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

GEOMETRY OF SUBSETS OF OPTIMALITY IN EXTRACTIVE DISTILLATION OF MULTICOMPONENT MIXTURES

Andrey V. Timoshenko, Boris B. Dolmatov, Elena A. Anokhina and Vladimir S. Timofeev
Lomonosov's Moscow State Academy of Fine Chemical Technology, Chemistry and Technology of Basic Organic Synthesis Dpt., 86, Vernadskogo ave., 119571, Moscow, Russian Federation

Abstract

Extractive distillation was investigated of the multicomponent mixtures: methanol – n-propylacetate – toluene (I); acetone – chloroform – n-butanol(II); benzene – n-butanol – ethylbenzene(III). Aniline was selected as entrainer for the I and III mixtures and dimethylformamide for the II mixture separation. The possible three columns distillation flowsheets were constructed for separation of each mixture. Then they were transformed into the partially thermally coupled complexes. Eight points were selected in each simplex of initial feed composition. All flowsheets were simulated and optimized for each composition on the criteria of minimum energy consumption. These results gave an ability to construct the energy consumption surfaces for each flowsheet under the initial feed compositions simplex. The mapping of these surfaces intersection into the initial feed compositions simplex gives the borders which separate different fields of initial feed composition. The each field is characterized by the existence of a single optimal flowsheet and can be described as the region or subset of optimality. The geometry of those subsets was detected for the different classes of flowsheets and for full flowsheets manifold. It was developed that the maximum of energy saving in the investigated field of initial feed compositions are about 14 % for mixture (I), more than 22% for mixture (II) and more than 36% for mixture (III). The best thermally coupled complex is better than the best three-column extractive distillation flowsheet.

Keywords: Extractive distillation, complex column

Introduction

The task of optimal flowsheet synthesis is one of the main in chemical engineering. It also referred to the separation subsystem which commonly is some sequence of the distillation columns linked with direct and reverse flows. The thermodynamic irreversible nature of the distillation leads to energy and entropy production dependence on the process path and therefore to necessity of distillation flowsheet structural optimization. The optimization task may be solved by different methods. The heuristic methods were most popular at the medium of the last century. One of the most complete lists of such rules can be found in the reviews[1, 2] and textbooks[3]. Unfortunately heuristic rules cannot guarantee optimal solution obtaining. This and the methods of mathematical modeling progress led to the development of distillation flowsheets optimization algorithmic methods.

Another important and interesting fundamental problem is the development of algorithms for synthesis of the whole manifold of distillation flowsheets. This seemingly simple combinatorial task was rigorously solved only recently even for the most simple conventional distillation columns sequences[4] although the empiric fractionally rational factorial equation had been known long ago. There is no analogous equation for all distillation flowsheets manifold including conventional and complex columns. To the present time only a graph-theory method was proposed to synthesis of distillation flowsheets with partially thermally coupled columns (PTCC)[5]. There is some attempt to determine the number of flowsheets with the columns with side streams[6]. The methods are actively developed for synthesis of thermodynamic efficient flowsheets with fully coupled thermal and material flows for multicomponent mixtures separation. It is known that these complexes have a fixed order of separation which is determined by the requirement of full distribution of components with intermediate relative volatility between bottom product and distillate [7]. However, such complex with a fixed number of sections may have different sections distribution between real columns [8-10] which improves controllability and manageability.

The synthesis of distillation flowsheets manifold for azeotropic mixtures separation is complicated by the presence of thermodynamic-topological restrictions on products composition. This means that preliminary the number and types of separation sets which can guarantee the quality of products flows is unknown. Thus, the problem must be solved of possible workable distillation flowsheets synthesis for azeotropic mixture separation. The basis for thermodynamic-topological restrictions overcoming is the principle of redistribution of the concentration fields between separation regions[11]. This principle can be realized by different ways for example by extractive distillation. On the base of this principle we have solved some tasks of azeotropic mixtures distillation flowsheets synthesis. The number of flowsheets was determined for separation of multicomponent mixtures with one azeotrop.The graph-theoretical algorithm was proposed for synthesis of extractive distillation flowsheets. It combines flowsheet graphs transformation and thermodynamic-topological analysis of vapor-liquid equilibrium diagrams[12]. The use of algorithms for synthesis of the full nonazeotropic mixtures distillation flowsheets manifold[5] to extractive distillation in two-withdraws columns has allowed us to obtain workable flowsheets with PTCC[13]. The PTCC using in extractive distillation provides energy consumption decreasing similarly to nonazeotropic mixture distillation[14].

It is well known that manifold of the initial feed compositions divides into some regions (subset of optimality). Each of those subsets is characterized by single optimal distillation flowsheet [3,15]. The number of subsets of optimality (SO) as a rule is equal to the number of flowsheets in the case of nonazeotropic mixtures distillation in conventional columns sequences. For all manifold of distillation flowsheets this rule does not satisfied [15]. A detailed study gives an ability to make the interesting observation: if at the first stage define the SO for conventional columns flowsheets and subsequently expand the flowsheets manifold by including the PTCC flowsheets then the SO of images (flowsheets with PTCC) will be located in the regions where on the first step were optimal their preimages (flowsheets of conventional columns)[16]. Therefore the hypothesis was proved on the correlation between the localization of subsets of optimality of preimages and images in concentration simplex of initial feed composition. The flowsheets classes differ on the depth of graph transformation (degree of thermal integration)[5]. By the transition from one class to another the flowsheet transforms by excluding of one zone of irreversible flows mixing. The structures of vapor and liquid flows and concentrations profiles have insignificant changes for the most sections. Thus the succession of flowsheet structure supports the succession of the energy consumption by the transition from one class to another. The initial flowsheet accumulates changes with the depth of transformation increasing, and therefore we can’t declare that SO borders for preimages are rigorous similar to SO for images.

2. Investigation objects

The purpose of this work is the identification of concentration subsets of optimality and their features for extractive distillation flowsheets of ternary azeotropic mixtures.

Extractive distillation was investigated of the multicomponent mixtures: (I) – methanol(M) – n-propylacetate(P) – toluene(T); (II) – acetone(A) – chloroform(C) – n-butanol(Bu); (III) – benzene(Be) – n-butanol (Bu) – ethylbenzene(Eb). Aniline (An) was selected as entrainer for the I and III mixtures separation and dimethylformamide for the II mixture separation. Mixture I has one binary azeotrop with minimum boiling point temperature in M-T system and one tangential azeotrop in M-P system near the point of pure P. Mixture II has one binary azeotrop with maximum boiling point temperature in A-C system. Mixture III has one binary azeotrop with minimum boiling point temperature in Bu-Eb system.

The influence of extractive agent was examined on the relative volatility of azeotrop formed components pairs. The locations of different α-varieties were calculated for mixtures I and III, the data[17] was used for α-varieties in mixture II. The vapor-liquid equilibriums were described for the II and the III systems by NRTL and for the I system by UNIFAC models. The models adequacies were estimated by experimental and calculated data comparison.

The possible three columns distillation flowsheets were constructed for separation of each mixture[12] (fig. 1). On the base of those flowsheets (preimages) the PTCC flowsheets were created[13] (fig.2).

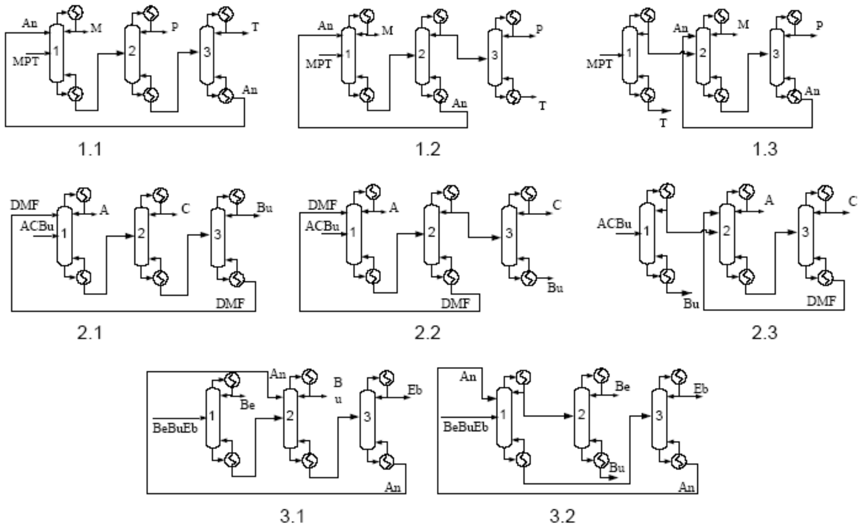


Fig.1 Flowsheets of two-withdraws columns (preimages) for ED separation of: M-P-T mixture with aniline as entrainer (1.1,1.2,1.3); A-C-Bu mixture with DMF as entrainer (2.1,2.2,2.3); Be-Bu-Eb mixture with aniline as entrainer (3.1,3.2)

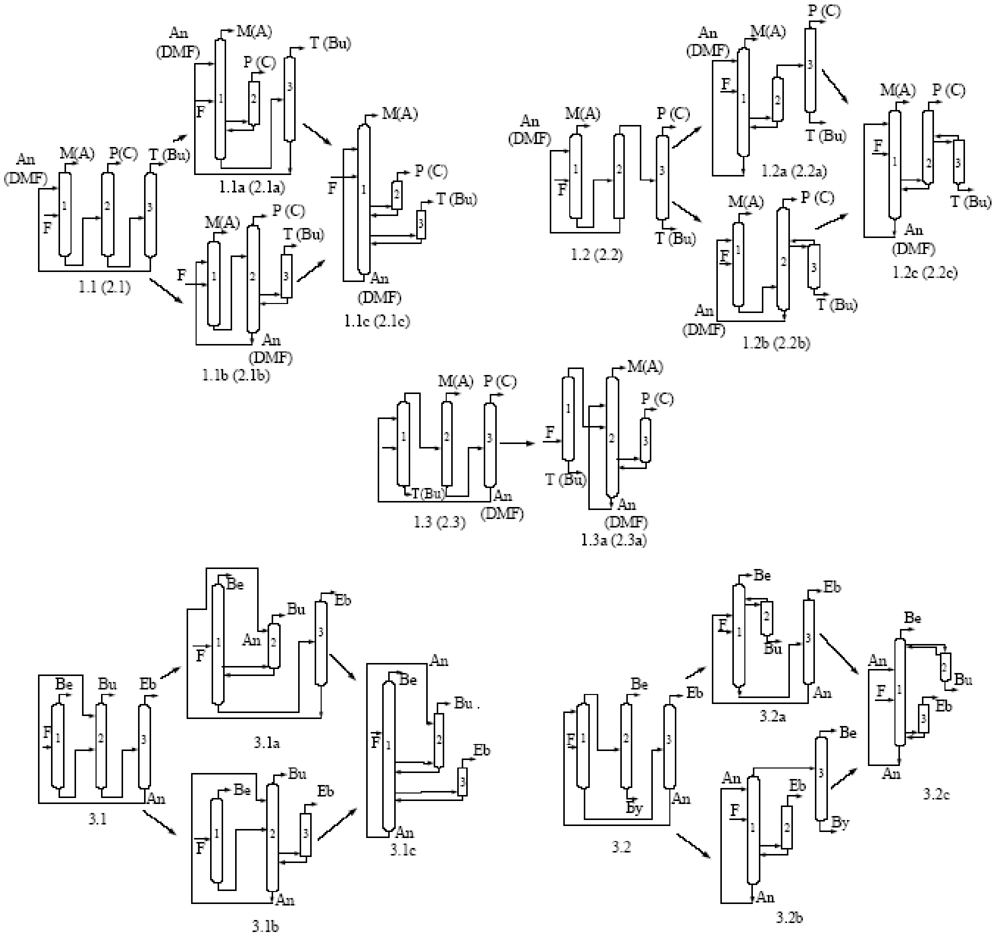


Fig.2 Extractive distillation flowsheets of two-withdraws columns (1.1,1.2,1.3, 2.1, 2.2, 2.3, 3.1, 3.2); two-columns PTCC flowsheets have index (a) or (b) and preimage number; one-column PTCC flowsheets have index (c) and preimage number.

Eight points were selected in each simplex of initial feed composition. Those points allocate the region in the initial feed composition simplexes with boundaries x_i=10% mol. All flowsheets for each of 8 points of initial feed composition were optimized on the criteria of minimum sum of energy consumption at the columns boilers. The initial feed has the boiling point temperature at 1 kg/cm^2 abs. pressure and flow rate equal 100 kmol/h. The products quality were fixed and equal 99.5% mol. for M, A, C, Bu; 99.0 mol. for Be, Eb; 98.5% mol. for P and T; 99.9% mol. for regenerated entrainer. The sum of the theoretical plates was fixed at all flowsheets for specific mixture separation. Optimization parameters for classic ED columns were the initial feed and entrainer feed plates location, the temperature and flow rate of the entrainer. Optimization parameter for entrainer regenerator was the initial feed plate location. For PTCC optimization parameters were the initial feed and entrainer feed plates location, the temperature and flow rate of the entrainer, the streams to and from side column locations and flow rates.

3. Results and discussion

M-P-T, A-C-Bu, Be-Bu-Eb mixtures separation by ED may be organized at various flowsheets (fig.2). The energy consumption values were estimated during optimization procedure for each points of initial feed composition and every possible flowsheets. We analyzed the energy consumption changes by initial feed composition variation at secants and cuts of concentration simplex. One example is presented on fig. 3. Then the scalar functions of energy consumption for each ED flowsheet was constructed under the vector field of initial feed compositions by data interpolation of energy consumption. One example is presented on fig.4. If for each point of the initial feed compositions select minimum energy consumption for all compared flowsheets and then map received piecewise surface in the initial feed compositions simplex, it would be divided into some subsets. Each of those subsets of optimality (SO) is characterized by single optimal distillation flowsheet [3,15]. It was detected that optimization criterion functions for all flowsheets are sufficiently smooth, almost monotonically increasing or decreasing and do not have extremes.

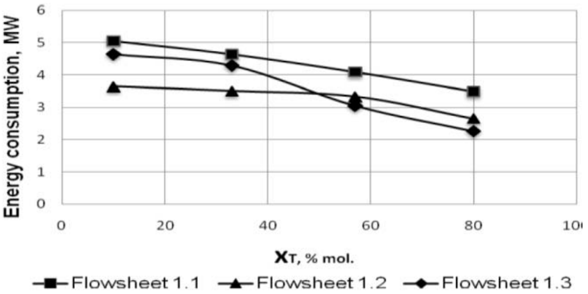


Fig. 3 Energy consumption of flowsheets 1.1, 1.2, 1.3 in the cut X_M = 10 % mol. as the function of toluene concentration.

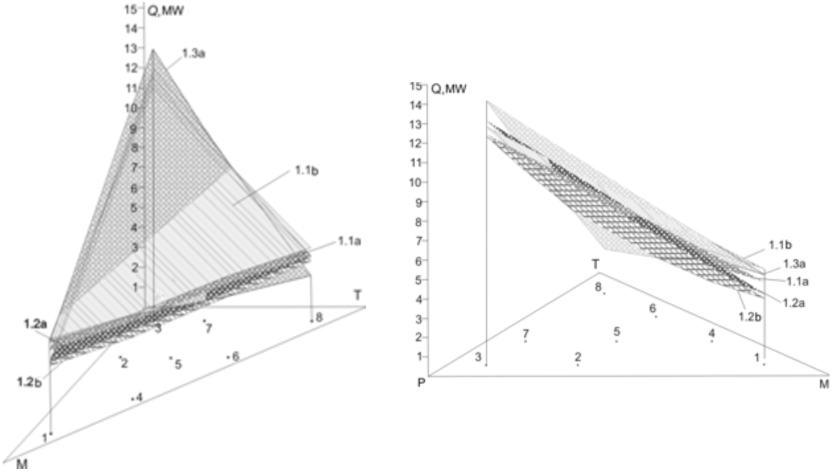
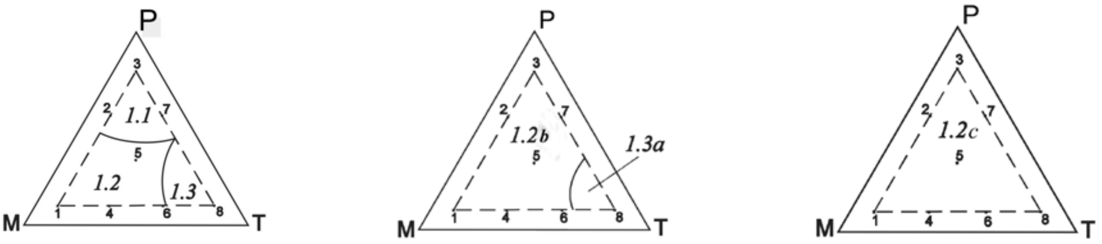


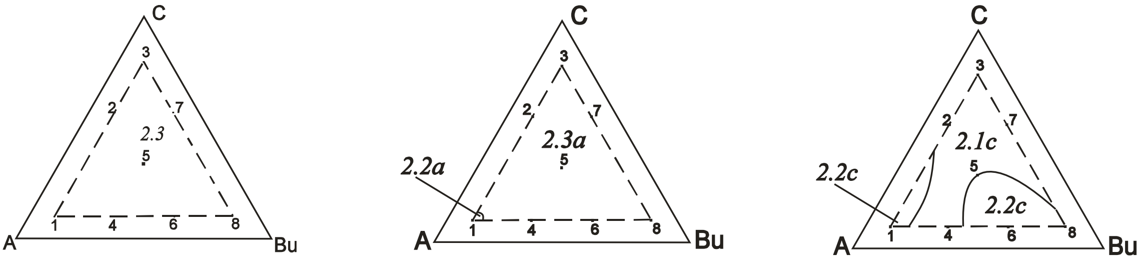
Fig. 4 Two views of the energy consumption surfaces for M-P-T extractive distillation at 1.1a, 1.1b, 1.2a, 1,2b, 1.3a flowsheets

The three SO were identify for M-P-T mixture extractive distillation at two-withdraws columns flowsheets (fig.5a), two SO for flowsheets consists of one simple and one complex column (fig. 5b) and only one SO for flowsheets consists of one complex column (fig.5c). The another data were obtained for A-C-Bu (fig. 6) and Be-Bu-Eb (fig. 7) mixtures separation.



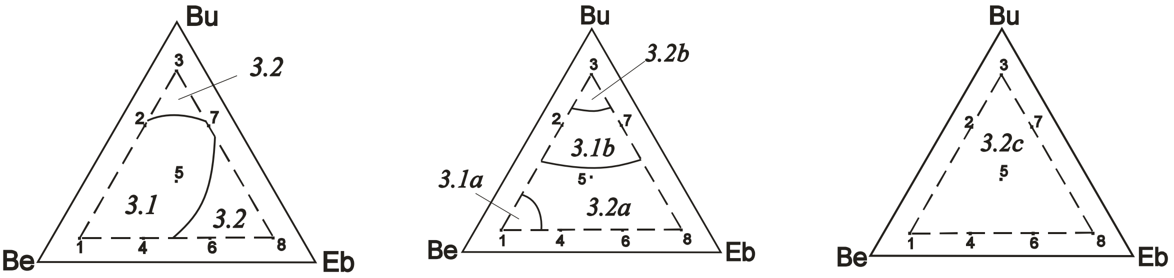
(a) (b) (c)

Fig. 5 The subset s of optimality for different classes of ED flowsheets for M-P-T mixture separation: flowsheets of two-withdraws columns (a); flowsheets consists of one simple and one complex column (b); flowsheets consists of one complex column (c).



(a) (b) (c)

Fig. 6 The subset s of optimality for different classes of ED flowsheets for A-C-Bu mixture separation: flowsheets of two-withdrawsl columns (a); flowsheets consists of one simple and one complex column (b); flowsheets consists of one complex column (c).



(a) (b) (c)

Fig. 7 The subset s of optimality for different classes of ED flowsheets for Be-Bu-Eb mixture separation: flowsheets of two-withdraws columns (a); flowsheets consists of one simple and one complex column (b); flowsheets consists of one complex column (c).

4. Conclusions

Generally, the PTCC flowsheets are better than traditional extractive distillation. The geometry and location of subsets of optimality are different for various mixtures. The number of SO may be equal or not equal to the number of flowsheets even at the single class of them. Sometimes all investigated manifold of initial feed composition is equal to the SO of unique flowsheet. Also we developed that the maximum of energy saving in the investigated field of initial feed compositions are about 14 % for mixture (I), more than 22% for mixture (II) and more than 36% for mixture (III). The best thermally coupled complex is better than the best three-column extractive distillation flowsheet. The thermally integration increasing leads to energy consumption decreasing.

Acknowledgements

We are grateful to our teacher professor L.Serafimov for discussion and useful consultations.
The part of this work was supported by the Russian Foundation for Basic Research. Grant # 08-08-00318.

References

1. N. Nishida G. Stephanopoulos and A.W. Westerberg, *AIChE J.,* 27(1981) 321-338.
2. A.W. Westerberg and O.Wahnschafft, *Adv. in Chem. Eng.*, 23(1996) 63-246.
3. J.G. Stichlmair and J.R. Fair, *Distillation: principles and practice*, Wiley-VCH (1998).
4. Serafimov L.A. et.al. *Theoretical Foundations of Chemical Eng.*, 27(1993) 292-299 (in russ.).
5. A. V. Timoshenko and L. A. Serafimov, *Theoretical Foundations of Chem. Eng.,* 35(2001) 567-572
6. S. Domenech et.al., *The Chem. Eng. J.*, 45(1991) 149-164.
7. F. B Petlyuk, V. M. Platonov and D. M. Slavinskii, *Int. Chem. Eng.,* 5 (1965) 555–561
8. R.Agrawal, *Trans. IChemE*, 78(2000) 454-464
9. R. Agrawal, *AIChE J.,* 49(2003) 379-401
10. B.-G.Rong and I. A Turunen, *Chem.Eng.Res. and Design*, 84(2006) 1095-1116.
11. L. A. Serafimov and A. K. Frolkova*, Theoretical Foundations of Chem. Eng*., 31(1997) 159-166.
12. L. V. Ivanova, et.al., *Theoretical Foundations of Chem. Eng.,*39(2005) 16-23
13. A. V. Timoshenko et.al**,** *Theoretical Foundations of Chem. Eng.,* 41(2007) 845-850
14. A. Timoshenko, E. Anokhina and V. Timofeev, *Russia Patent,* N2207896, (2003).
15. D.W.Tedder and D.F. Rudd, *AIChE J.,* 24(1978), 303-315.
16. O. D. Patkina, et.al., *Theoretical Foundations of Chem. Eng.,* 34(2000) 39-45
17. A.K. Frolkova, Dr. Sci. Thesis, MITHT, (2002) (in Russian)