PHASE EQUILIBRIA FOR QUATERNARY MIXTURES IN ESTERIFICATION REACTION SYSTEMS

E. A. CAMPANELLA[*] and B. A. MANDAGARAN

Instituto de Desarrollo Tecnológico para la Industria Química
(Universidad Nacional del Litoral – CONICET)
Güemes 3450 – 3000 Santa Fe – Argentina
tquique@ceride.gov.ar

Abstract-- **This paper examines the effect of the simultaneous chemical and phase equilibrium on the conceptual design of reactive distillation processes. Esterification of acetic acid with methanol, ethanol and butanol are examined. Using commercial software, azeotropic points, residue curve maps and distillation line diagrams having been calculated. The analyzed systems have showed different behavior when phase equilibrium parameters and chemical equilibrium constants are changed. The methyl acetate system does not change the topological features of residue curve maps and distillation line diagrams. The ethyl acetate system and the butyl acetate system change the topological features of the graphs when different chemical equilibrium constants are used.**

Keywords-- **Phase equilibrium, Chemical equilibrium, Reactive systems, Esterification, Reactive distillation.**

I. INTRODUCTION

In the last decade, reactive distillation has become an important alternative to the usual reaction separation processes. Agreda *et al.* (1990), Doherty and Buzad (1992) have described the advantages of reactive distillation in industrial applications. Other authors have considered different aspects of the reactive distillation. In particular, Doherty (Barbosa and Doherty 1988a, 1988b; Okasinski and Doherty, 1997, Chadda *et al.*, 2000) has examined the most relevant aspects of reactive distillation for the design of distillation sequences and columns. The first step of almost all design methods is an analysis of feasibility where residue curve maps or distillation line diagrams are very useful. An important point in analyzing reactive distillation feasibility is the influence of the chemical reaction and the phase equilibrium on residue curve maps and distillation line diagrams. The effect of property inaccuracies on process design has been reported earlier by Streich and Kistenmacher (1979), Nelson *et al.* (1983) and Hernandez *et al.* (1984). Studies that are more recent have analyzed the effect of model (Mandagarán *et al.*, 1999) and of thermodynamic data (Whiting *et al.*, 1999) on calculated process performance. Okasinski and Doherty (1997) explored the effect of the reaction equilibrium constant on the existence and location of reactive azeotropes for chemical equilibrium systems with a single chemical reaction. However, the combined effect of phase equilibrium and chemical equilibrium on reactive distillation have not been analyzed.

In this work, we present calculations to study the effect of phase and chemical equilibria on residue curve maps and distillation line diagrams for three esterification systems: methyl acetate, ethyl acetate and butyl acetate.

II. CALCULATION DESCRIPTION

In a residue curve map or in a distillation line diagram, pure component boiling points and azeotropic points are nodes (stables or unstables) or saddle points that set the topological feature of the graph. In this work, non-reactive systems are examined through residue curve maps, and reactive systems are looked through distillation line diagrams. The two graphs are necessary since reactive distillation is normally a sequence that involves separation with and without reaction.

The non-reactive azeotropy conditions are the equality of molar fraction for each component in the vapor phase and in the liquid phase. At a reactive azeotrope, the change in composition due to reaction is compensated by the change in composition due to phase equilibrium, and so a constant boiling mixture is achieved. For the esterification systems in this work (four component mixture involving one independent reaction) a convenient way to represent the reactive azeotropy condition is (Ung and Doherty, 1995).

$$X_i = Y_i \quad , i=1,...,3 \qquad (1)$$

where X_i and Y_i are a set of transformed mole fraction variables in the liquid phase and vapor phase respectively. The transformed mole fractions for acetic acid (AA), the alcohol (OH), the ester (AC) and water (W) are given as

$$X_{AA} = x_{AA} + x_{AC} \qquad (2)$$

$$Y_{AA} = y_{AA} + y_{AC} \qquad (2')$$

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[*] Author to whom correspondence should be addressed.