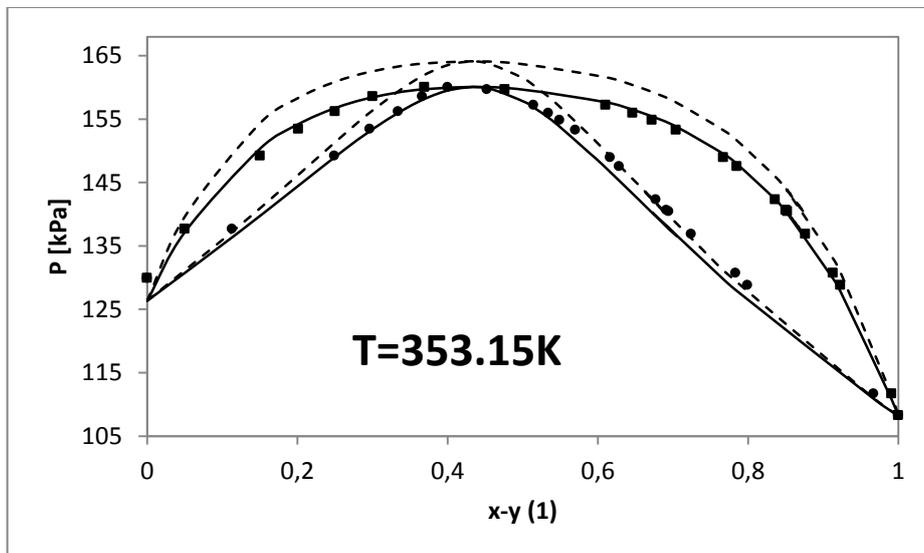


Figure 3. Ethanol (1) and ETBE (2) equilibrium. \blacksquare and \bullet equilibrium data for liquid and vapor phase, respectively [8]. — Prediction with calculated parameters. - - - Prediction with tabulated parameters.

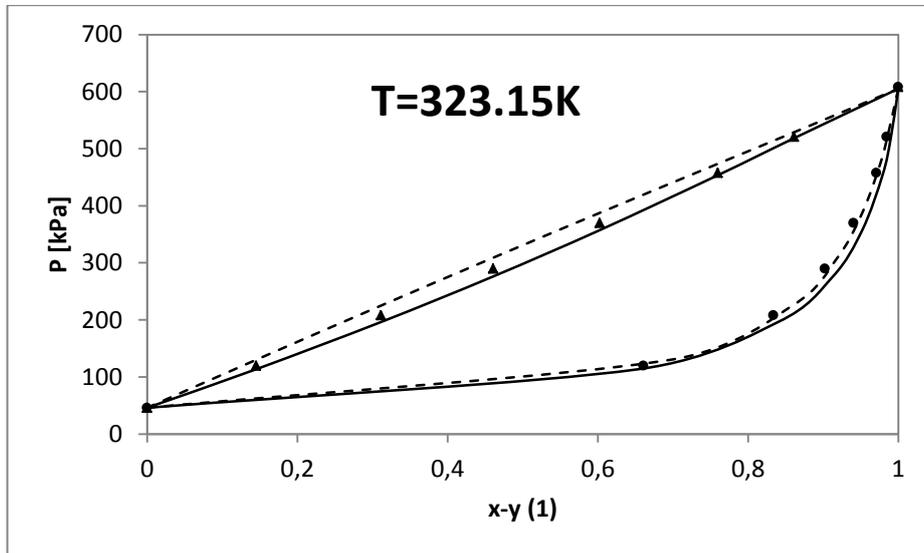


Figure 4. Isobutene (1) and ETBE (2) equilibrium. ▲ and ● equilibrium data for liquid and vapor phase, respectively [9]. — Prediction with calculated parameters. - - - Prediction with tabulated parameters.

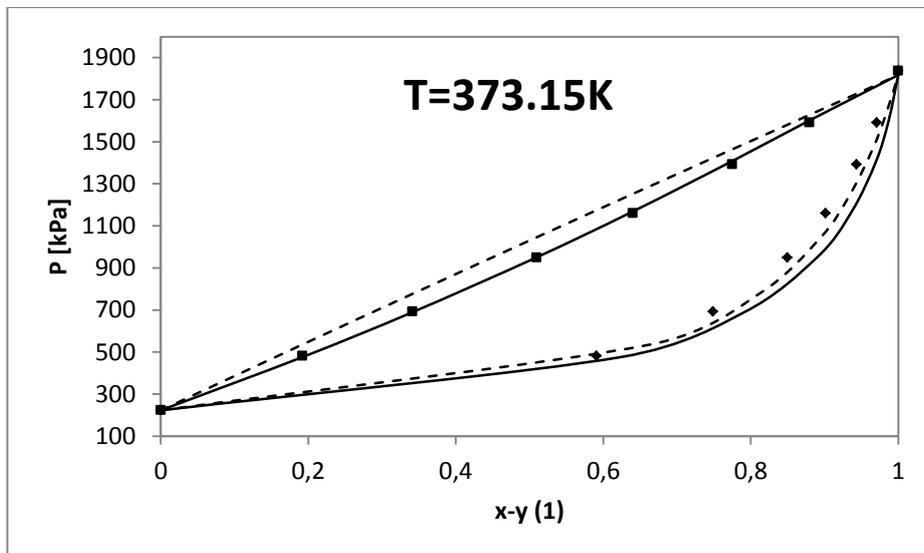


Figure 5. Isobutene (1) and ETBE (2) equilibrium. ■ and ◆ equilibrium data for liquid and vapor phase, respectively [10]. — Prediction with calculated parameters. - - - Prediction with tabulated parameters.

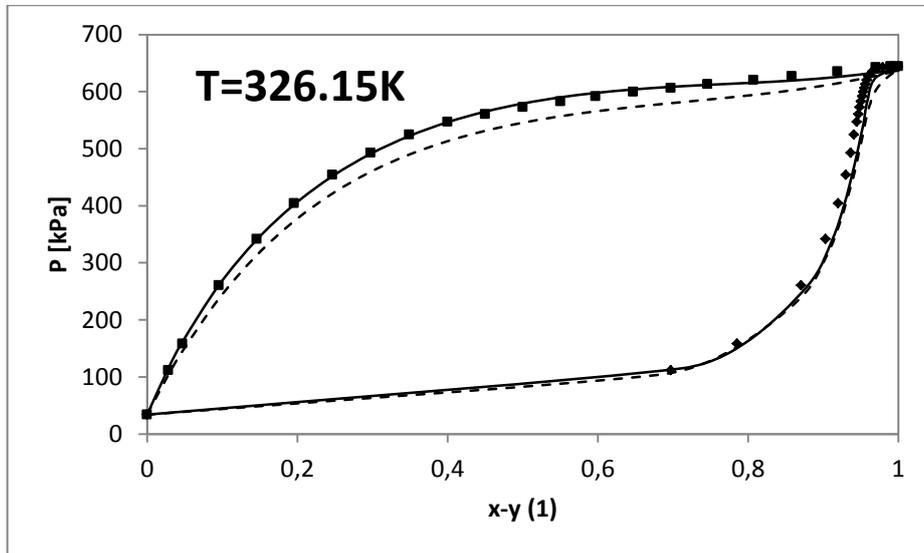


Figure 6. Butene(1) and Ethanol(2) equilibrium. ■ and ◆ equilibrium data for liquid and vapor phase, respectively [10]. — Prediction with calculated parameters. - - - Prediction with tabulated parameters.

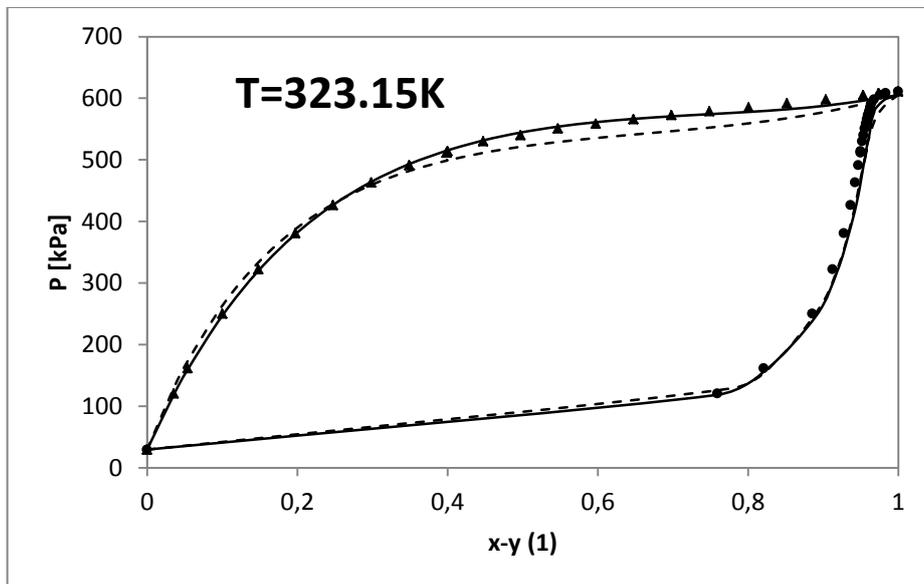


Figure 7. Isobutene(1) and Ethanol(2) equilibrium. ▲ and ● equilibrium data for liquid and vapor phase, respectively [11]. — Prediction with calculated parameters. - - - Prediction with tabulated parameters.

Figures 1 to 7 show the good agreement between the proposed thermodynamic model and experimental data. They also show the comparison between predicted P-y

with tabulated and estimated parameters and how the new parameters better predict the phase equilibrium of the binaries present in the reactive column.

Errors were more noticeable for the system isobutene-ETBE (Figures 4 and 5). Highest error is about 5.6 % which remains well below experimental error.

From Figures 6 and 7 it can be seen that experimental data for lower liquid compositions in the system isobutene-ethanol are unavailable, although the prediction for available compositions is very accurate.

The full set of equations representing the reactive distillation system can now be solved, within a nonlinear programming environment such as GAMS, minimizing the total costs, in order to obtain a feasible design at the minimum cost.

5 Conclusions

In this work, a full set of interaction parameters for a quaternary system ETBE-Ethanol-Isobutene-Butane is found by posing a nonlinear programming problem that minimizes the residuals. The model of the column is then implemented in GAMS, including rigorous thermodynamic model and hydraulic constraints. The main contribution of this work is the prediction of an important set of parameters required for simulating this system, which were unavailable in literature.

Reactive distillation poses an important challenge for process control [12], and ETBE production using these systems still constitutes an application yet not thoroughly explored [13]. These aspects will be addressed in future work, within a dynamic optimization environment.

6 Nomenclature

Subindexis

- i,k: molecule
- j,m,n: group
- ne= 1..7: number of set of experimental data
- d: number of experimental data in each set

UNIFAC

- $\gamma_{ne,d,i}$: activity coefficient
- $\gamma_{ne,d,i}^C$: combinatorial contribution
- $\gamma_{ne,d,i}^R$: residual contribution
- v_j^i : number of group of kind j in molecule i
- $\Gamma_{ne,d,j}$: residual activity coefficient of group j in a solution
- $\Gamma_{ne,d,j}^i$: residual activity coefficient of group j in a reference solution containing only molecules of type i
- $\Phi_{ne,d,i}$: molecular volume fraction
- $\Theta_{ne,d,i}$: molecular surface area fraction
- $X_{ne,d,i}$: mol fraction of molecule i

q_i : van der Waals surface area
 r_i : van der Waals volume
 Q_j : group surface area parameter
 R_j : group volume parameter
 $\Theta_{ne,d,m}$: group surface area fraction
 $X_{ne,d,m}$: group fraction
 $\Psi_{ne,d,m,j}$: parameter
 $a_{n,m}$: group interaction parameter
 T_{ne} : temperature of set of experimental data ne

Parameters estimation

$P_{ne,d}^{CALC}$: calculated pressure for datum d , in set of experimental data ne
 $P_{ne,i}^V$: vapor pressure of molecule i at T_{ne}
 $P_{ne,d}^{EXP}$: experimental pressure for datum d , in set of experimental data ne
 σ_P : standard percent relative deviation in pressure P
 σ_y : standard percent deviation in mole fraction y_1
 N_{ne} : number of points in set of experimental data ne

7 Acknowledgments

Authors greatly acknowledge CONICET, ANPCyT and Universidad Nacional del Sur for supporting their work through grants PIP 2011 11220110101078 (2013-2015), PICT 2012-2469 and PGI 24/M125 respectively.

8 References

1. Sharifzadeh, M. *Implementation of a steady-state inversely controlled process model for integrated design and control of an ETBE reactive distillation*. Chemical Engineering science 92 (2013) 21-39
2. Thiel, C., Sundmacher, K., Hoffmann, U. *Synthesis of ETBE: Residue curve maps for the heterogeneously catalyzed reactive distillation process*. Chemical Engineering Journal 66 (1997) 181-191.
3. Yee, K.F., Mohamed, A.R., Tan, S.H. *A review on the evolution of ethyl tert-butyl ether (ETBE) and its future prospects*. Renewable and Sustainable Energy Reviews 22 (2013) 604-620.
4. L. Domingues, L., Pinheiro, C. I. C., Oliveira, N. M. C., Fernandes, J., & Vilelas, A.. *Model Development and Validation of Ethyl tert-Butyl Ether Production Reactors Using Industrial Plant Data*. Industrial and Engineering Chemistry Research, 51 (2012) 15018–15031.
5. Brooke, Kendrick, Meerhaus, Raman. *GAMS 24.0 User Guide*. (2013)
6. Pretel, E. *The UNIFAC library*. (1997)
7. Al-Arfaj, M.A., Luyben, W.L. *Control study of ethyl tert-butyl ether reactive distillation*. Ind. Eng. Chem. Res. 41 (16) (2002) 3784–3796.

8. K. Kammerer, S. Schnabel, D. Silkenbaumer, R. N. Lichtenthaler. *Vapor – liquid equilibria of binary mixtures containing an alcohol and a branched ether. Experimental results and modeling*, Fluid Phase Equilibria, 162 (1999) 289–301.
9. A. Leu, D. B. Robinson, A. Tg, 1999, *Vapor-Liquid Equilibrium for Four Binary Systems*. Journal of Chemical Engineering data, 44, 398–400.
10. M. Laakkonen, J.-P. Pokki, P. Uusi-Kyyny, J. Aittamaa. *Vapour-liquid equilibrium for the 1-butene + methanol, + ethanol, + 2-propanol, + 2-butanol and + 2-methyl-2-propanol systems at 326 K*, Fluid Phase Equilibria, 206, 1-2 (2003) 237–252.
11. T. Ouni, P. Uusi-Kyyny, J.-P. Pokki, J. Aittamaa. *Isothermal vapour liquid equilibrium for binary 2-methylpropene+methanol to butanol systems*, Fluid Phase Equilibria, 232, 1-2 (2004) 90–99.
12. Nikacevic, N. M., Huesman, A. E. M., Van Den Hof, P. M. J., Stankiewicz, A. I. *Opportunities and challenges for process control in process intensification*. Chemical Engineering and Processing - Process Intensification, 52 (2011) 1–15.
13. Tian, Y.-C., Zhao, F., Bisowarno, B. H., Tadó, M. O. *Pattern-based predictive control for ETBE reactive distillation*. Journal of Process Control, 13(1) (2003) 57–67.