Distillation Absorption 2010
A.B. de Haan, H. Kooijman and A. Górak (Editors)

SYNTHESIS OF NOVEL TERNARY HETEROGENEOUS AZEOTROPIC DISTILLATION FLOWSHEETS

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Abstract
An algorithmic approach is presented for synthesising novel sequences for separating, by distillation and decanting, ternary heterogeneous azeotropic mixtures. Existing synthesis procedures that consider only simple single-feed columns with decanters and integrated decanters are extended to include more industrially relevant options such as columns with several heterogeneous stages, double-feed columns, columns with intermediate decanters, and those accepting a heterogeneous liquid feed. With these advanced column configurations included in the synthesis method, a wider range of sequences may be considered systematically, allowing sequences that are more economically attractive than conventional designs to be identified. A case study illustrates the application of the sequence synthesis approach and the novel flowsheets it can generate.

Keywords: heterogeneous azeotropic distillation, sequence synthesis, recycle heuristics

1. Introduction
The synthesis of separation sequences, for a given feed and products with required purities and recoveries, involves the selection of separations, the unit operations (and their operating conditions) for achieving these and the flow connections between them. The choices made should allow the resulting flowsheet to achieve the separation aims with a good performance in terms of energy demand or processing costs.

Separation sequence synthesis for heterogeneous azeotropic mixtures is challenging – it may not be possible to achieve desired purities or recoveries because of the presence of azeotropes; the number of alternative flowsheet structures to choose from may be large; recycles may be required to improve product recoveries or purities. Several alternative flowsheet structures may exist – both distillation columns and decanters may be used; the columns may carry out direct, indirect or intermediate (e.g. 'saddle-type') splits. Various column configurations may be used – columns may have one or two feeds, and decanters may be integrated with the column, at the top of the column or on an intermediate stage. Verifying that a proposed separation is feasible is also a significant challenge; identifying the most economic column designs poses yet another challenge, exacerbated by the difficulty of converging column simulations. When recycles are present, their source and destinations need to be selected; to solve the mass balance over each column, the recycle compositions and flow rates need to be determined in an iterative process. These challenges motivate the development of systematic approach for synthesising, testing and evaluating separation sequences.

Existing approaches for the synthesis of separation sequences for heterogeneous azeotropic mixtures have used inspection of residue curve maps[1,2] or algorithmic approaches[3,4]. A sub-problem of sequence synthesis is identifying which streams should be mixed or recycled to recover high-purity products – existing approaches use heuristics[3,4,5]. The existing algorithms and heuristics are restricted in the range of column and flowsheet configurations they address.

2. Existing Synthesis Approaches
The existing sequence synthesis algorithms[3,4] first generate separation sequences that are most probably feasible. Opportunities to use simple columns (with a single feed and two products) carrying out direct and indirect splits, and stand-alone decanters (separating a column product) or integrated

decanters (separating the two liquid formed on condensing the overhead vapour and returning part of the condensate as reflux) are addressed. A classification system allows those streams that are not desired products to be identified. Options for mixing these streams or recycling them are then generated. Those sequences identified as containing infeasible separations may be made feasible by introducing mixing of non-product streams or recycling of pure components so that the resulting stream can be separated in a decanter or a column.

Existing algorithms and heuristics[3,4] do not, however, take into account double-feed columns, columns with intermediate decanters or columns with heterogeneous feeds (where the two phases lie in different distillation regions). The configurations have been shown[6] to bring benefits for process economics, energy demand or feasibility. The existing synthesis approach[3,4] is extended in this work to include such complex column configurations. Including these novel options in the synthesis algorithm with allow a wider range of industrially important flowsheet structures to be identified, designed and evaluated, and thus will facilitate the development of flowsheets with better performance in terms of energy demand, cost, yield, etc.

3. Extended Synthesis Algorithm for Ternary Heterogeneous Azeotropic Mixtures

The existing approach to synthesis[3,4] is extended to include new features: heterogeneous column feeds where the compositions of the two-liquid phases lie in different distillation regions and double-feed columns with integrated decanters. A new algorithm to identify opportunities to use columns with intermediate decanters is also proposed. The synthesis algorithm, together with the two extensions discussed in Sections 3.1 and 3.2, is represented in Figure 1.

3.1 Heterogeneous feed to distillation column

In the existing approach, a heterogeneous liquid with its two equilibrium phases in different distillation regions is always separated in a decanter before being further separated. The option of introducing such a feed to a column directly is added to the algorithm, as such a column can allow new, potentially attractive, flowsheet structures to emerge (indicated by “[See 3.1]” in Figure 1, complementing flowsheet options that use a decanter.

3.2 Double-feed column with integrated decanter

A double-feed heterogeneous azeotropic distillation column is analogous to an extractive distillation column separating a homogenous azeotropic mixture; as such, it allows the recovery of intermediate-boiling ('saddle-type') products. A heavy component must be added near the top of the column to act as an entrainer – however, during flowsheet synthesis, it is not known what streams are available for this purpose. This separation option is added to the synthesis algorithm, initially assuming the heaviest component is the entrainer and later updating the assumption, once more information is available about what streams are present in the whole sequence. A new boundary value method[6,7] provides a feasibility check for the proposed column; the ratio of upper to lower feed flow rates is an important variable as it has a strong influence on feasibility.

3.3 Column with intermediate decanter

A column with an intermediate decanter is a column in which a heterogeneous liquid on a stage within a column is withdrawn, separated in a decanter to produce a sidestream product and a second stream that is returned to the column, typically one stage below the side draw. This complex column configuration is commonly used to recover water[8] and can reduce significantly energy requirements and/or capital cost[9].

A sequence with two columns and with two decanters that perform similar separations (Figure 2a) can be systematically merged into a sequence with two columns and a common decanter (Figure 2b) and subsequently into a column with an intermediate decanter (Figure 2c). An algorithm is added to the overall sequence synthesis algorithm to identify opportunities to use this complex configuration.

3.4 Flowsheet feasibility assessment and evaluation

A number of feasible sequences that separate a mixture into (nearly) pure components may be generated; these sequences need to be quantitatively evaluated, e.g. in terms of economic performance. For design of an individual column, the mass balance of the sequence determines the flow rates and compositions of all streams in the sequence. For sequences without a recycle loop, this calculation is straightforward, proceeding sequentially in the direction of material flow. For sequences that have one or more recycle loops, where the flow rate and composition of the recycle are not known at the outset, iterative approaches using 'tear' streams are need. The feasibility of proposed separations may be sensitive to the recycle composition and flow rate Therefore, the feasibility of each separation (distillation or decanting) must be assessed once the mass balance of the flowsheet is solved[3]. Then each column in the sequence can be designed for its best performance, e.g. applying the boundary value method for a range of key design variables, to allow the overall flowsheet to be evaluated.

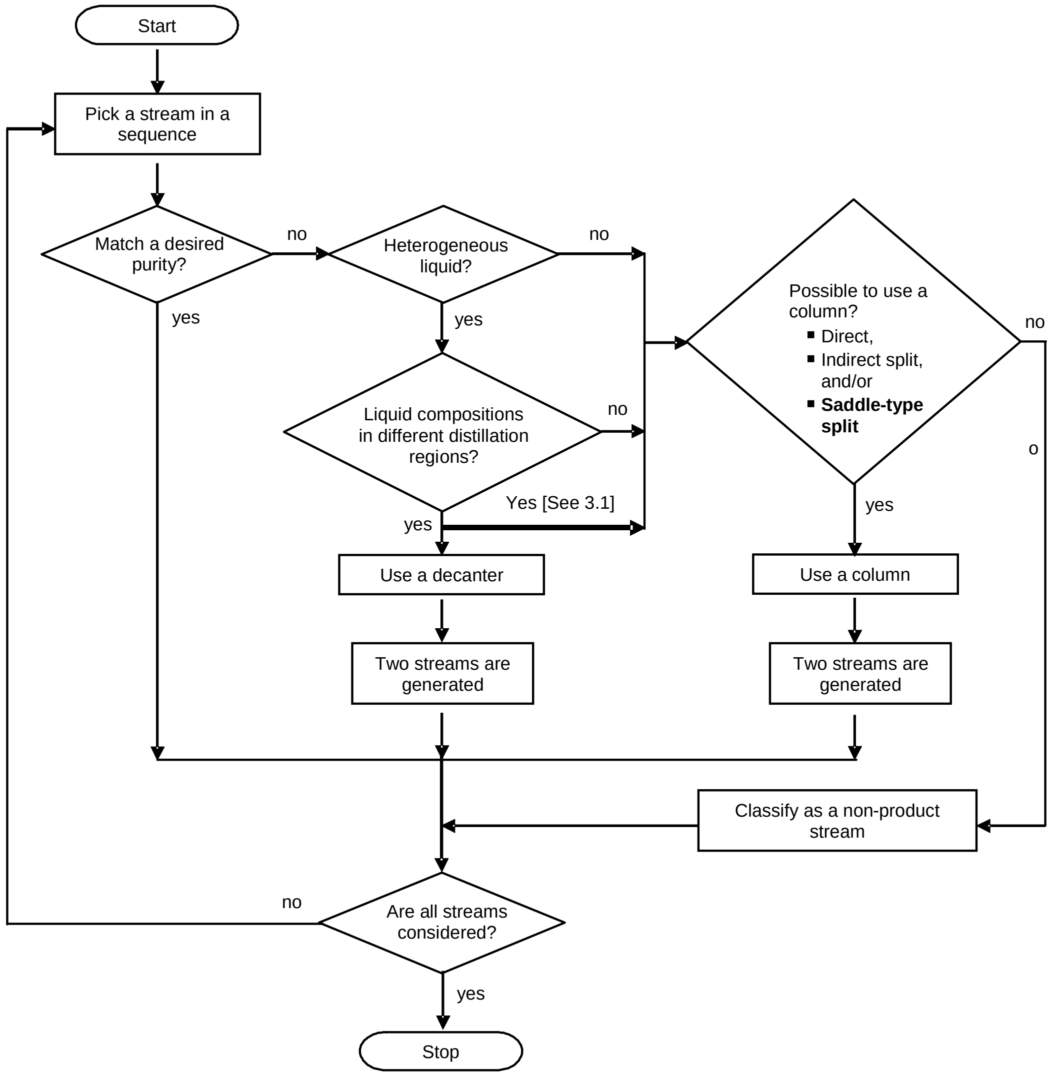


Figure 1. Existing algorithm[3,4] extended to include double-feed column and use of heterogeneous column feed (where equilibrium liquid compositions are in different distillation regions)[6].

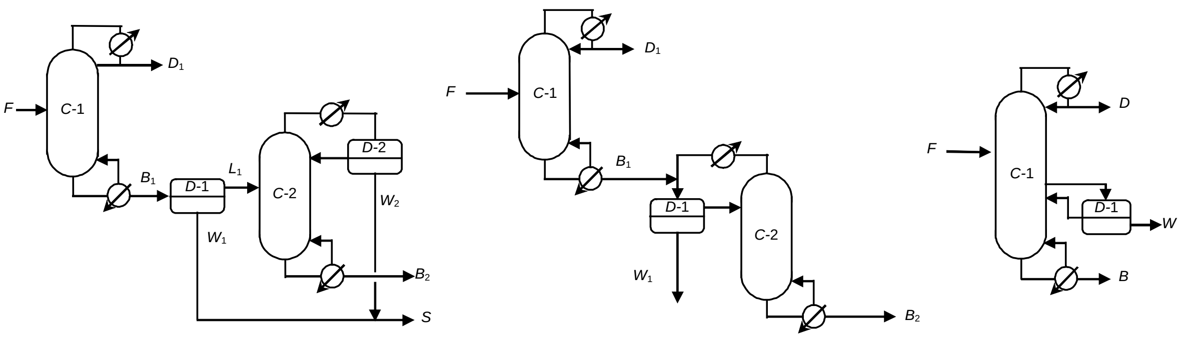


Figure 2. Two columns with two decanters carrying out similar separations can be merged to give a column with an intermediate decanter[6].

4. Example – n-butyl acetate–ethyl acetate–water separation

The synthesis of sequences for separation of an industrially relevant[10] ethyl acetate–water–n-butyl acetate mixture illustrates the approach. Alternative sequences are generated using existing synthesis algorithms[3,4] and the new extensions. The composition and flow rate of the feed stream and the desired product purities are given; the pressure of the separation units is fixed to 1 atm. The residue curve map is constructed, and presented in Figure 3, showing the azeotropes, distillation boundaries and 'compartments' (continuous distillation regions), the heterogeneous boiling envelope and associated vapour line for this mixture.

The synthesis algorithm is applied to generate four flowsheets – Option 1 (Figure 4) uses single-feed columns with integrated decanters; Option 2 (Figure 5) applies a two-feed column; Option 3 (Figure 6) introduces a heterogeneous liquid (with its equilibrium compositions in different distillation regions) to a single-feed column; Option 4 (Figure 7) develops Option 3 further to identify a column with an intermediate decanter. Once the feasible sequences have been generated, they may be evaluated on the basis of their total annualised cost and compared, to allow the most attractive sequence to be identified. Further results are presented elsewhere[6].

The extended synthesis approach allows additional sequences utilising new features to be generated. In the case presented, however, complex column configurations are not found to be economically attractive. Nonetheless, including those complex column configurations is important in sequence synthesis because they may make a separation feasible or may improve the economics.

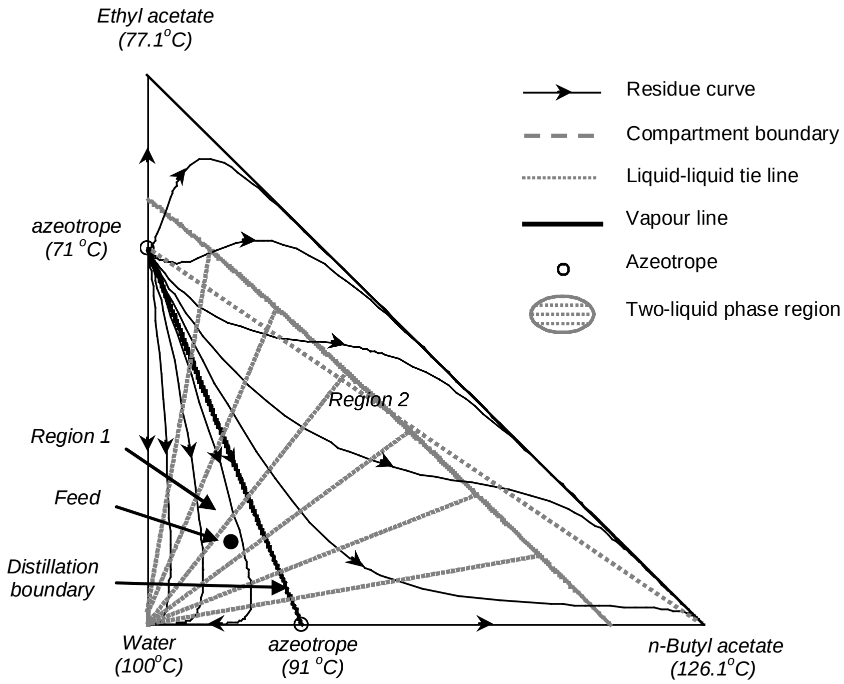
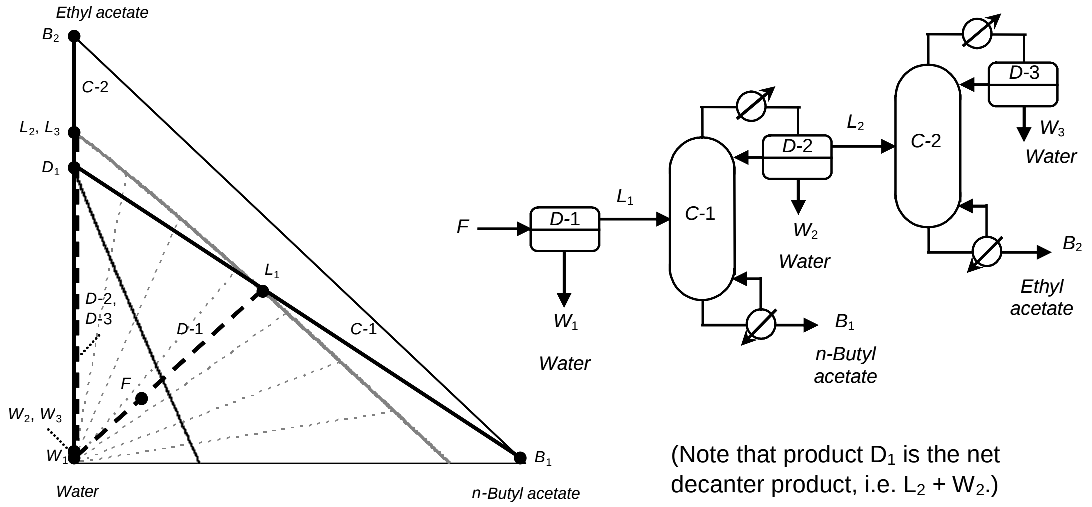
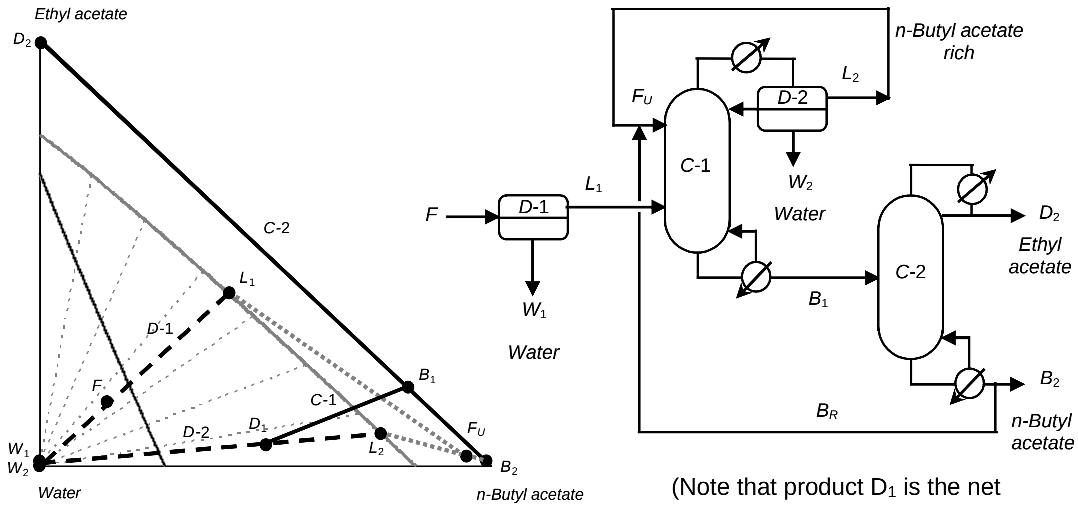


Figure 3. Residue curve map for n-butyl acetate–ethyl acetate–water mixture at 1 atm[6].



(Note that product D_1 is the net decanter product, i.e. $L_2 + W_2$.)

Figure 4. ***Option 1:*** Sequence with single-feed columns and integrated decanters[6].



(Note that product D_1 is the net decanter product, i.e. $L_2 + W_2$.)

Figure 5. ***Option 2:*** Sequence with double-feed column and recycle[6].

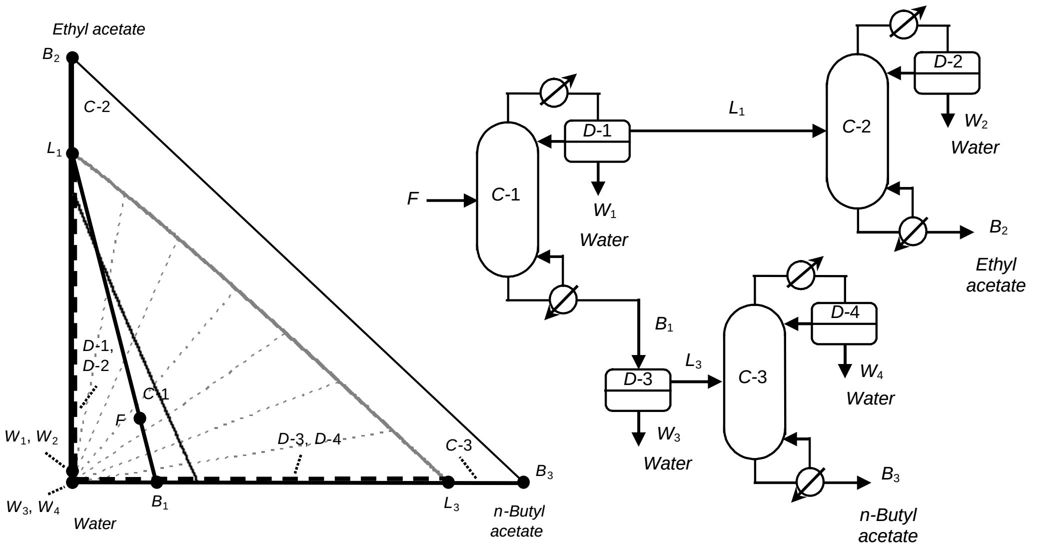


Figure 6. ***Option 3:*** Sequence with single-feed columns, and heterogeneous feed to Column 1[6].

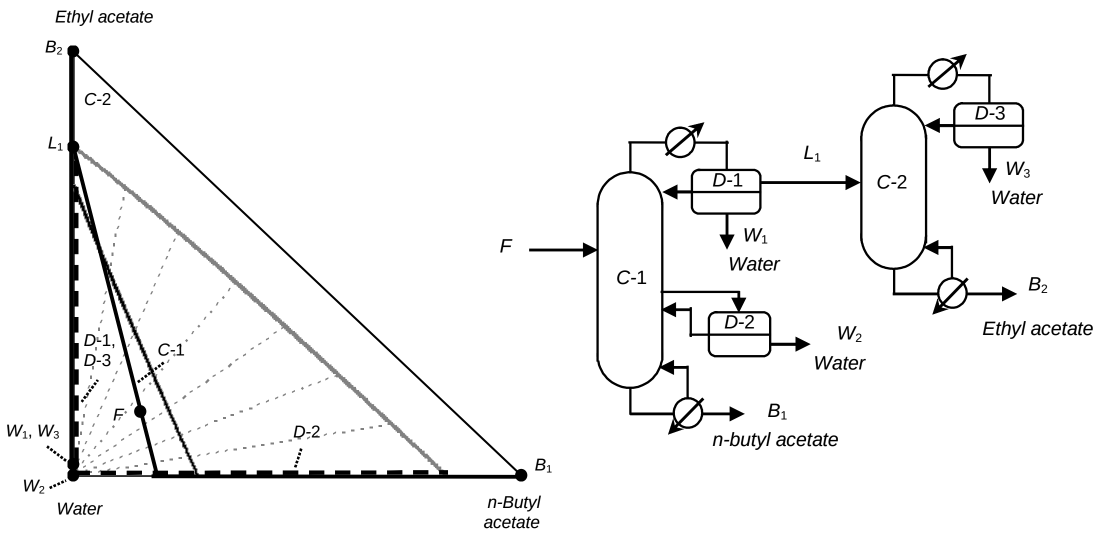


Figure 7. ***Option 4:*** Sequence evolved from Option 3, including column with intermediate decanter[6].

5. Conclusions

This paper extends existing approaches[3,4] for synthesising sequences to separate ternary heterogeneous azeotropic mixtures. Two novel options are introduced: heterogeneous liquid streams may be separated in either a decanter or a column, and double-feed columns with an integrated decanter can perform a saddle-type split. A new algorithm has been proposed for evolving sequences employing columns with intermediate decanters. The new features in the synthesis approach increase the number of separation sequences, allowing more attractive sequences to be found. The proposed approach is illustrated for the separation of a mixture of ethyl acetate–water–n-butyl acetate.

Separation sequences generated from the proposed synthesis approach can be evaluated using the iterative application of boundary value methods[6,7] (e.g. varying reflux ratios, phase reflux ratios, and upper-to-lower feed rate ratios). The total annualised cost of a flowsheet can then be estimated to allow quantitative evaluation of flowsheet alternatives.

The feasibility of a proposed separation in a single-feed column may be evaluated using the common saddle test[11]. A limitation of the synthesis approach is the lack of such a test for two-feed columns, for which feasibility may be assessed using a new boundary value method[7], given full product specifications. The proposed synthesis approach may be readily extended to consider the effects of operating pressure and decanter temperature.

Acknowledgements

The authors gratefully acknowledge the sponsorship of the Royal Thai government for Ms Prayoonyong's PhD studies at the University of Manchester.

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