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General design methodology for reactive liquid–liquid extraction: Application to dicarboxylic acid recovery in fermentation broth

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A B S T R A C T

A general design methodology for reactive liquid–liquid extraction is introduced in this paper. It is composed of three different steps: feasibility analysis, pre-design determination and simulation validation. This paper is focused on the first and the second step. This methodology leads to the design specifications of the units from the information concerning the physico-chemical behaviour of the studied system, exploiting the equilibrium and material balance equations. The results of this methodology are a good starting point for an optimization study or for an investment calculation process. This methodology has been applied to different case studies: two different strategies of extraction and several solvents to recover succinic acid in fermentation broth.

Keywords:

Reactive liquid–liquid extraction
Liquid–liquid diagram
Process design
Process synthesis
Physical and chemical equilibrium
Succinic acid
Fermentation broth

1. Introduction

The reactive separation involves the combination of reaction and separation in a same unit. Esterification is mainly chosen as case study in the literature. The transformation of the molecule in its esterified form confers better physico-chemical and equilibrium characteristics which can be used for an easier separation. Furthermore, merging reaction and separation in a single apparatus can lead to energy integration and process intensification.

The efficiency of reactive separation strategies (especially reactive distillation) has already been proved [13]. The advantages of reactive distillation are multiple: increased conversion, increased selectivity and energy integration or production quality can be cited. But distillation is energy consuming to maintain boiling and will be an expensive solution in the case of a very diluted system (especially in water). For this type of diluted system, a cost effective way to recover valuable products especially from fermentation, such as acids or alcohols, is reactive liquid–liquid extraction.

The work of Samant and Ng [11] proposes a calculation procedure for determining the design of a reactive liquid–liquid extraction column. They apply this procedure to a general pattern four reactive compounds at the maximum with an inert as an extracting agent.

The objective of this study is to adapt this procedure for real systems, and transcribe it in a design approach similar to the one introduced by Tuchlenski [14] for reactive distillation. A design methodology consists in determining the key structural parameters of an operation unit. This study proposes a design methodology for reactive liquid–liquid reaction.

The design approach developed here is based on thermodynamic equilibrium calculation to determine the design of the of reactive extraction process. The aim is to obtain the operating parameters such as possible raffinate and extract composition, solvent rate and number of theoretical stages. The design approach includes three parts: the feasibility analysis, the pre-design and the validation step. This article is focused on the first and second step of the approach

In the first part, the general design methodology for reactive liquid extraction is presented with the reactive liquid–liquid diagram. It shows the location of the compositions of the organic phase and the aqueous phase, which respect both chemical and phase equilibrium. The second step of the methodology is also

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Nomenclature

E	Molar organic phase flow (mol.s ⁻¹)
F	Molar feed flow (mol.s ⁻¹)
H	Liquid retention of the one stage extraction process (mol)
K_{eq}	Chemical equilibrium constant
M	Mixture of F and S flow or R_N and E_1 flow (mol.s ⁻¹)
m	Variable for RECM defined in the variable change
N_T^0	Initial total amount of mole for reactive liquid diagram (mol)
N_c	Number of compound
N_r	number of reactions
Q	fractional conversion
R	Molar aqueous phase flow (mol.s ⁻¹)
S	Molar solvent feed flow
(S/F)	Solvent rate
$(S/F)_{min}$	Minimum solvent rate
t	Time (s)
V	Variance
w	Molar composition of the liquid retention H
X	Reactive molar composition of phase
x	Molar composition of phase
z	Molar composition of feed flow F
Z	Reactive molar composition of feed flow F
γ	Activity coefficient
β	Fraction of phase I in the mixture
ξ	Chemical extent: mol
τ	Dimensionless time
ϑ	Stoichiometric coefficient
ϕ	Matrix of the reference compounds' stoichiometric coefficient

Exponents

I	Aqueous phase
II	Organic phase

Subscript

i	Component
j	Stage
L	Limit
N	Last stage
r	Reaction
ref	Reference

Acronym

DMS	Di-Methyl succinate
DOS	Di-octyl succinate
MeOH	Methanol
MMS	Mono-Methyl succinate
MOS	Mono-Octyl succinate
NTS	Number of theoretical stage
OcOH	Octanol
P-X	Para-Xylene
RECM	Reactive extraction curves map
rLLD	Reactive liquid-Liquid diagram
rLLE	Reactive liquid-Liquid extraction
SMILES	Simplified molecular input line entry specification
SA	Succinic acid

detailed; it is the pre-design method. It allows to evaluate the minimum solvent flow rate and the number of theoretical stages based on this reactive liquid-liquid diagram. The model equations

are explained and a graphical illustration of the method is proposed using the reactive liquid-liquid diagram.

In the second part of this article, the design methodology is applied to succinic acid recovery. The production of succinic acid by fermentation of biomass presents a viable alternative [19,20]. The recovery of succinic acid in the fermentation medium is quite complicated because of the presence of a large amount of water. Several separation techniques have been studied such as crystallization [3-5], electrodialysis [2,16] or reactive extraction with tertiary amines [1]. However, all these methods have a high operation cost and this is a serious brake to the development of alternative ways of production. Several reactive liquid-liquid extraction strategies will be considered, including the number of reactive or not reactive compounds.

2. General design methodology for reactive liquid-liquid extraction

2.1. Strategy

Fig. 1 presents the principle of the design methodology that we proposed, based on the analogy with reactive distillation. It is composed of three steps [13]. This method allows us to determine the design parameters of the extraction column with the introduction of more complexity along the method and from known data:

- Thermodynamic property of the system (thermodynamic models parameters, chemical reaction constant);
- The chemical data (stoichiometric coefficient for each reaction);
- The product purity, rate recovery or conversion rate, objectives to achieve.

Step 1: Feasibility analysis

The feasibility analysis allows to verify that the separation specifications are thermodynamically feasible. If applicable, the maximum attainable compositions of the organic and aqueous phase respecting the separation specifications are determined. If these are not feasible separation objectives are revised. In the feasibility step, two tools have been identified: the reactive liquid-liquid diagram (rLLD) and the reactive extractive curve map (RECM). These tools allow to determine the thermodynamically feasible composition useful for the next step of the methodology. The last part of the article on the application of the method shows that in some cases, the application of the reactive liquid-liquid diagram is sufficient and that in more complex cases, RECM are needed to determine thermodynamically feasible compositions. That's why the two tools are identified.

The cited tools are respectively based on the work of [10] and [15]. The feasibility analysis involved some simplified assumptions on infinite solvent rate, infinite intern organic and aqueous phase flow. They allow to identify the feasible composition for the organic and the aqueous phase from a thermodynamic point of view and independently of material balances consideration.

Step 2: Pre-design

In the pre-design step, the studied physical-chemical phenomena are more complex, and this step allows the determination of a column configuration required to achieve the separation goals by using data from the previous step. For the pre-design step the structural parameters of the column are determined. To begin with, the minimum and maximum solvent rates are calculated. Then, the aqueous and organic phase compositions of the process are determined. To complete this step, the design of the column is made (number of theoretical stages, composition and flow profile). The boundary value design method introduced by Wuithier and Giraud book, [17,18] for simple extraction process and expanded to

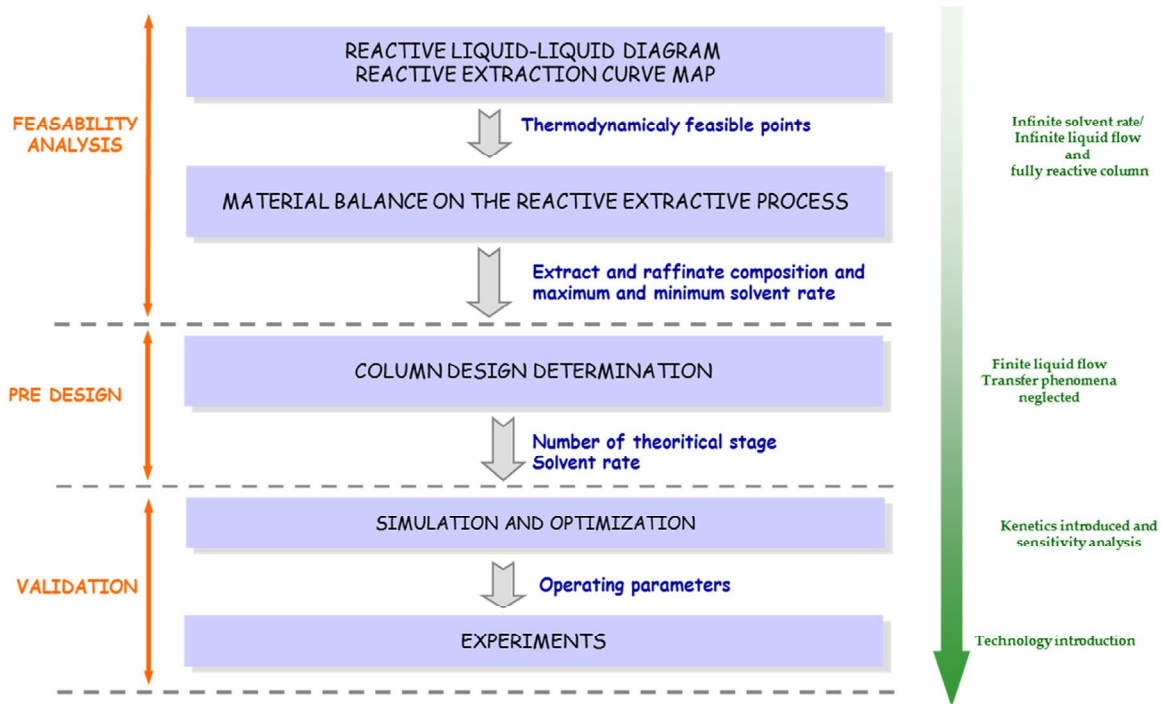


Fig. 1. Organigram of the conception methodology for reactive separation process.

reactive extraction by [11] is used exploiting the data of feasibility analysis.

Step 3: validation and design

The validation steps allow to validate the previously determined configuration of the column. From the perspective of industrialization and investment analysis, sensitivity analysis and optimization of structural and operating parameters of the column are performed to make the commercially viable and feasible extraction column. Complex physical phenomena are introduced like kinetics and mass transfer limitation. This validation step can also include experiments to validate the accuracy of the calculations performed throughout the pre-design step. The experimental results may also be compared to the simulation results in order to prove the precision of the simulation model.

In the first part of this article, the necessary tools for the first two steps, feasibility analysis and pre-design, are described.

2.2. Reactive liquid-liquid phase diagram

To consolidate and exploit thermodynamic information, liquid-liquid diagrams are implemented. They represent the locus of aqueous and organic phases which respected the chemical and phase equilibrium. In this section, the calculation method and the representation of reactive phase equilibrium are presented.

Building a reactive liquid-liquid diagram (rLLD) requires to perform coupled chemical and phase equilibria calculations for a given system with set pressure and temperature. Descriptive equations of such a system with N_c component and N_r independent reactions, in thermodynamic equilibrium at fixed pressure and temperature are described below. There are the N_r chemical equilibrium equation, the N_c physical equilibrium, N_c partial material balance and sum to unity for the molar composition of phase I.

$$\prod_{i=1}^{N_c} (\gamma_i x_i^I)^{\theta_{i,r}} = K_{eq,r} \quad r = 1, \dots, N_r \quad (1)$$

$$\gamma_i^I \cdot x_i^I - \gamma_i^{II} \cdot x_i^{II} = 0 \quad i = 1, \dots, N_c \quad (2)$$

$$\beta \cdot x_i^I + (1 - \beta) \cdot x_i^{II} - z_i + \sum_{r=1}^{N_r} \vartheta_{i,r} Q_r = 0 \quad i = 1, \dots, N_c \quad (3)$$

$$\sum x_i^I = 1 \quad (4)$$

This system of $2N_c + N_r + 1$ equations and $3N_c + 2N_r + 1$ variables admits $N_c + N_r$ freedom degrees which are the composition x_F and the equilibrium constant K_{eq} . The unknown variables are the molar composition of each phase (x^I, x^{II}), the fraction of phase I in the mixture (β) and the fractional conversion ($Q_r = \frac{\xi_r}{N_{I,r}^0}$) for each reaction. The resolution of this non-linear algebraic system is done with a Matlab algorithm with the Simulis[®] toolbox. The algorithm uses the "fsolve" function and uses the trust-region dogleg algorithm. The algorithm is a variant of the Powell dogleg method described in the work of [9].

Once the resolution is done, the reactive compositions are calculated by choosing successively the reference compounds and the independent variables (Appendix A). These variables are then represented in the reactive composition domain.

According to the variance of the system, the shape of the field of reactive compositions can have different forms. At fixed temperature and pressure the expression of the variance is:

$$V = N_c - N_r - 1 \quad (5)$$

The variance represents the space dimension needed for the representation of the system. If the variance is equal to 2, the system is representable in two dimensions. For a variance equal to 3 the representation of the LLD is in three dimensions. The example

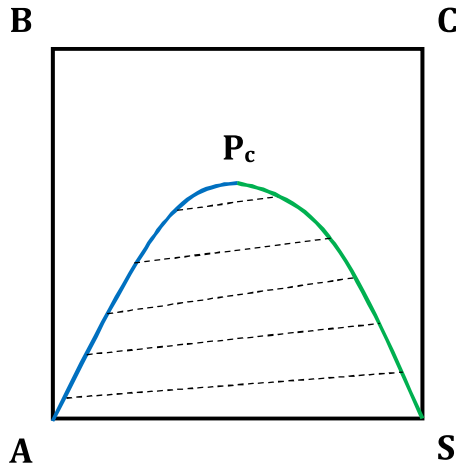
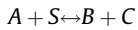


Fig. 2. Reactive liquid-liquid diagram for a system with 4 compounds and 1 reaction $V=2$.

presented in Fig. 2 is for a system with four compounds and one reaction:



In that case the variance is 2 and a planar representation of composition space is required.

The Curve A- P_c -D represents the phase envelope and point P_c represents the critical point. The blue line is the locus of aqueous phase composition and the green line is the locus of organic composition. Each composition is connected in pairs to a composition at the chemical and physical equilibrium by a tie line represented by the black dotted line.

This general example shows that the number of chemical reactions reduces the space compositions accessible by the system. When the variance (Eq. (5)) is strictly greater than 3, the composition range is no longer limited to a curve but it is a surface. The handling and use of such a diagram with three-dimensional representation for the feasibility analysis is more complex. The tool introduced in the next paragraph, RECM, is introduced to overcome this difficulty in determining thermodynamically feasible compositions.

2.3. Reactive extraction curve map (RECM)

For this study a new conceptual tool has been developed by analogy with the reactive distillation to determine thermodynamically feasible compositions, the reactive extractive curves map (RECM). The RECM are the transposition to liquid-liquid reactive extraction of Residue Curve Map (RCM) in reactive distillation. The RCM is a very useful tool for the feasibility analysis of a reactive distillation process. It allows to identify the stable unstable nodes and the distillation regions [13]. The RCM is obtained from the simulation of a simple distillation process "Rayleigh distillation" [8,15]. A reactive residue curve is the locus of points compositions of the liquid phase in equilibrium with the vapor phase in a single distillation operation and involving a system, the seat of one or more chemical reaction. A residue curve is a good approximation of liquid composition at infinite solvent ratio.

The objective of this section is to extend this concept to the reactive liquid-liquid extraction. Fig. 3 illustrates the one-stage extraction process. It is a decanter with a total constant retention, a free interface and fed by the light phase (phase II). The liquid is at chemical and phase equilibrium. The decanter is fed with pure solvent flow and a flow of organic phase is recovered. The reactive extractive curves represent the evolution of the composition over

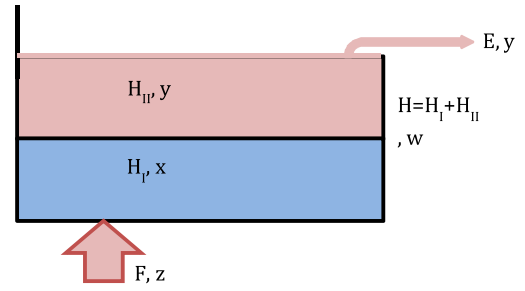


Fig. 3. Dynamic extraction process.

time in a single-stage reactive extraction process. This system being still fed over time of pure solvent, the solvent ratio can be regarded as infinite, and the amount of solute extracted maximum. The extraction curves therefore represent a sequence of equilibrium state that can be compared to a composition profile in a multi-stage extraction column, operating at infinite solvent rate. So the reactive extraction curves reflect the feasibility of the process. The RECM can be drawn for phases I and II.

We consider a system with N_c compounds and N_r independent reactions in a one stage extraction process presented in Fig. 3. The operation is at fixed temperature and pressure and the following assumptions are formulated:

- The total molar retention H is constant but H_I and H_{II} are variable.
- System at liquid-liquid and chemical equilibrium.

The input data of the system are H representing the constant liquid retention system, the feed flow F and the composition z of the N_c compounds in the feed flow.

The unknown variables are:

- w , the global composition of the retention H
- x^I , the composition of the aqueous phase (I)
- x^{II} , the composition of the organic phase (II)
- β , the fraction of phase I in the mixture
- ξ the chemical extent of each reaction

The following equation system is expressed to describe the dynamic extraction process (Fig. 3).

The N_c partial material balances on each component are expressed here:

$$H \frac{dw_i}{dt} - Fz_i + Ex_i^{II} + \sum_{i=1}^{N_r} H \vartheta_{i,r} \frac{d\xi_r}{dt} = 0 \quad i = 1, \dots, N_c \quad (6)$$

$$w_i = x_i^I \beta + x_i^{II} (1 - \beta) \quad i = 1, \dots, N_c \quad (7)$$

The developed algorithm uses the ode function which integrates the differential equations system $y' = f(t, y)$. It is easier to solve an equation with only one differential term, so variable changes are performed to simplify the system of equation.

The following changes of variables are being made:

$$m_i = H \left(w_i - \sum_{i=1}^{N_r} \vartheta_{i,r} \xi_r \right) \quad i = 1, \dots, N_c \quad (8)$$

This material balance is expressed in function of the variables m_i described previously:

$$H \frac{dm_i}{dt} - Fz_i + Ex_i^{II} = 0 \quad i = 1, \dots, N_c \quad (9)$$

A new time step τ is defined which is non-dimensional:

$$\tau = \frac{Ft}{H} \quad d\tau = \frac{Fdt}{H} \quad (10)$$

The material balance can now be written:

$$F \frac{dm_i}{d\tau} - Fz_i + Ex_i^{II} = 0 \quad i = 1, \dots, Nc \quad (11)$$

$$\frac{dm_i}{d\tau} - z_i + \frac{E}{F}x_i^{II} = 0 \quad i = 1, \dots, Nc \quad (12)$$

The Nc liquid-liquid equilibrium equations:

$$x_i^I \gamma_i^I - x_i^{II} \gamma_i^{II} = 0 \quad i = 1, \dots, Nc \quad (13)$$

The Nr chemical equilibrium equations:

$$K_{eq,r} - \prod_{i=1}^{Nc} (x_i^I \gamma_i^I)^{\nu_{i,r}} = 0 \quad r = 1, \dots, Nr \quad (14)$$

The sum equation on the variable x^I :

$$1 - \sum_{i=1}^{Nc} x_i^I = 0 \quad (15)$$

The sum equation on the variable m :

$$\sum_{i=1}^{Nc} m_i - H \left(1 - \sum_{i=1}^{Nc} \sum_{r=1}^{Nr} \nu_{i,r} \xi_r \right) = 0 \quad (16)$$

This system of $2Nc + Nr + 2$ equations and of $2Nc + Nr + 2$ variables ($m_i, x_i^{II}, \xi_r, E/F, \beta$) is solved thanks to a Matlab algorithm with the Simulink[®] toolbox. The algorithm uses the "ode15s" solver which is a multistep solver. It is a variable order solver based on the numerical differentiation formulas (NDFs).

The results of the calculation are represented on the rLLD. From the initial state with the global composition w of the retention, the Matlab integration is performed in the forward and backward direction from this point. This figure enables to choose a feasible separation specification (x_N^I) for the next step of the design methodology, the synthesis and design step, particularly for the steady state analysis.

2.4. Feasibility analysis: minimum solvent rate determination, column static analysis

Fig. 4 shows the reactive extraction column. This step of the feasibility analysis allows to determine the flow and the composition of all the input and output streams E_1, F, S and R_n .

Static analysis provides the accessible composition at the boundary of the process. The available data are the feed flow rate, the feed composition (F, z) and the solvent composition (x_{N+1}^{II}). The separation objectives set by at the feasibility analysis with the RECM allow to determine the composition of the aqueous phase R_N (x_N^I).

First, the minimum solvent flow rate is calculated; the design calculation requires the solvent ratio to be higher than the minimum solvent ratio so the corresponding solvent rate is taken between 1.3 and 1.6 times the minimum solvent rate [12]. The determination of the minimum solvent rate is analogous to the method used for simple liquid-liquid extraction. The tie line through the feed point is the richest organic phase composition that can be obtained with a counter-current extraction (E_L). Knowing the composition of the limit extract, partial material balances can be written on the column and the minimum solvent

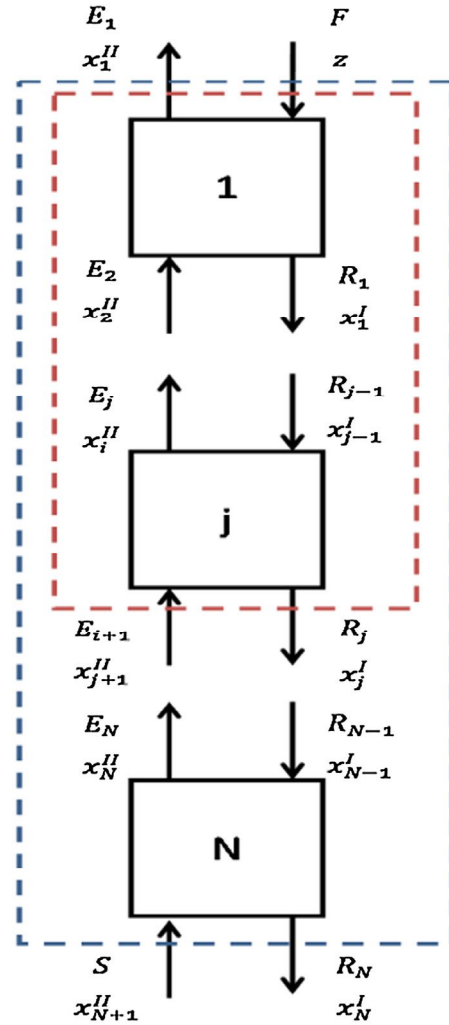


Fig. 4. Schema of a counter-current multistage reactive extraction.

flow rate can be calculated. The material balances are written with the reactive composition (Appendix A) to avoid a reactive term and remove the fractional conversion variable. Fig. 5 is the graphical representation of Eq. (17), the crossing between the feed-solvent line (line F-S) and the organic-aqueous line (R_N-E_1) defines point M_L

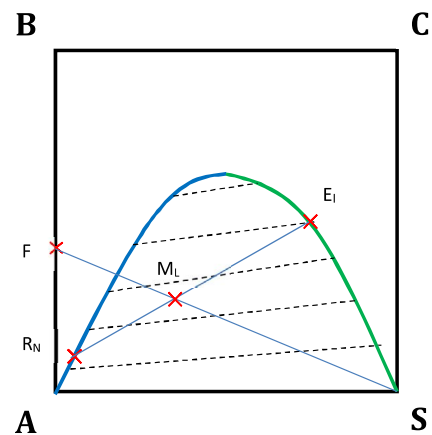


Fig. 5. Graphical representation of the minimum solvent rate determination.

which allows to calculate the minimum solvent rate.

$$\begin{aligned}
 F + S &= M_L \\
 FZ_i + SX_i &= M_L X_{M_L,i} \\
 FZ_i + SX_i &= (F + S)X_{M_L,i} \\
 F(Z_i - X_{M_L,i}) &= S(X_{M_L,i} - X_i) \\
 \left(\frac{S}{F}\right)_{\min} &= \frac{(Z_i - X_{M_L,i})}{(X_{M_L,i} - X_i)} \\
 \left(\frac{S}{F}\right) &= 1.6 * \left(\frac{S}{F}\right)_{\min} \leftrightarrow S = F * 1.6 * \left(\frac{S}{F}\right)_{\min}
 \end{aligned} \quad (17)$$

The last unknown variables of the system are calculated from the resolution of the following equation system which is composed of the overall material balance and partial material balances on the column written with the reactive compositions (equation 18 and 19) and the physical and chemical equilibrium equations (Eqs. (20) and (21)).

$$S - R_N - E_1 + F = 0 \quad (18)$$

$$S \cdot X_{N+1}^I - R_N \cdot X_N^I - E_1 \cdot X_1^I + F \cdot Z_i = 0 \quad i = 1, \dots, Nc - Nr \quad (19)$$

$$K_{eq,r} - \prod_{i=1}^{Nc} (x_i^I \gamma_i^I)^{\theta_{i,r}} = 0 \quad r = 1, \dots, Nr \quad (20)$$

$$x_{i,1}^I \cdot \gamma_i^I - x_{i,1}^{II} \cdot \gamma_i^{II} = 0 \quad i = 1, \dots, Nc \quad (21)$$

$$\sum_{i=1}^{Nc} x_{i,1}^{II} - 1 = 0 \quad (22)$$

This system of $2(Nc + 1)$ variables and equations is solved with a Matlab procedure using the “fsolve” function. The result can be plotted on the reactive liquid–liquid diagram and the data are used to determine the number of theoretical stages in the following step.

2.5. Pre-design step: number of theoretical stage determination

The pre-design step and the determination of the number of theoretical stages can be done with the data determined in the feasibility analysis. It allows to determine the number of theoretical stages and the compositions profiles inside the column. The phase equilibrium equation, the material balance and chemical equilibrium equation can be expressed over j different stages.

- for the j^{th} stage $j \neq 1$ and $j \neq N$:

$$x_{i,j}^I \cdot \gamma_i^I - x_{i,j}^{II} \cdot \gamma_i^{II} = 0 \quad i = 1, \dots, Nc \quad (23)$$

$$E_j \cdot X_{i,j+1}^I - R_{j-1} \cdot X_{i,j-1}^I - E_1 \cdot X_{i,1}^I + F \cdot Z_i = 0 \quad i = 1, \dots, Nc - Nr \quad (24)$$

$$K_r - \prod_{i=1}^{Nc} (x_i^I \gamma_i^I)^{\theta_{i,r}} = 0 \quad r = 1, \dots, Nr \quad (25)$$

$$\sum_{i=A}^C x_{i,j}^I - 1 = 0 \quad (26)$$

$$\sum_{i=A}^C x_{i,j}^{II} - 1 = 0 \quad (27)$$

The set of Eqs. (23)–(27) allows to perform the design method from the known flows and compositions of F and E_1 stream if the method starts at the top of the column. The boundary value design method is based on this property. From the top or the bottom of the column, the design of the column is defined with a succession of equilibrium lines, which is the solution of the equilibrium equation, and operating line, which is the solution of the material balance and chemical equilibrium equations. This is for graphical representation and can be easily translated in equation for the resolution algorithm on Fig. 6.

3. Application to succinic acid recovery

The previous parts present the general method for the design determination of a reactive–extractive column. Now this method is applied to different liquid–liquid systems involving Succinic acid, different heavier or lighter alcohols, water and the corresponding mono–ester and di–ester. Selected n -alcohols are ethanol (C_2), 1-butanol (C_4) and 1-octanol (C_8). This choice allows to identify the effect of alcohol carbon length on the biphasic zone and on the column design. Another system is studied with a non-reactive compound (para-xylene) used as a solvent. In that case the number of compounds is $Nc=6$ and in these conditions the graphical representation is tridimensional.

3.1. Thermodynamic model

In this article the reactions of succinic acid with different alcohols (methanol, ethanol, butanol or octanol) and with or

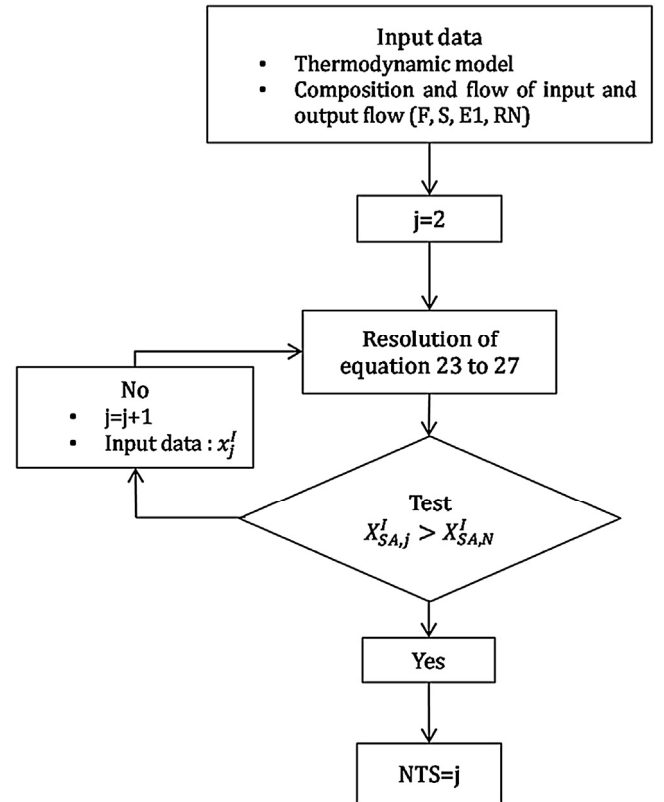
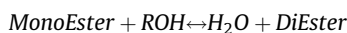
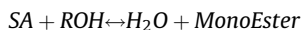


Fig. 6. Algorithm for the pre-design step, determination of the NTS.

without inert compounds are considered. The main compounds are listed in Table A1 of Appendix B.

The esterification reaction of succinic acid with an alcohol is composed of two consecutive reactions: initially, the formation of a mono-ester and then the formation of a di-ester. The assumption that there is no secondary reaction is formulated.



The data on chemical reaction are the results of the work of Orjuela et al. [6] on the esterification of succinic acid. These chemical data are considered the same regardless of the alcohol chosen, in accordance with the literature [7]; the same order of magnitude can be found for the chemical equilibrium constant (Table 1).

The UNIFAC thermodynamic model is chosen for the representation of the liquid–liquid equilibrium. The major difficulty is the lack of some molecules in the data base, especially for mono-ester and for long carbon chain on the alkoxy group. The unknown molecules are created on Simulis[®] with the regression tools and from the Simplified Molecular Input Line Entry Specification (SMILES), the UNIFAC decomposition.

3.2. Strategy A: solvent is the reactant

3.2.1. Choice of solvent

The main component of the aqueous phase is water while in the organic phase it is non-polar or slightly polar molecules. The higher the molecular mass of the reactive alcohol will be, the more non-polar mono-ester and di-ester will be. As a consequence the composition in the organic phase will also increase. The envelope of the two phases area depends on the initial composition in

Table 1
Chemical reaction constant for the two consecutive reactions.

	$K_{eq}(-)$
Succinic esterification	48.9
Mono-ester esterification	10.14

reactive alcohol, hence, the heavier the alcohol will be, the more non-polar the mono-ester and di-ester will be. A high composition in alcohol widens the two phase area.

Fig. 7 shows this phenomenon, it presented the different bi-phasic zones for a system with different carbon length alcohols. As discussed previously, for the heavier alcohol: octanol (C₈), the bi-phasic zone will be larger than for the lighter one: butanol (C₄) and ethanol (C₂).

Then, different types of reactive liquid–liquid equilibria can be identified as for liquid ternary diagrams. In accordance with a ternary diagram, the immiscibility or partial immiscibility between different compounds can be deduced from reactive liquid diagrams. If a binary mixture considered separately does not present total or partial immiscibility, the diagram is type 0 (see the example of reactive mixture with ethanol). If the diagram presents an immiscible binary, it will be type I (see the example of reactive mixture with butanol and octanol), and a diagram with two or more immiscible binary can be expected, in this case then the diagram will be type II or higher.

The design methodology for reactive extractive column is applied to these different systems. The shape of the two-phase area has an impact on the design of the column and according to the system, particularly the molecular weight of the alcohol, the separation may be more or less easy. For butanol and octanol, the diagrams are type I, but for octanol the two phase's area is larger. Therefore reactive extraction process is possible with both alcohols but it is most favourable with octanol. This part of the article deals with the design method for a reactive liquid–liquid extraction column which is illustrated by the extraction of succinic acid with octanol.

3.2.2. Design determination of the reactive liquid–liquid extraction column

3.2.2.1. Feasibility analysis. Fig. 8 represents the reactive liquid–liquid diagram which shows the bi phasic zone and the mono phasic zone. If the composition of the system is in the bi phasic zone, the mixture splits in two phases with compositions corresponding to the end point of the tie line. For the system chosen, Fig. 8 presents the reactive composition domain composed of five vertexes which represent the pure component. The blue and green curves represent respectively the aqueous and organic phase

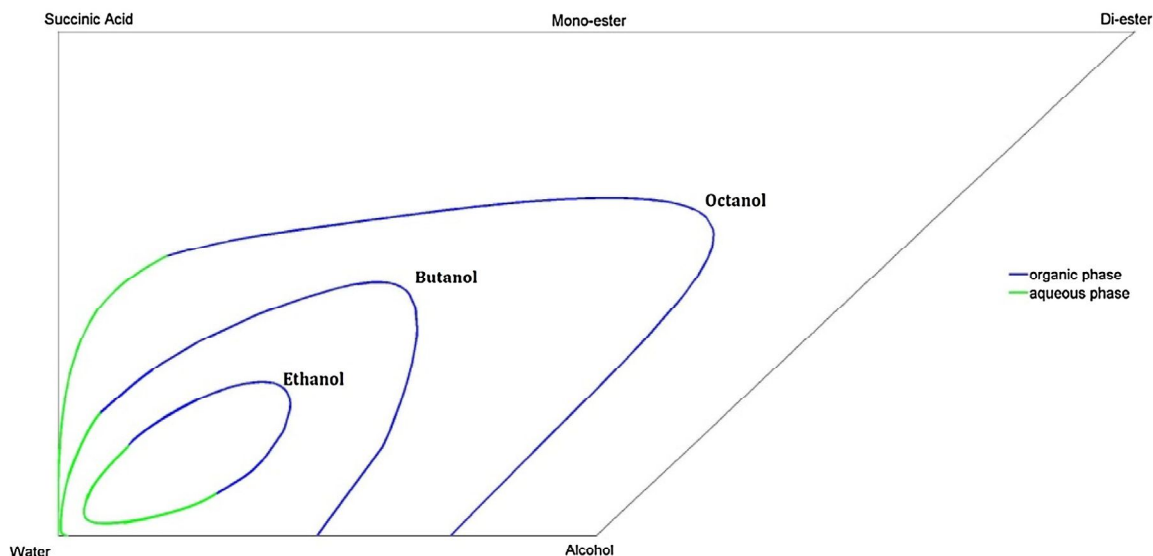


Fig. 7. Reactive liquid–liquid diagram for the examples chosen.

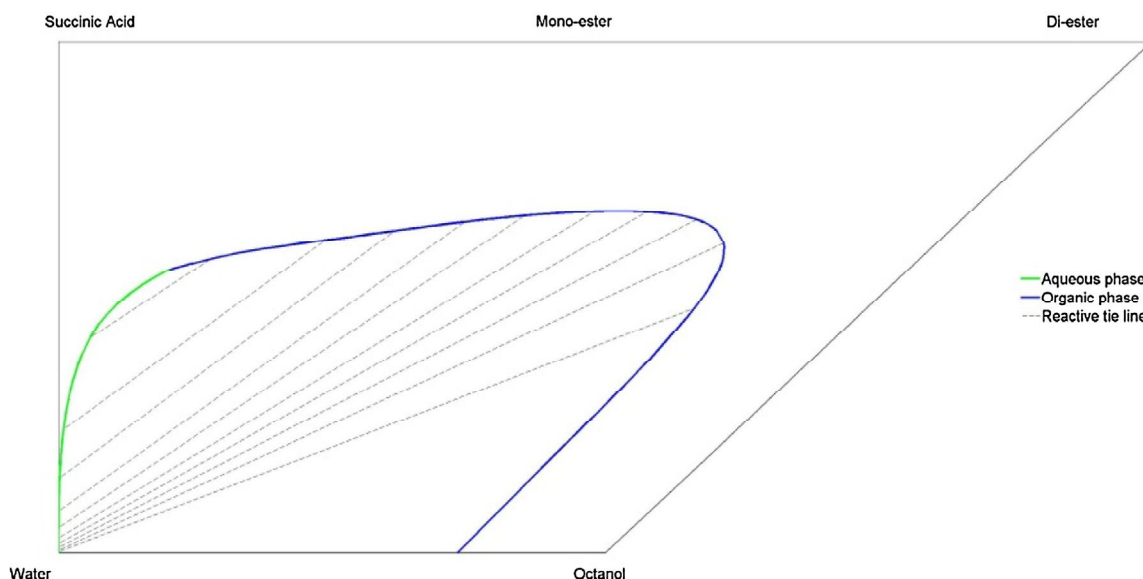


Fig. 8. Reactive liquid-liquid diagram for system $N_c=5$ $N_r=2$ succinic acid, octanol, water, mono-ester, di-ester represented in reactive coordinates.

and the black dotted lines represent the tie-line. As for a simple liquid-liquid diagram, the tie-lines tend to approach a critical point marked by the intersection of the aqueous and organic phase. The conservative appearance of balances and summation equations allows us to use the same tool and properties as the lever rule or design methodologies for the simple extraction process. Therefore, the liquid-liquid reactive diagram is an essential tool for the design method that must be developed; it will be the core of the design methodology.

The following task of the feasibility analysis is to determine the separation specifications with the rLLD and the RECM. The RECM for the system can be presented on the reactive liquid-liquid diagram. The aqueous composition is located on the blue aqueous curves of the reactive liquid-liquid diagram. Each point represents a thermodynamically feasible point. The RECM starts at the critical point which can be considered as the unstable node and tend to end at the binary water-alcohol mixture on liquid-liquid equilibrium which is the stable node. Since this system has a variance of 2, the phase envelope is a curve, and the RECM correspond exactly to this equilibrium curve. Thus, we can conclude that the RECM analysis does not give any more information than the equilibrium diagram for system with a variance less or equal to 2.

The separation objective is set on the aqueous composition, the higher the composition of the water compound in the aqueous flow, the higher the C_4 compounds are recovered (C_4 represent all the molecules with 4 carbons, succinic acid, and the two ester). This example is to determine the design of a column with the objective, the best yield of C_4 molecules recovered in the extract flow. The compositions of the raffinate phase at the boundary of the process can be set directly on the reactive liquid-liquid equilibrium diagram. The following table gives this chosen composition (Table 2).

Other strategies to fix the separation specifications are possible, such as choosing the highest possible composition of the extract flow or by formulating the separation objectives with recovery

Table 2
Compositions of the R_N flow fixed with the feasibility analysis.

	SA	OcOH	H ₂ O	MMS	DMS
Compositions	0.0005	0.0005	0.999	0	0

rate. This example however is confined to the strategy and the composition set above.

3.2.2.2. Pre-design. With the aqueous composition as input data determined at the last step (feasibility analysis), the design methodology can be pursued. A Matlab algorithm was developed to resolve the equation described in the previous section synthesis and design. All the results obtained here are calculated with this algorithm.

Fig. 9 is the representation of the steady states analysis. From the chosen separation specification, the boundary values of the process (useful for the next step) are determined. Here the material balance on the entire column is used to calculate the solvent rate, the aqueous and organic phase flows and composition.

The steady states analyses allow to determine the boundary value thanks to separation specification. The method is as follows; first point M representing the mixing of feed F and solvent S (alcohol) is placed with the minimum solvent ratio. Secondly, thanks to the steady states analyses the compositions of E_1 are resolved.

The next step is the determination of the column design with the resolution of Eqs. (23)–(27). Fig. 10 is the graphical representation of the results with the boundary value of columns F, E_1 , R_N and S depicted by the vertex alcohol. For this example the column has four theoretical stages.

Table 3 summarizes all the design results of the reactive liquid-liquid extraction column for the recovery of succinic acid with alcohol as reactant and extractant.

It may be necessary when the selected alcohol cannot act as both reagent and solvent (examples of ethanol and butanol) to use an inert compound that only plays the role of solvent. However, the use of an inert in a system with already five compounds makes it more difficult to represent the reactive phase equilibrium as explained in the next section.

3.3. Strategy B: solvent is an inert

The system chosen for this part has six compounds with two reactions. Methanol, the selected alcohol is too miscible with water and the separation could be complex as seen previously in part 2.2.1. It is necessary to use a compound as inert solvent for the reaction. The design of a reactive extraction column appears as the

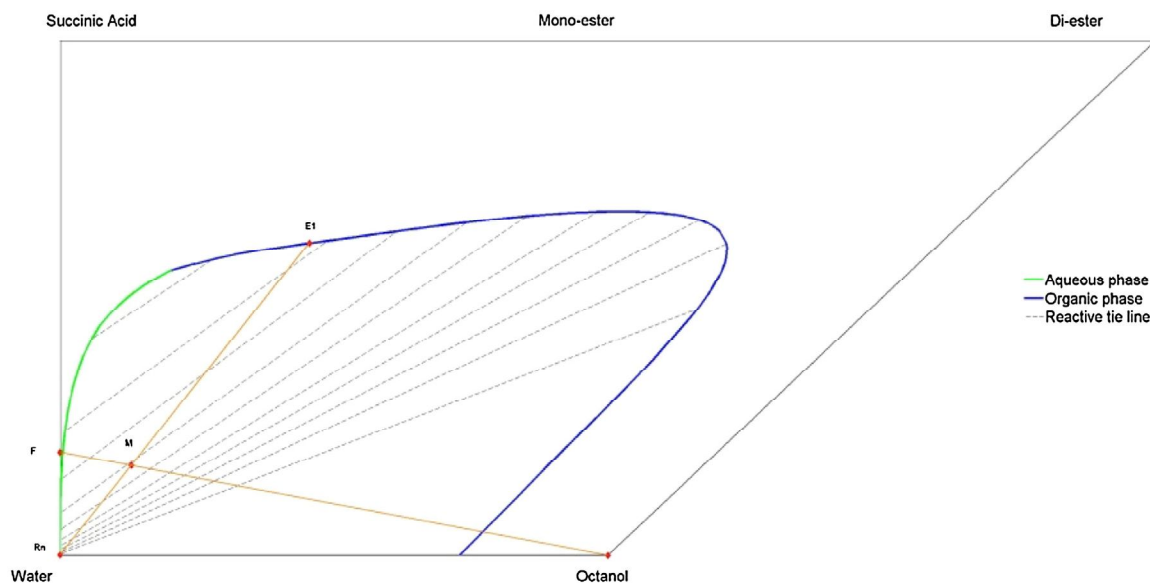


Fig. 9. Minimum and work Solvent rate determination.

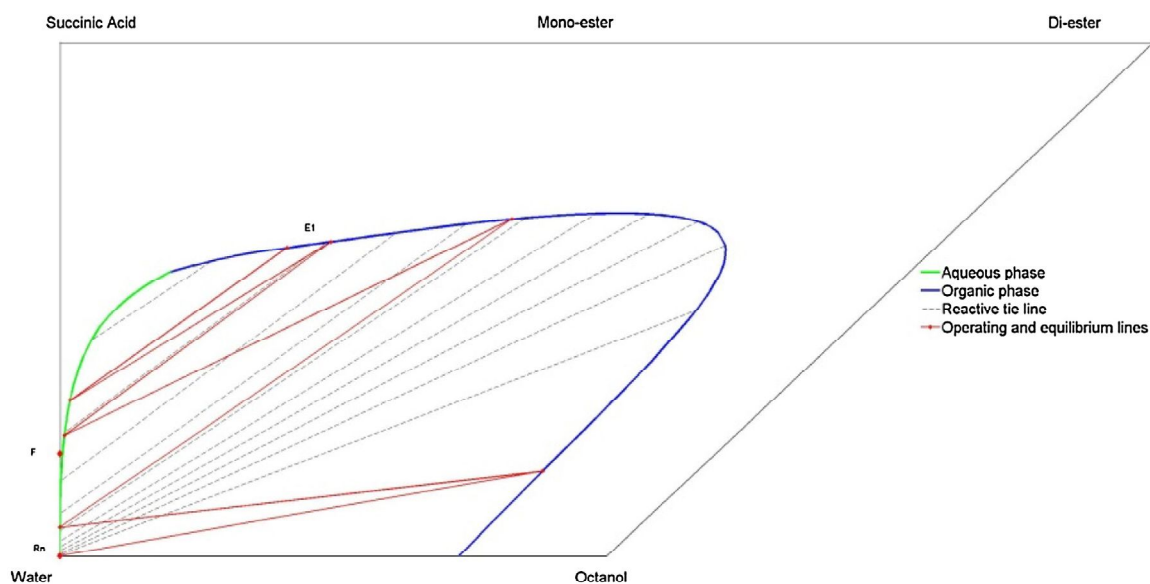


Fig. 10. Number of theoretical stage determination.

Table 3

Design parameters for the reactive extractive column processing the succinic acid recovery.

Composition						
	Flow (mol.s ⁻¹)	SA	OcOH	H ₂ O	MOS	DOS
F	2.000	0.200	0	0.800	0	0
S	0.301	0	1.000	0	0	0
E1	0.658	0.224	0.0168	0.382	0.355	0,0227
Rn	1.643	0,0004391	0,000195	0.999	0	0
(S/F) _{min} = 0.100 (S/F) = 0.150						
NTS = 4						

real challenge for this system. Our design methodology is applied in the same way but the representation is more complex because of the pentahedron form of the reactive composition domain.

Fig. 11 presents the reactive phase cover which is representative of the reactive liquid-liquid equilibrium.

To understand the phase diagram, the reagent composition range can be decomposed into a succession of triangular plans around the axis Para-Xylene-Water. The first and last plans of this series are represented by the unreactive ternary Water-Methanol-Para-xylene system which is Type I and P-Xylene-water-acid Type II (Figs. 12a and d). The reactive succession plan describing the reactive phase envelope is thus transformed from a type I into a type II.

This representation with the succession of reactive planes, allows identifying a critical curve, formed with all the critical point of the reactive liquid-liquid equilibrium lines of the different planes. This remarkable line starts at the critical point of the ternary Water-methanol-Para xylene system and finishes at the critical point of the ternary Succinic acid-mono ester-Para xylene

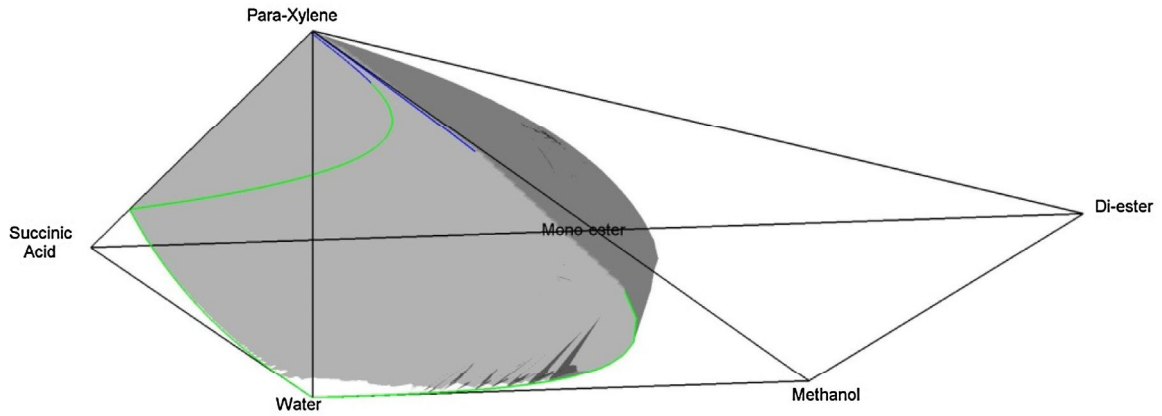


Fig. 11. Reactive liquid-liquid diagram of the system succinic acid/methanol/water/mono-ester/di-ester/para-xylene.

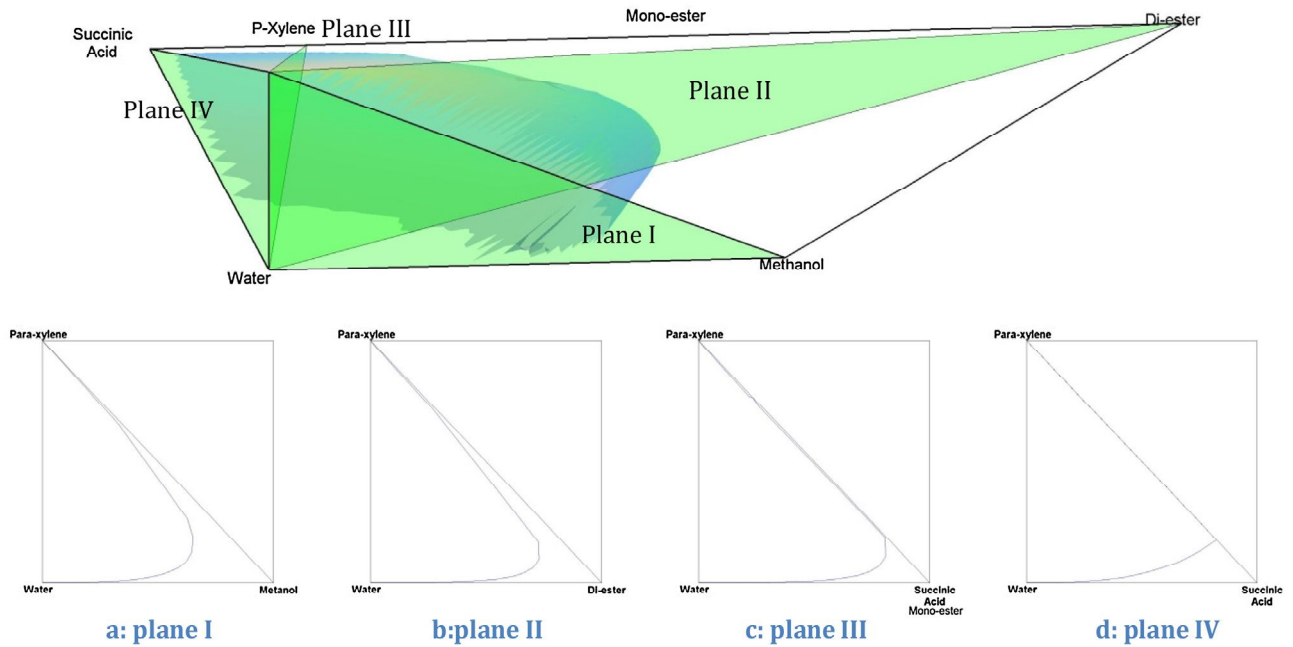


Fig. 12. Decomposition of the phase envelope in a reagent triangular plane succession.

system (Fig. 12b and c). The design methodology is applied to this system.

3.3.1. Feasibility analysis

The RECM is calculated for this system with the proposed method. For this system the variance (Eq. (5)) is equal to 3. For this kind of system, the RECM allows to observe the composition

evolution of the retention on this surface. The reactive RECM of the system succinic acid-methanol-water-mono-ester-di-ester-para-xylene is represented in Fig. 13. The RECM is very useful in this case to fix a thermodynamically feasible separation specification, that is to say from the phase envelope. The RECM represents the thermodynamic path for a reactive liquid extraction.

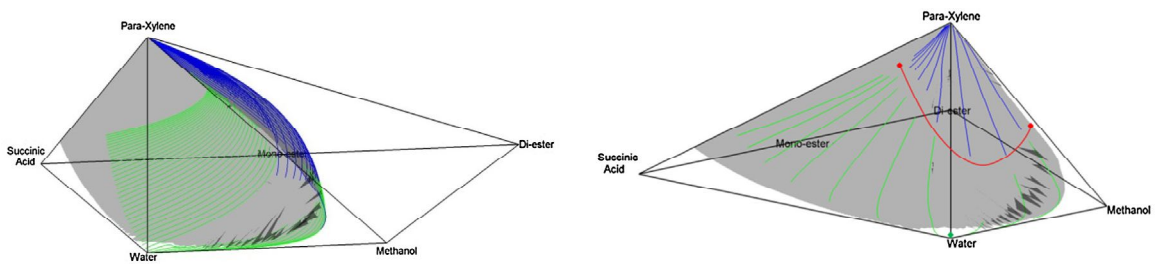


Fig. 13. Feasibility analysis, Reactive Extractive Curve Map of the system succinic acid/methanol/water/mono-ester/di-ester/para-xylene.

For the aqueous phase, the green curves, all the RECM starts at an unstable node represented by the critical points represented on the red line, and ends at the stable node symbolized by the aqueous phase of the unreactive alcohol-water-para-xylene system symbolized by the green point. This is in accordance with the dynamic reactive extraction process. Initially the system presents a succinic acid quantity which will decrease over time. Ultimately, all the succinic acid would be consumed and the aqueous mixture composed only by alcohol, water and para-xylene.

The blue curves on Fig. 13 represent the evolution of the composition of the extract flow. The points of these curves represent the composition at physical and chemical equilibrium with the composition of aqueous phase. The blue curves start at the corresponding critical point on the red curve and end at the vertex

Table 4
Compositions of the R_N flow fixed with the feasibility analysis.

	SA	MeOH	H ₂ O	MOS	DOS	P-X
Compositions	0.00564	0.00604	0.988	0.000467	0	0

Table 5
Results of the static analysis on the extraction column for the $N_c = 6$ and $N_r = 2$ case study.

Stream	Flow	Composition					
		SA	MeOH	W	MMS	DMS	P-X
F	2	0.156	0.220	0.624	0	0	0
S	10	0	0	0	0	0	1
R_N	1.67	0.00564	0.00604	0.988	0.000468	0	0
E_1	10.33	0.00210	0.00111	0.00199	0.0138	0.0133	0.968
NTS=4							

representing the pure compound para-xylene. The critical points and the vertex para-xylene can be respectively related to unstable node and stable node.

The principal node is the common point to all the extractive curves can be spotted near the vertex water. This composition is thermodynamically feasible and because it is near the vertex water, it is the composition that is the richest in water and the poorest in organic molecules. These characteristic could be chosen as a separation specification since the aqueous flow of the process is poor in valuable molecules. As a matter of fact, the recovery rate obtained here was the best.

The Table 4 presents the fixed composition for the raffinate as the composition with the fewest valuable compounds.

3.3.2. Pre-design

Table 5 gathered the results of the static analysis on the entire column. All the data needed for the static analysis are presented in this Table 5. They are the feed flow chosen to be processed with a reactive liquid extraction column (F, z), the composition of solvent flow (x_{N+1}^I) and the separation specification as the composition of the aqueous phase (x_N^I). This data are input data for the static analysis procedure described in part 1.4 and they are exploited to calculate the last variables as x_1^I composition R_N , S and E_1 flow. The results of the static analysis are presented on the reactive liquid diagram.

Figs. 14 present the results of the static analysis plotted in three dimensions (Fig. 14a) and according to the two static analysis plane, the green and red planes (Figs. 14b and c). For the first plane the point representing the composition of feed and solvent flow are coplanar, whereas the points representing the compositions of extract and raffinate are on either side of the plane. For Fig. 14c, it is the contrary, the point representing the raffinate and extract composition are coplanar and on the phase envelope while the S and F points are on either side of the green plane.

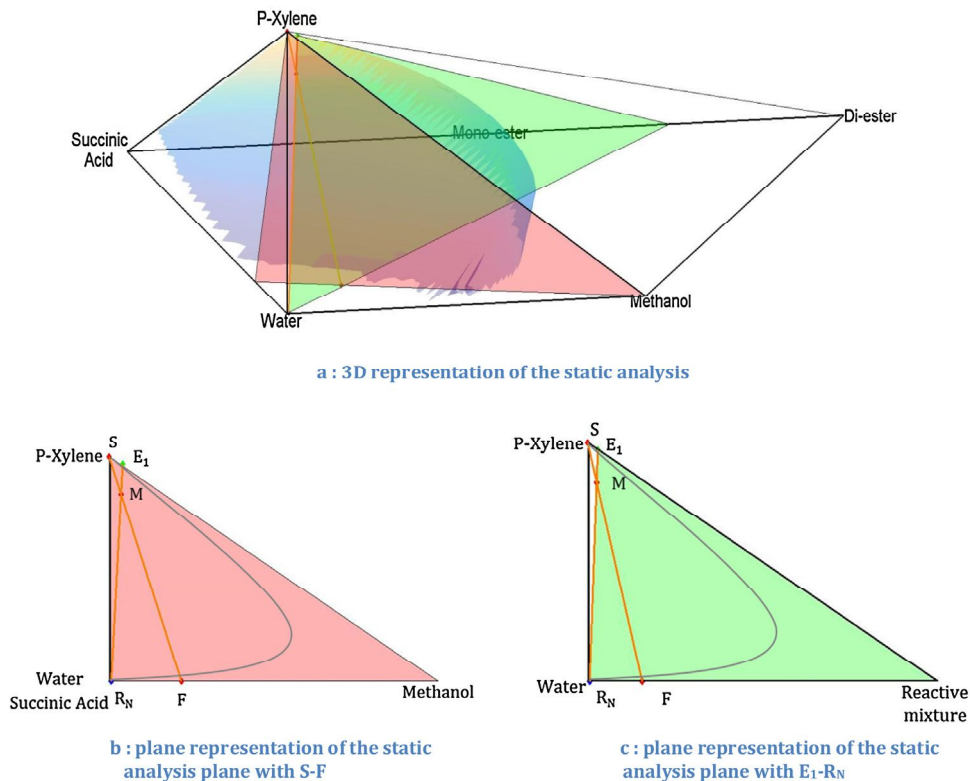


Fig. 14. a: 3D representation of the static analysis. b: plane representation of the static analysis plane with S-F. c: plane representation of the static analysis plane with E_1-R_N .

This representation is the graphic interpretation of the static analysis equation (Eqs. (18)–(22)). It illustrates the alignment of the FMS point and of the E_1MR_N according to the global material balance and the positioning of the E_1 and R_N points on the phase envelope due to the reactive liquid–liquid equilibrium.

The set composition of $R_N x_N^I$ and the objective composition of $E_1 x_1^II$ are now exploited as starting data for the determination of the number of theoretical stages. For this, Eqs (23)–(27) are solved with the following stopping criterion. The role of the reactive extractive column is to recover the C_4 molecules (succinic acid, mono-ester and di-ester), the stopping criterion is the reactive composition of succinic acid $X_{SA,1}^{II}$ since the latter is the addition of the three real compositions of valuable molecules. The value of this reactive composition is $X_{SA,1}^{II} = 0.0292$.

On Fig. 15, the succession of equilibrium lines and operating lines are represented on the three-dimension representation. For this representation it is difficult to determine the number of theoretical stages.

Different representations presented on Figs. 16 and 17 allow to determine the number of theoretical stages.

Fig. 16 represents the evolution of the reactive organic composition for the reactive compound, succinic acid and methanol along the column. The horizontal lines represent the separation objective $X_{SA,1}^{II}$. When the profile curves cut the objective line, the number of theoretical stages is determined. For this example the number of theoretical stages is five.

The distribution diagram proposed on Fig. 17 presents the equilibrium curve and the operating curves required to determine the number of theoretical stages. The composition of succinic acid in the extract (x_{SA}^{II}) is plotted as a function of the succinic acid in the raffinate (x_{SA}^I). It is another representation of the number of theoretical stages in a manner analogous to McCabe Thiele for distillation. The number of points on the equilibrium curves represents the number of theoretical stages, and the exploitation of this method returns the same result, the number of theoretical stages is equal to five.

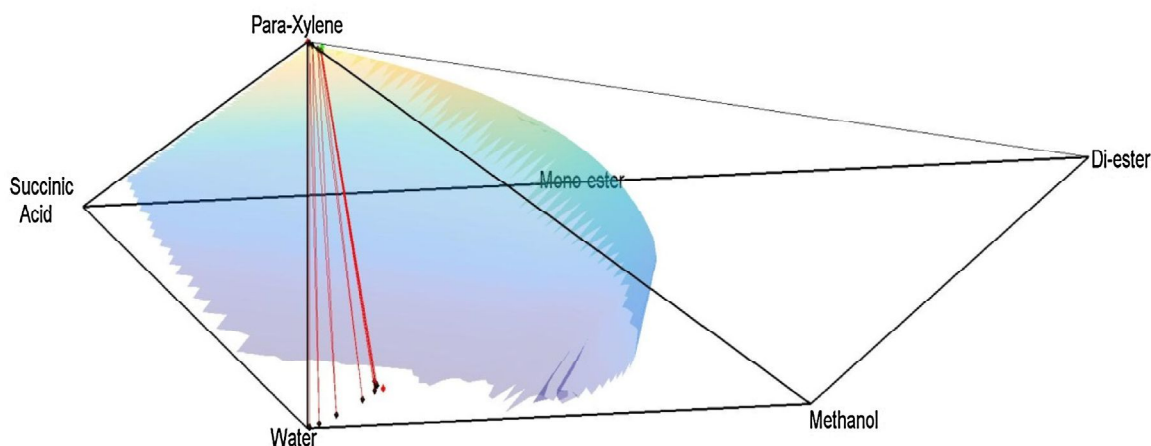


Fig. 15. Pre-design step for the $N_c = 6$ system.

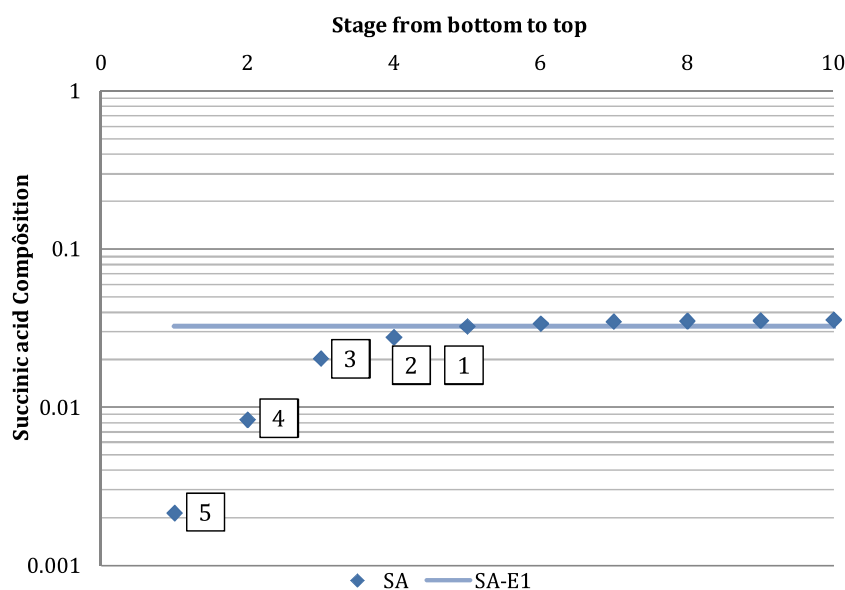


Fig. 16. Reactive organic phase composition profile for Succinic Acid and Methanol. NTS determination, NTS = 5.

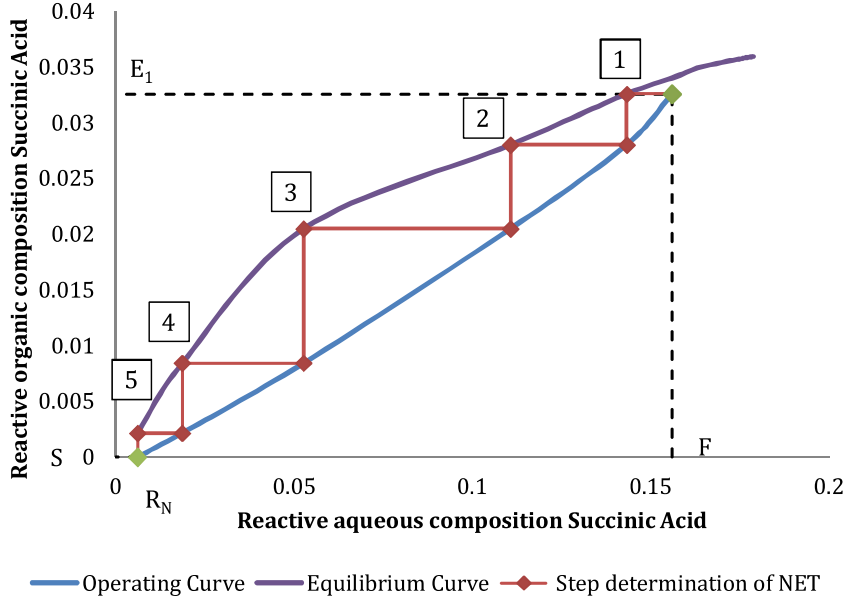


Fig. 17. Distribution diagram for the NTS determination.

4. Conclusion

A method for determining the design of a liquid–liquid extraction column is proposed in this article. This method is based on three stages: a feasibility analysis, a shortcut step also called a pre- column design and a final step of simulation. Throughout this method, the complexities in the study of physical phenomena are introduced. The developed method is based on work done on reactive separation processes such as reactive distillation. The aim of this method is the determination of the reactive extractive column design and its operating parameters. This method has been applied to different reactive systems with different strategies and numbers of compounds, with succinic acid, and leads to the design of a reactive extractive column. To complete this study, the simulation step must be performed to identify the kinetics and transfer effects on the design configuration and on the operating parameters.

Appendix A. Definition and benefits of reactive composition (Barbosa and Doherty, 1987)

We consider a system with N_c reacting compounds and N_r independent reactions. If the composition of the compounds' compositions are expressed according to the N_r reference compounds, N_r composition variables can be removed. A set of composition variables with the same dimension as the variance of the system ($N_c - N_r$) is obtained. The expression of the reactive composition variables is as follows:

$$X_i = \frac{x_i - v_i^T \cdot \phi_{(r)}^{-1} \cdot x_{(r)}}{1 - v_i^T \cdot \phi_{(r)}^{-1} \cdot x_{(r)}} \quad (28)$$

with,

- v_i^T : row vector of stoichiometric coefficients of component i in each N_r reactions.

$$v_i^T = (v_{i,1}, v_{i,2}, \dots, v_{i,N_r})$$

- v_i^T : row vector composed of the sums of stoichiometric coefficients for each N_r reactions.

$$v_i^T = (v_{i,1}, v_{i,2}, \dots, v_{i,N_r})$$

- $\phi_{(r)}^{-1}$: square matrix of stoichiometric coefficients for the N_r reference component in the N_r reaction equation.

$$\phi_{(r)} = \begin{pmatrix} v_{(N_c - N_r + 1),1} & \dots & v_{(N_c - N_r + 1),N_r} \\ \vdots & & \vdots \\ v_{N_c,1} & \dots & v_{N_c,N_r} \end{pmatrix}$$

$x_{(r)}$: column vector of the compositions for the N_r reference component.

$$x_{ref} = (x_{(c-r+1)}, x_{(c-r+2)}, \dots, x_c)^T$$

The matrix $\phi_{(r)}$ must be invertible, so the choice of the reference components was subject to some conditions:

- No rows or columns of the matrix can be equal to zero. That is to say, each chemical reaction needs to match at least one reference component. An inert compound cannot be selected as a reference compound.
- Two reference compounds cannot have the same stoichiometric coefficients in each reaction.

The main benefit of using reactive composition is that the final result does not depend on the reaction and the chemical extent ξ (Eq. (29)), in addition to the fact that the sum of the molecular composition is always equal to 1.

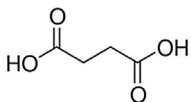

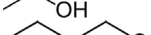

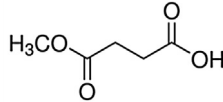
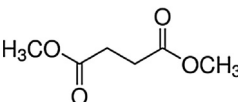
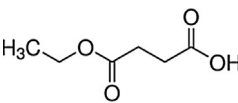
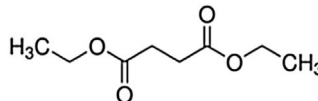
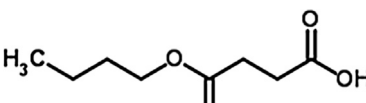
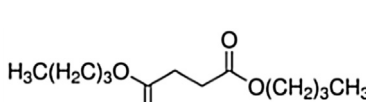
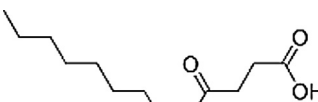
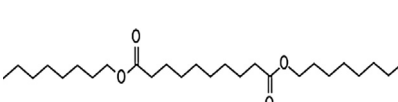
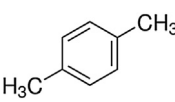
$$X_i(0) = X_i(\xi) \quad \forall \xi \quad i = 1, 2, \dots, N_c - N_r \quad (29)$$

$$\sum_{i=1}^{N_c - N_r} X_i = 1 \quad \sum_{i=1}^{N_c - N_r} Y_i = 1 \quad (30)$$

Appendix B.

Table A1.

Table A1
Compounds studied in this application.

Name of the molecules	Empirical chemical formula	developed chemical formula	Molecular weight (g.mol ⁻¹)
Succinic Succinic (SA)	C ₄ H ₆ O ₄		118.09
Methanol (MeOH)	C ₁ H ₄ O		32.04
Ethanol (EtOH)	C ₂ H ₆ O		46.07
Butanol (BuOH)	C ₄ H ₁₀ O		74.12
Octanol (OcOH)	C ₈ H ₁₈ O	CH ₃ (CH ₂) ₆ CH ₂ OH	130.23
Water	H ₂ O	H ₂ O	18.02
Mono-Methyl Succinate (MMS)	C ₅ H ₈ O ₄		132.11
Dimethyl Succinate (DMS)	C ₆ H ₁₀ O ₄		146.14
Mono-Ethyl Succinate (MES)	C ₆ H ₁₀ O ₄		146.14
Diethyl Succinate (DES)	C ₈ H ₁₄ O ₄		174.19
Mono-Butyle Succinate (MMS)	C ₈ H ₁₄ O ₄		174.19
Dibutyle Succinate (DMS)	C ₁₂ H ₂₂ O ₄		230.30
Mono-Octyl Succinate (MOS)	C ₁₂ H ₂₂ O ₄		230.30
Diocetyl Succinate (DOS)	C ₂₀ H ₃₈ O ₄		342.51
Para-xylène	C ₈ H ₁₀		106.17

References

- [1] C.S.L. Garzón, A.J. Straathof, Recovery of carboxylic acids produced by fermentation, *Biotechnol. Adv.* 32 (2014) 873–904.
- [2] D.A. Glassner, P. Elankovan, D.R. Beacom, K.A. Berglund, Purification process for succinic acid produced by fermentation, *Appl. Biochem. Biotechnol.* 51–52 (1995) 73–82.
- [3] Q. Li, D. Wang, Y. Wu, W. Li, Y. Zhang, J. Xing, Z. Su, One step recovery of succinic acid from fermentation broths by crystallization, *Sep. Purif. Technol.* 72 (2010) 294–300.
- [4] H. Lin, G.N. Bennett, K.-Y. San, Metabolic engineering of aerobic succinate production systems in *Escherichia coli* to improve process productivity and achieve the maximum theoretical succinate yield, *Metabolic Eng.* 7 (2005) 116–127.
- [5] R. Luque, C.S.K. Lin, C. Du, D.J. Macquarrie, A. Koutinas, R. Wang, C. Webb, J.H. Clark, Chemical transformations of succinic acid recovered from fermentation broths by a novel direct vacuum distillation-crystallisation method, *Green Chem.* 11 (2009) 193–200.
- [6] A. Orjuela, A.J. Yanez, A. Santhanakrishnan, C.T. Lira, D.J. Miller, Kinetics of mixed succinic acid/acetic acid esterification with Amberlyst 70 ion exchange resin as catalyst, *Chem. Eng. J.* 188 (2012) 98–107.
- [7] V.K.S. Pappu, V. Kanyi, A. Santhanakrishnan, C.T. Lira, D.J. Miller, Butyric acid esterification kinetics over Amberlyst solid acid catalysts: the effect of alcohol carbon chain length, *Bioresour. Technol.* 130 (2013) 793–797.
- [8] H.N. Pham, M.F. Doherty, Design and synthesis of heterogeneous azeotropic distillations—II: Residue curve maps, *Chem. Eng. Sci.* 45 (1990) 1837–1843.
- [9] M.J.D. Powell, A fortran subroutine for solving systems of nonlinear algebraic equations, in: P. Rabinowitz (Ed.), *Numerical Methods for Nonlinear Algebraic Equations*, 1970 (Ch. 7).
- [10] K.D. Samant, K.M. Ng, Synthesis of extractive reaction processes, *AIChE J.* 44 (1998) 1363–1381.
- [11] K.D. Samant, K.M. Ng, Design of multistage extractive reaction processes, *AIChE J.* 44 (1998) 2689–2702.
- [12] J.D. Seader, E.J. Henley, *Liquid–Liquid extraction with ternary systems*. In: *separation process principles: chemical and biochemical operations 3rd edition* John Wiley and sons, Inc (2011) 299–358 (ISBN: 978-0-470-48183-7).
- [13] R. Thery, X.M. Meyer, X. Joulia, M. Meyer, Preliminary design of reactive distillation columns, *Chem. Eng. Res. Des.* 83 (2005) 379–400.
- [14] A.B. Tuchlenski, Reactive distillation industrial applications: process design and scale-Up, *Chem. Eng. Sci.* 56 (2001) 387–394.
- [15] S. Ung, M.F. Doherty, Calculation of residue curve maps for mixtures with multiple equilibrium chemical reactions, *Ind. Eng. Chem. Res.* 34 (1995) 3195–3202.
- [16] R.C. Wu, Y.Z. Xu, Y.Q. Song, J.A. Luo, D. Liu, A novel strategy for salts recovery from 1,3-propanediol fermentation broth by bipolar membrane electro dialysis, *Sep. Purif. Technol.* 83 (2011) 9–14.
- [17] P. Wuithier, A. Giraud, *Le Pétrole: Raffinage Et génie Chimique*, Technip, Paris, 1972 (Tome I. Editions).
- [18] P. Wuithier, A. Giraud, *Le Pétrole: Raffinage Et génie Chimique*, Technip, Paris, 1972 (Tome II. Editions).
- [19] J.G. Zeikus, Chemical and fuel production by anaerobic bacteria, *Annu. Rev. Microbiol.* 34 (1980) 423–464.
- [20] J.G. Zeikus, M.K. Jain, P. Elankovan, Biotechnology of succinic acid production and markets for derived industrial products, *Applied Microbiology Biotechnology* 51 (1999) 545–552.