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DESIGN OF COMPLEX DISTILLATION COLUMNS SEPARATING TERNARY HETEROGENEOUS AZEOTROPIC MIXTURES

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Abstract
The boundary value method for design of distillation columns separating ternary heterogeneous azeotropic mixtures is extended to include complex configurations, i.e. columns with integrated decanters and with multiple heterogeneous stages; double-feed columns; columns with intermediate decanters. The methods can be used for establishing product feasibility in a column and evaluating a column design on a basis of cost. Multiple feasible designs can be generated for a given set of product specifications, according to the reflux ratio, number of heterogeneous stages and liquid phase ratio; these designs may be evaluated with respect to operating and equipment costs. Case studies illustrate the design method.

Keywords: heterogeneous azeotropic distillation, complex columns, boundary value method

1. Introduction

Separation of heterogeneous azeotropic mixtures using distillation columns is an important industrial process for which systematic design approaches are lacking. Column and flowsheet design using conventional process simulation software is challenging, because of difficulties converging simulations involving these non-ideal mixtures, and because conventional simulation software does not lend itself to systematic and comprehensive exploration of design alternatives. The boundary value method for assessing feasibility of proposed separations and for designing columns separating ternary azeotropic mixtures can overcome these difficulties. The boundary value method is well established, but there are significant gaps in its capabilities in the area of heterogeneous azeotropic distillation.

This paper presents a methodology to generate, simulate and evaluate complex column configurations for separating ternary heterogeneous azeotropic mixtures. The column design method exploits the boundary value method for establishing separation feasibility and for assessing economic performance, following from previous work[1,2]. Single- and double-feed columns with integrated decanters and columns with intermediate decanters are addressed. The design method provides preliminary column design information, e.g. number of stages, feed locations and heat duties, which allows estimation of capital and operating costs. Thus many alternative designs may be readily generated and evaluated, which is valuable in the synthesis of separation flowsheets.

1.1 State of the art in design of ternary heterogeneous azeotropic distillation columns

Established methods for assessing separation feasibility and/or column design to ternary heterogeneous azeotropic distillation – namely the boundary value method[1,2] and the continuous distillation region-based method[3] – have certain limitations to their applicability. The new design approach does not restrict two liquid phases only to the top decanter[1,2], does include the reflux phase split ratio as a degree of freedom for design[1,2,3], and does not need the maximum number of heterogeneous stages to be specified[3]. Furthermore, the design method should not be computationally intensive[3] to be relevant and applicable to flowsheet synthesis.

The boundary value method may be used to assess feasibility of a proposed separation and to generate column designs, given fully specified product compositions. The liquid composition profiles for the rectifying and stripping sections are generated in mole fraction space by stage-by-stage mass balance and phase equilibrium calculations (and often, as in this paper, with enthalpy balances as

well) starting with the product compositions. An intersection of the composition profiles indicates that a continuous profile connecting the product compositions may be obtained, and thus that the proposed separation is feasible. Information about the design – i.e. number of stages in each section and reflux ratio – of the corresponding column may be retrieved and used to evaluate the column design[1]. The capital and/or operating costs of the column can thus be estimated, allowing design alternatives to be compared. The most attractive designs need to be evaluated further, based on other important issues, such as operability and controllability.

By varying the reflux and/or reboil ratio and/or feed condition, different column designs are readily generated and evaluated with respect to their energy demand or economic performance[1,4,5,6]. This capability makes the boundary value method a powerful tool for sequence synthesis and preliminary column design. The boundary value method is therefore adopted in this work, and extended to address some significant gaps in the design of ternary heterogeneous azeotropic distillation columns, n particular the complex column configurations depicted in Figure 1.

2. New Design Methods for Complex Column Configurations

In these new boundary value methods, as with existing methods, the feed composition and product composition of one product need to be fully specified, and one purity specification needs to be given for the remaining product. These specifications fix the mass balance. The operating pressure is specified and assumed constant in the column. Two variables from the reflux ratio, reboil ratio and feed condition fix the column energy balance. The composition profiles are generated for each section, applying stage-by-stage mass balances and calculating the phase equilibrium. Energy balances are also incorporated, as the assumption of constant molar overflow is found to be inadequate for highly non-ideal systems. The intersection between the profiles is identified using a line intersection search algorithm[7]. As with the classical McCabe-Thiele boundary value method for column design, a fractional number of stages may result. In order to verify the design approach and its results, column designs generated by the boundary value method are simulated in Aspen HYSYS 2004.1; the performance of the columns, in terms of composition profiles, product purities and reboiler and condenser duties, etc., is compared to that predicted by the boundary value method. Multiplicities – where different design inputs and specifications give identical outputs (i.e. product compositions and flow rates) – predicted by the boundary value method may be verified by conventional simulation[8].

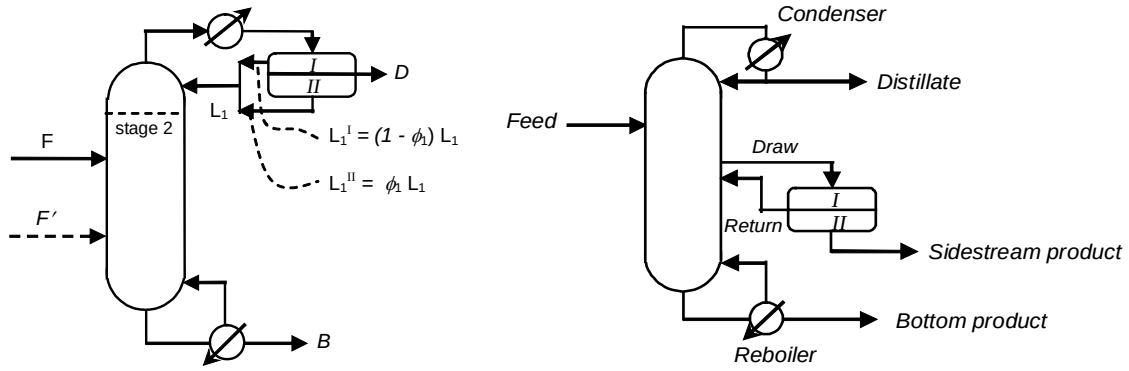
Designs generated by the boundary value method are evaluated in terms of their economic performance using appropriate cost models[8]. The capital cost models take into account column height, diameter, shell thickness; heat transfer area of heat exchangers; vessel size of decanters, etc.[9]. Several designs may be generated by varying key degrees of freedom – such as reflux ratio, feed condition and phase split ratio – and evaluated using the cost models.

The models are implemented in Matlab 7.0 code; physical, thermal and phase equilibrium properties of fluid streams are calculated in HYSYS and retrieved by Matlab[8]. Prior to applying the boundary value method, the vapour-liquid-liquid-equilibrium behaviour is computed, and represented as a liquid-liquid region and a ‘vapour line’, i.e. the set of corresponding equilibrium vapour compositions.

2.1 Single-feed Column with an Integrated Overhead Decanter

In an integrated decanter the condensed overheads of the column – a two-phase liquid – are separated by decanting, allowing the reflux to have a different composition to the distillate. The design method of Pham et al.[1] restricts the existence of two-phase liquids to the decanter. However, in industrial columns two liquid phases frequently occur within the column as well[10–13] and such columns may be economically advantageous[3]. The boundary value method is extended to accommodate a two-phase reflux being returned to the column from the overhead decanter, as illustrated in Figure 1(a).

To generate the rectifying composition profile, the reflux phase split ratio (the ratio of the molar flow of the heavy liquid to that of the total liquid flow[8]) must be specified. There is a reflux phase split ratio that causes two liquid phases to appear within the column. The number of heterogeneous stages in the column and the phase split ratio on the last heterogeneous stage of the column are however not unique, allowing multiple profiles to be generated.



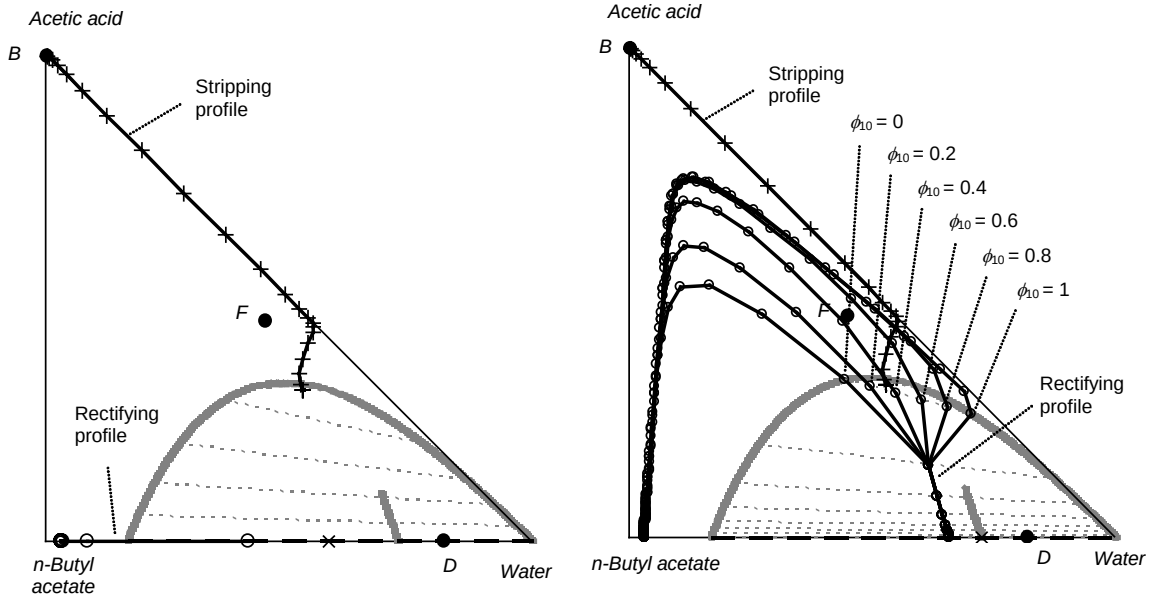
(a) (b)

Figure 1. (a) Column with integrated decanter (i.e. stage 1) and one or two feeds; (b) Column with intermediate decanter[8]

When generating heterogeneous rectifying profiles, preliminary tests establish whether the final heterogeneous stage has been reached and hence the maximum number of heterogeneous stages that may exist. Once the rectifying profile leaves the two-phase region, the computation of the profile is carried out in the conventional manner. The corresponding stripping composition profile must also be generated. Heterogeneous stages may be encountered in the stripping section; in this case the phase split ratio does not need to be specified as it is implicit in the calculations.

Example – Single-feed column with integrated decanter

Figure 2 presents boundary value method results for a column separating the mixture acetic acid–n-butyl acetate–water. For the specified reflux ratio, the separation is not feasible when a two-phase liquid appears only in the decanter (in Case (i) the profiles do not intersect) but it is feasible for a column with a heterogeneous liquid leaving the top stage (Case ii). Note that the reboil ratio depends on the phase split ratio of the reflux via the column energy balance. The maximum number of heterogeneous stages in the column is 10; four of the six values of the phase split ratio on the last heterogeneous stage (0.4, 0.6, 0.8 and 1) lead to feasible column designs. The boundary value method may be applied repeatedly for different numbers of heterogeneous stages as well as for different reflux ratios. In this case, designs with fewer heterogeneous stages are found to need more theoretical stages overall, which would indicate that their capital costs would be higher.



(i) (ii)

Figure 2. Composition profiles of a column recovering acetic acid: Case (i) two-phase liquid occurs only in the decanter (ϕ_1 = 0.3); Case (ii) heterogeneous liquid within column ($\phi°_1$ = 0.589). Profiles for six different phase split ratios on the final stage are shown.[8]

2.2 Double-feed Column with an Integrated Overhead Decanter

Double-feed columns are commonly used for separating homogeneous azeotropic mixtures by introducing a high-boiling component towards the top of the column. Heterogeneous azeotropic distillation may also be made feasible or more economic by using two feeds[2]. Typically a heavy boiling compound that is partly immiscible with the binary feed mixture is added as an upper feed, shown as F in Figure 1(a).

Available graphical design methods for double-feed columns[2,14] do not explain how to accommodate multiple heterogeneous stages in the rectifying section, are computationally intensive or do not directly generate column design information. The boundary value method for a single-feed column with an integrated decanter is extended to include double-feed columns.

Additional inputs and specifications to the boundary value method are the composition and flow rate of a second feed, the phase split ratio of the reflux stream and either the reboil ratio or the thermal condition of the second feed. The product specifications must satisfy product purity constraints and the overall material balance. Liquid phase splitting may occur only in the decanter or two liquid phases may appear in the column, depending on the reflux phase split ratio. As with double-feed homogeneous distillation columns designs[15,16], there may be a maximum reflux ratio above which the desired separation is no longer feasible, and there may be a limited range of upper- to lower-feed flow ratios leading to feasible column designs.

The new method generates the composition profile of the middle section after generating the rectifying and stripping profiles as described in Section 2.1. The middle-section profile is generated upwards starting from a specified stripping stage (a degree of freedom in design); the phase split ratio does not need to be explicitly specified. If a middle-section profile leaves the composition space, it cannot intersect the rectifying profile. Feasible column designs, i.e. the number of theoretical stages in each section, can be identified from the transition from the stripping section to the middle section and from the intersection of the middle-section and rectifying composition profiles.

Example – Double-feed column with an integrated overhead decanter

A double-feed column separating a mixture of 1-propanol and water using 1-butanol as an entrainer demonstrates the new approach. Figure 3 illustrates the performance of columns where two-phase liquids are restricted to the decanter (Case i) and where they exist within the column (Case ii). The two cases are comparable, as both designs require a similar number of stages and the reboiler and condenser duties are similar. In this case, designs with multiple heterogeneous stages are found not to be as attractive as those in which two-phase liquids are restricted to the decanter.

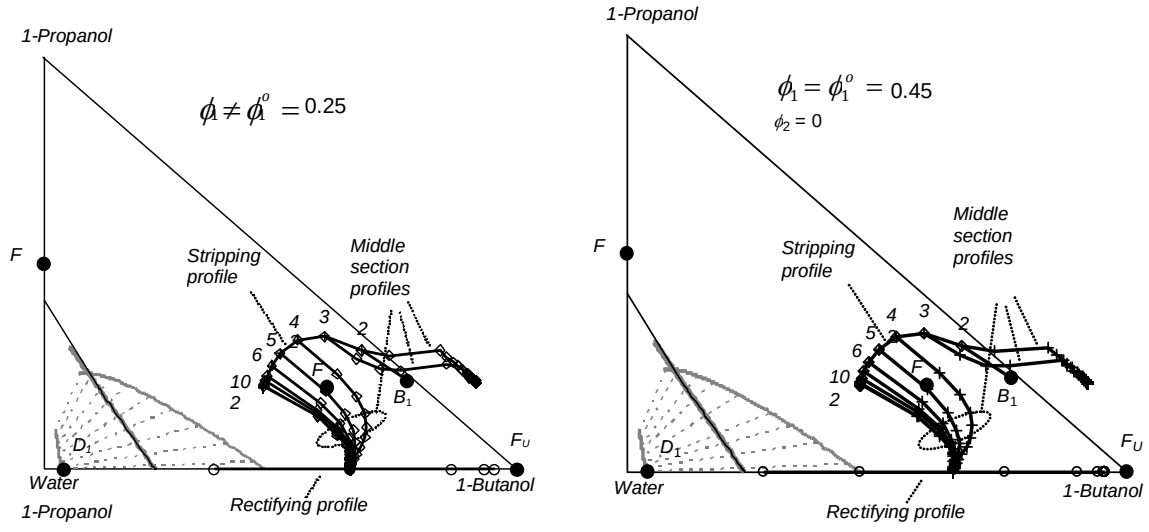


Figure 3. Liquid composition profiles for double-feed distillation column with integrated overhead decanter. Case (i) two-phase liquid appears only in the decanter (ϕ_1 = 0.25); Case (ii) heterogeneous liquid within column (decanter ϕ°_1 = 0.45; stage2 ϕ_2 = 0)[8]

2.3 Column with an Intermediate Decanter

In columns with intermediate decanters, a heterogeneous liquid is withdrawn to a decanter – one phase is recovered as a side-stream (typically the aqueous phase); the other is returned to the column one stage below the draw stage[17], as shown in Figure 1(b). Alternatively, a built-in 'donut' decanter tray on the draw stage with an interface controller can facilitate the removal of the aqueous phase[10,18]. The use of an intermediate decanter may reduce the number of columns and/or decanters required in a separation sequence. Design of such a column configuration could be carried out by trial and error, through simulation of alternative column designs, but would most probably be plagued by convergence issues. The method applying the concept of continuous distillation regions[14] allows feasibility to be assessed but does not give directly column design details.

In this new boundary value method, additional specifications for design of a column with an intermediate decanter are the composition of the side-stream, specified by choosing a water-rich composition on the boundary of the two-phase region, and the flow rate, which must satisfy the overall column mass balance. As in the boundary design methods discussed in Sections 2.1 and 2.2, the column design is obtained by the intersection of composition profiles. The new method generates the composition profile of the middle section after generating the rectifying and stripping profiles as described in Section 2.1. Note that the rectifying section may or may not include an integrated decanter.

The middle section profile is calculated upwards from the stripping profile once the decanter position has been specified – this is a degree of freedom in the design. It is assumed that the 'return' stage, to which the organic liquid phase from the intermediate decanter is returned, is one stage below the decanter draw stream. The composition, flow rate and enthalpy of the liquid leaving the return stage are known from the stripping section profile. The mass and energy balances over the column section (including the return stage and decanter) determine the flow rate and composition of the liquid entering the decanter. This liquid must be heterogeneous, if any separation is to take place in the decanter – this provides an additional feasibility constraint. Multiple middle-section profiles may be generated for a given stripping profile. The intersection information and transition from stripping to middle section determine the number of stages in each column section; capital and operating costs of the column can then be estimated.

Example – Column with an intermediate decanter

The recovery of 1-butanol, from acetone–butanol–water mixtures is relevant to biofuel production by fermentation[19]. Figure 4 presents composition profiles for the proposed separation. It may be seen that the feasibility of the design is sensitive to location of the draw stream.

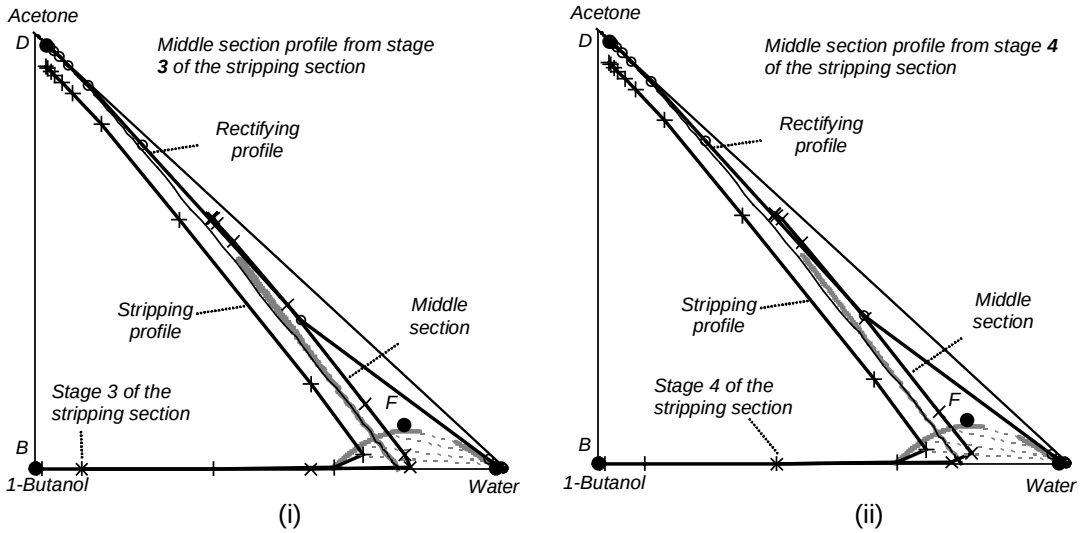


Figure 4. Composition profiles for a column with an intermediate decanter. Case (i) return stage 3: liquid on draw stage is not heterogeneous – infeasible design; Case (ii) return stage 4: liquid on draw stage lies in two-phase region – feasible design[8].

3. Conclusions

Complex column configurations for separating ternary heterogeneous azeotropic mixtures may offer advantages over simpler configurations with respect to feasibility and cost. However, the complexity of these columns presents a challenge for design and simulation. New boundary value methods are presented in this paper. Single- and double-feed columns with integrated decanters and columns with intermediate decanters are addressed. These methods allow multiple designs to be generated and screened for feasibility and cost, and also provide useful initial values for conventional process simulation software such as HYSYS. The new methods overcome limitations of existing design methods, avoid the time-consuming, iterative option of design-by-simulation, and allow multiple designs to be generated and hence screened prior to more detailed simulation and design.

The boundary value method provides a useful approach for preliminary design and evaluation of ternary azeotropic distillation columns and facilitates generation and screening of alternative flowsheets[8]. A complementary paper[20] provides further information on this application.

A drawback of boundary value methods is that the product compositions must be fully specified and that no systematic approach exists for doing so. The feasibility and design results can be highly sensitive to the mole fraction of minor components in the products, especially for multicomponent mixtures. Another limitation of boundary value methods is that fractional numbers of stages may be found; such results limit the usefulness of the boundary value methods for preliminary design or for initialisation of more conventional process simulations.

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