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## A graphical design method for reaction–extraction processes in quaternary systems

M.A. Olán-Acosta, V. Rico-Ramírez, G. González-Alatorre,  
E.O. Castrejón-González\*

Departamento de Ingeniería Química, Instituto Tecnológico de Celaya, Av. Tecnológico y A. García Cubas s/n, Celaya, Guanajuato, CP 38010, Mexico

### ABSTRACT

This paper proposes a graphical design method for quaternary systems in simultaneous chemical and physical liquid–liquid equilibrium (reaction–separation process). The reactive phase equilibrium data and the stage by stage calculation are represented into two projections diagrams with rectangular coordinates. The graphical method has been applied to reversible reactive systems where all of the components of the reaction have the same stoichiometric coefficient. This graphical method allows estimating the number of reactive theoretical stages, the limits of the solvent to feed ratio ( $D/F$ ), the extent of reaction and the conversion. Results obtained for seven design problems (involving four different reactive systems) are in good agreement with state of the art simulation software and with literature.

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**Keywords:** Reaction–extraction; Diagram projection; Calculation of stages; Reactive quaternary systems; Reactive liquid–liquid equilibrium; Chemical equilibrium; Self induced system

### 1. Introduction

In reaction–separation processes the integration effects provide the possibility of bypassing the equilibrium limitations imposed by a reversible reaction. Then, these processes can be used as a useful alternative for improvement in yield and selectivity of a desired product and ease of separation (Moulijn and Stankiewicz, 2003). Another advantage of this integration is that a more compact technological configuration can be used; the advantages should be considered in both the conceptual design and the practical design (Zimmerman et al., 2007).

In the particular case of the reaction–extraction process, an interaction is obtained between the reaction and the separation of two liquid phases. The separation of the phases, caused by immiscibility, may occur naturally (when one of the

components of the system acts as a solvent) or may be induced by the addition of a solvent (Samant and Ng, 1998a).

The reaction–extraction process has been classified according to its main goal. If the main goal is the synthesis of chemical products, then it is classified as an extractive reaction; on the contrary, if the goal is the separation of chemical substances, then the process is referred to as a reactive extraction (Samant and Ng, 1998a; Cardona and Gutiérrez, 2007a). In this paper, no particular distinction is made between these two processes.

The reaction–extraction process is used for the purification of solvents, the extraction of products, or the selective separation of physically similar components. It is applied to separate metals or pharmaceuticals, for wastewaters treatment and in the purification of organic mixtures (Schmidt-Traub and Górak, 2006). Most of these applications are experimental,

**Abbreviations:** CCMS, countercurrent multicomponent stage; IC, interpolation curve; MESH, mass balance, equilibrium relations, summation of fractions, heat balance equations; OL, operating line; RLLE, reactive liquid–liquid equilibrium; RLLEC, reactive liquid–liquid equilibrium curve; RTL, reactive tie line; SS, single stage.

\* Corresponding author. Tel.: +52 461 6117575.

E-mail addresses: [omar@iqcelaya.itc.mx](mailto:omar@iqcelaya.itc.mx), [eocastrejjon@gmail.com](mailto:eocastrejjon@gmail.com) (E.O. Castrejón-González).

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and the research effort is limited to verifying the advantages of the process to obtain certain products (Cardona and Gutiérrez, 2007b). Theoretically, in the area of process design, the reaction–extraction process has been analyzed with esterification reactions (Minotti et al., 1998; Gutiérrez, 2008); ester hydrolysis (Krause et al., 2010), polymerization of alkenes (Schmidt-Traub and Górák, 2006) and hypothetical reactions to achieving different design goals (Samant and Ng, 1998a).

There are both qualitative and quantitative methods for the analysis, synthesis and process design of reaction–extraction processes. Qualitative methods require only thermodynamic and chemical equilibrium data. They represent tentative paths of the process in tetrahedron diagrams or in transformed coordinates diagrams (Samant and Ng, 1998a; Gutiérrez, 2008; Krause et al., 2010). The quantitative methods are applied to multicomponent systems and require additional information such as extent of reaction, number of reactive stages and feasible operation regions (Samant and Ng, 1998b; Minotti et al., 1998; Pai et al., 2004). Among all of these methods, only the qualitative methods represent a systematic strategy to verify if a reactive system could be implemented in practice as a reaction–extraction process.

Several researchers, such as Samant and Ng (1998b), Harjo et al. (2004) and Rivera and Cardona (2004) argue that the visualization of the behavior of the phases constitutes a key element in the development of the process since it allows the definition of feasible operation configurations to achieve a given objective.

In multicomponent systems, drawing the phase and reaction equilibrium surfaces and identifying the compositions that satisfy both phase and reaction equilibrium are difficult tasks when using mole fraction coordinates. The difficult task results when we try to visualize in an effective manner the functional relationships of the system variables. However, it is possible to use cuts or projections that describe projected subspace and the representation is simpler (Ung and Doherty, 1995; Wibowo and Ng, 2002; Harjo et al., 2004).

Graphical methods applied to reaction–extraction systems include methods that determine the number of reactive stages and those methods used as tools for the synthesis and design of the reactive system. In the first category, Machhammer (1994) proposed a method based on the McCabe–Thiele and applied to the removal of metal salts. The diagram is made on a logarithmic scale with four quadrants. Each quadrant represents the ionic charges of the equilibrium reaction.

In the second category, Rivera and Cardona (2004) represented the reactive liquid–liquid equilibrium in composition space (in mole fraction) on a tetrahedron diagram. The diagram is used to trace the path attempts and generate process flow diagrams that help to identify whether or not it achieves the purposes of the process (increased yield, selectivity and ease of separation). Further, Samant and Ng (1998a,b) used the transformed coordinates for reducing the size of the system and the process is analyzed in the phase diagram in the transformed coordinate space.

Lee et al. (2000) argue that, in diagrams based on transformed mol fractions coordinates, it is difficult to analyze how the reaction proceeds in the original composition space (mol fraction). To the best of our knowledge, a graphical method for extraction–reaction systems (represented either in a regular tetrahedron or through projections) would simultaneously find (i) the number of reactive stages, (ii) the extent of reaction, (iii) the feasible region of operation, and (iv) the minimum solvent ratio for mixtures with more than three components,

and further allows a better visualization of the process has not been reported to date.

In this paper we present an alternative method to design graphical reactive–extractive columns. The method is based on the diagrams of projections given by Ruiz et al. (1984) for the non-reactive processes. This work has been applied to two types of reactions: (a) reactions where there is no change in the number of total moles, and (b) reactions where the total number of moles changes. Particular attention has been given to reactions where the stoichiometric coefficients of the reactants and products are equal because, in that case, the extent of reaction is implicit in one of the projections and does not need to be specified.

The proposed design method allows to estimate: (i) the number of reactive equilibrium stages in order to achieve a specified product composition in the stream of extract (*E*) or raffinate (*R*), (ii) the extent of reaction, (iii) the conversion, (iv) the limits of the solvent to feed ratio (*D/F*) and (v) the composition of the phases that leave each stage (in multistage design problems).

The extent of reaction is defined as  $\xi = (n_i - n_{i0})/\pm \nu_i$ , where  $n_i$  are the moles of *i* unreacted,  $n_{i0}$  moles of *i* in the feed and  $\nu_i$  is the stoichiometric coefficient of *i*. The stoichiometric coefficient for the reactants is negative and that for the products is positive. The extent of reaction has units of (mol) for a batch process and (mol/h) if the process is continuous. The conversion is the disappearance of reactants during reaction; the conversion is defined as the percentage of reactant converted into products inside a unit process.

In this work, the results obtained by the proposed method are compared to those obtained from state of the art simulation software and from the literature (when the information is available).

## 2. Method

The design of the equipment needed for separation processes based on equilibrium are performed by using the MESH (mass balance, equilibrium relations, summation of fractions and heat balance) equations. The resulting system of equations can be solved through stage by stage calculations. In the case of reactive liquid–liquid extraction, if the enthalpy effects are neglected, the mass balance equations are required to relate the streams which flow between two consecutive stages (operating line); whereas the equilibrium relations are used to connect the two equilibrium (chemical and physical) phases which leave each stage (reactive tie lines). Previous information is required to RLLE representation:

1. Reactive liquid–liquid equilibrium (RLLE) data. This data can be obtained either experimentally (Maeda et al., 1997) or by using thermodynamic models such as NRTL, UNIQUAC or UNIFAC (Samant and Ng, 1998a; Gutiérrez, 2008; Iglesias-Silva et al., 2006; Bonilla-Petriciolet et al., 2008; Avami and Yadollah, 2011). However, the accuracy of the proposed design method can be affected by the fit made to the experimental data to obtain the thermodynamic parameters.
2. A method to interpolate or to calculate the Reactive Tie Line (RTL). According to the Gibbs' phase rule, for reactive systems with four components, two phases and one constraint (for the reaction), there is one degree of freedom. The region generated is therefore a curve. This enables the

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