

## Effect of adjusted parameters of NRTL model in design, optimization, and control of homogeneous azeotropic distillation columns

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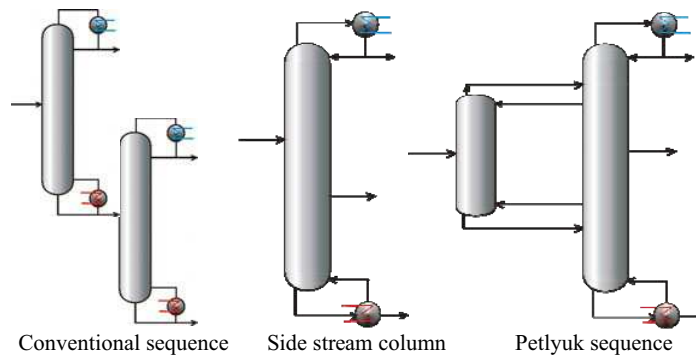
### Abstract

In this work we use adjusted parameters obtained with Simulated Annealing and those from Dechema Collection [1] for the NRTL model, in order to analyze their effect in the design, optimization, and control of homogeneous azeotropic distillation columns. For the design of the azeotropic sequences we use short design methodologies [2, 3], while a multiobjective genetic algorithm with constraints coupled to Aspen Plus [4] is used to optimize them. Theoretical control properties are evaluated with Singular Value Decomposition technique. Results show remarkable differences in structure, energy consumption, and performance of the sequences.

### Introduction

A key step in the design of azeotropic distillation systems is the choice of the thermodynamic model. These thermodynamic models utilize adjusted parameters that are obtained from non linear regressions of the experimental data. In most of the cases, the objective function in nonlinear parameter estimation problems is non-convex and may have multiple local optima [5]. Therefore, assuming that experimental equilibrium data are thermodynamically consistent, it is clear that the use of different methods to make the non linear regression affects, without doubt, the obtained adjusted parameters, and as consequence the predicted phase equilibrium. The high nonlinearity of the problem of parameters estimation suggests that only global optimization techniques can be used. However, in most of the cases the estimation is based on a least squares or maximum likelihood analysis [5]. For instance, Gau et al [6] found that for some of the equilibrium data published in Dechema Collection the adjusted parameters are just a local optima. This finding is very important, because design, simulation, optimization, and even control of reactive and separation process relies on estimation of thermodynamic properties.

Several works have been focused in studying the effect of the thermodynamic uncertainties on the design, or the simulation, or the control of distillation columns [5, 7, 8, 9, 10, 11]. However, no formal analysis has been made to study the effect that adjusted parameters have in design, optimization, and control of distillation sequences, either conventional or thermally coupled. So, in this work we use adjusted parameters obtained with a stochastic technique, Simulated Annealing, SA, and those taken from Dechema Collection, DC, [1] for the NRTL model, in order to analyze their effect in the design, optimization, and control of homogeneous azeotropic distillation columns. We consider three azeotropic sequences: conventional direct, side stream and Petlyuk (Figure 1), which are designed with short design methodologies [2, 3]; while a multiobjective genetic algorithm coupled to Aspen Plus [4] is used to perform the optimization task. Theoretical control properties are evaluated with Singular Value Decomposition technique, SVD. Results show considerable differences in the structure, energy consumption, and performance of the sequences.



**Figure 1.** Schemes for separation of the azeotropic mixture.

### Strategy solution

In order to obtain the optimal designs of the considered distillation schemes, we consider two set of adjusted parameters for NRTL model: one from DC, and other obtained by SA. Our numerical experience indicates that this stochastic method is a reliable strategy for parameter estimation in VLE modeling [12]. SA method overcomes most of the numerical difficulties that local optimization methods show. Due to the statistical nature of the SA, a local minimum can be hopped much more easily than in conventional methods. For the case of complete VLE data, excess Gibbs energy equations are widely applied for phase equilibrium modeling. In the present study, the SA code use [13, 14] an objective function, commonly used for data fitting, based on activity coefficients:

$$F_{obj} = \sum_{j=1}^{ndat} \sum_{i=1}^c \left( \frac{\gamma_{ij}^{exp} - \gamma_{ij}^{calc}}{\gamma_{ij}^{exp}} \right)^2 \quad (1)$$

where  $\gamma_i^{exp}$  and  $\gamma_i^{calc}$  are the experimental and calculated values for the activity coefficient of component  $i$ , and  $c$  is the number of components in the mixture, respectively. This formulation is equivalent to assuming that the standard error in the measurement of  $\gamma_{ij}$  is proportional to its value. All experimental data are taken from DC. We use the following initial intervals for NRTL parameters in the global

optimization of objective function:  $A_{12}, A_{21} \in (-2000, 5000)$  and  $\alpha_{12} \in (0.01, 10)$ . With the adjusted parameters calculated with SA and those from DC, we use short design methodologies in order to have the preliminary feasible designs. These methodologies consider algebraic material balances and the complete phase equilibrium calculation. For more detailed information about these design procedures the reader is referred to the original works [2, 3]. Since we are working with azeotropic mixtures, it is so important to give an initial design feasible to avoid that the algorithm explores in regions not feasible; this requirement is due to the nature of the mixture itself, and it is not a limitation of the genetic algorithm. Then, preliminary designs become initial designs for the optimization procedure [4], which is explained next.

The optimal design problem of the azeotropic sequences implies the simultaneously optimization of the heat duty of the sequence,  $Q_i$ , and the number of stages in each shell,  $N_i$ : 4, 2, and 3 objectives for conventional, side stream and Petlyuk sequences, respectively. Also, the purities required in each product stream, 3, must be reached. This optimization problem can be expressed as:

$$\begin{aligned} \text{Min}(Q_i, N_i) &= f(R, F_k, N_{in,k}, N_{out,k}, N_F, N_S, N_i) \\ \text{subject to} & \\ y_k &\geq x_k \end{aligned} \quad (2)$$

Where  $R$  is the reflux ratio,  $F_k$  is the interconnection flow  $k$ ,  $N_F$  is the feed stage of the sequence,  $N_S$  is the side stream stage,  $N_{in,k}$  and  $N_{out,k}$  are the number of stage where comes and leaves the interconnection flow  $k$ , and required and obtained purities are the vectors  $x_k$  and  $y_k$ , respectively. All these manipulated variables are considered if they applied for each scheme.

This optimization problem is solved through a multiobjective genetic algorithm with constraints [4]; since the code is coupled to Aspen Plus all results consider the complete MESH equations and rigorous calculations of phase equilibrium. This optimization procedure allows obtaining the Pareto front of optimal designs, which includes optimal designs from minimum reflux ratio to minimum number of stages, and all designs between these extremes. From the Pareto front, the design with the best compromise between heat duty and number of stages is chosen, for each scheme and set of adjusted parameters, to study their control properties. Theoretical control properties of selected designs are evaluated using the SVD technique, which can be defined as:

$$G = V\Sigma W^H \quad (3)$$

Here,  $G$  is the matrix target for SVD analysis and  $\Sigma$  is a diagonal matrix which consists of the singular values of  $G$ . The singular values of the open-loop frequency function matrix of a process at a given frequency are the gains of the process at this frequency, in the directions of the corresponding input singular vectors (as the input singular vectors form a basis in the input space, the gain can be calculated in every direction). These gains play an important role when performing controllability analysis of a process, and for a complex analysis they must be evaluated in all frequency domain. The Morari Resiliency Index (MRI) is the smallest singular value ( $\sigma_*$ ) of the process open-loop frequency function matrix. The larger its value, the more controllable the process is. If it is zero, this means that there is an input

direction where the gain is zero and the matrix is not invertible. Condition number ( $\gamma$ ) is the ratio of the largest and smallest singular values of the process open-loop frequency function matrix. If it is large, then the matrix has strong directionality, which means that the gains vary strongly depending on input directions. Such a matrix is said to be ill-conditioned. A large  $\gamma$  means that the system is sensitive to input and model uncertainty and therefore the process is less controllable. Systems with higher  $\sigma_*$  values and lower  $\gamma$  are expected to show the best dynamic performance under feedback control.

This methodology is applied to the separation of an equimolar azeotropic mixture of acetone-isopropanol-water, introduced as saturated liquid; the separation is performed in conventional direct, side stream and Petlyuk sequences, which operate at 30 psia. Required purities of acetone, isopropanol, and water in their respective product stream are 0.90/0.65/0.99.

### Analysis of results

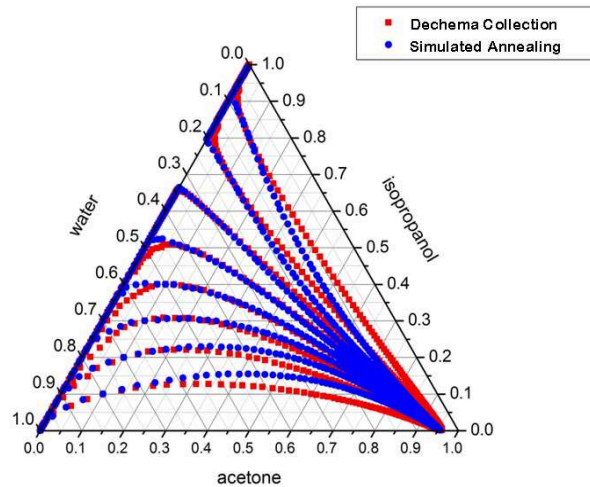
In Table 1, we observe that adjusted parameters for binary pairs isopropanol-water and acetone-water have the same values as in DC as in SA. Nevertheless, remarkable differences are found in the binary pair acetone-isopropanol; which do not affect the calculated composition of the azeotropic points, Table 2. On the other hand, the residue curve maps present small differences between them, as can be seen in Figure 2.

**Table 1.** Adjusted parameters from Dechema Collection and Simulated Annealing.

	Adjusted parameter	acetone (1) isopropanol (2)	isopropanol (1) water (2)	acetone (1) water (2)
Dechema Collection	A12	536.728000	39.854100	750.318100
	A21	-97.821600	1659.257200	1299.397000
	$\alpha$ 12	0.301800	0.325500	0.585600
Simulated Annealing	A12	402.816000	39.854100	750.318100
	A21	9634.610000	1659.257200	1299.397000
	$\alpha$ 12	0.419480	0.325500	0.585600

**Table 2.** Azeotropic point's compositions with both adjusted parameters.

	Azeotrope	$X_{\text{acetone}}$	$X_{\text{isopropanol}}$	$X_{\text{water}}$
Dechema Collection	Binary 1	0.96060831		0.03939069
	Binary 2		0.68236521	0.31763379
Simulated Annealing	Binary 1	0.96060831		0.03939069
	Binary 2		0.68236521	0.31763379



**Figure 2.** Residue curve maps with both set of adjusted parameters.

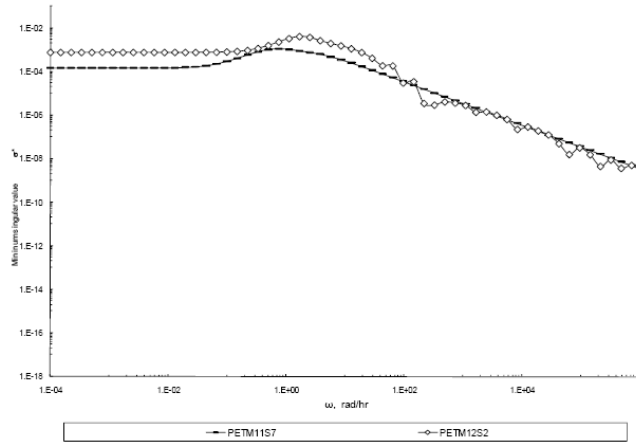
In the adjusted parameters, we observe that there is a match in two binary pairs, and the last one presents notable differences. In spite of this, the azeotropic point's compositions are the same, and they are just lightly differences in the residue curve maps. Therefore, we can expect minor differences in the design and control properties of the optimal designs with both set of adjusted parameters. Nevertheless, the optimal designs present notable differences in the heat duty,  $Q$ , and total number of stages,  $N$ , as can be noted in Table 3.

**Table 3.** Optimal designs of the azeotropic schemes with both adjusted parameters.

Sequence	Dechema Collection		Simulated Annealing	
	N	Q, BTU/h	N	Q, BTU/h
Conventional	24	9,654,746.83	24	8,688,388.50
Side stream	25	14,247,716.20	21	5,902,515.26
Petlyuk	45	3,522,565.61	43	2,516,847.94

For all sequences, designs resulting from using the adjusted parameters of SA, called from here SA designs, have lower energy consumptions, with respect to the designs obtained with parameters of the DC, called from here DC designs. Basically, the SA designs require 10.01%, 58.58%, and 28.56% less energy than the DC designs, in the conventional direct, side stream, and Petlyuk sequences, respectively. The found differences are huge, considering that just one binary pair does not match between DC and SA; it is worth to mention that the components of this binary pair do not form azeotropes. In the number of stages we observe the same tendency, but the differences are very small, no more of 4 stages.

Finally, the control studies reveal that the SA design of Petlyuk sequence is the best conditioned, of all schemes, to the effect of the disturbances, as a result of its greater minimum singular value, Figure 3. Therefore, for this case the Petlyuk sequence has the better energy consumptions and also the best control properties, when the adjusted parameters obtained with SA are used. From Figure 3 we also can observe the deterioration in the control properties with the use of adjusted parameters of DC.



**Figure 3.** Minimum singular value for Petlyuk sequence optimal design with DC (PETM11S7) and SA (PETM12S2).

### Concluding remarks

A formal analysis to study the effect of the adjusted parameters of model NRTL on the design, optimization, and control of azeotropic sequences has been presented. Results show that optimal designs with best energy consumption and control properties are obtained when global optimum for adjusted parameters are used. In spite of some discrepancies in the designs with both set of parameters were expected, results show that small differences in the phase equilibrium analysis are translated and maximized in the later stages of design, optimization and control. For the study case analyzed, the energy consumptions differ until 40%, even when the prediction of azeotropic points does not change. Also, the control properties are deteriorating just changing the parameters used. The huge variation in energy savings and control properties represent a serious problem, since new separation schemes and/or improvement of existing plants are evaluated through design and control studies, principally; and they determine if the structure or improvement can be implemented or not in practical applications.

### Acknowledgements

Financial support of this work provided by CONACyT (México) through the Project 84552 is gratefully acknowledged.

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