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STEP-BY-STEP CALCULATION OF REACTIVE EXTRACTION CASCADES APPLYING THE EQUILIBRIUM MODEL

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ABSTRACT

This paper presents a step-by-step calculation algorithm for reactive extraction cascade simulation. The theoretical basis is taken from reactive liquid-liquid equilibrium thermodynamics. This method can be applied to parallel, countercurrent, and cross-current arrangements, operating with the most important practical specifications: splitting of solvent and feed streams, location of reaction zone, choice of feed points, and specification of transferred heat flow. To illustrate the usefulness of this approach, reactive extraction technological schemes for the synthesis of n-amyl acetate from aqueous acetic acid solutions were simulated. Although the examples are designed to prove algorithm adequacy, it was also found that the n-amyl acetate production by reactive extraction has strong limitations on conversion and separation. In addition, it is not an interesting alternative to increase the economic value of acetic acid and water streams.

KEYWORDS: Reactive extraction; Reactive liquid-liquid equilibrium; Esterification systems; N-amyl acetate; step-by-step calculation algorithm.

CÁLCULO SECUENCIAL DE CASCADAS DE EXTRACCIÓN REACTIVA APLICANDO EL MODELO DE EQUILIBRIO

RESUMEN

Se presenta un algoritmo de cálculo etapa por etapa para la simulación de cascadas de extracción reactiva. El fundamento teórico se encuentra en la termodinámica del equilibrio líquido – líquido reactivo. El método puede tratar arreglos en paralelo, contracorriente y cruzados, operando con las especificaciones más importantes en la práctica: división de flujos de solvente y alimento, localización de la zona de reacción, elección de los puntos de alimentación y la especificación del flujo de calor transferido. Para ilustrar la utilidad de las ideas se simularon esquemas tecnológicos de extracción reactiva para la síntesis de n-amilacetato a partir de soluciones acuosas de ácido acético. Aunque

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los ejemplos se encuentran orientados a demostrar las capacidades del algoritmo, también se pudo establecer que la producción de n-amilacetato por extracción reactiva presenta fuertes limitaciones a la conversión y a la separación y no representa una alternativa interesante para incrementar el valor económico de las corrientes de ácido acético y agua.

PALABRAS CLAVE: extracción reactiva; equilibrio líquido – líquido – reactivo; sistemas de esterificación; n-amilacetato; algoritmo etapa a etapa.

CÁLCULO SEQÜENCIAL DE CASCATAS DE EXTRAÇÃO REATIVA APLICANDO O MODELO DE EQUILÍBRIO

RESUMO

Apresenta-se um algoritmo de cálculo etapa a etapa para a simulação de cascatas de extração reativa. O fundamento teórico se encontra na termodinâmica do equilíbrio líquido - líquido reativo. O método pode ser utilizado para cascatas com contato multiestágio em paralelo, cruzado e contracorrente operando nàs especificações mais importantes na prática: divisão de fluxos de solvente e alimentação, localização da zona de reação química, escolha dos pontos de alimentação e especificação do fluxo de calor transferido. Para ilustrar a utilidade das ideias, foram simulados esquemas tecnológicos de extração reativa para a síntese de n-amil acetato a partir de soluções aquosas de ácido acético. Embora os exemplos são orientados para demonstrar as capacidades do algoritmo, foi igualmente estabelecido que a produção de n-amil acetato por extração reativa tem fortes limitações pela conversão e separação e não representa uma alternativa interessante para aumentar o valor econômico das correntes de ácido acético e água.

PALAVRAS-CHAVE: Remoção de equilíbrio reativo Liquefeito - sistemas de esterificação reativa; n-amylacetate algoritmo passo a passo - líquidos.

1. INTRODUCTION

Reactive extraction (RE) is the combination of liquid-phase reaction and chemical reaction to improve a solvent's capacity or to complete reactions limited by equilibrium. The main limitation to these processes is that they must operate in conditions under which liquid-liquid phase separations and chemical reactions take place simultaneously (Krishna, 2002; Kulprathipanja, 2002; Gutiérrez, 2008; Górak, 2011). When "compatibility" exists between reaction and separation, it is possible to displace the chemical equilibrium through in situ removal of the product formed. This possibility offers two main advantages when compared to homogeneous phase processes: 1) conversion and selectivity are increased, and 2) the number of recycle flows, processing costs, and capital costs are reduced (Krishna, 2002; Kulprathipanja, 2002; Gutiérrez, 2008; Górak, 2011). The best-known RE applications in the industry are related with the production of fuel (especially biodiesel), antibiotics, acetates, and the recovery of acids and alcohol produced during fermentation processes (Krishna, 2002; Kulprathipanja, 2002; Pai et al., 2002; Bouraqadi et al., 2007; Cadavid et al., 2011).

The solution to the mathematical model controlled by equilibrium (chemical equilibrium plus phase equilibrium) is a tool for basic analysis of ER processes. At this level, the following aspects are established: a) forms of contact, b) positioning of the reaction zone, c) maximum conversion, and d) use of different technological schemes (Gorissen, 2003; Cardona & Gutiérrez, 2007a-b; Gutiérrez, 2008). Quantifying these aspects for reactive extractor arrangements requires robust algorithms able to manage different sets of specifications. Research into numerical techniques for solving the equilibrium model in RE processes is therefore relevant. It must also be considered that commercial chemical process simulators (ASPEN PLUS® being the most representative) do not have specialized modules for simulating RE cascades, although it is possible to obtain approximations through reactor and liquid-liquid separator combinations.

This study extended the calculation algorithm for non-reactive extraction cascades proposed by Sánchez et al. (2009). It was observed that this strategy is valid for reactive cascades since it is founded on the calculation of different types of flash. This method can handle specifications such as the type of arrangement (parallel, cross-current, and countercurrent), the location of the reaction zone (number of reactive phases in hybrid arrangements), and transferred heat (isothermal, adiabatic, and specified heat flow stages). The case with specified heat flow constitutes an improvement with regards to the studies presented in the literature, in which this effect is generally not included (Minotti et al., 1998; Rivera, 2004; Rivera & Cardona, 2004; Gutiérrez, 2008). The method's foundation is in reactive liquid-liquid equilibrium (RLLE) calculations, RLLE with heat transfer (RLLET), and the analysis of material stability developed by Michelsen (Michelsen, 1982a-b; Michelsen & Mollerup, 2007).

An RE cascade addresses an arrangement of phases in equilibrium in which each reactive extractor is modeled as a flash with a chemical reaction. The type of flash is determined by the specifications. For example, in isothermal or adiabatic cascades, the type of flash is isothermal or adiabatic, respectively. This point of view allows for easily covering different types of configurations and situates the problem of resolving a reactive cascade model within the sphere of thermodynamics. The methodology is therefore centered on the ordered use of RLLE (or RLLET) in a step-by-step algorithm to simulate RE cascades. The solutions to RE cascades (especially composition profiles) are represented using the transformed molar fractions proposed by Ung & Doherty (1995) in order to decrease the spatial dimension of compositions and demonstrate the possibility of using graphic methods of conventional extraction on reactive phase diagrams with coordinate transformation.

The algorithm's performance is demonstrated in examples related to n-amyl acetate production through reactive extraction. This system is an appropriate object of study for two reasons: 1) the presence of a reactive partial solubility area that is favorable for liquid-liquid separation, and 2) the distillation processes are limited by the existence of multiple azeotropes.

2. METHODOLODY

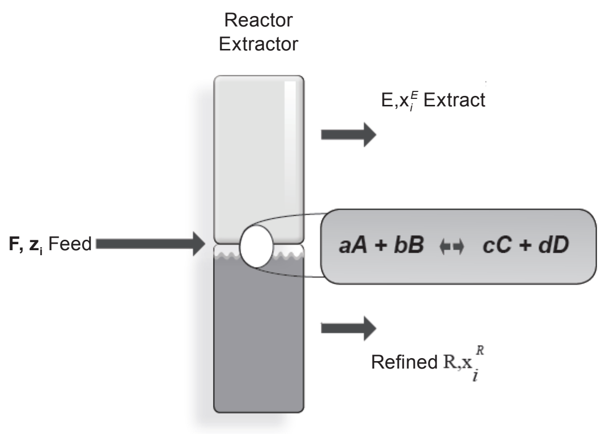
This section presents the procedures used for calculation of the reactive phase equilibrium and how these calculation routines can be combined to solve a reactive phase cascade. To calculate the RLLE and the RLLET, we modified the reactive variable suggested by Henley & Rosen (1973) in the Rachford & Rice algorithm. The step-by-step procedure suggested by Sánchez et al. (2009) was used for the RE cascade to manage the non-reactive case.

2.1. Reactive Liquid-liquid Isothermal Flash

Let us consider the reactive extractor represented in **Figure 1**. An isothermal flash is defined as when the feed (flow and composition) is specified, along with temperature and pressure. The problem is to calculate the composition of the phases (conventionally called refined phases, or RF, and extract phases, or EF) and the relationship between their amounts (the fraction of extracts) (Henley & Rosen, 1973). In general, the solution to the system of equations that models the reactive separator in **Figure 1** can be approached using four alternatives: a) simultaneous correction like the Newton-Raphson and its variations (Bonilla et al., 2008), b) continuation techniques using homotopies (Jalali & Seader, 1999 & 2000), c) relaxation methods (Wasylkiewicz & Ung, 2000), and d) step-by-step procedures based on Rachford & Rice's equations (Henley & Rosen 1973; Sánchez et al., 2011).

This study uses a generalization of the Rachford & Rice algorithm to include the effect of a chemical reaction (see **Figure 2**). The origin of these ideas is found in the study by Henley & Rosen (1973). The information flow diagram (see **Figure 2**) uncouples phase equilibrium from chemical equilibrium: the two internal connections correspond with the Rachford & Rice algorithm for non-reactive systems (Henley & Rosen, 1973; Henley & Seader, 2006; Sánchez, 2009) and are executed keeping the reaction coordinate constant; the most external connection is meant to

Figure 1. Equilibrium stage. Simultaneous reaction-extraction process.



Note that in Figure 1, the feed refers to the mix of feed to be separated and the extractive solvent. It is expressed as a single feed to simplify the equations.

check compliance with the chemical equilibrium condition. The flow diagram in **Figure 2** is simplified for the non-reactive case when the reaction does not proceed ($\xi = 0$), eliminating the most external iterative cycle.

The objective function of the internal cycle, called the Rachford & Rice function, is the product of combining the balances of matter, the liquid-liquid equilibrium relationships, and the moral fraction restrictions (Henley & Rosen, 1973):

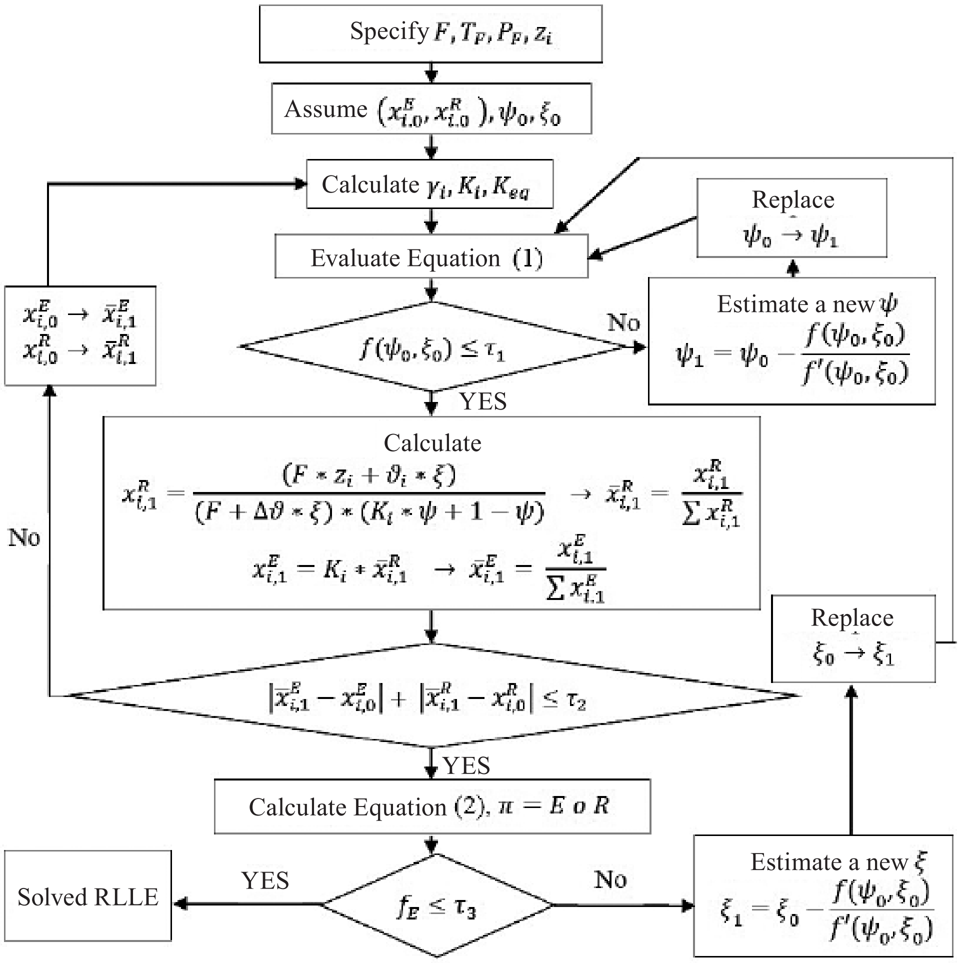
$$f(\psi,\ \xi) = \sum_{i=1}^{c} \frac{(F * z_i + \vartheta_i) * (K_i - 1)}{(F + \Delta\vartheta * \xi) * (K_i * \psi + 1 - \psi)} \qquad (1)$$

In the equation above, the variables have the following meanings: ψ is the fraction of extracts (E/F), K_i is the distribution coefficient of component i (γ_i^R/γ_i^E), z_i is the molar fraction of component i in the feed, $\Delta\vartheta$ is the change in the moles caused by the reaction (the sum of the stoichiometric coefficients, positive for products and negative for reactives), and ξ is the reaction coordinate. If there is no reaction ($\xi = 0$), the **Equation 1** takes the form of the Rachford & Rice function for non-reactive systems (Henley & Rosen, 1973; Henley & Seader, 2006). The **Equation 1** is general and applies to systems both with and without a change in the number of moles. The objective function for the external connection (see **Figure 2**) is the condition of chemical equilibrium for systems with a reaction in the liquid phase (Smith et al., 2007):

$$f_E \equiv K_{eq} - \prod_{i=1}^{m} [x_i^\pi * \gamma_i^\pi]^{\vartheta_i} = 0 \qquad (1)$$

In the **Equation 2**, π refers ton e of the phases in equilibrium (extracts or refined), and K_{eq} is the constant of chemical equilibrium. The convergence of the Rachford & Rice algorithm for reactive systems is strongly influenced by the initial estimates. This situation can be addressed by generating the initial estimates in two steps: 1) resolving the chemical equilibrium in the homogeneous phase, and 2) analyzing the material stability of the resultant solution after reaching chemical equilibrium. If the solution is materially stable, the equilibrium is homogeneous; conversely, if the solution is materially unstable, the equilibrium is heterogeneous. The results of the material stability analysis give excellent estimates for the LLE calculation (Michelsen, 1982a-b; Firoozabadi, 1999; Michelsen & Mollerup, 2007) and the RLLE calculation (Jalali & Seader, 1999 & 2000; Wasylkiewicz & Ung, 2000; Sánchez, 2011). Note that this initialization procedure

Figure 2. RLLE solution algorithm



is equivalent to requiring that the pseudo-initial mix in chemical equilibrium be materially unstable.

Given that the phase separation and the chemical reaction take place at the separator conditions (see **Figure 1**), the algorithm presented in **Figure 2** is also valid for reactive extractors with multiple feeds by using the composition of the solution that would result from mixing the different feeds in a non-reactive process (Prieto, 2012). It should be observed that once the reactive isothermal flash is solved, it is possible to calculate the heat transfer flow by applying an energy balance to the reactive extractor. In accordance with the above: in an isothermal flash calculation, the energy balance is disconnected from the material balances and the equilibrium relationships.

2.2. Reactive Liquid-liquid Flash with Heat Transfer

Figure 1 defines a liquid-liquid flash with heat transfer when the feed (molar flow, temperature, pressure, and composition), the reactive extractor's operation pressure, and the transferred heat flow are specified. The problem is calculating the composition of the refined products and the extracts, the fraction of the extracts, and the operation temperature. Due to the set of specifications, the energy balance is coupled with the material balances and the equilibrium relationships.

In this study, it was observed that classic solution strategy presented in the textbooks for non-reactive systems (Manning & Thompson, 1995; Henley & Rosen, 1973; Henley & Seader, 2006; Sánchez, 2009) was valid for reactive liquid-liquid flash with heat transfer. The information flow diagram is shown in **Figure 3**. It should be observed that the classic algorithm is reduced if LLE is used instead of RLLE (see block 3 in **Figure 3**). The temperature varies in an external cycle, applying a step from the Newton-Raphson to an objective function defined in terms of the energy balance:

$$f(T) \equiv F * H_F \pm Q - E * H^E - R * H^R \qquad (3.1)$$

$$T^{i+1} = T^i - \frac{f(T^i)}{f'(T^i)} \qquad (3.2)$$

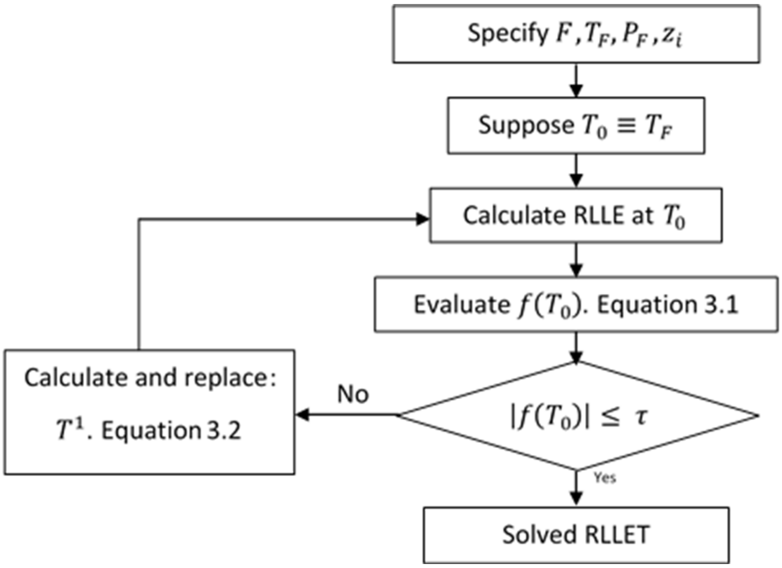
2.3. Reactive Extraction Cascades

Figure 4 illustrates the three most common cascade arrangements (parallel, cross-current, and countercurrent) for liquid phase extraction processes (Treybal, 1968; Rydberg, 2004; Benítez, 2009). The cascades are different in two aspects: 1) the direction in which the currents flow differentiates the parallel and cross-current arrangements from the countercurrent arrangement, and 2) the use of one or more solvent flows differentiates the cross-current arrangement from the parallel and countercurrent arrangements.

From a computational point of view, parallel and cross-current cascades are simple problems because the calculations can be made in a step-by-step manner, following the order that corresponds to the arrangement physically. **Figures 4a** and **4b** show that each reactive extractor is only affected by the extractor immediately preceding it, and there is therefore no recirculation of currents or of information. In synthesis: in parallel and cross-current arrangements, the reactive extractors are uncoupled.

The total equilibrium model applied to parallel cascades easily leads us to conclude that a reactive extractor is only necessary because it is not possible to increase the equilibrium conversion without manipulating the operating conditions of later stages. If the conversion must be increased to include more extractors, the temperature in stage 2 and the following stages must be "programmed" to displace the equilibrium as required. The solutions to the total equilibrium model correspond with the asymptotic limits of the

Figure 3. RLLET solution algorithm



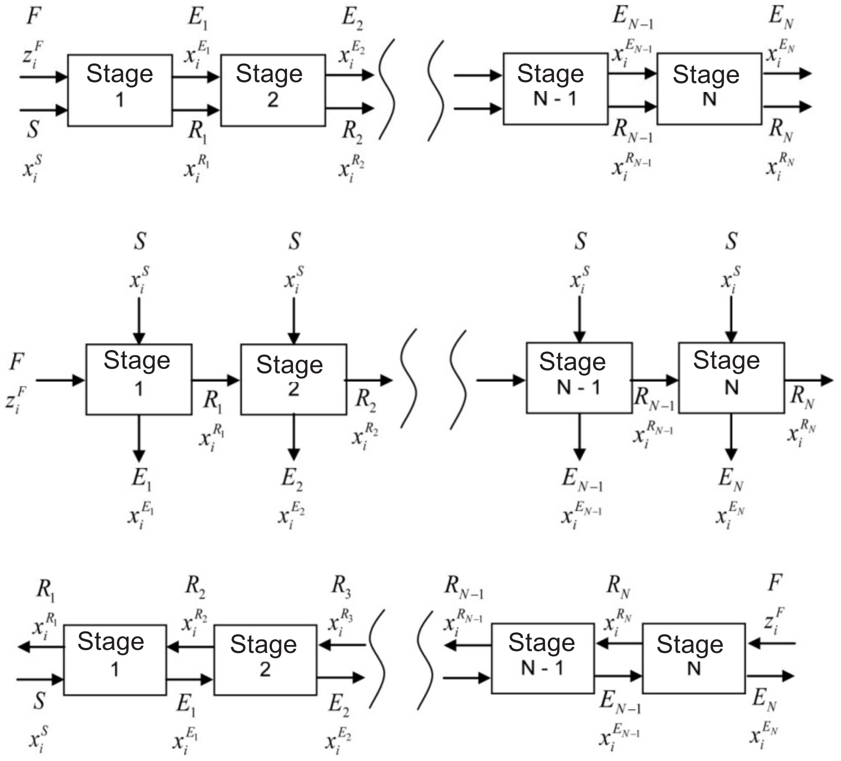
kinetics-controlled model for long residence times achieved with multiple extractors (Minotti et al., 1998; Gutiérrez, 2008).

In the countercurrent arrangement (see **Figure 4c**), a reactive extractor is coupled with the following and the previous reactors, creating a calculation process that requires complete consideration of the cascade. In principle, the methods used in reactive distillation (RD) can be adapted to solve the mathematical model. However, in the specific area of the simulation, no research considering the necessary adaptations for this purpose has been found in the open literature.

For the countercurrent cascade solution, the method proposed by Sánchez et al. (2009) was generalized to address non-reactive arrangements. Due to the fact that this model is founded in the routines for different types of flash (isothermal, adiabatic, vaporized fraction, etc.), it can be adapted for systems with chemical reactions by using the reactive versions of the different types of flash. **Figure 5** shows the information flow diagram. This algorithm is easy to implement because it only has one iterative connection and manipulates the equations by subsets associated with each reactive extractor. Block 3 of the algorithm in **Figure 5**, called "consecutive evaluation of the extraction cascade," consists of calculating the arrangement by beginning with the first stage and proceeding consecutively until the final extractor is reached using the type of flash that corresponds with the specifications. The initial estimates are obtained by solving a reactive extractor and using the results to specify profile graphs for temperatures, flows, and compositions throughout the cascade. The convergence criterion is determined when the change in the fractions between two consecutive cycles is less than or equal to the desired precision:

$$\tau = \sum_{j=1}^{N} \sum_{i=1}^{C} \Delta x_{i,j} \leq 10^{-6} \tag{4}$$

Figure 4. Typical RE cascade arrangements: a) parallel, b) cross-current, and c) countercurrent.



$$\Delta x_{i,j} = |x_{i,j}^{k} - x_{i,j}^{k-1}| \qquad j=1,2,3\ldots N;\ i=1,2,3\ldots C \qquad (5)$$

The algorithm in **Figure 5** is step-by-step and its structure is valid independent of the numerical method used to solve the reactive flash. This aspect is important because it offers the versatility of using the techniques available in the literature for solving the flash. Based on wide experience with the use of the algorithm, the authors have observed that for arrangements with multiple stages, 30 iterations of the external cycle in **Figure 5** are typically required.

3. RESULTS AND DISCUSSION

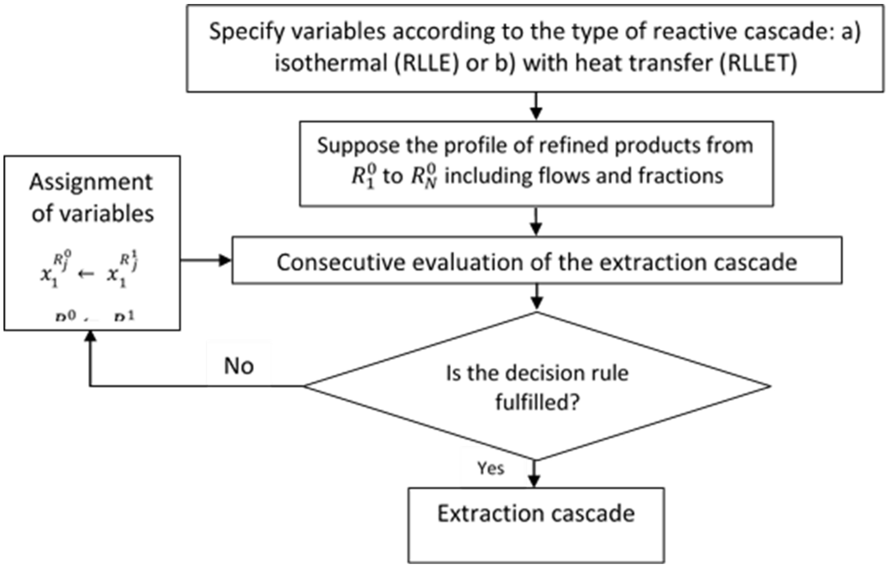
N-amyl acetate is widely used as a solvent in the production of lacquers and paints, as well as in the creation of adhesives, coatings, and paint thinners. Its synthesis can prove interesting based on an esterification reaction using reactive separation processes (mainly distillation, extraction, and membranes) in order to displace the chemical equilibrium and avoid limiting factors to separation that exist in the non-reactive system.

First, the reactive phase equilibrium for the acetic acid + 1-Butanol + n-Butyl acetate + water system (case study 1) is calculated in order to have a point of comparison in a recurrent system in the literature (Bonilla et al., 2008-1; Bonilla et al., 2008-2; Gutiérrez, 2008, Rivera, 2004, Minotti et al., 1998). Then, examples of reactive extraction cascades created for synthesizing n-amyl acetate are addressed using different technological schemes. For the solutions in case study 1, the activity coefficients are calculated with the UNIQUAC model and the interaction parameters reported by Minotti et al (1998). For the acetic acid + 1-Pentanol + n-amyl acetate + water solutions (case study 2), the NRTL model was used with the parameters reported by Chiang et al (2002). The equilibrium constant for the esterification reactions were taken from Wyczesany (2009) and Minotti et al (1998) for the n-amyl acetate cases and the n-Butyl acetate cases, respectively. The case with the transferred heat flow specification was only evaluated for n-amyl acetate taking the calorific capacity as a liquid for the acetic acid, 1-Pentanol, and n-amyl acetate compounds from Yaws, (2003) for water from NIST, (2012) and enthalpies of formation as a liquid from NIST, (2012).

Example 3.1. RLLE for an Acetic Acid + 1-Butanol + n-Butyl Acetate + Water Solution

In order to validate the calculation of reactive phase equilibrium, the RLLE was calculated in the

Figure 5. Solution algorithm. Countercurrent arrangement extraction cascades



context of an example studied by Minotti et al (1998) corresponding to a parallel cascade for the esterification system in case study 1. The inflow information is found in **Table 1**.

Tabla 1. Operating conditions. Acetic acid + 1-Butanol + n-Butyl acetate + water system (case study 1)

Operating conditions: Temperature = 293.15 K Pressure = 1 bar
Feed Flow F = 100 mol/h Solvent Flow S = 100 mol/h
Feed Composition: $z_1^F = 0.25$; $z_2^F = 0.00$; $z_3^F = 0.00$; $z_4^F = 0.75$
Solvent Composition: $x_1^S = 0.00$; $x_2^S = 1.00$; $x_3^S = 0.00$; $x_4^S = 0.00$
Equilibrium Constant: $K_{eq} = 66.1$

In the study by Minotti et al (1998), a kinetics-controlled model is considered and an expression of the law of speed is used in order to calculate the residence time for a known conversion. In this approach, the representation of chemical equilibrium is achieved using long residence times (theoretically, an "infinite" amount of time). According to Minotti et al (1998), the equilibrium conversion is approximately 91%.

Table 2. Results obtained for RE cascade, parallel arrangement, acetic acid + 1-Butanol + n-Butyl acetate + water system (case study 1)

Phase	Flow (mol/h)	Composition
EF	24.4726	$x_1^E = 0.0239$; $x_2^E = 0.0107$; $x_3^E = 0.9122$; $x_4^E = 0.0532$
RF	175.5274	$x_1^R = 0.0089$; $x_2^R = 0.4380$; $x_3^R = 0.0030$; $x_4^R = 0.550$
Acetic acid conversion: 91.40 %		

The information flow diagram from **Figure 2** was used to solve the RLLE, and the results shown in **Table 2** were found. The conversion calculated is equal to 91.4% and concurs reasonably with that reported by Minotti et al (1998). Considering that the equilibrium model is an asymptotic solution of the kinetics-controlled model, other examples addressed in the article by Minotti et al (1998) were checked (for reasons of space, they are not presented here), also finding a good correspondence.

Example 3.2. N-amyl Acetate Production.

3.2.1. Countercurrent Cascades

The study of n-amyl acetate production was completed by evaluating various design schemes that all maintain the countercurrent arrangement. The selection of this arrangement stems from the knowledge that it is the most widely used in the industry for the following reasons: a) there is a gradual enrichment of the solute in the solvent phase throughout the entire extractive process, b) the quantities of solvent necessary to complete the process are considerably less than those required for other kinds of arrangements, for example, cross-current arrangements, which imply obtaining richer extract phases in the solute of interest, and c) the guide force for completing the extraction is minimized (Rydberg, 2004). Initially, it is a reactive extraction cascade in four stages operating in a countercurrent arrangement. The operating conditions are described in **Table 3**; the results are obtained after 30 iterations and are reported in **Figure 6**.

Table 3. Operating conditions. Acetic acid + 1-Pentanol + n-amyl acetate + water system (case study 2)

Feed Flow F = 100 mol/h	Solvent Flow: S = 50 mol/h
Feed Composition:	Solvent Composition:
$z_1^F = 0.30$; $z_2^F = 0.00$; $z_3^F = 0.00$; $z_4^F = 0.70$	$x_1^S = 0.00$; $x_2^S = 1.00$; $x_3^S = 0.00$; $x_4^S = 0.00$
T = 363.15 K P = 1 bar	$K_{eq}(T) = -56.8133 + (0.178352 \cdot T)$; T [=] K

It can be observed in **Figure 6** that between the third and fourth stages, the extract flows (E3 and E4) and refined products (R3 and R4) do not show relative changes in their composition. This suggests that the specification of four stages is close to the maximum for a reactive extraction cascade in a countercurrent arrangement. To confirm the maximum number of reactive stages, ten reactive extraction cascades were evaluated in which each cascade contained a different number of stages, from 1 to 10. The results are summarized in **Figure 6a**, where it can be observed that the reactive limit conversion (acetic acid) remains approximately constant from stage 4 on. Including more reactive stages does not provide a benefit given that the relative change in concentration and reactive limit conversion (acetic acid) is not significant.

Figure 6b illustrates the usefulness of graphically expressing the results obtained for the arrangements of reactive extraction cascades in isothermal conditions using the transformation of coordinates in Ung & Doherty (1995) given that an approximation of the maximum number of reactive stages for a countercurrent arrangement can be made based on this graphic. This conclusion, at a numerical level, is not easily deduced previously because of the need of simulating an arrangement with more than four stages to find the answer. Additionally, **Figure 6b** also proposes the possibility of completing posterior graphic analyses since they are very similar to known analyses in the literature for extraction cascade arrangements in ternary numeral systems. Based on the results obtained for the reactive extraction cascades in an isothermal condition, the heat flow necessary to maintain this condition was calculated (see **Figure 6b**). Endothermic behavior in which the heat flow is greater for the stage of feed introduction is observed, and this flow decreases as the extractive solvent inflow stage is approached. This suggests that the process's global calorific needs are determined by the feed stage.

3.2.2. Flow Division

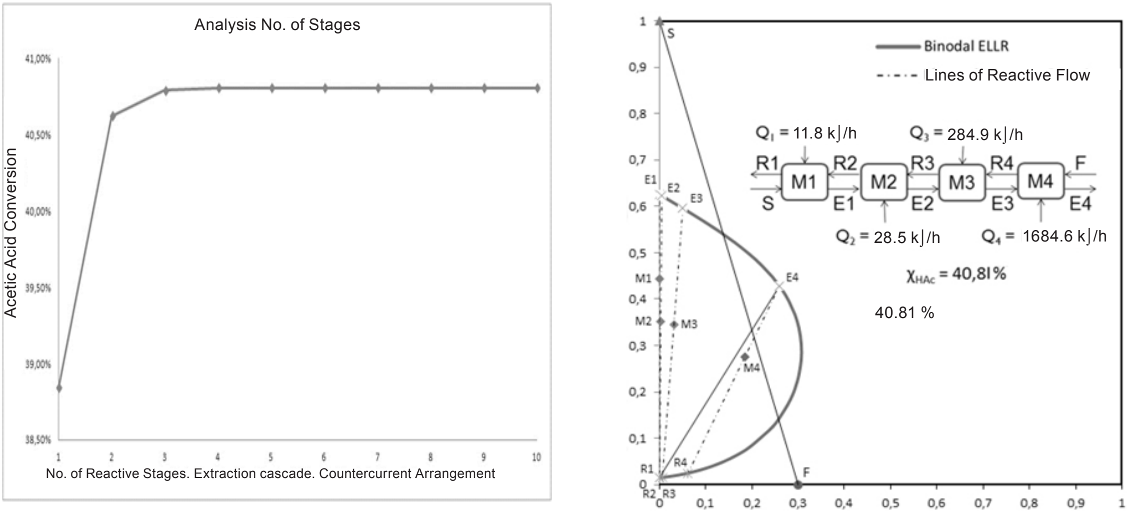
Another of the design schemes analyzed is a division of feed and solvent flows in countercurrent reactive extraction cascades (see **Figure 7**).

For the case study, the effect of feed and solvent division on a countercurrent reactive extraction cascade in four stages using the same specifications described in **Table 3** was analyzed. It is worth highlighting that this division was considered equimolar, and the results are summarized in **Figure 7**. It is observed that the calculation algorithm is versatile since it allows for including specifications different from the conventional ones, and the total conversion is not benefitted by the feed or solvent flow being divided since the greatest total conversion is obtained when working with a conventional arrangement (see **Figure 6**).

3.2.3. Hybrid Cascades

To complement the analysis, the effect of including localized reaction zones within the extraction cas-

Figure 6. RE cascade in countercurrent

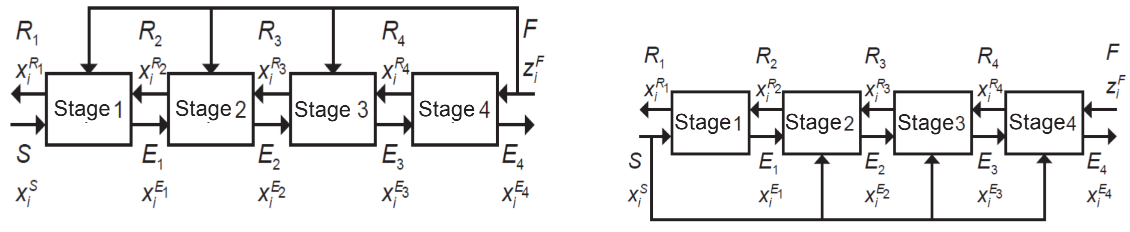


a) Analysis of # of reactive stages

b) RE cascade, four stages

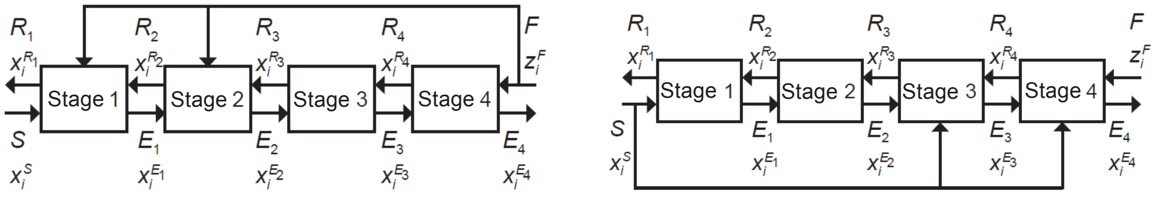
Figure 7. Division of feed and solvent flows. RE cascade - 4 stages.

Feed Flow Division (FFD)	Solvent Flow Division (SFD)



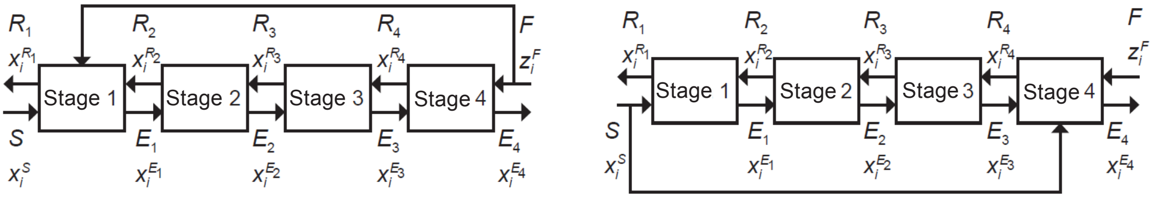
(a) FFD in Stages 1, 2, 3, and 4.
$X_{total\ HAc}$= 40.39 %

(b) SFD in Stages 1, 2, 3, and 4.
$X_{total\ HAc}$ = 39.09 %



(c) FFD in Stages 1, 2, and 4.
$X_{total\ HAc}$= = 40.24 %

(d) SFD in States 1, 3, and 4.
$X_{total\ HAc}$ = 38.49 %



(e) FFD in Stages 1 and 4.
$X_{total\ HAc}$= 39.98 %

(f) DFS en etapas 1 y 4.
$X_{total\ HAc}$ = 40,80 %

cades was also determined. This type of configuration has only been worked with in the literature in reactive distillation schemes to improve the performance of solute separation in the reactive zone and reduce costs since a reactive zone is considerable more expensive when compared to a non-reactive stage (Agarwal, Thotla & Mahajani, 2008).

The results obtained from evaluating the hybrid extraction cascades using the same specifications described in **Table 3** are summarized in **Figure 8**. In concordance with **Figure 9**, the conversion obtained in a hybrid extraction cascade with a single reactive stage is similar to the conversion obtained in extraction cascades with two, three, and four reactive stages. This suggests that a production process can have arrangements that are not completely reactive since increasing the number of reactive stages does not show significant improvements in regards to the conversion, and each reactive stage has a significant impact on the investment and operation costs. To analyze the behavior of the composition profiles of the arrangements addressed in **Figure 8**, the values of the molar fractions for one of the equilibrium phases in each of the cascades considered have been summarized (see **Table 4**).

In agreement with the results, it has been observed that the behavior of compositions is similar for cascade arrangements with two, three, and four reactive stages. However, there is an evident change for the hybrid extraction cascade that works with a single reactive stage. The separation and recovery of acetic acid and amyl alcohol in this hybrid cascade is greater since these components react in only one stage. In addition, a clear decrease in the separation and recovery of n-amyl acetate has been observed given that the molar fractions obtained for this compound are very low in comparison with the other hybrid arrangements and the arrangement with a non-localized reaction zone.

Table 4 also shows the heat profiles for the arrangements addressed in **Figure 8**. The esterification reaction for n-amyl acetate production is endothermic, and it is therefore necessary to add heat in the stages

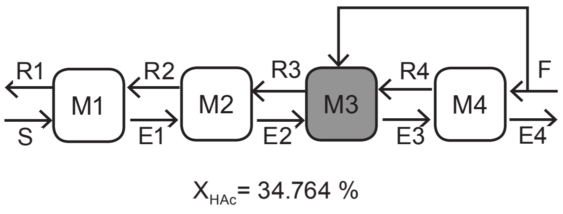
Table 4. Composition profiles by component - heat profiles (kJ/h)

Fig.	Profiles of Component (Extract) Composition – Heat Flow			
	Stage 1	Stage 2	Stage 3	Stage 4
9 a)	$x_1^E = 0.0018$	$x_1^E = 0.0105$	$x_1^E = 0.0502$	$x_1^E = 0.1537$
	$x_2^E = 0.6227$	$x_2^E = 0.6065$	$x_2^E = 0.5292$	$x_2^E = 0.3225$
	$x_3^E = 4.08E-08$	$x_3^E = 1.03E-05$	$x_3^E = 0.0017$	$x_3^E = 0.1060$
	$x_4^E = 0.3756$	$x_4^E = 0.3830$	$x_4^E = 0.4190$	$x_4^E = 0.4179$
	7.811	-2.662	-11.597	2014.810
9 b)	$x_1^E = 8.19E-04$	$x_1^E = 0.0050$	$x_1^E = 0.0261$	$x_1^E = 0.1537$
	$x_2^E = 0.6244$	$x_2^E = 0.6167$	$x_2^E = 0.5713$	$x_2^E = 0.3224$
	$x_3^E = 3.93E-07$	$x_3^E = 1.04E-04$	$x_3^E = 0.0245$	$x_3^E = 0.1060$
	$x_4^E = 0.3748$	$x_4^E = 0.3782$	$x_4^E = 0.3780$	$x_4^E = 0.4179$
	8.469	-1.745	319.000	1683.870
9 c)	$x_1^E = 4.27E-04$	$x_1^E = 0.0026$	$x_1^E = 0.0261$	$x_1^E = 0.1537$
	$x_2^E = 0.6251$	$x_2^E = 0.6204$	$x_2^E = 0.5713$	$x_2^E = 0.3224$
	$x_3^E = 9.16E-06$	$x_3^E = 0.0025$	$x_3^E = 0.0245$	$x_3^E = 0.1060$
	$x_4^E = 0.3745$	$x_4^E = 0.3745$	$x_4^E = 0.3780$	$x_4^E = 0.4179$
	8.866	32.019	285.190	1683.750
9 d)	$x_1^E = 2.33E-04$	$x_1^E = 0.0026$	$x_1^E = 0.0261$	$x_1^E = 0.1537$
	$x_2^E = 0.6254$	$x_2^E = 0.6204$	$x_2^E = 0.5713$	$x_2^E = 0.3224$
	$x_3^E = 2.23E-04$	$x_3^E = 0.0025$	$x_3^E = 0.0246$	$x_3^E = 0.1060$
	$x_4^E = 0.3741$	$x_4^E = 0.3745$	$x_4^E = 0.3780$	$x_4^E = 0.4179$
	11.751	28.535	284.899	1684.648

in which the chemical reaction occurs. According to the results found, the process's global heat needs are very similar among all the arrangements addressed in **Figure 8** (cascades with localized and non-localized reaction zones) with the exception of the arrangement with a single reactive stage. The reason for this is that the system distributes the calorific needs according to the presence of reactive stages in the process, and in the arrangement with a single stave, all the heat falls to the feed stage.

In order to analyze the importance of the feed stage, a hybrid extraction cascade with a reactive "heart" was evaluated, and the position of this heart was changed using the same conditions described in **Table 3**. The acetic acid conversions achieved were 33.439%, 34.526%, and 34.764% for an inflow of 80% of the feed for reactive stage 1, 2, and 3, respectively, with the remaining 20% entering in stage 4. By way of example, **Figure 9** shows the case in which part of the feed entered in stage 3.

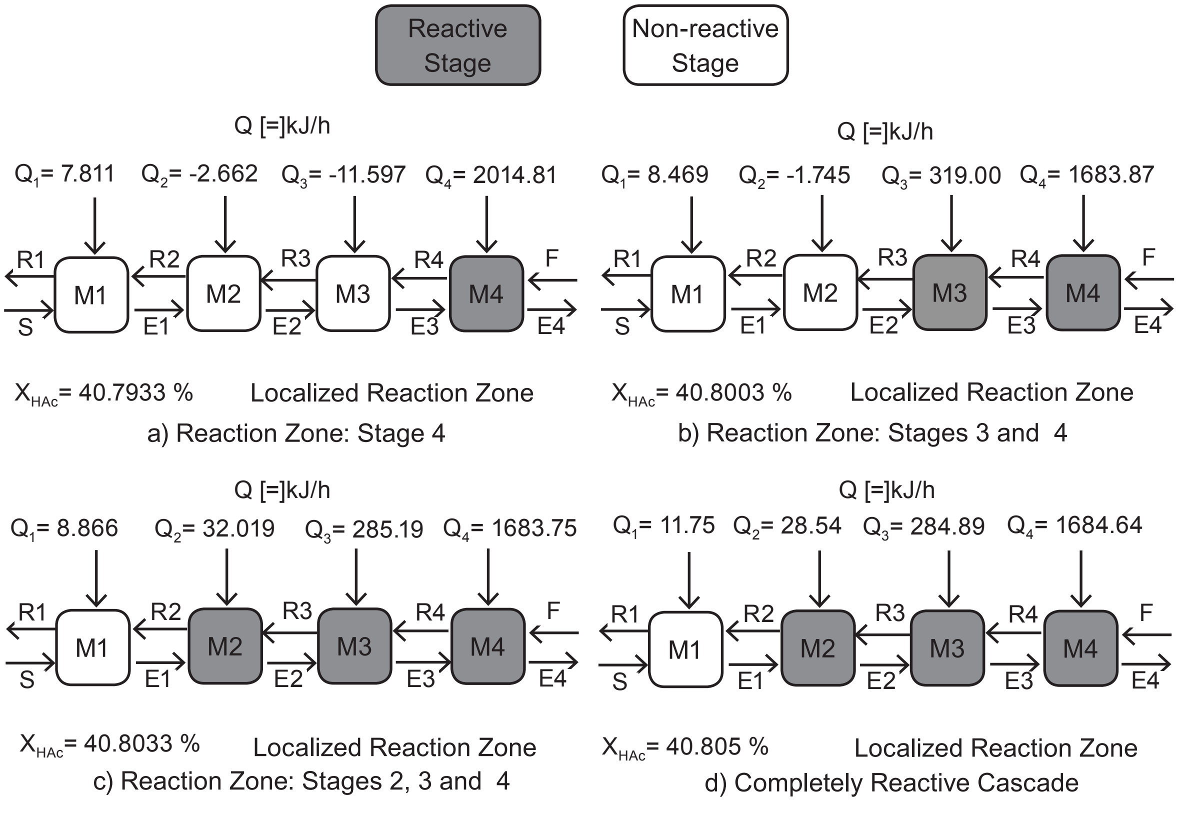
Figure 9. Extraction cascade with a reactive heart.



3.2.2. Specified Heat Flow

To prove that the calculation algorithm also supports conditions with specified heat transfer, a reactive extraction cascade in a countercurrent arrangement was calculated for three stages. The operating conditions are summarized in **Table 5**.

Figure 8. Extraction cascades with localized and non-localized reaction zones.



a) Reaction Zone: Stage 4

b) Reaction Zone: Stages 3 and 4

c) Reaction Zone: Stages 2, 3 and 4

d) Completely Reactive Cascade

Table 5. Operating conditions. Case study system 2

Equilibrium Constant: $K_{eq}(T) = -56.8133 + (0.178352 \cdot T)$; T [=] K
Feed Flow F = 100 mol/h Solvent Flow S = 50 mol/h T Feed = 373.15 K T Solvent = 353.15 K Feed Composition: $z_1^F = 0.30$; $z_2^F = 0.00$; $z_3^F = 0.00$; $z_4^F = 0.70$ Solvent Composition: $x_1^S = 0.00$; $x_2^S = 1.00$; $x_3^S = 0.00$; $x_4^S = 0.00$
$\dot{Q}$ by Stage (kJ/h): Stage 1 = 100; Stage 2 = 250; Stage 3 = 2000

Table 6. RE Cascade with Heat Transfer. Countercurrent Arrangement.

Esterification of N-amyl Acetate - Global Acetic Acid Conversion χ_{HAc}: 37.8066% Flow [mol/h] Enthalpy [kJ/mol]		
Stage 1 T [K] 358.3205	EF	Flow E1 =80.7335 Enthalpy =-317.5839 $x_1^E = 0.0025$; $x_2^E = 0.6228$; $x_3^E = 0.0021$; $x_4^E = 0.3726$
	RF	Flow R1 = 30,5004 Enthalpy =-282.0119 $x_1^R = 0.0005$; $x_2^R = 0.0141$; $x_3^R = 0.0000$; $x_4^R = 0.9854$
Stage 2 T [K] 356.4345	EF	Flow E2 = 86.1675 Enthalpy = -321.5003 $x_1^E = 0.0269$; $x_2^E = 0.5735$; $x_3^E = 0.0212$; $x_4^E = 0.3784$
	RF	Flow R2 = 61.2339 Enthalpy = -283.2781 $x_1^R = 0.0062$; $x_2^R = 0.0143$; $x_3^R = 0.0001$; $x_4^R = 0.9794$
Stage 3 T [K] 359.4169	EF	Flow E2 = 119.4995 Enthalpy = -337.8836 $x_1^E = 0.1559$; $x_2^E = 0.3199$; $x_3^E = 0.0949$; $x_4^E = 0.4292$
	RF	Flow R2 = 66.6679 Enthalpy = -294.1685 $x_1^R = 0.0607$; $x_2^R = 0.0232$; $x_3^R = 0.0018$; $x_4^R = 0.9143$

The results are obtained after 18 iterations, and they are summarized in **Table 6**.

With the results from the tables above, it is therefore shown that the calculation algorithm allows us to know the influence of the transferred heat flow independently (RLLET) or dependently (RLLE). This confirms its robust characteristics and the possibility of working with different processing conditions.

4. CONCLUSIONS

A step-by-step algorithm was presented for the simulation of countercurrent reactive extraction cascades operating in the total equilibrium condition (simultaneous phase equilibrium and chemical equilibrium). The method was tested with an esterification reaction and diverse technological schemes for the production process. The algorithm can handle specifications relevant to the practice, such as: a) division of solvent and feed flows; b) cascades with a localized reaction zone; c) different feed points; and c) specification of the heat transfer flow.

The method presented is easily implemented in a computer program because it includes a single iterative connection. The foundation of each execution of the procedure lies in well-established knowledge: the calculation of the different types of flash for systems with two liquid phases. This final aspect offers the advantage of using the algorithms available in the literature for reactive liquid-liquid equilibrium as subroutines.

The graphic representation using transformed molar functions by Ung & Doherty (1995) allow for simplifying the analysis of reactive cascades. In this sense, one of the examples illustrates the approximation of the maximum number of reactive stages for the countercurrent arrangement and suggests the possibility of using graphic methods developed for non-reactive ternary numeral systems in the calculation of reactive extraction for systems with two degrees of freedom.

The production of n-amyl acetate by reactive extraction from aqueous acetic acid solutions is strongly limited by thermodynamic restrictions on reaction and separation. The highest conversions found are around 40% in cascades with countercurrent arrangements. In this case, the reactive extraction process must be completed with a distillation sequence to manage separation. It is likely that reactive distillation offers better perspectives.

NOMENCLATURE

$\Delta\vartheta$: Change in the molecules caused by the reaction

γ: Activity coefficient

K_i: Coefficient of component i distribution

K_{eq}: Constant of chemical equilibrium

X: Conversion

ξ: Reaction coordinate

τ: Convergence criterion

z_i: Molar fraction of component i in the feed

x_i: Molar fraction of component i

Ψ: Fraction of extracts

F: Feed flow (mol/h)

H: Enthalpy (kJ/mol)

S: Solvent flow (mol/h)

$\dot{Q}$: Heat flow (kJ/h)

T: Temperature (K)

P: Pressure (bar)

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