



# Synthesizing alternative sequences via a P-graph-based approach in azeotropic distillation systems<sup>☆</sup>

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## Abstract

The present work proposes a P-graph based approach capable of systematically generating all combinatorially feasible alternative sequences for both continuous and batch azeotropic distillation systems when the feeds, products, and operating units and their concomitant intermediate materials are known. To facilitate synthesis, a highly effective method has been established to identify processing or operating units necessary for constructing azeotropic-distillation systems by means of first principles and logical sequencing of such units. The materials represented in the space of the residue curve map are partitioned into lumped materials bounded by thermodynamic boundaries and pinches, e.g. distillation boundaries and liquid–liquid phase equilibrium envelope. Subsequently, the operating units are identified on the basis of these lumped materials. The proposed approach automatically discards the operating units and intermediates whose inclusion will lead to infeasible sequences. The efficacy of the approach is illustrated with a realistic example. © 2000 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

While some notable accomplishments, predominantly based on heuristic methods, have been reported, no method is available for systematically identifying the plausible operating units for azeotropic-distillation systems (see, e.g. Malone and Doherty [1]; Westerberg and Wahnschafft [2]; Widagdo and Seider, 1996 [3]). It appears that neither the conventional heuristic methods nor the available algorithmic methods are capable of ensuring optimality of the alternative sequences synthesized; this is largely attributable to the combinatorial complexities encountered. The development of a rigorous and robust method is deemed highly desirable for expeditiously and rigorously synthesizing all feasible sequences by overcoming combinatorial complexities.

A set of operating units must be conceived or available prior to synthesizing any process. Hence, to identify all plausible operating units is the first task for synthesizing, i.e. developing the flowsheet of an azeotropic-distillation

system, or any process system for that matter. Undertaking this task, however, for a azeotropic-distillation system is exceedingly complex since the existence of thermodynamic pinches, e.g., azeotropes and distillation boundaries, almost always appreciably magnify the chemical/physical complexity of the subsystem. To cope with the situation mentioned above, substantial domain knowledge of the system and various mathematical techniques need be incorporated into the method to deal with the system specificity. For example, residue curve maps (RCM's) serve to represent the system (see, e.g. [2] and [3]), and materials partitioning, classification of operating units, and numerical curve fitting come into play to systematize and automate the method. This work aims at developing a systematic and efficient method to identify processing or operating units required in establishing the flowsheets of azeotropic-distillation systems which are ubiquitous in chemical and allied industries which is essential for implementing various synthesis approaches such as the process graph-based, or P-graph-based in short, process synthesis method (see e.g. Siirola, 1996 [4]). To facilitate the presentation, each major step of the proposed method is delineated with the example of a well-known azeotropic-distillation system, the production of pure ethanol from its aqueous solution with toluene as the entrainer (see, e.g., Partin, 1996 [5]).

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## 2. Overcoming thermodynamic pinches and/or crossing distillation boundaries

Various means have been proposed to overcome the thermodynamic pinches either heuristically or based on the first principles [1–4]. Those dealing with a specific type of thermodynamic pinches are adopted here; a distillation boundary, which should be of particular concern in designing any azeotropic-distillation system, is an instance of such thermodynamic pinches.

## 3. Partitioning materials

A countless number of plausible materials may be identified for a three or more component system: the RCM of such a system is a two-dimensional plane, i.e. area, or higher dimensional space. For generalization, therefore, a need exists to partition all the materials within each of the areas or spaces defined by various boundaries in the RCM. Generally, the products and feed for any distillation column should be in the same region created by distillation boundaries. When the extreme curvature of a distillation boundary is exploited, however, the products and feeds can be in different regions on the two sides of this boundary [3]. Nevertheless, in this situation, the design and operation of the distillation columns are severely affected, often negatively, by the reliability of thermodynamic data; frequently, these data contain appreciable error. It is, therefore, advisable to circumvent the situation.

### 3.1. Partitioning materials according to the critical curves and lines

As can be discerned in Fig. 1, distillation boundaries XH, YH and ZH divide the entire RCM into three regions which cannot be crossed by simple distillation; in other words, simple distillation, can only be implemented inside a single region. With the exception of those located infinite-simally close to each of the three boundaries and the singular points, E, W, T, and F, the materials in the RCM are partitioned into three classes, i.e., lumped materials  $L_1$ ,  $L_2$ , and  $L_3$ , thereby resulting in azeotropes X, Y, Z, and H. They are not classified as separate classes of materials since they are the terminal points of the distillation boundaries. Note that the lumped materials identified are not illustrated in Fig. 1 since they will be partitioned further, nor are any lumped materials to be identified later if they are to be partitioned further. The materials along distillation boundary XH on the sides of regions XHZWX and EYHXE are classified as lumped materials  $L_{4,W}$  and  $L_{4,E}$ , respectively, since the materials in the former and the latter can be fed into distillation columns producing water (W) and ethanol (E), respectively; the materials along distillation boundary YH on

the sides of regions EYHXE and YTZHY are classified as lumped materials  $L_{5,E}$  and  $L_{5,T}$ , respectively, since the materials in the former and the latter can be fed into distillation columns producing ethanol (E) and toluene (T), respectively; and the materials along distillation boundary ZH on the sides of regions YTZHY and XHZWX are classified as lumped materials  $L_{6,T}$  and  $L_{6,W}$ , respectively, since the materials in the former and the latter can be fed into distillation columns producing toluene (T) and water (W), respectively.

Further partitioning of lumped materials according to phase splitting is desirable since it may facilitate overcome the thermodynamic pinch attributable to the ethanol–water azeotrope. For this purpose, additional critical points are identified; they are point S where the two branches of the liquid–liquid equilibrium envelope merge; points Q and V, the terminal points of the first tie line totally located in region EYHXE; points P and R, the two terminal points of the first tie line with a single terminal point, i.e. the latter, located in region EYHXE; point U where distillation boundary XH and tie line PR cross each other. Note that distillation boundary XH and liquid–liquid envelope WST cross each other at point Q while distillation boundary YH and liquid–liquid envelope WST cross each other at point R. The further partitioning of the lumped materials is accomplished as follows:

Lumped material  $L_1$  is partitioned into lumped material  $L_{1,1}$  in homogeneous region ERSQE; lumped material  $L_{1,2}$  on curve QSV which is part of liquid–liquid equilibrium envelope WST and in heterogeneous region QSVQ where phase splitting leads to the crossover of neither distillation boundary XH nor distillation boundary YH; lumped material  $L_{1,3}$  on distillation boundary VR; lumped material  $L_{1,4}$  in heterogeneous region QVRUQ where phase splitting leads to the crossover of distillation boundaries XH; and lumped material  $L_{1,5}$  in heterogeneous region URHU where phase splitting leads to the crossover of both distillation boundary XH and distillation boundary YH. Lumped material  $L_2$  is partitioned into lumped material  $L_{2,1}$  in homogeneous region YTRY; lumped material  $L_{2,2}$  on curve RT which is part of liquid–liquid equilibrium envelope WQSRT; and lumped material  $L_{2,3}$  in region RTZHR. Lumped material  $L_3$  is partitioned into lumped material  $L_{3,1}$  in region HZWPQH; lumped material  $L_{3,2}$  on curve WP which is part of liquid–liquid equilibrium envelope WQSRT; lumped material  $L_{3,3}$  in region QUPQ; lumped material  $L_{3,4}$  on curve PQ which is part of liquid–liquid equilibrium envelope WQSRT; and lumped material  $L_{3,5}$ , in region XQWX. Note that in contrast to the situation of distillation boundaries, curves RT and WQ are not classified further since the materials on both sides of either of these curves are situated in identical regions bounded by the distillation boundaries.

As illustrated in Fig. 1, lumped material  $L_{4,E}$  is partitioned into lumped material  $L_{4,E,1}$  along curve XQ

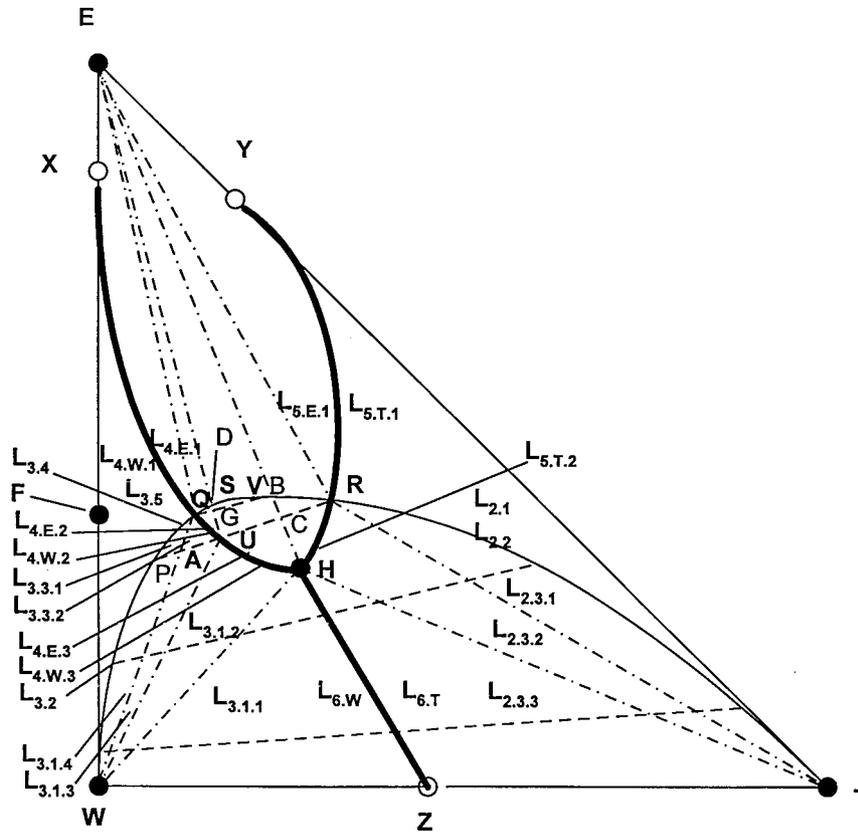


Fig. 1. RCM of the ethanol(E)–water (W)–toluene (T) system illustrating the partitioning of materials.

which is the homogeneous part of distillation boundary XH and on the side of region EYHXE; lumped material  $L_{4.E.2}$  curve QU which is one of the two heterogeneous parts of distillation boundary XH and on the side of region EYHXE; and lumped material  $L_{4.E.3}$  along curve UH which is another portion of the heterogeneous part of distillation boundary XH and on the side of region EYHXE. Note that lumped material  $L_{4.E.2}$  splits into lumped materials  $L_{1.2}$  and  $L_{3.2}$  while lumped material  $L_{4.E.3}$  splits into lumped materials  $L_{2.1}$  and  $L_{3.2}$ . Lumped materials  $L_{4.W}$  is partitioned into lumped material  $L_{4.W.1}$  along curve XQ which is the homogeneous part of distillation boundary XQ and on the side of region XHZWX; lumped material  $L_{4.W.2}$  along curve QU which is one of the two heterogeneous parts of distillation boundary XH and on the side of region XHZWX; and lumped material  $L_{4.W.3}$  along curve UH which is the remaining heterogeneous part of distillation boundary XH and on the side of region XHZWX. Lumped material  $L_{5.E}$  is partitioned into lumped material  $L_{5.E.1}$  along curve YR which is the homogeneous part of distillation boundary YH and on the side of region EYHXE; and lumped material  $L_{5.E.2}$  along curve RH which is the heterogeneous part of distillation boundary YH and on the side of region EYHXE. Lumped material  $L_{5.T}$  is partitioned into lumped material  $L_{5.T.1}$  along curve YR which is the homogeneous part of distillation

boundary YH and on the side of region YTZHY; and lumped material  $L_{5.E.2}$  along curve RH which is the heterogeneous part of distillation boundary YH and on the side of region YTZHY.

### 3.2. Further partitioning of the lumped materials according to the uniqueness of intermediate products from separation

The materials in an area-occupying or curve-occupying subregion may not yield a unique intermediate lumped material upon separation. For instance, besides product E, the materials in region EYRHUQXE, i.e., the region representing lumped material  $L_{1.1}$ , may yield intermediate lumped material  $L_{4.E.1}$ ,  $L_{4.E.2}$ ,  $L_{4.E.3}$ ,  $L_{5.E.1}$ , or  $L_{5.E.2}$  depending on the locations or compositions of the materials. It is, therefore, deemed desirable to further partition the materials in some area-occupying subregions. As clearly discernable in Fig. 1, this has been accomplished by supplying additional boundaries, i.e. the dotted dashed lines, thus giving rise to the area-occupying lumped materials, each indicated by a triple subscript, as elaborated in the succeeding paragraph.

Lumped material  $L_{1.1}$  is partitioned into lumped material  $L_{1.1.1}$  in region EQXE; lumped material  $L_{1.1.2}$  in region EDQE; lumped material  $L_{1.1.3}$  in region EBVSDE; lumped material  $L_{1.1.4}$  in region ERBE; and

lumped material  $L_{1,1,5}$  in region EYRE. Lumped material  $L_{1,2}$  is partitioned into lumped material  $L_{1,2,1}$  in region DGQD; and lumped material  $L_{1,2,2}$  in region SVBGDS. Lumped material  $L_{1,3}$  is partitioned into lumped material  $L_{1,3,1}$  on curve VB; and lumped material  $L_{1,3,2}$  in curve BR. Lumped material  $L_{1,4}$  is partitioned into lumped material  $L_{1,4,1}$  in region GUQG; lumped material  $L_{1,4,2}$  in region VBCUGV; and lumped material  $L_{1,4,3}$  in region BRCB. Finally, lumped material  $L_{1,5}$  is partitioned into lumped material  $L_{1,5,1}$  in region UCHU; and lumped material  $L_{1,5,2}$  in region CRHC. Lumped material  $L_{2,3}$  is partitioned into lumped material  $L_{2,3,1}$  in region RTR; lumped material  $L_{2,3,2}$  in region RTHR; and lumped material  $L_{2,3,3}$  in region HTZH. Lumped material  $L_{3,1}$  is partitioned into lumped material  $L_{3,1,1}$  in region HZWH; lumped material  $L_{3,1,2}$  in region UHWU;

lumped material  $L_{3,1,3}$  in region AUWA; and lumped material  $L_{3,1,4}$  in region QAWPQ. Similarly, lumped material  $L_{3,3}$  is partitioned into lumped material  $L_{3,3,1}$  in region QAPQ; and lumped material  $L_{3,3,2}$  in region QUAQ.

**4. Identifying the plausible operating units and concomitant materials**

The plausible operating units will be identified along with the concomitant materials that have been lumped.

*4.1. Identifying the indispensable operating units*

All plausible operating units necessary for producing the desired products, E and W, are identified at the

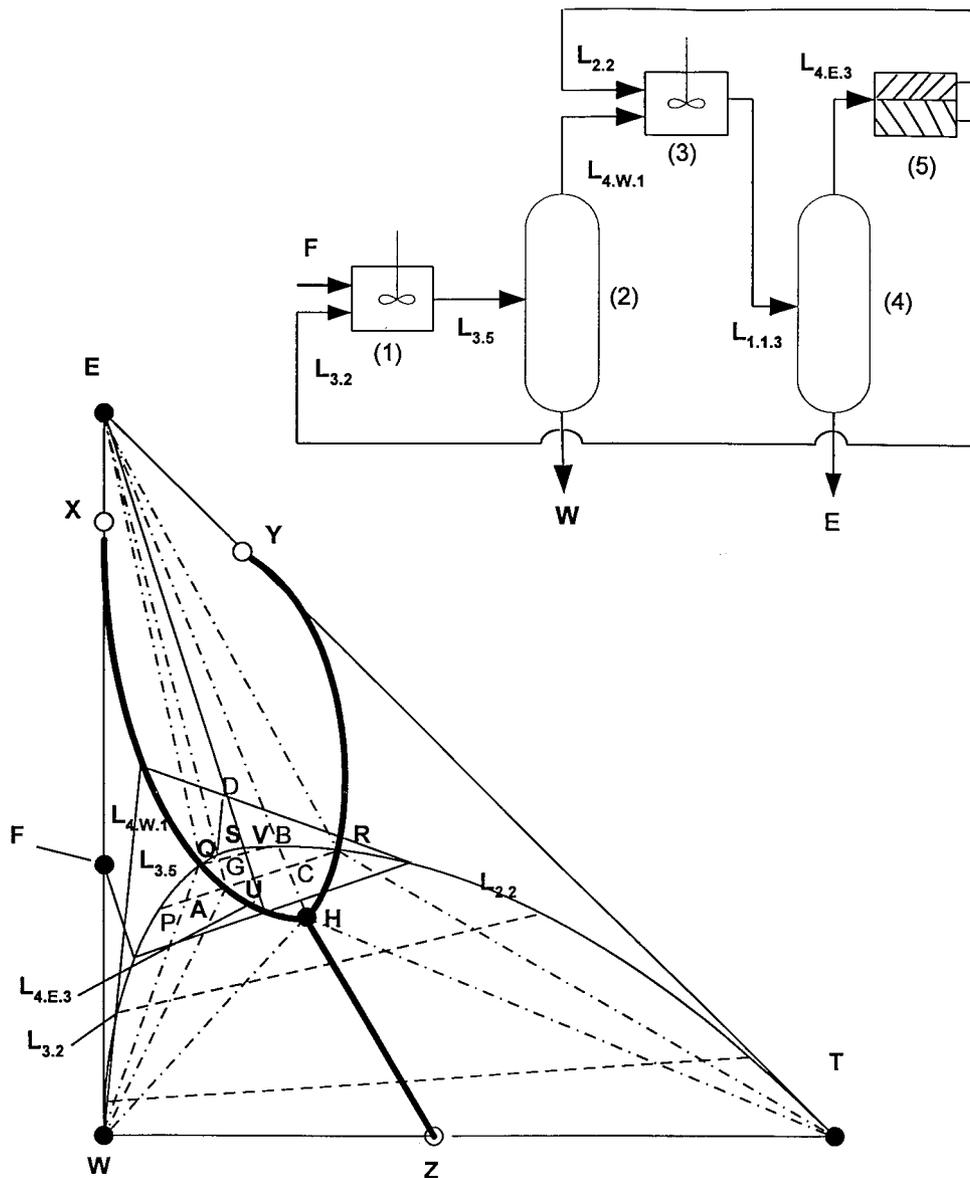


Fig. 2. RCM of the ethanol(E)–water(W)–toluene(T) system to generate flowsheet for the example: (1) mixer; (2) distillation column; (3) mixer; (4) distillation column; (5) decanter.

outset; for example, they are distillation column ( $\{L_{1.1.1}\}$ ,  $\{E, L_{4.E.1}\}$ ) producing E and distillation column ( $\{L_{3.5}\}$ ,  $\{W, L_{4.W.1}\}$ ) yielding W. To avoid or overcome thermodynamic pinches, another class of operating units, decanters, is indispensable; an example is decanter ( $\{L_{1.4.2}\}$ ,  $\{L_{1.3.2}, L_{3.4}\}$ ).

#### 4.2. Identifying the operating units for generating the feeds to the indispensable operating units selected and other plausible operating units facilitating separation

Mixers, for instance, ( $\{F, L_{5.T.1}\}$ ,  $\{L_{1.1.1}\}$ ) and ( $\{F, L_{4.E.1}\}$ ,  $\{L_{3.5}\}$ ), are the principle means of producing the feeds for indispensable operating units, so are the decanters identified in the preceding sub-section since one or more products may be located in a region segregated by distillation boundaries, in which no raw material or feed to the entire process, i.e. feed F, is situated. Moreover, the pure entrainer is usually recycled in a feasible sequence or flowsheet. Consequently, any operating unit capable of regenerating T, e.g., distillation columns ( $\{L_{2.1}\}$ ,  $\{L_{5.T.1}, T\}$ ) and ( $\{L_{2.2}\}$ ,  $\{L_{5.T.1}, T\}$ ), are also identified.

## 5. Application

Obviously, the present method is applicable to the flowsheeting or synthesis of azeotropic-distillation or similar processes in conjunction with a conventional method heavily guided by heuristics in a rather straightforward manner (see e.g. Feng and Fan [6, 7]). A resultant flowsheet is illustrated in Fig. 2; it comprises distillation columns ( $\{L_{1.1.3}\}$ ,  $\{E, L_{4.E.3}\}$ ) and ( $\{L_{3.5}\}$ ,  $\{W, L_{4.W.1}\}$ ), mixers ( $\{L_{4.W.1}, L_{2.2}\}$ ,  $\{L_{1.1.3}\}$ ) and ( $\{F, L_{3.2}\}$ ,  $\{L_{3.5}\}$ ), and decanter ( $\{L_{4.E.3}\}$ ;  $\{L_{2.2}, L_{3.2}\}$ ). In addition, more than 100,000 combinatorially feasible flowsheets have been generated by means of a P-graph-based method (see e.g. Friedler et al. [8–10]).

## 6. Concluding remarks

An immensely effective method has been established in the current work for synthesizing alternative sequences of azeotropic-distillation systems. The efficacy of this method has been amply demonstrated generating

feasible flowsheets for the production of pure ethanol from its aqueous solution with azeotropic-distillation via a heuristic approach. The method can be readily extended to complex processes involving phase transition and/or phase separation. The method possesses great potential to be an integral part of any conventional or heuristic flowsheeting. Nevertheless, its full potential can probably be realized only when applied in conjunction with a robust algorithmic approach to process design and flowsheeting, i.e. process synthesis [8–10].

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