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Thermodynamic analysis of reaction-distillation processes based on piecewise linear models

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A U T H O R - H I G H L I G H T S

- Approach for conceptual process design suited for industrial applications.
- Covers homogeneous and heterogeneous reaction-distillation processes.
- Third paper of a series which extends the applicability to reaction-distillation processes.
- Method attractive as a first step in a process design work flow.
- Method gives excellent starting values for rigorous simulations.

A R T I C L E I N F O

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In this work a short-cut method for the conceptual process design is presented which enables an analysis of arbitrary flow sheets consisting of reactors, distillation columns, decanters, mixers, splitters, and component splitters. It is based on previous work (Ryll et al., 2012b, 2013), which is extended here to include reactors. Besides the flow sheet structure and the model for the physico-chemical properties only information on the feed streams and a set of desired product specifications is needed. The method is based on the consideration of thermodynamic limiting cases: for distillation columns ∞/∞ -analysis is used (Ryll et al., 2012b, 2013). Decanters are described assuming equilibrium between the phases which are withdrawn from Ryll et al. (2013). The reactors are either described assuming that chemical equilibrium is reached or by specifying the conversion. The number of chemical reactions is not restricted. By applying a piecewise linearization to the separatrices of the vapor-liquid(-liquid) equilibrium diagram for distillation, to the liquid-liquid equilibria in decanters as well as to the chemical equilibrium surfaces of the reactions, the nonlinear process model is replaced by a piecewise linear model (Feng et al., 2003). An existing software tool in which these methods are implemented is extended to include reactors. The tool allows for a thermodynamic analysis of arbitrary reaction-distillation processes, e.g. for feasibility or multiplicity studies, without using simplifying assumptions on thermodynamic properties. Two examples for applications are discussed.

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1. Introduction

For the conceptual design of distillation processes graphical methods based on residue curve maps or distillation line diagrams are often used (Doherty and Malone, 2001; Stichlmair and Fair, 1998). These methods can be applied to homogeneous and heterogeneous azeotropic distillation processes (Van Dongen and Doherty, 1985; Doherty and Caldarola, 1985; Pham and Doherty, 1990a,b; Kiva et al., 2003; Królikowski et al., 2011). Recently, the authors discussed the application of ∞/∞ -analysis to homogeneous and

heterogeneous distillation processes for computer-aided feasibility studies (Ryll et al., 2012b, 2013). This paper presents an extension of the method to processes including reactors. The processes to be analyzed by the extended method consist of an arbitrary number and arrangement of reactors, distillation columns, decanters, mixers, splitters, and component splitters and are denoted, hereafter, simply as reaction-distillation processes. In particular, they may contain an arbitrary number of recycles. Studying the feasibility of such processes is demanding, even when the limitations of each of their units are well understood. The main idea of the approach followed in the present work is the investigation of all units at their thermodynamic limits. This has two advantages: the number of process variables is reduced and the performance of all units is only restricted by the physico-chemical properties of the studied system.

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No compromises are made regarding the modeling depth of these properties.

For distillation, the maximum attainable separation is achieved in a column of infinite height operating under infinitely high reflux ratio. These limiting conditions are reflected in ∞/∞ -analysis (Petlyuk and Avet'yan, 1971; Serafimov et al., 1973; Petlyuk and Serafimov, 1983; Bekiaris et al., 1993; Bekiaris and Morari, 1996). ∞/∞ -Analysis is useful for feasibility and multiplicity analysis of homogeneous and heterogeneous azeotropic distillation processes (Bekiaris et al., 1993, 1996; Bekiaris and Morari, 1996; Güttinger and Morari, 1996; Müller and Marquardt, 1997; Müller, 1998; Esbjerg et al., 1998; Ulrich, 2002; Ulrich and Morari, 2003; Ryll et al., 2012b, 2013). It yields stream tables, which are usually excellent starting values for rigorous process simulations (Ryll et al., 2006; Grützner et al., 2007; Ryll et al., 2008; Burger, 2012; Burger and Hasse, 2013). ∞/∞ -Analysis can be easily applied as a graphical method based on structural residue curve maps or distillation line diagrams (denoted, hereafter, as vapor–liquid (–liquid) equilibrium diagrams) to analyze the behavior of a single distillation column in ternary systems (Petlyuk and Avet'yan, 1971; Serafimov et al., 1973; Petlyuk and Serafimov, 1983; Bekiaris et al., 1993; Bekiaris and Morari, 1996), whereas its application in quaternary mixtures is restricted to systems with a simple phase behavior (Bekiaris and Morari, 1996; Petlyuk, 1998; Blagov et al., 2000). However, even for systems with only three components a graphical analysis of distillation sequences with recycles becomes difficult (Ryll et al., 2012b, 2013), and for systems with more than three components and a complex phase behavior a graphical analysis is unfeasible and numerical approaches are needed (Pöpken, 2000; Pöpken and Gmehling, 2004; Bellows and Lucia, 2007). Furthermore, for these systems tools for synthesis of the vapor–liquid equilibrium diagrams needed for ∞/∞ -analysis have only recently become available (Blagov and Hasse, 2002).

For mixtures with more than three components the multidimensional separatrix (distillation boundaries) of the vapor–liquid (–liquid) equilibrium can only be determined numerically (Pöpken, 2000; Pöpken and Gmehling, 2004; Bellows and Lucia, 2007) and are usually described by piecewise linear approximations. By combining piecewise linear approximation of the separatrix with the evolutionary approach of Blagov and Hasse (2002) piecewise linearized vapor–liquid (–liquid) equilibrium diagrams of arbitrary complexity can be generated (Ryll, 2009; Ryll et al., 2012b, 2013). Thus, the reported difficulties in finding a well-defined mathematical description of the thermodynamic process limitations (Bekiaris et al., 1993; Müller, 1998) are overcome. Furthermore, since the original, nonlinear process model is replaced by piecewise linear sub-models (Feng et al., 2003), the attainable product compositions of ∞/∞ -separations are described by linear equations and inequalities. This approach was also recently applied to decanters, which extends the applicability of the method to heterogeneous azeotropic distillation (Ryll et al., 2013). Furthermore, not only single units can be treated with the method but arbitrary flow sheets consisting of any number of these units. Besides distillation columns and decanters, these flow sheets may also contain mixers, splitters and component splitters (Ryll et al., 2013). Based on this approach, a software tool was developed which enables an analysis of homogeneous and heterogeneous distillation processes for ternary and quaternary systems (Ryll, 2009; Ryll et al., 2012b, 2013).

Using simplified descriptions of reaction systems, e.g. chemical equilibrium or fixed degree of conversion, reaction–distillation processes with recycles can be analyzed, too (Blagov et al., 2000; Bonet et al., 2007; Nazanskii et al., 2001). In line with the idea underlying the ∞/∞ -analysis of distillation columns, i.e. maximum separation capacity, for reactors, the limiting case of an equilibrium reactor is considered here, where the mixture in the reactor outlet is always in chemical equilibrium. For kinetically

controlled reversible reactions this regime is formally attainable in a reactor of infinitely large volume thus providing the infinite residence time. To extend the applicability of the analysis to irreversible reactions and kinetically limited equilibrium reactions, alternatively, also the conversion can be specified.

In this paper, only single phase reactors are considered. Similar to the product manifolds in distillation, the reactor product manifold defined by the chemical equilibrium is generally nonlinear. By applying a piecewise linearization to the chemical equilibrium manifold the original nonlinear reactor model is replaced by piecewise linear sub-models (Feng et al., 2003), and the attainable product compositions of reactors are modeled by linear equations and inequalities. The algorithm for the piecewise linearization of the reactor product manifold used in the present work is similar to that described by Tishaeva et al. (2005).

Using the methods described above the model of the reaction–distillation process is an under-determined system of linear equations with a specific set of linear inequalities (Ryll, 2009; Ryll et al., 2012b, 2013). It can be solved without numerical problems by applying linear optimization, e.g. the simplex algorithm. Hence, reliable and robust feasibility studies for reaction–distillation processes can be carried out without restrictions on the type and depth of the model used to describe the physico-chemical properties and which give rise to the thermodynamic limitations of the process. These methods are implemented in a software tool which is restricted to systems up to four components, since a visualization of the composition simplex is only possible for these systems. The proposed method has been successfully applied to the development of a new distillation based process for the production of trioxane (Grützner et al., 2007) and oxymethylendimethylethers (OME) (Burger, 2012; Burger and Hasse, 2013). In the present work feasibility studies for the production of ethyl tert-butyl ether (ETBE) and 1-butyl acetate are discussed as examples.

2. Linear unit operation models

In the present work, the original nonlinear model of any unit operation, e.g. reactor, distillation column or decanter, is replaced by an appropriate set of linear sub-models. Each linear sub-model is comprised of an equation and an inequality part (Ryll, 2009; Ryll et al., 2012b, 2013). The equation part is modeled by a system of linear equations

$$\underbrace{\mathbf{A}}_{J \cdot N_C \times J \cdot N_C} \cdot \underbrace{\dot{\mathbf{n}}}_{J \cdot N_C \times 1} = \underbrace{\mathbf{b}}_{J \cdot N_C \times 1}, \quad (1)$$

where the vector $\dot{\mathbf{n}}$ represents the molar component flow rates \dot{n}_i^j of all J feed and product streams involved in the respective unit operation. Eq. (1) generally expresses different types of relationships:

1. equations for all known feed streams,
2. mass-balance equations including stoichiometry,
3. equations for the attainable product manifolds given by the respective thermodynamic limitations or
4. unit specific equations, e.g. for splitters and component splitters.

The inequality part

$$\underbrace{\mathbf{C}}_{N_{IQ} \times J \cdot N_C} \cdot \underbrace{\dot{\mathbf{n}}}_{J \cdot N_C \times 1} \leq 0 \quad (2)$$

may contain different types of relationships:

1. inequalities defining the boundaries for the attainable product compositions of the considered linear sub-model,
2. trivial inequalities excluding unphysical results, e.g. $\dot{n}_i^j \geq 0$,

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