

New Algorithm for the Determination of Product Sequences of Batch Azeotropic and Pressure Swing Distillation

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In multicomponent azeotropic mixtures (e.g. waste solvents), the products obtainable by batch distillation and their maximal amount is highly dependent on the charge composition. A method is presented for the determination of product sequences for any number of components based only on the boiling points of pure components and azeotropes, and azeotropic compositions, without the knowledge of further VLE data. The method is suitable for heteroazeotropes and pressure swing distillation as well. The results are presented for the system acetone-chloroform-methanol-ethanol-benzene with and without pressure change, as well.

1. Introduction

Batch distillation is a common solvent recovery technology in the pharmaceutical and specialty chemical industries. The components of waste solvents usually form multicomponent azeotropic mixtures therefore the sequence of cuts and the maximum recovery in each cut is highly dependent on the charge composition. For the successful recovery it is essential to predict the feasibility of recovering components in pure form. For ternary mixtures, the distillation boundaries were determined on the basis of only the boiling points (BP) of pure components and azeotropes, and azeotropic compositions by Foucher et al. (1991).

For mixtures with arbitrary number of components methods were suggested by Safrit and Westerberg (1997) and Ahmad et al. (1998), which require the knowledge of the type of all stationary points demanding the use of a VLE model. The method of Safrit and Westerberg (1997) may for globally undetermined systems, which, however, haven't been reported. Ahmad et al. (1998) assumed that the maximum number of unstable and stable nodes (UN, SN) is two. Lang and Modla (2006) proposed a method for the determination of batch distillation regions of heteroazeotropic distillation.

This article presents a rapid and automatic method

- for generating product sequences for batch distillation of a mixture containing any number of components,
- based only on the BPs of pure components and azeotropes, and azeotropic compositions (including the compositions of liquid phases in the case of heteroazeotropes),

- making unnecessary the knowledge of further VLE data (e.g. binary interaction parameters), test runs in pilot columns and detailed dynamic simulations,
- which is suitable also for mixtures containing heteroazeotropes.

The algorithm was implemented in Visual Basic for Applications. Microsoft Excel was used as a data interface. Calculations were performed among others for the system acetone-chloroform-methanol-ethanol-benzene (Ahmad et al., 1998).

2. Description of the algorithm

The following simplifying assumptions are applied:

- Maximal separation.
- The boundaries are straight lines.
- The mixture does not contain quinary azeotrope.
- The quaternary azeotrope cannot be SN and it is the common point of all distillation regions in a quaternary mixture.
- In an n-component mixture there is maximum one azeotrope of n-component.
- The ternary submixtures occur in practice (present in Reshetov's statistics).

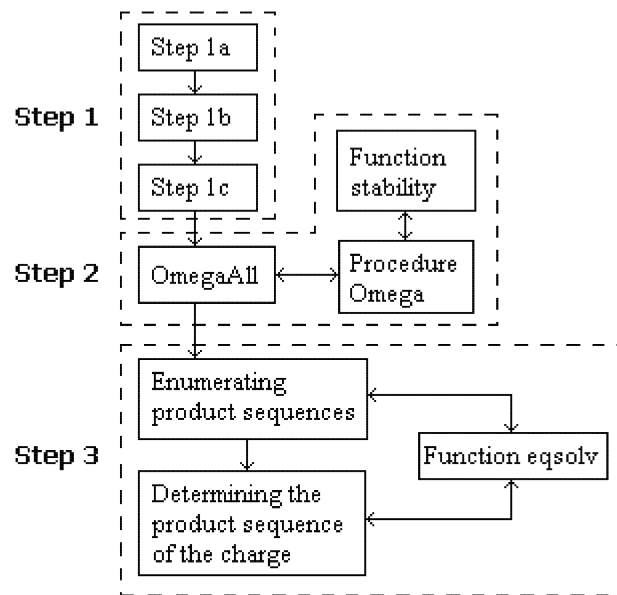


Figure 1: The overall structure of the algorithm

The structure of the algorithm is presented in Fig. 1. The main steps are the following:

1. Determination of the type of all stationary points.
2. Completing the adjacency matrix of fixed points which represent the topological structure of the composition simplex by the method of Ahmad et al. (1998).
3. Determination of all product sequences and the relative amount of cuts for the given charge.

Step 1, which is the new part of the algorithm, consists of the following steps:

- a. Determination of the type of stationary points in ternary submixtures.
- b. Unification of ternary submixtures into quaternary ones.
- c. Unification of quaternary submixtures into quinary ones etc.

The main steps are described with more details below. In the case of a heteroazeotrope, the azeotropic composition is replaced with that of the product phase before Step 1.

2.1 Step 1: determination of the type of all stationary points

In this step, the stability of fixed points in all ternary submixtures is determined, then these stabilities are revised as the ternary submixtures are joined into quaternary ones, quaternary submixtures into quinary ones, etc.

2.1.1. Step 1a: ternary submixtures

From the pure components, all ternary submixtures are created, and the azeotropes are assigned to the corresponding ternary submixtures. After that, the stability of all fixed points is determined within the ternary submixtures. The stability of pure component vertices is obtained by comparing their BPs with those of the neighbour fixed points on the edges, which can be pure components or binary azeotropes. If after the identification of the fixed points with minimum and maximum BP, there is no point with unknown stability, this step is ended for the given ternary submixture.

The next step depends on the presence and the stability of a ternary azeotrope. If there is a ternary azeotrope, which is UN, the binary ones are saddles. If the ternary azeotrope is a S, the type of binary azeotropes depends on their number:

- 1: if any of the neighbour vertices is UN (SN), it will be a SN (UN);
- 2: if there are two vertices, which are UNs (SNs), the binary azeotropes will be SNs (UNs), in the opposite case, one of the azeotropes is an UN, the other one is a SN;
- 3: in this case there is only one vertex which is a node, whose stability determines those of binary azeotropes. Two of the azeotropes will have the same stability as the vertex, the third one will be a node of opposite stability.

If there is no ternary azeotrope, the stability of the binary ones depends on their number:

- 1: it is a S,
- 2: the stability of the two azeotropes depends on the stability of the common (pure) component. If it is UN (SN), the azeotrope with lower BP is S (UN), the other one is SN (S). If it is S (Serafimov-type: 2.0-2a), the stability of binary azeotropes can not be determined on the basis of temperatures only,
- 3: the stability depends on that of the pure components. If all vertices are SNs, the azeotrope with the lowest BP is UN, the other ones are saddles, otherwise, the binary azeotropes form an UN, a S and a SN, respectively.

2.1.2. Step 1b: quaternary submixtures

From the ternary mixtures all quaternary submixtures are created. The stability of all pure components and binary azeotropes are updated. If a point is S in any ternary mixture, it will be a S otherwise it will remain a node. The next step depends on the presence of the quaternary azeotrope. If there is a quaternary azeotrope and it has the lowest BP of the submixture, it is the single unstable node, otherwise it is S.

If there is no quaternary azeotrope, but there is a ternary UN and still another UN, Step 1b is continued, otherwise it is ended for this submixture. We investigate whether this

other UN is a pure component, and if there are boundaries on all the three ternary submixtures not containing the ternary UN. If both above conditions are satisfied the stabilities are not modified, otherwise the UN with higher BP becomes S.

2.1.3. Step 1c: submixtures of higher dimension

The n-component mixture is decomposed into submixtures of n-1 components by omitting one component for each submixture. This procedure is continued until we have a set of five component submixtures, then to all submixtures of each level, the stationary points are assigned. The stability of the stationary points in the quinary submixtures are determined by comparing their stabilities in the quaternary submixtures. If a point is S in any quaternary mixture, it will be a S otherwise it will remain a node. If in the quaternary submixtures to be united, there are more than one quaternary azeotropes, which are UNs, the azeotrope with the lowest BP remains an UN, while the other(s) become(s) S. This comparison is repeated at every higher level until the stabilities in the n-component mixture are determined.

2.2 Step 2: Completion of adjacency matrix (Ahmad et al., 1998)

In this step we implement the procedures OmegaAll and Omega by Ahmad et al. (1998). Since we study only the mixtures occurring in practice, the number of topological structures to be considered decreases from the 13 distinguished by Ahmad et al. (1998) to 9. A further difference is, that for the evaluation the stabilities of fixed points in the common unstable boundary limit set, we have to use the same method as in Step 1 (calling the function “stability”) because of the lack of the knowledge of the number positive and negative eigenvalues, respectively.

2.3 Step 3: Determination of product sequences

All possible sequences of cuts must be enumerated satisfying the criteria 1 and 2 of Ahmad et al. (1998), that is, a sequence consists of n fixed points, and each subsequent product cut has to be an element of the unstable boundary limit sets of all the preceding product cuts. The list of possible sequences of cuts has to be checked if they fulfil also criterion 3, that is, the fixed points form an n-1 simplex. If the first point is a linear combination of the others, they form an n-1 simplex. This check is performed by the function “eqsolv”. In the case of ternary and quaternary mixtures, it may occur that some of the batch distillation (BD) regions overlap. In this case it must be checked if the azeotrope containing all components is located in the interior of a BD region. If so the region, which is a subset of another one, is not a real BD region, and it must be omitted. By this omission, the region which contains the non-real region becomes concave, therefore if the charge happens to lie in the omitted, non-real region, it will actually lie in a third, convex region.

The composition of the charge is the linear combination of those of the fixed points of its corresponding BD region. If this set of equations is solved for all regions (by the function “eqsolv”), and the coefficients are between 0 and 1, the charge is located in the corresponding region, and the coefficients give the relative amount of the cuts.

It is possible to take pressure change during the process into account by giving the necessary data for the second pressure (P_2), and by specifying the cut, after which the

pressure change occurs. The cut(s) obtained for P_1 are withdrawn from the original charge, and the algorithm is repeated for the modified charge using the data for P_2 .

3. Results

Calculations are presented for the five-component system acetone (A) – chloroform (C) – methanol (M) – ethanol (E) – benzene (B), studied by Ahmad et al. (1998). The calculations were performed for $P_1=1.01$ and for $P_2=10$ bar. For P_1 , we have used the BPs and compositions (Table 1) published by Ahmad et al. (1998), except the BP of the acetone-chloroform (AC) azeotrope, which was taken from CRC Handbook of Chemistry and Physics. The missing data for P_2 was calculated by ChemCAD using the NRTL model. The azeotropes are denoted by joining the letters of forming components.

Table 1: Boiling points and compositions of the test system (1.01 bar/10 bar)

Fixed point	A	C	M	E	B	BP (K)
CMB	-/0	-/0.340	-/0.522	-/0	-/0.138	-/400.8
CM	0/0	0.658/0.455	0.342/0.545	0/0	0/0	326.5/401.9
AM	0.778/0.38	0/0	0.222/0.62	0/0	0/0	328.0/407.0
A	1	0	0	0	0	328.9/416.1
ACMB	0.316/-	0.228/-	0.436/-	0/-	0.020/-	329.9/-
ACM	0.340/-	0.232/-	0.428/-	0/-	0/-	329.9/-
MB	0/0	0/0	0.607/0.728	0/0	0.393/0.272	330.8/407.2
AE	-/0.711	-/0	-/0	-/0.289	-/0	-/414.3
CE	0/0	0.845/0.57	0/0	0.155/0.43	0/0	332.1/415.6
C	0	1	0	0	0	333.9/426.8
ACE	0.357/0.18	0.464/0.39	0/0	0.179/0.42	0/0	335.5/415.9
M	0	0	1	0	0	337.3/409.9
AC	0.346/-	0.654/-	0/-	0/-	0/-	337.9/-
CEB	-/0	-/0.09	-/0	-/0.63	-/0.28	-/418.9
EB	0/0	0/0	0/0	0.444/0.647	0.556/0.353	340.5/418.8
E	0	0	0	1	0	351.1/423.9
B	0	0	0	0	1	352.9/451.8

First, the calculations were done without pressure change for P_1 . The stabilities calculated without using a VLE model agree with the ones obtained by Ahmad et al. (1998) requiring the knowledge of VLE parameters. For testing Steps 2 and 3, we determined all feasible product sequences and the relative amount of the cuts for two different charge compositions located in different BD regions (Table 2). The 25 product sequences calculated agree with the ones obtained by the method of Ahmad et al. (1998). The above results verify that our algorithm is suitable for the determination of the sequence of the cuts without using a VLE model.

For one composition, the results are also given for pressure change after the first cut (Table 2, 3rd row). In this case, six cuts were obtained, which differ from the cuts obtained without pressure change.

Table 2: The sequence and relative amounts (%) of products for different charges

Pressure (bar)	Charge composition	Cuts						
		CM:	ACMB:	ACE:	EB:	E:		
1.01	0.2, 0.2, 0.2, 0.2, 0.2	3.0	43.5	17.5	34.5	1.6		
1.01	0.15, 0.15, 0.4, 0.15, 0.15	6.4	47.4	28.2	5.4	12.6		
1.01 (1 st cut), 10	0.15, 0.15, 0.4, 0.15, 0.15	6.4	31.7	34.3	2.8	21.9	2.9	

4. Conclusions

A method is presented for the determination of product sequences of batch distillation for any number of components based only on the BPs of pure components and azeotropes, and azeotropic compositions. Previously published algorithms required the use of a VLE model for more than three components. The method is suitable for heteroazeotropes and for pressure swing distillation as well. The stability of fixed points is determined in every ternary submixture, assuming they occur in Reshetov's statistics. The stabilities are updated as the ternary submixture are joined into quaternary ones, quaternary submixtures into quinary ones, etc. On the basis of the stabilities, we enumerate all feasible product sequences using the algorithm of Ahmad et al. (1998). Finally, the relative amount of cuts is determined assuming maximal separation for the given charge composition. The results are presented for the system acetone-chloroform-methanol-ethanol-benzene. The stabilities and the set of product sequences calculated without using a VLE model agree with the ones obtained by Ahmad et al. (1998). These results verify that our algorithm is suitable for the determination of the sequence of the cuts without using a VLE model.

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