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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 preliminary 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.

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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.

Nomenclature

A, B, C	name of element
A_{ji}	number of reaction invariant elements j in molecule i
$\boldsymbol{b}$	vector of element amounts
b^D	total element in distillate
b_j	total element of j (j = A, B, C for the cases studied)
b^{l}	total liquid element
b^{v}	total vapor element
b_j^{l}	element j in liquid phase (j = A, B, C for the cases studied)
b_j^{v}	element j in vapor phase (j = A, B, C for the cases studied)
D_b	rate of distillate element
$D_{b,0}$	rate of distilled element when $t = 0$
F	degrees of freedom
$G(n)$	total Gibbs free energy
$h_b^{\mathrm{l}}, h_b^{\mathrm{v}}$	element enthalpy for liquid and vapor phases
H_b	liquid element holdup in the still
$H_{b,0}$	total liquid element in the still when $t = 0$
M	number of elements
n	total moles in the system
n_i	moles of the species i
NC	number of components
NP	number of phases
NR	number of independent reactions
Q	rate of heat transfer
S	number of special restrictions
W_j^D	element fraction in distillate (j = A, B, C)
W_j^{l}	liquid element fraction (j = A, B, C)
W_j^{v}	vapor element fraction (j = A, B, C)
x_i	liquid mol fraction (i = 1, 2, ..., NC)

Greek letters

λ_j	Lagrange multipliers
μ_i	chemical potential for component i
τ	dimensionless time

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:

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

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

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 ↔ MTBE	$B \leftarrow CH_4O$ $C \leftarrow$ 1-butene (inert)	
$(CH)_2O(H_2O) + CH_4O \leftrightarrow H_2O + (CH)_2O(CH_4O)$	$A \leftarrow (CH)_2O$ $B \leftarrow CH_4O$	$AC + B \leftrightarrow C + AB$
AA + MOH ↔ water + MA	$C \leftarrow H_2O$	
$C_3H_6O_3 + C_2H_6O \leftrightarrow H_2O + C_5H_{10}O_3$ LA + EOH ↔ water + EL	$A \leftarrow C_3H_4O_2$ $B \leftrightarrow C_2H_6O$ $C \leftrightarrow H_2O$	$AC + B \leftrightarrow C + AB$

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

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