Reactive residue curve maps
A new study case

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Abstract

Using a methodology based on the element concept instead of the usual molar concept, a calculation procedure and meaning of the reactive residue curves are described. Through two well known industrial production processes (MTBE and methyl acetate), characteristics and advantages of the residue curve maps are depicted in order to analyse and design *reactive* distillation processes. Based on this, a new case is examined: esterification of lactic acid and ethanol to ethyl lactate, a biodegradable and non-toxic solvent that has been studied and obtained by reaction/pervaporation. Some alternatives via reactive distillation are discussed.
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1. Introduction

In the twenties of the last century Backhaus [2] carried out experiments combining distillation with reaction and developed several patents in order to manufacture esters. Since then, these kinds of processes have been intensively studied specially when MTBE and methyl acetate industrial production by reactive distillation (RD) were implemented [17,1]. Through RD, it is possible to overcome reaction equilibrium limitations, minimise side-reactions, obtain high purity products and, by employing the heat of reaction in situ, energy consumption is reduced. However, reactive distillation is not a universal solution; every case should be studied theoretically and experimentally [5,7–9,11,14].

RD is complex because of the competition among equilibrium trends, mass transfer between liquid and vapour phases, reaction rate and diffusion inside catalyst, when there is a heterogeneous reaction [19].

The thermodynamic behaviour of reactive distillation processes (three components or more) in chemical and physical equilibrium (CPE) can be graphically illustrated by *reactive* residue curves (RRC) whose complete composition space shapes a *reactive* residue curve map (RRCM). Based on this, a prelim-

inary or conceptual design can be located [3,27] for developing a more detailed and realistic design [16].

In this work, RRCM and conceptual design are shown for three production processes: MTBE,[1] methyl acetate (MA) and ethyl lactate (EL), all of them highly non-ideal reactive system. The chemical kinetic effects over the RRCM have been investigated by other authors [20,25,26].

For binary (in component) reactive systems, other graphical design approaches have been implemented [10].

Based on the element concept, the approach used in this work was applied to RD for the first time by Pérez-Cisneros et al. [13]. This approach allows graphic representation of the reactive distillation processes in a simple way, its analysis and design becoming easier. Additionally, the mathematic models look like distillation models without reaction.

2. Methodology

The methodology used in this work is supported by the element concept (atom, molecule or fragment of molecule) as an alternative to the usual *molar* concept [12]. The amount of element is not changed even though non-symmetric stoichiometric reactions take place. Therefore, since the elements are not consumed by reactions, the differential equations describing the

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[1] Methyl-*tert*-butyl-ether.

simple reactive distillation, a dynamics process represented in the *reactive* residue curves, become analogous to those from batch distillation without reaction. In addition, although the reactive mixtures studied are made up of four components, according to phase rule of Gibbs for reactive components, the degrees of freedom are reduced to three.

2.1. Problem definition in terms of element

The phase rule of Gibbs for reactive components points out the degrees of freedom (F) for the reactive system rely on phase number (NP) and the minimum number of substances (M) which should be present in order to attain a system with NC species:

$$F = 2 - NP + M \tag{1}$$

$$M = NC - NR - S \tag{2}$$

Specifically, M symbolizes the independent element number making up the complete system. These can be atoms, molecules or atom groups, but not necessarily the elements of the periodic table. Given that in RD processes only vapour and liquid coexist (NP = 2), the degrees of freedom are matched by element number of the reactive system.

In agreement with Eq. (2), when one reaction (NR = 1) occurs in a ternary mixture (NC = 3) without stoichiometric restriction (S = 0), the system becomes binary in terms of elements (M = 2). Therefore, in these cases study and design can be carried out through graphical procedures like McCabe-Thiele and Ponchon-Savarit originally proposed for distillation without reaction [6,15,16].

The reactive systems in order to produce MTBE, methyl acetate and ethyl lactate are made up of four components; only one reaction takes place and no stoichiometric restriction is displayed; as a result, according to Eq. (2), they become ternary systems in elements (M = 3).

An element definition fulfilling Gibbs's phase rule is shown in Table 1. It should be noticed for the first reaction that elements A, B and C are components while the product MTBE was represented by combining AB. In contrast, reactions for producing MA and EL include a molecule fraction as element A.

The relationship between molar and element quantities can be seen through the formula matrix (or element composition

Table 1
Element definition (production of MTBE, MA and EL)

Reaction in components	Elements	Reaction in elements
$C_4H_8 + CH_4O \leftrightarrow C_5H_{12}O$	A $\leftarrow C_4H_8$	A + B $\leftrightarrow$ AB
IB + MOH $\leftrightarrow$ MTBE	B $\leftarrow CH_4O$	
	C $\leftarrow$ 1-butene (inert)	
$(CH)_2O(H_2O) + CH_4O \leftrightarrow H_2O + (CH)_2O(CH_4O)$	A $\leftarrow (CH)_2O$	AC + B $\leftrightarrow$ C + AB
	B $\leftarrow CH_4O$	
AA + MOH $\leftrightarrow$ water + MA	C $\leftarrow H_2O$	
$C_3H_6O_3 + C_2H_6O \leftrightarrow H_2O + C_5H_{10}O_3$	A $\leftarrow C_3H_4O_2$	AC + B $\leftrightarrow$ C + AB
LA + EOH $\leftrightarrow$ water + EL	B $\leftrightarrow C_2H_6O$	
	C $\leftrightarrow H_2O$	

IB: isobutene; MOH: methanol; 1-B: 1-butene; AA: acetic acid; MA: methyl acetate; LA: lactic acid; EOH: ethanol; EL: ethyl lactate.

Table 2
Formula matrix

Element	Component			
	IB (1)	MOH (2)	1-B (3)	MTBE (4)
MTBE production				
A	1	0	0	1
B	0	1	0	1
C	0	0	1	0
	AA (1)	MOH (2)	Water (3)	MA (4)
Methyl acetate production				
A	1	0	0	1
B	0	1	0	1
C	1	0	1	0
	LA (1)	EOH (2)	Water (3)	EL (4)
Ethyl lactate				
A	1	0	0	1
B	0	1	0	1
C	1	0	1	0

matrix) in Table 2. For example, for EL production considering equimolar mixture (1 mol) the results shown in Table 3 could be acquired defining:

$$\text{Element fraction } j = \left[\frac{\text{Element Quantity } j}{\text{Total Quantities of Elements}} \right] \quad (3)$$

Therefore, for MTBE production each element fraction would be:

$$W_A^l = \frac{x_1 + x_4}{1 + x_4}, \qquad W_B^l = \frac{x_2 + x_4}{1 + x_4}, \qquad W_C^l = \frac{x_3}{1 + x_4} \quad (4)$$

Based on a similar reasoning, for methyl acetate and ethyl lactate production element fractions should be evaluated in the same way because they have identical formula matrix. The corresponding equations would be:

$$W_A^l = \frac{x_1 + x_4}{1 + x_1 + x_4}, \qquad W_B^l = \frac{x_2 + x_4}{1 + x_1 + x_4},$$
$$W_C^l = \frac{x_1 + x_3}{1 + x_1 + x_4} \quad (5)$$

2.2. Calculation of the residue curves

In one stage of reactive batch distillation the chemical reaction takes place in liquid phase (residue) while vapour phase is continuously removed. Due to volatility differences as well as the chemical reaction taking place, compositions of both phases

Table 3
Element fraction calculation (EL production)

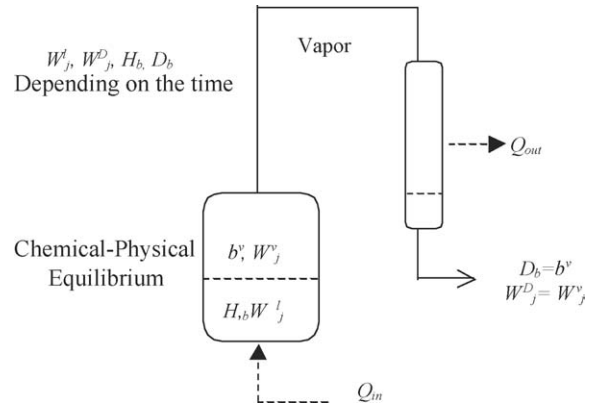|	Moles	Moles A	Moles B	Moles C
Lactic acid (1)	0.25	0.25	0	0.25
Ethanol (2)	0.25	0	0.25	0
Water (3)	0.25	0	0	0.25
Ethyl lactate (4)	0.25	0.25	0.25	0
Total	1	0.5	0.5	0.5

Fig. 1. Batch distillation with reaction in terms of elements.

change as time passes; in addition, residue is depleted especially in the more volatile component. A schematic description of reactive batch distillation is shown in Fig. 1.

Appendix A contains description of differential equation system (6) and (7) whose solution requires to know the vapour phase element fractions (W_j^v) corresponding to the specified composition (initial condition) for the mixture charged in the still ($W_{j,0}^l$).

$$\frac{dW_j^l}{d\tau} = W_j^l - W_j^v = W_j^l - W_j^D, \quad j = 1, 2, \ldots, M,$$
$$\tau = \frac{D_{b,0}}{H_{b,0}} t \quad (6)$$

$$\frac{d(H_b h_b^l)}{d\tau} = -H_b h_b^v + \frac{H_{b,0}}{D_{b,0}} Q_{in} \quad (7)$$

Assuming chemical and physical equilibrium (CPE) a reactive bubble point calculation is carried out in order to cover that requirement. The approach employed minimises the total Gibbs free energy [Eq. (8)] assuming the multicomponent CPE as a phase equilibrium problem for a mixture of M elements (representing the problem). The mathematic general formulation is as follows (see notation):

$$\min G(n) = \sum_{\beta=1}^{NP} \sum_{i=1}^{NC} n_i^\beta \mu_i^\beta \quad (8)$$

subject to the M restrictions:

$$\sum_{\beta=1}^{NP} \sum_{i=1}^{NC} A_{ji} n_i^\beta - b_j = 0, \quad j = 1, 2, \ldots, M \quad (9)$$

Eq. (9) represents the M independent element mass balances, where the coefficients A_{ji} symbolize the number of reaction invariant elements j in molecule i as described in Table 2 and b_j is the total number of gram-atoms of element j in the system.

The solution of this equation system was carried out through the Lagrange multiplier formulation by Pérez-Cisneros [12]

defining the corresponding Lagrangian function as:

$$\hat{L} = \sum_{\beta=1}^{NP}\sum_{i=1}^{NC} n_i^\beta \mu_i^\beta - \sum_{j=1}^{M}\lambda_j \left(\sum_{\beta=1}^{NP}\sum_{i=1}^{NC} A_{ji} n_i^\beta - b_j \right) \quad (10)$$

and the necessary conditions for a stationary point as:

$$\frac{\partial\hat{L}}{\partial n_i^\beta} = \mu_i^\beta - \sum_{j=1}^{M} A_{ji}\lambda_j = 0,$$

$$i = 1, 2, \ldots, NC, \quad \beta = 1, 2, \ldots, NP \quad (11)$$

$$\frac{\partial\hat{L}}{\partial\lambda_j} = -\sum_{\beta=1}^{NP}\sum_{i=1}^{NC} A_{ji} n_i^\beta + b_j = 0, \quad j = 1, 2, \ldots, M \quad (12)$$

Given that the equation system (11) and (12) has $NC \times NP + 2M + 2$ variables [$NC \times NP$ molar compositions (n_i^β), M element compositions (b_j), M Lagrange multipliers (λ_j), P and T], the corresponding degrees of freedom are:

$$F = NC \times NP + 2M + 2 - (NC \times NP + M) = M + 2 \quad (13)$$

Therefore, using any thermodynamic model that provides chemical potentials, given P, T and all the W_j^l (or $\mathbf{b}$, the vector of element amounts) Eqs. (11) and (12) can be solved for the $NC \times NP + M$ unknowns. As a bubble point calculation in phase equilibrium, T could be supposed as well as the check condition of sum to unity of the vapour mole fractions is applied.

Founded the answer to the CPE calculation, Eqs. (6) and (7) could be solved in order to obtain the reactive residue curves. As can be seen in Appendix A, in this equation a specific heating strategy (or policy) has been proposed that enables to define a new dimensionless time variable (τ), reducing by one the total number of variables in the system and achieving an explicit relationship between H_b and τ.

$$H_b = H_{b,0} \exp(-\tau) \quad (14)$$

Considering that W_j^l and W_j^v should be in equilibrium at certain P and T, our equation system comprises $M + 2$ equations [(6), (7) and (14)] and $2M + 5$ variables (W_j^l, W_j^v, P, T, τ, H_b and Q_{in}), therefore, the degrees of freedom are:

$$F = 2M + 5 - (M + 2) = M + 3 \quad (15)$$

As a result, given W_j^l, P, T and τ the problem could be solved. An alternative model would be obtained by omitting the energy balance. In this case, the system would comprise M equations [(6)] and $2M + 3$ variables (W_j^l, W_j^v, P, T and τ) remaining the same degrees of freedom. These results support the consistency of the model proposed. Finally, three issues should be noted: h_b^l and h_b^v rely on the variables coming from the solution for the equilibrium model, the stoichiometry does not need to be symmetric and, all the more, reaction stoichiometry is unnecessary in this approach.
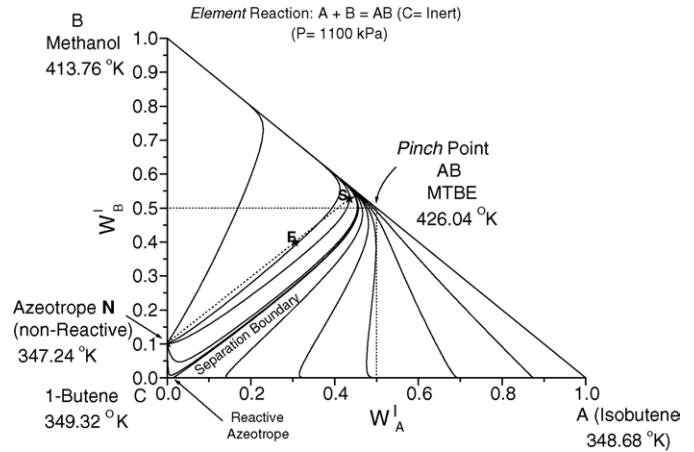

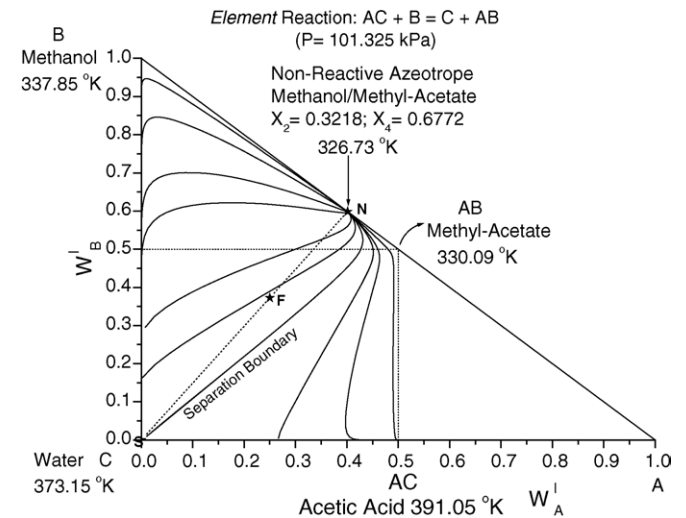
Fig. 2. Residue curve map. MTBE production.

Fig. 3. Residue curve map. MA production.

3. Residue curve map analysis

Figs. 2–4 show *reactive* residue curve maps (RRCM) for the non-ideal reactive systems proposed. It is suitable to observe
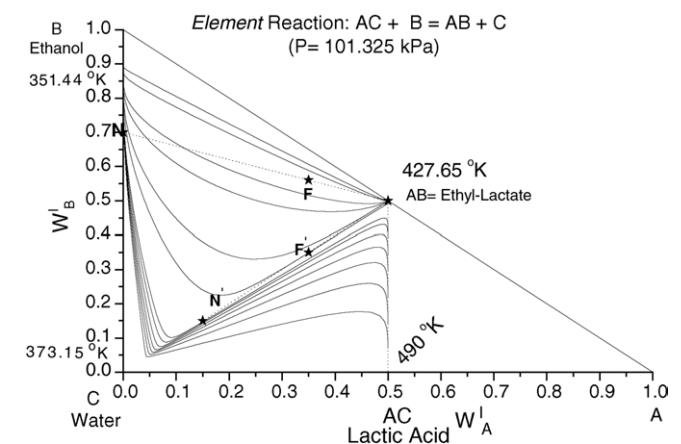

Fig. 4. Residue curve map. EL production.

in these figures that, consistently with the element definition in Table 1, isobutene is symbolized by element A in Fig. 1 while element A represents no one component in Figs. 2 and 3 but an atom group as was set in Table 1. NRTL model and ideal gas were considered for all of them (binary parameters and thermodynamics constants were taken from Aspen-Plus 11.1 simulator).

3.1. General features of the reactive residue curve map

- A RRCM shows explicitly regions and separation boundaries, being useful concepts to determine feasible options for reactive distillation. The separation boundaries delimit feasible specification regions.
- The singular points on the RRCM correspond to reactive azeotropes, non-reactive azeotropes and pure components as shown by Ung and Doherty [21,22].
- The residue curves can converge to the singular points but not always. Certain singular points could work like attracting points (the residue curves are curved towards it with different strength) and other as *pinch* points (the residue curves are noticeably curved towards it but none of them exactly converges to the point).
- Residue composition always changes towards increasing temperature.
- By using the lever rule, RRCM allows for implementation of conceptual design.

3.2. MTBE production

Fig. 2 shows two feasible regions for reactive distillation separated by a boundary due to reactive azeotrope displayed close to the 1-butene corner [18]. In the upper region, methanol composition (element B) prevails over isobutene (element A), both reagents; on the other hand, residue curves in this region address from the non-reactive azeotrope (1-butene/methanol) to the pure methanol attracted by the singular point AB (MTBE). In opposition, in the lower region (Fig. 2), there is higher isobutene ratio with respect to methanol and residue curves going from isobutene to methanol, but strongly attracted by MTBE (*pinch* point). As a result, pure MTBE cannot be attained in chemical and physical equilibrium conditions (non-reactive stages would be necessary).

Two extreme points inside a residue curve, for instance, S and N in Fig. 2, depict bottom and top products, respectively, for a continuous distillation column with chemical reaction happening in all its stages. Point S represents a rich mixture in MTBE and point N is located right on the non-reactive azeotrope.

In agreement with the lever rule, i.e. the total mass balance, an intermediate point over the right line S–N such as F (isobutene as limit reagent) would be a feasible feed for this case.

Based on the *transformed composition variable* concept, Ung and Doherty [22] elaborated for the first time a *reactive* residue curve map for MTBE production, while a conceptual design located in the lower region was proposed by Ung and Doherty [23].

3.3. Methyl acetate production

Fig. 3 shows *reactive* residue curves above the separation boundary leaving from non-reactive azeotrope (methanol/methyl acetate) to the reaction product, water (element B). However, below the separation boundary, RRC tend to the reagent acetic acid (point AC). Methanol (point B) and methyl acetate (point AB) work as attracting points becoming impossible to obtain pure methyl acetate as top product when only reactive stages exist in the column. Separation boundary (*reactive* residue curve departing from N to S) clearly describes opportunity for acquiring highly pure water from the bottom of a distillation column with only reactive stages. However, according to lever rule (line S–F–N in Fig. 3), an azeotrope methanol/methyl acetate would be obtained from the top, which could be separated through further extractive distillation, an impractical choice due to the increase in energy, equipment and hence costs.

By modelling and experiments, Agreda et al. [1] showed acetic acid is a good extractive agent in order to decompose the azeotrope methanol/methyl acetate. Therefore, by counter-flow between acetic acid (reagent) and azeotrope inside column, methyl acetate can be separated. Interesting and complete studies about MA production have been carried out by Pöpken et al. [14] and Huss et al. [7].

3.4. Ethyl lactate production

Ethyl lactate is an environmentally benign solvent because it is biodegradable and non-toxic. Benedict et al. [4] have shown advantages to producing it through reactor/pervaporation combination. The following analysis depicts some possibilities for using reactive distillation as an alternative.

Fig. 4 highlights the water role as attracting point as well as an incomplete separation boundary exactly on the diagram diagonal. RRC in upper region move from neighborhood of the point B (ethanol) to the pure ethyl lactate (point AB). A mass balance in this region as indicated by line AB–F–N shows the possibility for acquiring high purity ethyl lactate through RD at the bottom while ethanol–water mixture could be obtained at the top which would have to be purified in other equipment. A feed like F in Fig. 4 includes an ethanol excess.

Below the separation boundary, RRC start nearby ethanol (point B) addressing to the lactic acid (point AC) but being attracted by the ethyl lactate (point AB). To implement RD in this region is not attractive because both products (bottom and top) would be very impure. However, another opportunity could be over the diagonal. Line AB–F′–N′ in Fig. 4 indicates that high purity ethyl lactate can be attained at the bottom while a multi-component mixture would leave at the top of the column. In this case an equimolar feed could be used.

A further design work combining experiments and simulation will be necessary to reach a feasible design for this system.

4. Conclusions

By applying a methodology supported on the element concept, reactive batch distillation (one stage) in chemical and physical equilibrium for three highly non-ideal systems has been studied. Through an algorithm based on *reactive* bubble point calculation *reactive* residue curves and residue curve maps were elaborated. By defining the reactive system in terms of element according to the Gibbs phase rule for reactive systems, the number of composition variables representing the system is reduced and the graphical representation is simplified; therefore, comprehension of reactive distillation processes becomes relatively straightforward. Additionally, the mathematic models have a similar appearance to distillation models without reaction.

By considering two reactive distillation processes (MTBE and methyl acetate production) studied by many authors and successfully implemented industrially, a systematic description has been developed regarding *reactive* residue curve map characteristics and advantages. From this, an analysis was worked out that allows for discerning feasible opportunities for carrying out reactive distillation.

Finally, ethyl lactate production, a biodegradable and nontoxic solvent that has been obtained by reactor/pervaporation combination, was analysed using the studied tools. Some conceptual alternatives for producing ethyl lactate via reactive distillation were depicted.

Appendix A. Model based on the element concept for calculating *reactive* residue curves

$$\text{Element balance}: \quad \frac{d(H_b W_j^l)}{dt} = -D_b W_j^v, \quad j = 1, 2, \ldots, M \tag{A.1}$$

$$\text{Total element balance}: \quad \frac{dH_b}{dt} = -D_b \tag{A.2}$$

$$\text{Energy balance}: \quad \frac{d(H_b h_b^l)}{dt} = -D_b h_b^v + Q_{in} \tag{A.3}$$

where H_b: liquid element holdup in the still; D_b: rate of distillate element; h_b^l and h_b^v: element enthalpy for liquid and vapor phases; Q: rate of heat transfer.

Developing left side in (A.1) and combining with (A.2) we have:

$$\frac{H_b}{D_b} \frac{dW_j^l}{dt} = W_j^l - W_j^v \tag{A.4}$$

Assuming a heating strategy such that the rate of distillate element is decreased in constant proportion to the liquid element holdup in the still [24,26]:

$$\frac{D_b}{H_b} = \frac{D_{b,0}}{H_{b,0}} = \text{Cte} \tag{A.5}$$

or

$$\frac{D_b}{D_{b,0}} = \frac{H_b}{H_{b,0}} \tag{A.6}$$

A dimensionless time could be defined:

$$\tau = \frac{D_{b,0}}{H_{b,0}} t \tag{A.7}$$

where $H_{b,0}$: total liquid element in the still when $t = 0$; $D_{b,0}$: rate of distilled element when $t = 0$.

Considering (A.5) and (A.7) in (A.4):

$$\frac{dW_j^l}{d\tau} = W_j^l - W_j^v \tag{A.8}$$

Substituting (A.6) and (A.7) in the energy balance (Eq. (A.3)) and ordering:

$$\frac{d(H_b h_b^l)}{d\tau} = -H_b h_b^v + \frac{H_{b,0}}{D_{b,0}} Q_{in} \tag{A.9}$$

Eqs. (A.8) and (A.9) along with physical and chemical equilibrium model described in Section 2.2 form the equation system for calculating reactive residue curves. Additionally, an explicit relationship between H_b and τ should be considered (Eq. (A.10)).

Combining (A.6) with (A.2) and integrating we obtain:

$$H_b = H_{b,0} \exp\left(-\frac{D_{b,0}}{H_{b,0}} t\right) = H_{b,0} \exp(-\tau) \tag{A.10}$$

To carry out the model solution, $D_{b,0}$ should be evaluated in the following way. From (A.10) $D_{b,0}$ could be known setting initial and final element holdup ($H_{b,0}$ and $H_{b,f}$) for a reactive distillation time (t_f) wanted [24]:

$$D_{b,0} = \frac{H_{b,0}}{t_f} \ln\left(\frac{H_{b,0}}{H_{b,f}}\right) \tag{A.11}$$

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