THERMODYNAMIC ANALYSIS OF MULTICOMPONENT DISTILLATION-REACTION PROCESSES FOR CONCEPTUAL PROCESS DESIGN

Oliver Ryll, Sergej Blagov[1], Hans Hasse
Institute of Thermodynamics and Thermal Process Engineering, University of Stuttgart, 70569 Stuttgart, Germany, E-mail: hasse@itt.uni-stuttgart.de

A short-cut method for conceptual process design is presented which is solely based on fundamental thermodynamic data and allows an analysis of arbitrary flow sheets consisting of distillation columns and reactors. The required information on the process is reduced to a minimum: besides the model for vapor-liquid and chemical equilibrium, only the flow sheet structure, information on the overall feed streams and a suitable set of desired product specifications are needed. The approach is based on the consideration of thermodynamic limiting cases: for distillation columns ∞/∞–analysis is applied. The description of reactors is based on the assumption that chemical equilibrium is reached. Thus nonlinearities of the process model are only caused by fluid properties like the shape of distillation boundaries and chemical equilibrium surface. By applying a suitable piece-wise linearization of these thermodynamic properties the process model can be represented by a set of linear sub-models. This allows reliable finding of all possible solutions and, hence, comprehensive feasibility and multiplicity analysis. In the current work a brief overview of the underlying theory will be given followed by the presentation of the developed software tool and its application to a number of industrial processes.

KEYWORDS: process simulation, conceptual design, distillation, reaction, ∞/∞-analysis

INTRODUCTION

In conceptual process design generally many process alternatives have to be considered. Feasible ones must be identified and then ranked according the estimated efficiency. By using rigorous process simulators the feasibility analysis of different process alternatives is very time consuming, especially for complex process arrangements with recycles. Furthermore, there may exist multiple steady states. Conventional process simulators calculate only one steady state (depending on initial guesses and the solution algorithm). Disregarding other solutions may eventually mislead the process designer, so that reliable multiplicity analysis is an important part in conceptual process design. More generally, it is desirable to get an overview over the entire solution space for any considered process under its specifications. All this can only be achieved by applying suitable short-cut methods in conceptual process design.

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[1] Presently with: INEOS Paraform GmbH, Hauptstr, 30, 55120 Mainz, Germany

An important short-cut method based on residue curve or distillation line maps is ∞/∞−analysis [1−3]. The main idea of ∞/∞−analysis is to investigate the behaviour of a distillation process in the limiting case of infinite separation capacity which is not achievable in practice but allows highlighting the thermodynamic restrictions of the process. This limiting case is achieved in an imaginary, infinitely high column operating at infinitely large reflux. Under these conditions, for a given feed and pressure, only the split in the column can be varied, thus tremendously reducing the complexity of the model to be analyzed. Furthermore, because infinite separation capacity is assumed, only limiting separations are possible [1, 4]. To investigate these limiting separations, only information on the topology of vapor-liquid equilibrium diagrams is needed, i.e. it only has to be known how many singular points there are for a given mixture and how these points are connected. In other words, only information on the geometry of the distillation boundaries in the composition space has to be supplied. Despite these simplifications, the basic process characteristics are usually retained, so that the method can efficiently be used to support various tasks in conceptual distillation process design like feasibility, multiplicity studies and bifurcation analysis [1].

The basic idea of ∞/∞−analysis can be extended in a straightforward manner to other unit operations. For chemical reactors it is assumed that chemical equilibrium is reached. But in principle the method can be further extended to kinetically controlled reactions. By combining these ideas for distillation and reaction, ∞/∞−analysis can also be applied to reactive distillation [7]. However this can only be done under the assumption of simultaneous physical and chemical equilibrium resulting in a restricted feasibility region. Furthermore, it has been shown that ∞/∞−analysis can successfully be used to study flow sheets combining more than one unit operation, e.g. [2−7].

∞/∞−analysis for distillation-reaction processes requires besides the flow sheet information only thermodynamic models of phase and chemical equilibrium. The lack of tools to synthesize phase diagrams for more than three components has hindered up to now the use of ∞/∞−analysis in many practical problems. Because of the highly non-linear nature of the phase equilibrium behavior the determination of the topology of multicomponent vapor-liquid equilibrium diagrams is generally a difficult task. It has only recently been shown that this task can be solved for multicomponent mixtures of arbitrary complexity by two different strategies [8]. These strategies were implemented in the present work for the first time in a computer tool. Furthermore, general approaches for the determination of chemical equilibrium diagrams are available. The one that is being used here is similar to the algorithm described by Tishaeva et al. [9].

Based on these methods a software tool was developed in the present work which allows comprehensive thermodynamic analysis of arbitrary distillation-reaction processes by applying ∞/∞−analysis. No simplifying assumptions on the thermodynamic properties of the studied system are needed; in principle any state-of-the art thermodynamic model can be used. The program can be coupled to any fluid property part of any process simulator. Presently an interface to ASPEN Properties is used. Furthermore, the program is up to now limited to systems with not more than four components. Apart from the fact that visualization of concentrations is only possible for systems with not

more than four components (three degrees of freedom), this limititation is only of technical nature.

METHODOLOGY

Different methods for synthesis of complex chemical processes which are based on $\infty/\infty-$analysis are described in the literature [10, 11]. Bertok et al. [11] have shown that complex phase equilibrium behavior may lead to enormous combinatorial complexity in process synthesis that may result in a huge number of flow sheet candidates to be analyzed. This is due to the non-linear constraints of the mathematical problem which may be caused in particular by thermodynamic restrictions in form of non-linear distillation boundaries. By applying an appropriate linearization to distillation boundaries in case of vapor-liquid equilibrium diagrams the original non-linear problem can be reformulated in form of linear sub-problems [11], and hence nonlinearities can be avoided.

The idea of the linearization approach which is also used in the present work is explained here for a vaporliquid equilibrium diagram of an azeotropic ternary mixture shown in Figure 1. In this simple case the distillation boundary can be linearized by polygonal lines, in the example in Figure 1 three linear segments are enough to retain the character of the original non-linear separatrix. The linearization of distillation boundaries allows a full mathematical description of the phase diagram in terms of linear equations and inequalities [11].
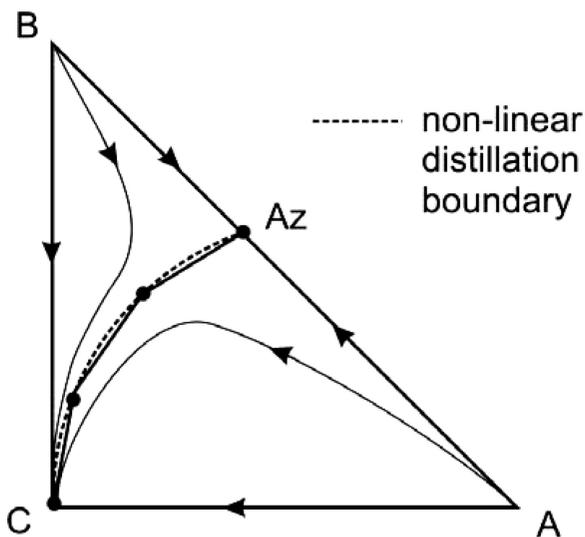

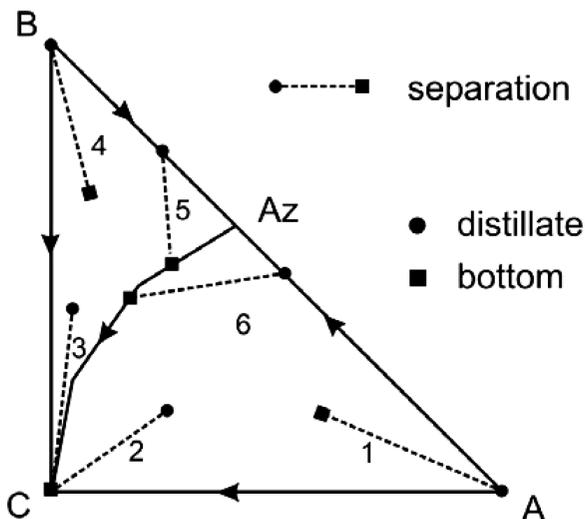**Figure 1.** Linear approximation of the non-linear distillation-boundary

Figure 2. Limiting separations for linearized vapor-liquid equilibrium

In case of $\infty/\infty-$analysis only limiting separations are possible [1]. For the considered example there exist three types of limiting separations for each distillation region resulting in six types of limiting separations which are shown in Figure 2. Based on the linearization of the vapor-liquid equilibrium the limiting separations can also be described by a set of linear equations and inequalities. Thus a distillation column can be analyzed with the aid of linear algebra. Similar methods can also be applied to chemical equilibrium diagrams.

The linearization approach is not restricted in the number of components, although the software developed in the present work currently only supports work on systems with up to four components. For quaternary mixtures the chemical equilibrium surface and the distillation boundaries are 2D-surfaces which are triangulated for linearization.

In the following, some examples are presented that give an idea of what can be achieved with the methods briefly described above when they are suitably implemented. First the geometry and topology of vapor-liquid equilibria of a very complex quaternary mixture is studied: the system Chloroform–Ethanol–Acetone–n-Hexane. For modeling the vapor-liquid equilibrium of that mixture NRTL was used assuming ideal behavior of the gas phase. At the pressure of 1.01325 bar this system shows nine azeotropes: five binary and three ternary azeotropes and also a quaternary one. Figure 3 gives an impression of the complexity of the topology of the diagram. The analysis shows that four 2D-distillation boundaries and different distillation regions exist in that system
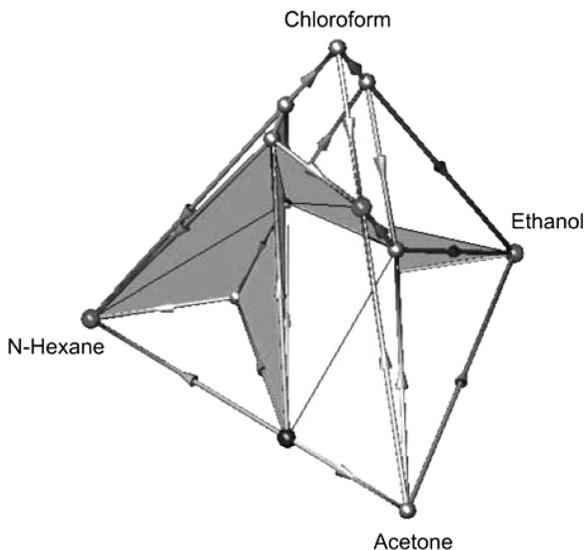
Figure 3. Linearized vapor-liquid equilibrium diagram for quaternary system of Chloroform–Ethanol–Acetone–n-Hexane at 1.01325 bar

which can not all be seen in the single picture shown in Figure 3. Diagrams like the one shown in Figure 3 can be calculated safely without any manual interaction with the software developed here. The software allows rotating the tetrahedron used to represent the concentration space.

With the new software, it is also possible to visualize the interaction between the vapor-liquid and chemical equilibrium in one diagram. As an example, the reactive system of Ethanol (EtOH)–Isobutene (IB)–n-Butane (NBUT)–Ethyl-Tertiary-Butyl-Ether (ETBE) was studied at 8 bar, with the reaction

$$EtOH + IB \; \rightleftharpoons \; ETBE \qquad (1)$$
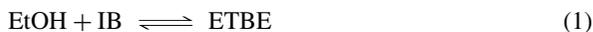
in the liquid phase (cf. Figure 4). For the description of the chemical equilibrium a temperature dependent chemical equilibrium constant is used [13], the vapor-liquid equilibrium was modeled using NRTL taking into account the nonideality in the gas phase by the Redlich-Kwong-Equation. The system has a 2D-distillation boundary and therefore two distillation regions. The 2D chemical equilibrium surface intersects with the distillation boundary forming a line.

A distillation-reaction process consists of an arrangement of distillation columns and chemical reactors. Each unit-operation (distillation column and reactor) is
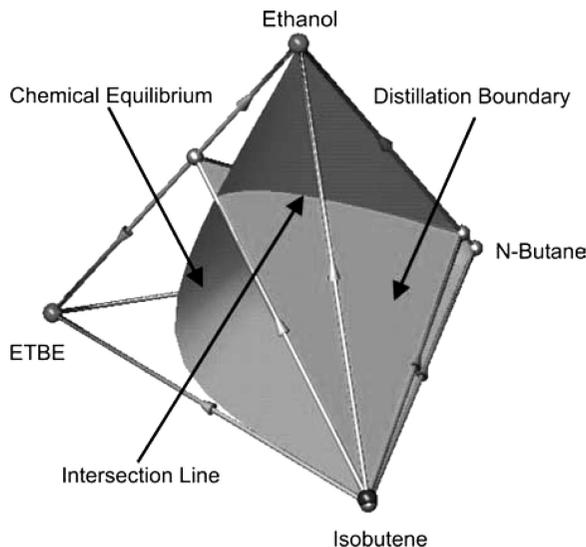
Figure 4. Combined vapor-liquid and chemical equilibrium diagram for reactive quaternary system of Ethanol–Isobutene–n-Butane–ETBE at 8 bar

mathematically described by equations of several types (mass-balances, stoichiometric equations, fixed feed specification, etc.) and inequalities representing process constraints (desired product qualities, distillation boundaries, chemical equilibriums, etc.). In the stage of conceptual process design the flowsheet is usually not fully specified (e.g. recycle streams are unknown), thus resulting in an under-determined process-model. A comparison of the number of equations and the number of unknowns usually shows that there remain degrees of freedom. Still, it is possible to solve uniquely the under-determined mathematical problem by formulating a constrained optimization.

In the present case, due to the linearization a set of mathematically similar linear sub-models is obtained for unit-operations which are combined to the model of the entire process. The constrained optimization problem can hence be solved here using linear programming tools. Thus the linearization method allows reliably finding all solutions of the problem and, hence, comprehensive feasibility and multiplicity analysis of any studied process. Further benefits include deeper insight in the process behavior, e.g. through comprehensive parametric studies information can be obtained easier than with conventional process simulators. Finally the results of the thermodynamic analysis can be used to generate initial guesses for rigorous simulations of promising process alternatives.

ANALYSIS OF MULTICOMPONENT DISTILLATION-REACTION PROCESSES

Most industrial distillation-based processes contain recycles, which are needed to overcome limitations in the reaction or separation due to kinetic or thermodynamic restrictions. Comprehensive analysis of a complex flow sheet with recycles is not straightforward with rigorous process simulators. Based on the approach described above such studies can efficiently be carried out for arbitrary distillation-reaction processes. In following this is illustrated using a feasibility study of an industrial process as an example, the synthesis of ETBE, cf. equation (1).

Figure 5 shows the Huels-Process for the synthesis of ETBE which consists of two reactors and three distillation columns [12]. That process was initially developed for MTBE production but can also be applied to ETBE. The flow sheet is used here to illustrate the procedure. As external feed streams to the first reactor R1 pure Ethanol (Stream 1) and a C4-Cut (Stream 2) from a refinery as a source of Isobutene are used. The C4-Cut is assumed to contain 40 mol% of Isobutene and 60 mol% of inert components which are represented by n-Butane here. The present study is carried out for the case of a molar excess of ethanol in the overall feed of 10%. Note that it would have been possible to include this quantity in the optimization described below. In distillation column C1 the produced ETBE, eventually containing Ethanol, (Stream 5) is separated from the rest of the product of reactor R1 (Stream 4) which is fed to a second reactor R2 to increase Isobutene conversion. In the second distillation column C2 the ETBE is purified (Stream 7) and non-reacted Ethanol is recycled back to the first step reactor R1 (Stream 6). Distillation column C3 separates the product stream of second stage reactor in a binary mixture of ETBE and Ethanol which is recycled to the first stage reactor (Stream 10) and a distillate stream containing still some Ethanol (the binary low-boiling azeotrope of Ethanol and n-Butane) which is sent to the Ethanol-Recovery (Stream 9).

For this case study was assumed that all columns are operated at 8 bar. The corresponding vapor-liquid equilibrium for these operating conditions was already shown in Figure 4. The reactors are modeled as isothermic liquid phase reactors operating at 50 °C.
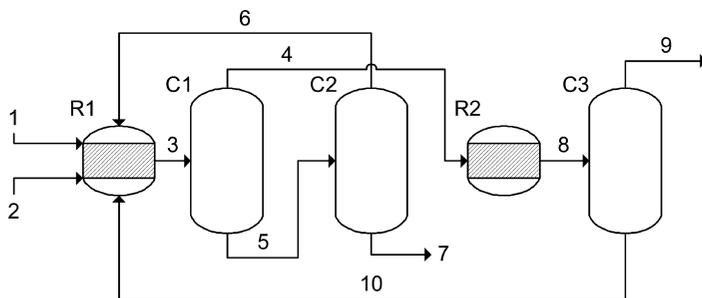

Figure 5. Huels process for ETBE production

The feasibility study of a process should reveal optimal solutions for desired product qualities. Thus besides the external feed rates and compositions the product qualities (compositions of Streams 7 and 9) also have to be specified. There is no need to specify any other variable in order to answer the question whether the flow sheet shown in Figure 3 is feasible or not. As mentioned above the linear problems are still underdetermined. From the physical point of view the flow rates of the recycle streams (Streams 6 and 10 in Figure 5) and the split ratio between the flow rates of the overall system products (Streams 7 and 9 in Figure 5) have not been specified yet.

To solve the problem of feasibility analysis an optimization criterion has to be formulated. The minimization of the overall system recycle (sum of Streams 6 and 10) seems to be a reasonable choice for this case. The existence of the optimal solution also proves the feasibility of the flowsheet. This solution for the considered flowsheet is presented in Table 1.

Bifurcation diagrams of single columns allow analyzing which product streams are feasible in a column for a given feed by varying the split ratio. In Figures 6 and 7 bifurcation diagrams for columns C1 and C3 (cf. Figure 5) are presented. The molar distillate-to-feed-ratio is used as bifurcation parameter for feed compositions according to Stream 3 and 8 of Table 1. The dashed line corresponds to the split ratios of the optimal solution (cf. Table 1). For these cases no multiplicitiy occur for the considered columns, but in other cases possible multiple steady states would be revealed and a multiplicity region can be identified.

As expected the optimal solution from ∞/∞–analysis (in the sense of the minimal overall recycle) corresponds to the case for which sharp separations are realized in the columns. It seems to be reasonable that for the optimal solution the maximum separation degree is achieved in each column. An Isobuteneconversion of 98.8% is achieved in this case. Recycle stream 6 is calculated to zero and the recycle stream rate of stream 10 is found to be about 5% of the overall feed rate (sum of stream 1 and 2) for the chosen optimization criteria. Therefore distillation column C2 is not needed (no separation takes place in the column) to meet the product qualities. In this case the analysis has directly lead to another industrially used process: the Oxeno-Process (Figure 8).

The results of the feasibility analysis were excellent initial guesses for a rigorous simulation of the Oxeno-Process. That simulation was mainly carried out to validate the

Table 1. Optimal solution with minimal recycle for the ETBE-synthesis

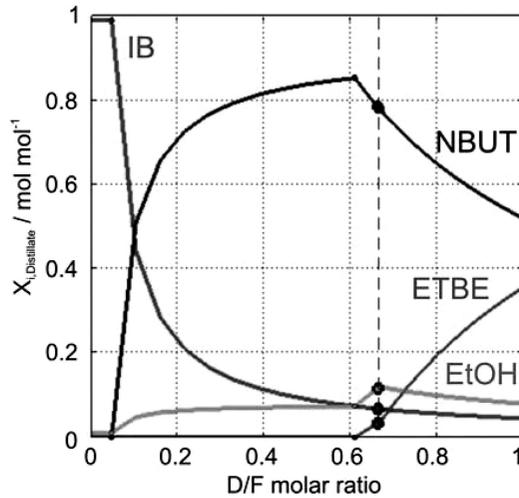| Stream	1	2	3	4	5	6	7	8	9	10
n/kmol s^{-1}	0.44	1	1.16	0.766	0.394	0	0.394	0.717	0.649	0.068
$x(IB)$/mol mol^{-1}	0	0.4	0.045	0.068	0	–	0	0.005	0.005	0
$x(NBUT)$/mol mol^{-1}	0	0.6	0.517	0.784	0	–	0	0.837	0.924	0
$x(EtOH)$/mol mol^{-1}	1	0	0.08	0.115	0.01	–	0.01	0.055	0.061	0
$x(ETBE)$/mol mol^{-1}	0	0	0.358	0.033	0.99	–	0.99	0.103	0.01	1

Figure 6. Bifurcation diagram for distillate mole fractions of column C1 with molar distillate to feed ratio as bifurcation parameter
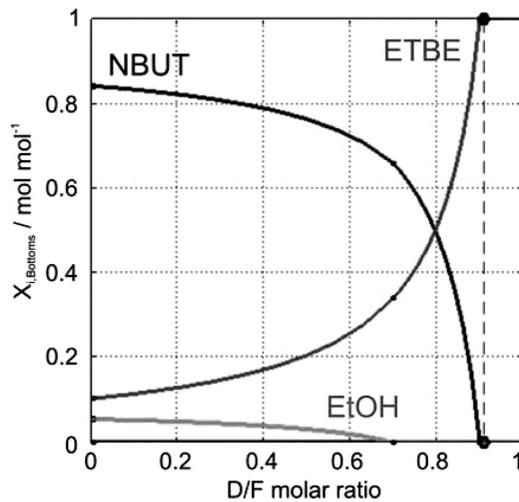

Figure 7. Bifurcation diagram for bottom mole fractions of column C3 with molar distillate to feed ratio as bifurcation parameter
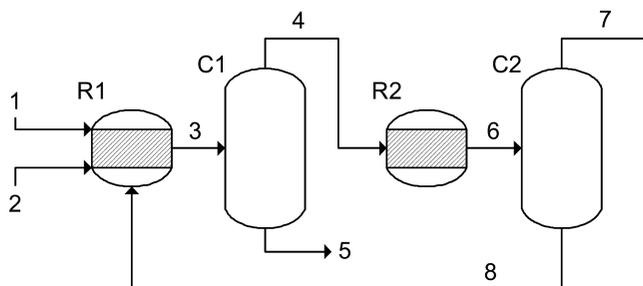
Figure 8. ETBE-synthesis with Oxeno-process

Table 2. Rigorous simulation results for the Oxeno-process (Streams 5, 6, 7, 8 from this table correspond to streams 7, 8, 9, 10 of Table 1, otherwise direct correspondences)

Stream	1	2	3	4	5	6	7	8
$n/\text{kmol s}^{-1}$	0.44	1	1.138	0.744	0.394	0.716	0.648	0.068
$x(IB)/\text{mol mol}^{-1}$	0	0.4	0.026	0.04	0	0.003	0.004	0
$x(NBUT)/\text{mol mol}^{-1}$	0	0.6	0.527	0.807	0	0.837	0.925	0
$x(EtOH)/\text{mol mol}^{-1}$	1	0	0.061	0.094	0	0.059	0.065	0
$x(ETBE)/\text{mol mol}^{-1}$	0	0	0.385	0.059	1	0.1	0.006	1

results from the ∞/∞–analysis and therefore, the number of stages and the reflux ratio in all columns were set to large numbers. The result of this simulation is presented in Table 2. For the same recycle flowrate an Isobutene-Conversion of 99% is calculated which is similar to the result of the feasibility study. The expected difference is caused on the one hand by the application of linearized vapor-liquid and chemical equilibrium diagrams. On the other hand the columns in the rigorous simulation have a finite column height and a finite reflux rate.

Similar algorithms have been developed for identifying multiple steady states (multiplicity analysis). The only difference between feasibility and multiplicity studies is the specified input to the linear optimization problems. Algorithms for the visualization of the feasibility and multiplicity regions which help understanding the process behavior are currently being developed.

CONCLUSION
The presented short-cut method allows reliable analysis of distillation-reaction processes without any restriction concerning the thermodynamic behavior of the system. The developed software was successfully applied to a number of industrial relevant distillation-reaction processes in the framework of the EU-Project INSERT. The presented

methodology is not restricted in the number of components and its application can be extended to other unit operations, e.g. decanters or reactive distillation.

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