Acyclic Directed Graphs Based on Residue Curves for Feasibility Analysis

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Residue curve maps (RCMs) provide a rapid and graphical way to visualize the feasibility of separation, taking into account the azeotropic constraints and boundaries. Unfortunately, due to its graphical nature, they are mainly used for azeotropic ternary systems. RCM represents the composition column profiles for distillation units operated at infinite reflux flow rate. When checking the feasibility, the present paper proposes to use acyclic directed graphs since the column profile of compositions are not so relevant compared to the singular points joined by them.

Keywords: acyclic directed graph, feasibility, residue curve maps (RCMs)

Distillation is the most used operation to purify products and recycle non reacted compounds, which consumes high amounts of energy. The combinatorial problem generates a number of alternative processes that increases greatly as the number of mixture components increases. Sometimes there is also the freedom to choose the desired extractive agent or entrainer [1]. Not all the alternative separations are feasible, for instance, in an ideal mixture it is not feasible to collect a compound at the distillate meanwhile a lower boiling point compound is collected at the bottom. When the mixture is not ideal, i.e. presents azeotropes, then the feasibility of a certain split is not straightforward. The residue curve maps (RCMs) are a useful tool to check the feasibility for nonideal mixtures and compare different separations, even for batch sequences [2]. A residue curve matches with the composition column profile of a distillation column operated at infinite reflux flow rate. Therefore, RCM represents all the infinite reflux composition column profiles for a certain mixture. The existence of a feasible column profile between distillate and bottoms compositions is a necessary condition for the feasibility of a certain separation. Obviously, the industrial distillation columns have not infinite reflux flow rate, but if a separation is feasible with infinite reflux then it must be industrially feasible when a high enough reflux is used. It is important to notice that this is a sufficient condition but not necessary. The feasibility based on RCM implies that it is industrially feasible, but a separation can be industrially feasible at a low reflux and not at infinite reflux, e.g. a double feed reactive distillation column. Despite this fact, RCM provides the main tool to check the distillation feasibility when considered together with the mass balance conservation equations. Unfortunately, RCMs can only be visualized clearly in two dimensions (2D), when the number of degrees of freedom of the mixture is two. The two dimensional maps more common are non-reactive ternary mixtures (triangle) and reactive quaternary mixtures at chemical equilibrium (square). For a ternary mixture, there are two compositions as variables and the third becomes fixed by the sum of composition fractions to one. If there is a fourth compound then a new free variable appears and the map must be presented in a tri-dimensional tetrahedron. But when a reaction occurs, assumed at equilibrium, the chemical equilibrium equation decreases the degrees of freedom of the mixture and it can be presented in two dimensions in a square. The reactive RCMs can be applied to kinetically controlled reactions, but the advance of the reaction adds a new degree of freedom [3]. The application of the residue curves to multicomponent systems with a large number of compounds is not a mathematical limitation but a graphical one when representing the calculated results. The total number of possible residual curve maps for ternary systems is 49, the types of tetrahedral surface diagrams, which are the same for the systems having a four component azeotrope and the systems having none, increase to 530 [4]. The present paper proposes the use of graph theory to overcome the feasibility analysis of multicomponent mixtures.

The illustrative examples provided imply the use of distillation columns, but nowadays the RCMs are applied to other separation units, e.g. membrane separation [5] or adsorption [6].

Experimental part

Methodology

The graph theory was developed by Euler in 1735 to solve the problem of the Seven Bridges of Königsberg. Euler pointed out that the choice of route inside each land mass is irrelevant and the only important feature for the feasibility is that no more than two pieces of land are connected to the rest by an odd number. To check the feasibility of a complex problem becomes thus very simple. In a similar way, for distillation feasibility purposes, the compositions followed by the residue curve are irrelevant and what it is important is which singular points become connected. In analogy to the problem solved by Euler, the residue curves are the bridges and the singular points are the pieces of land, i.e. the vertices and the edges of the graph, respectively. An important particularity of a feasible column profile is that it can pass through several singular points or nodes, but always in the same direction of monotonically changing temperature, i.e. the feasibility graphs obtained are acyclic directed graphs. When two singular points can be connected by a column profile, passing through several singular points, then it is also feasible a column profile

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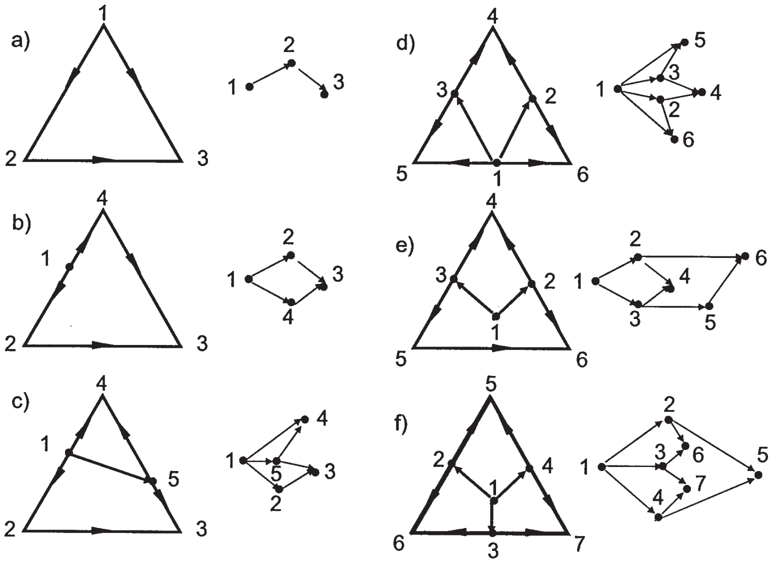

Fig. 1. Feasibility graphs for some ternary mixtures

connecting them without passing through the intermediate singular points. It is important to take into account this fact as the directly connected links are not required to be plotted, simplifying its representation. Notice that the term singular point is used as the azetropes and pure components are treated in the same way.

Results and discussions

Feasibility graphs are not necessary to use for ternary mixtures as they can be represented properly by means of RCMs. However, they are useful as illustrative examples. In the case of ternary mixtures, the feasibility graphs can be more complex than the RCMs but the RCMs provide more information, e.g the minimum number of transfer units required [7]. For instance, Figure 1a shows the distillation of an ideal ternary mixture. In these schemes, only the singular points, edges and boundary lines are presented in the RCM, but the representation of the residue curves provides additional information as the composition column profiles. The compositions, besides the mass and mole fraction, can be expressed as elemental [8] or reactive compositions [9] and the mass balance is presented in the map as a straight line joining the distillate, feed and bottoms compositions. The deviation of the residue curves to one of the vertex when a node is approached implies a higher chemical affinity between the compounds of this vertex than with the other compound. The map represents concentrations and the feasibility graph represents only which singular points are connected but not how. For this reason, in Figure 1a, when the feasibility graph is presented, the edge between 1 and 3 is not presented because it is already indicated by the fact that 1 and 3 are connected passing by 2.

The feasibility graph of a ternary mixture with one azeotrope but without boundary lines is equivalent to the feasibility graph of a quaternary mixture without azeotropes. This is a clear example that in the feasibility graph, the singular points taken into account are treated as a pure component than as an azeotrope. The sense of the arrows in the residue curve map is the same than in the feasibility graph. Figure 1c and 1d are clear examples of how different distillation regions are visible in the feasibility graph as surfaces delimited by edges. Figure 1c has two distillation regions, figure 1d has three distillation regions, while figure 1e has two different distillation regions. In the feasibility graph one region can overlap another, i.e. the region 1-2-4-3 overlap the region 1-2-6-5-3. It does not mean that really are overlapped, but it is just to represent it in a more compact way. The way the nodes are represented in space in the feasibility graph is not important, but the connectivity between them is. The overlap in the representation could be avoided representing the node 4 at the right of node 1, but then it would be more difficult to identify visually the unstable and stable nodes. However, the arrows define unequivocally each kind of node. Figure 1f shows a feasibility graph with three distillation regions. Any of the stable nodes could be placed in the biggest area of the feasibility graph without any special meaning about it. Notice that the RCMs without taking into consideration the triangle edge distances are also a possible representation of the feasibility graph. However, when the singular points are all situated in vertices and the singular points are situated in different positions (unstable, saddle or stable points), then their identification is more straightforward. Nevertheless, the abstraction is not a clear advantage over the RCMs for ternary mixtures, but its advantage becomes more obvious as the number of compounds increases, as it is shown in the following paragraphs. Figure 1 only represents a few illustrative examples of ternary diagrams, a more complete topology of diagrams is provided by [4] or [10].

As mentioned previously, the limitation to check the feasibility is due to the visualization limitations of the RCMs. Blagov and Hasse (2002) [11] proposed to present it as a table with 0 and 1, according to their connectivity between singular points. Although it is not graphical, it can be used for any number of compounds. The unstable nodes are easily identified because they correspond to singular points, with the entire column with zero value (no other singular point is connected towards it). The stable nodes are easily identified because they correspond to singular points with the entire row with zero value (it is not connected towards any other singular point). From the table, the residue curve map becomes perfectly identified but the overall view provided by the graphical presentation to show at a view the entire problem is lost and the distillation regions are not identified at a glance.

The quaternary mixture n-hexane (0)–chloroform (1)–ethanol (3)–acetone (7) at 1 bar is presented as a tri-dimensional tetrahedron by [11]. Its visualization, although feasible, is a bit confusing due to the large amount of lines and points in a three dimensional space. When it is represented as a feasibility acyclic directed graph, its visualization becomes simplified (fig. 2). The direction of the arrows has been kept as in the mentioned paper, following the sense from high to low temperatures. The system presents five binary azeotropes: n-hexane/ethanol (4), n-hexane/chloroform (2), n-hexane acetone (8),

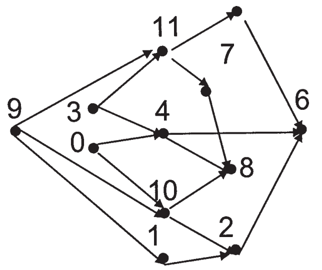

Fig. 2. Example of feasibility acyclic directed graph for the mixture n-hexane (0)–chloroform (1)–ethanol (3)–acetone (7) at 1 bar

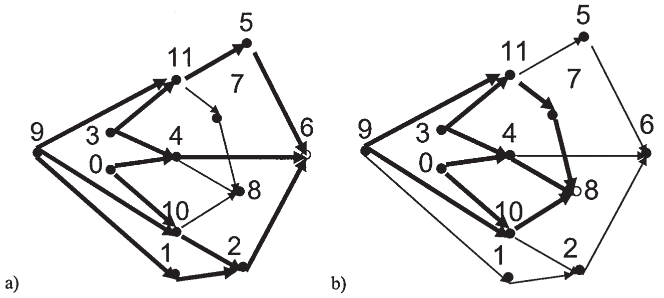

Fig. 3. Mixtures that provides composition (a) 6 or (b) 8 at the column distillate

ethanol/acetone (5), and chloroform/acetone (9), all of them being minimum boiling azeotropes, except the last one. It also presents three ternary azeotropes: hexane/ethanol/acetone (6), chloroform/hexane/acetone (10) and chloroform/ethanol/ acetone (11) and a quaternary azeotrope (12), all of them are saddles, except the first one that is a stable node. The saddle, stable and unstable nodes are easily identified on the feasibility graph, first of all due to the convergence and/or divergence of the arrows and secondly, due to their position at the left, centre of right of the feasibility graph. The distillation regions can also be easily identified as the edges that are between the same unstable and stable nodes. However, the main use is to check the feasibility of certain separations.

Figure 3 shows the edges associated to each one of both unstable nodes. Overlapping figures 3a and 3b, all the edges become associated at least to one of them as expected. The compositions on the edges correspond to the mixtures that can be obtained by mixing the compositions at the extremes of this edge. The edges associated to a certain node will define a closed area. Therefore, the mixtures that can be obtained by combining the compositions on the vertices are attainable from the mentioned node. For instance, when the distillate of the column corresponds to the hexane/ethanol/acetone (6) minimum boiling azeotrope, the bottoms composition can be at any value except the ones that can be obtained by combining the compositions inside the area 10-0-4-3-11-7-8. When the distillate corresponds to the binary azeotrope n-hexane/acetone (8), the bottoms composition can be at any composition except the one obtained by mixing the compositions corresponding to the values 11-3-4-0-10-9-1-2-6-5. Notice that the composition defined at the boundary 11-3-4-0-10-9 is common for both distillate compositions. For instance, it is feasible a column collecting the maximum boiling azeotrope chloroform/acetone (9) at the bottoms and the distillate at 6 or 8 depending on the initial feed composition. Therefore, there are regions attainable, depending on the distillate composition and some other common to both.

Figure 4a and 4b show that the both stable nodes can be attained in the bottoms, independent of the unstable node attained in the distillate. However, the distillation regions defined by the stable nodes are only coincident in the edges and not in the distillation region. The previous discussion is taken into account that the distillate or bottoms are nodes. However, the graph is also useful to check saddle points.

For instance, figure 5 presents how the graph can be interpreted to recover pure acetone (7). Pure acetone has only an arrow going towards the binary azeotrope acetone/n-hexane (8), this means that if pure acetone must be collected by the column bottoms, then the distillate can be at maximum the binary mixture acetone/n-hexane. As the feed must be a mixture of distillate and bottoms means that only if the feed is a binary mixture of acetone/*n*-hexane richer in acetone than the azeotrope, then it is feasible to collect pure acetone at the bottoms. On the other hand, the acetone can be collected pure at the distillate. To determine the region of feed composition where it is feasible, the arrows reaching the pure acetone (7) must be followed backwards. Notice that an open area is obtained. However, according to the fact that if there is an edge between A-B-C then it is also possible an edge A-C. Therefore, the bottoms and distillate compositions must be obtained by mixing 7-11-3 or 7-11-9.

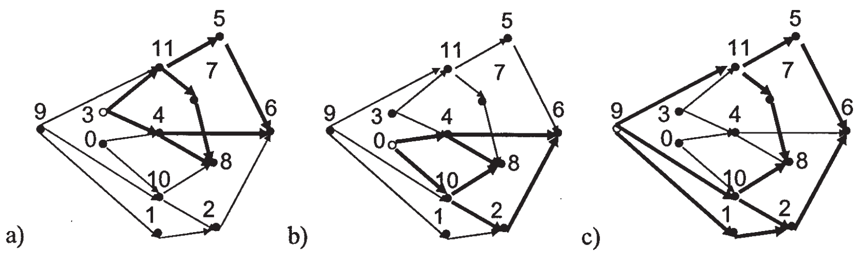

Fig. 4. Mixtures that provides composition (a) 3, (b) 0 or (c) 9 at the column residue

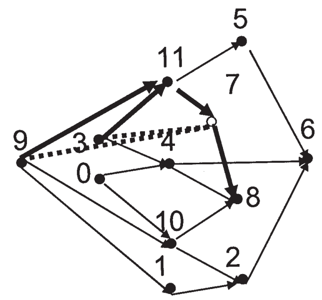

Fig. 5. Feasible distillation regions when a saddle composition of the graph must be collected pure

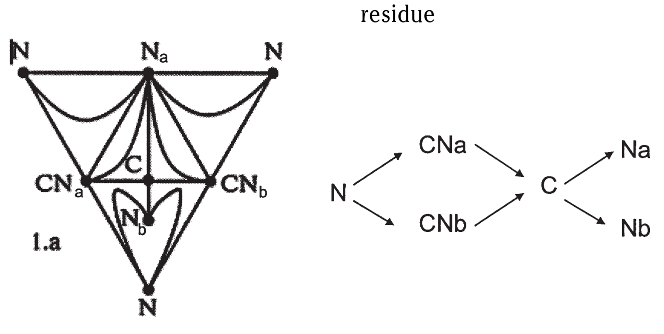

Fig. 6. Comparison of a surface residue map with a feasibility graph

Medvedev and Serafimov (2011) [4] represent the tetrahedron composition in two dimensions, based on the fact that a tetrahedron surface is composed of four triangles. As illustrative example, figure 6 shows how the surface representation can be converted to a feasibility graph.

As a final remark, the feasibility graph cannot represent the minimum number of transfer units, but it could include the values of the minimum energy requirements for the separation [12].

Conclusions

Industrially, many systems are made of multicomponent mixtures with more than three components. Unfortunately, the visualization to get a first insight on the column behaviour based on thermodynamic data is limited nowadays to ternary mixtures. The present paper shows that the acyclic directed graphs represent a topological tool that allows the visualization of complex distillation behaviour in a relatively simple way. The use of graphs is very old to solve complex problems, but at our knowledge it is the first time that it is used for feasibility studies with application to separation units, e.g. distillation.

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