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RESEARCH ARTICLE

Features of distillation separation of multicomponent mixtures

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Abstract

Objectives. *To improve the process of developing energy-efficient flowsheets for the distillation separation of multicomponent aqueous and organic mixtures based on a comprehensive study of the phase diagram structures, including those in the presence of additional selective substances.*
Methods. *Thermodynamic-topological analysis of phase diagrams; modeling of phase equilibria in the AspenTech software package using the equations of local compositions: Non-Random Two Liquid and Wilson; computational experiment to determine the column parameters for separation flowsheets of model and real mixtures of various nature.*
Results. *The fractionation conditions of the origin multicomponent mixture due to the use of sharp distillation, pre-splitting process, extractive distillation with individual and binary separating agents were revealed. The columns operation parameters and the energy consumption of the separation flowsheets ensuring the achievement of the required product quality with minimal energy consumption were determined.*
Conclusions. *Using the original methods developed by the authors earlier and based on the generalization of the results obtained, new approaches to the synthesis of energy-efficient multicomponent mixtures separation flowsheets were proposed. The provisions that form the methodological basis for the development of flowsheets for the separation of multicomponent mixtures and supplement the standard flowsheet synthesis plan with new procedures were formulated.*

Keywords: *distillation, technological flowsheet, phase diagram structure, separatrix manifold, extractive distillation*

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НАУЧНАЯ СТАТЬЯ

Особенности ректификационного разделения многокомпонентных смесей

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Аннотация

Цели. *Совершенствование процесса разработки энергоэффективных схем ректификационного разделения многокомпонентных водных и органических смесей на основе комплексного исследования структуры фазовой диаграммы, в том числе в присутствии селективных дополнительных веществ.*
Методы. *Термодинамико-топологический анализ фазовых диаграмм; моделирование фазовых равновесий в программном комплексе AspenTech с использованием уравнений локальных составов Non-Random Two Liquid, Вильсона; вычислительный эксперимент по определению параметров работы колонн схем разделения модельных и реальных смесей разной природы.*
Результаты. *Выявлены условия фракционирования исходной многокомпонентной смеси за счет использования промежуточного заданного разделения, предварительного расслаивания, экстрактивной ректификации с индивидуальными и бинарными разделяющими агентами. Определены параметры работы колонн и энергозатраты схем разделения, обеспечивающие достижение требуемого качества продуктов при минимальных энергозатратах.*
Выводы. *С использованием разработанных ранее авторами оригинальных методик и на основе обобщения полученных результатов предложены новые подходы к синтезу энергоэффективных схем разделения многокомпонентных смесей. Сформулированы положения, которые составляют методологическую основу разработки принципиальных схем разделения многокомпонентных смесей и дополняют типовой план синтеза схем новыми процедурами.*

Ключевые слова: *ректификация, технологическая схема, структура фазовой диаграммы, сепаратрическое многообразие, экстрактивная ректификация*

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INTRODUCTION

The development of technology for the production and isolation of organic substances is a complex scientific and technical task. The specificity of its solution is due to the complexity of the resulting mixtures, the nonlinearity of the dependencies of the mixture properties on the composition, and the presence of alternative process structuring options. One of the key problems is the polyvariance of technological solutions at each of the stages (chemical transformation and separation stages) of technology development (Fig. 1) [1–4].

The most energy-consuming processes in organic petrochemical synthesis technologies and in related industries are the processes of distillation separation of mixtures aimed at isolating required quality products, unreacted raw materials, additional substances, etc.

Figure 2 shows a flowchart describing the relationship between the various stages of the separation flowsheet synthesis procedure.

The determining role is assigned to the mixture physicochemical properties study, which determine the structure of the phase equilibrium diagram (SPED)

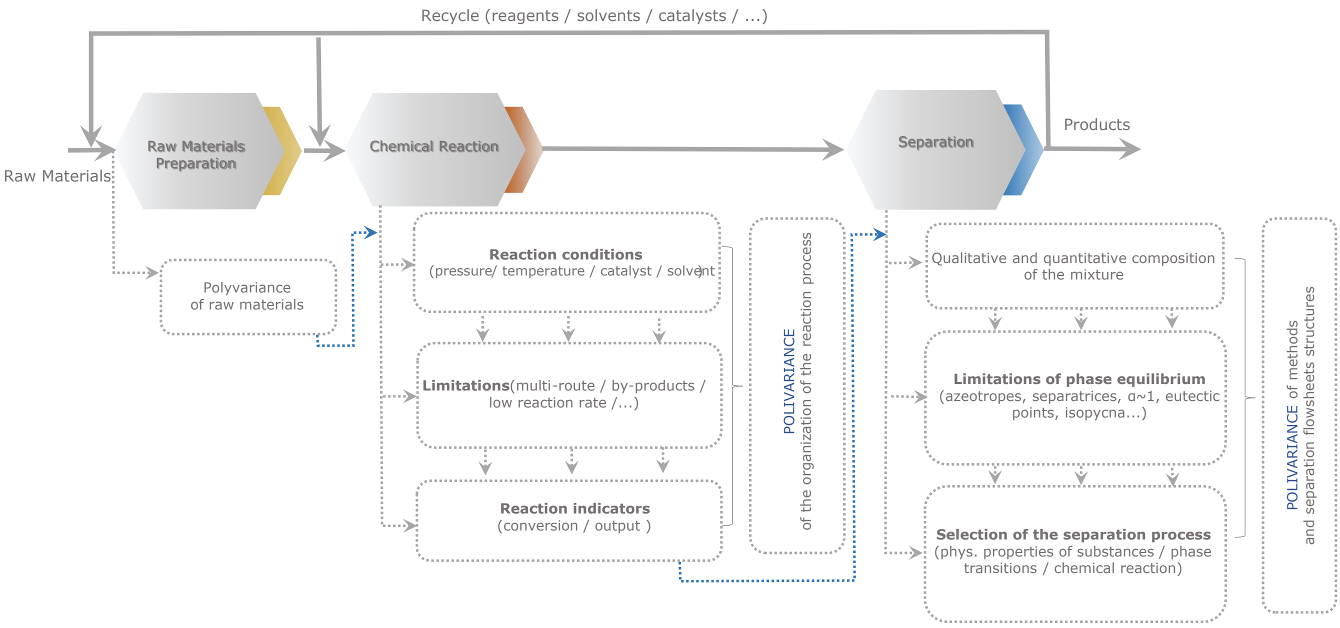


Fig. 1. Main stages of the organic compound production technology development.

(liquid–vapor, liquid–liquid, liquid–liquid–vapor). Data on the diagram structure and the system behavior when external parameters change (for example, pressure) underlie the choice of separation methods that can potentially be used in the flowsheets. Further, possible separation flowsheets are synthesized, and the structure of the latter directly depends on the belonging of the point of composition of the mixture to the specific distillation subregion (or splitting area) in the diagram. Moreover, the process from which separation begins is selected (conventional distillation, splitting, addition of separating agents (SA), etc.). For multicomponent mixtures, essentially, we are talking about methods of its fractionation—separation into parts containing fewer components, which allow us to use a large amount of accumulated information about the separation features of binary and triple systems.

At the next stage, it is possible to discriminate between individual options, for example, by the number of devices in the flowsheet, the limitations inherent in a particular method or separation mode. In this case, qualitative criteria and heuristic rules are used for the formation of a set of alternative

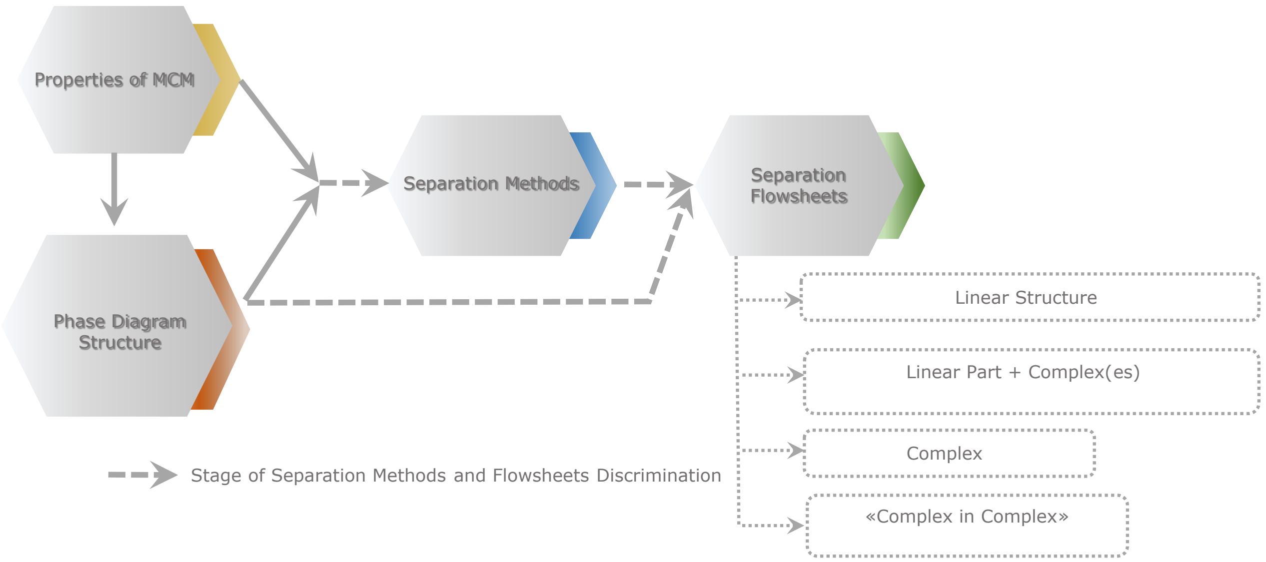


Fig. 2. Flowchart of the procedure for the synthesis of technological distillation flowsheets.

flowsheets that are subject to comparison by the selected criterion. These flowsheets can have a linear structure (a direct sequence of devices) or contain separation complexes as elements [5–7]. A characteristic feature of separation complexes is the presence of reverse (recycle) flows. There are virtually no qualitative criteria for screening flowsheets at this stage. According to the results of work [6], preference should be given to a simpler variant in structure (without feedbacks or with a minimum number of recycling flows). The final choice of the separation flowsheet is carried out only after simulating the processes and determining the device design and operating parameters (parametric optimization stage).

This algorithm in an enlarged form reflects a typical plan for the synthesis of basic technological distillation flowsheets (TDFS) [3], forms the basis of engineering research and has powerful information support in the form of modern software systems based on phase equilibria and processes mathematical modeling methods and on the use of extensive databases of physicochemical, thermodynamic data, and model parameters. The scientific and technical literature predominantly presents studies of binary and ternary mixtures [8–16], less often quaternary mixtures [17–21]. Review works [22, 23] are also devoted to the separation of binary and ternary mixtures, in particular, extractive distillation (ED). At the same time, quite a few multicomponent systems with internal azeotropes have been found [24–30].

The information presented in the appendices to [5] partially reflects the existing picture of the study of systems containing a different number of components (Table 1).

Usually, one method of separating a specific composition mixture and a fixed structure flowsheet is proposed, which is subject to parametric optimization. In rare cases, alternative separation methods and all possible separation flowsheet structures are considered. Since distillation is the main method for separation in large-scale production of basic organic and petrochemical synthesis in related industries, we will consider this method in the future, which, despite its energy intensity, dominates in modern chemical technologies. The development of fundamental TDFS is based on the achievements of the scientific school of Professor L.A. Serafimov, created at the M.V. Lomonosov Moscow State Academy of Fine Chemical Technology in the 1960s and 1970s and has not lost the relevance of his research at the present time.

The synthesis of a TDFS set is based on the thermodynamic-topological analysis of the SPED [1, 3], the principle of redistribution of composition fields between separation areas [3, 5], the already mentioned standard plan containing the stages and procedures for the development of possible TDFS. This work is devoted to improving the procedures for developing and creating energy-efficient flowsheets for the distillation separation of multicomponent aqueous and organic mixtures based on a comprehensive study of the initial system phase diagram structure, as well as the properties of derived systems containing selective additional substances (SA). The choice of complex *n*-component systems as objects (where *n* takes values of 4 and higher) dictates the need to create new methods for studying multidimensional phase diagrams and the use of complex structure flowsheets representing a combination of a linear part and complexes with recycling flows, several functional complexes, and complexes in a complex.

Multicomponent systems (MCS), on the one hand, are closest in their properties to real

Table 1. Ratios of the number of publications devoted to the separation of mixtures with different numbers of components (based on materials [5])

Number of components in mixture	Number of systems studied	Number of separation variants suggested
2	70 (48.3%)	187 (72.5%)
3	43 (29.7%)	37 (14.3%)
≥ 4	32 (22.0%)	34 (13.2%)
Total	145 (100%)	258 (100%)

mixtures formed at different chemical production stages, which increases the practical value of the recommendations being developed. On the other hand, the MCS phase diagrams and their thermodynamic transformations have a number of features that distinguish them into a MCS class, which is determined by the composition space multidimensionality. It can be stated [31–33] that ternary mixtures occupy an intermediate position between binary and quaternary ones and in some cases it is impossible to extend the known laws of constructing phase diagrams of ternary systems to systems with a large number of components. This is confirmed by the new approaches to the study of the internal space of composition simplices of four- and five-component systems, developed by us [32]. A technique for studying the internal space of phase diagrams of *n*-component systems based on the analysis of the simplex two-dimensional boundary space structure was created. This technique has been successfully tested on the example of fifteen quaternary and four five-component systems containing substances of different classes and characterized by different complexity of phase behavior: the presence of azeotropes of different compositions and types, including those five with internal singular points. In particular, previously unknown quaternary azeotropes have been predicted in the ethyl acetate–ethanol–hexane–water and ethanol–chloroform–cyclohexane–water systems. In the latter, the presence of azeotrope is confirmed by our own field experiment. Using the example of the acetone–methyl acetate–chloroform–cis-dichloroethylene system, the specificity of the formation of a two-dimensional separatrix in a tetrahedron in the absence of a closed contour on a two-dimensional scan of the simplex is shown: some of the boundary elements of the separatrix coincide with the edges of the tetrahedron.

The study of the evolution of vapor–liquid equilibrium (VLE) diagrams of acetone–chloroform–ethanol–water systems (appearance/disappearance of a quaternary azeotrope of the saddle type, ternary nodal azeotrope) and chloroform–ethanol–cyclohexane–water systems (appearance/disappearance of a quaternary azeotrope of the node type) [34] demonstrates the possibilities of directional transformation of phase diagram structures with varying pressure and the creation of more favorable conditions for the separation of complex mixtures.

This article provides an overview of the authors' current work, as well as presents new results that illustrate certain provisions of the methodology for the synthesis of basic TDFS mixtures containing four or more components.

RESULTS AND DISCUSSION

The study of the problem of separation of complex chemically inert multicomponent mixtures allows us to identify a number of fundamental points that complement to varying degrees the algorithm for the synthesis of flowsheets described in [3]. Most of the systems considered contain components, including homologues belonging to different classes of organic compounds, and water. These systems are characterized by the presence of azeotropes of different composition, separatric manifolds of different structures (simplex, complex), and regions of two- and three-phase splitting. With a complex structure of the phase diagram, the elements of the TDFS most often are not single columns, but separation functional complexes based on one or different special separation techniques [1, 3, 5].

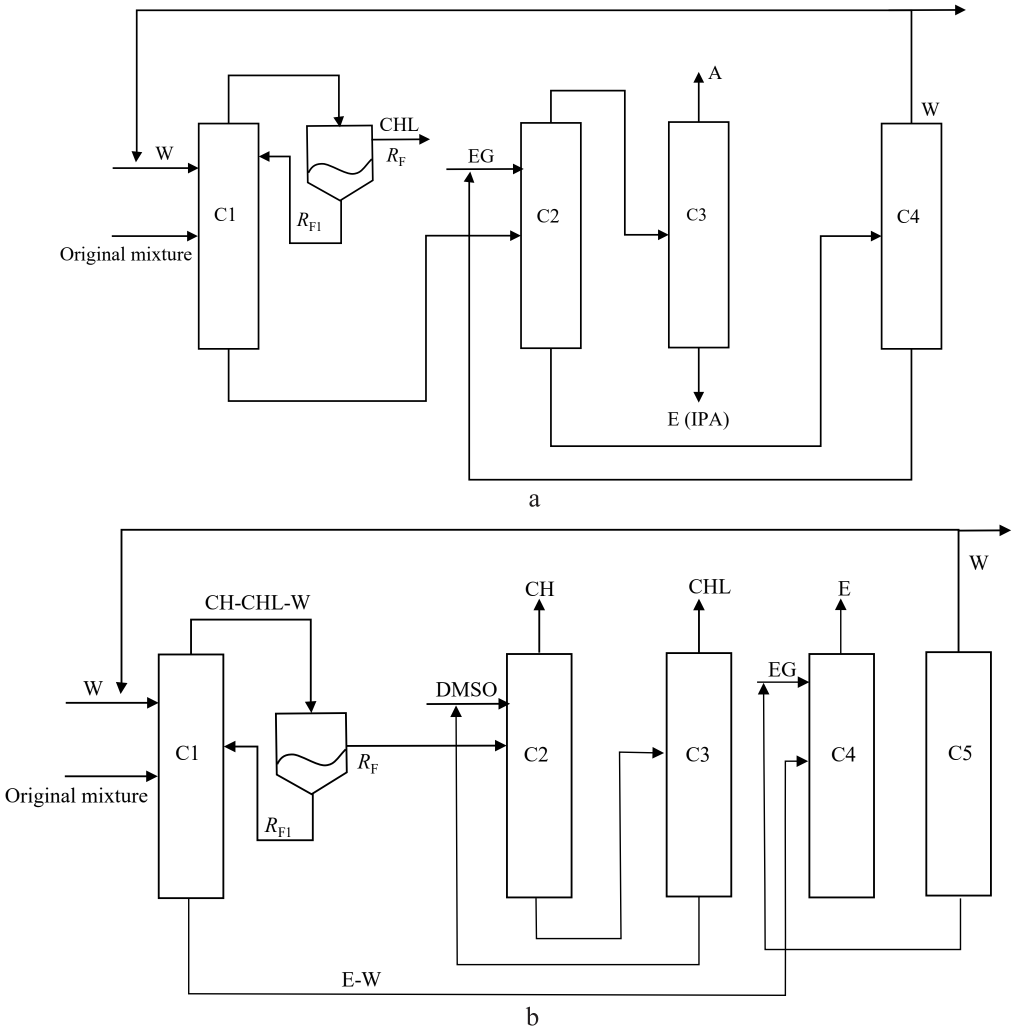
For the separation of mixtures of different compositions belonging to different distillation regions, a promising technique is the fractionation of the initial multicomponent mixture already at the first stage (in the first apparatus of the flowsheet). We have considered the following methods of fractionation of initial mixtures: 1) organizing an sharp distillation (absence of components distributed between distillate and bottom products) [35–39]; 2) preliminary splitting the mixture (in the case of a favorable arrangement of liquid–liquid tie-lines, which allows obtaining compositions of equilibrium layers in different regions of distillation); 3) use of ED in the presence of SA, selective with respect to the group of initial components [40, 41].

The possibility of implementing these MCS fractionating methods depends on the specifics of the system phase behavior and the initial mixture composition. The use of the sharp distillation at the first distillation stage is limited to system classes in which there are no internal separating surfaces, as well as areas of compositions of the initial mixture favorable for such separation [35]. This type of fractionation has shown its advantage over the modes of the direct and indirect sequences in the industrial mixtures separation flowsheets for the production of cyclohexanone [42, 43], methyl isobutyl ketone [36], and acetic anhydride [37, 38], as well as in the various solvents regeneration processes [36, 37].

The use of preliminary fractionation due to the mixture splitting is associated with the liquid–liquid and liquid–vapor equilibrium peculiarities. The use of this technique is advisable if, as a result of separation, one or more components are almost in full in one of the equilibrium layers. The mutual arrangement of separating manifolds and splitting simplices plays an important role. As an example, the separation of a mixture of solvents water–cyclohexanone–dichloroethane–butanol-1–dimethylformamide can be given here [20]. Water forms azeotropes with almost all components, however, when splitting the mixture of the composition supplied for separation, this component is present in the organic layer in impurity quantities that do not affect further separation. The mixture is separated in conventional distillation columns, with the exception of a cyclohexanone–dimethylformamide pair forming a positive azeotrope.

The use of SA, selective with respect to a group of components in the ED process or forming a heteroazeotrope with a group of components in heteroazeotropic (extractive-heteroazeotropic) distillation, is also an effective mixture fractionation method. It is advisable to use this technique when none of the listed above methods can be implemented. Most often, this situation is observed for systems characterized by a complex structure of the VLE diagram. The presence of water in the initial mixture, which increases the volatility of some components relative to others, allows it to be used as a solvent for the (auto)extractive, heteroazeotropic or extractive-heteroazeotropic distillation process [44–47]. Figure 3 shows the separation flowsheets of a number of mixtures listed above, and Table 2 shows the static parameters of the columns and energy consumption in the columns and flowsheets.

If the size and localization of the splitting area in a quaternary system does not allow isolating all the components in flowsheets combining distillation and liquid splitting, then it is possible to apply an ED of an aqueous mixture with a specially selected SA. This SA should be selective with respect to azeotrope-forming components, and its introduction does not increase the splitting area in the derivative system separable mixture + SA [40]. An example is the ED of a mixture of methanol (M)–*tert*-butyl alcohol (TBA)–methyl *tert*-butyl ether (MTBE)–water (W), the phase diagram of which is characterized by the presence of three azeotropes and a separatric manifold (Fig. 4). The separation of the M–TBA–MTBE–W mixture is proposed to be carried out in a flowsheet consisting of two-column ED complexes and a distillation column (Fig. 5).



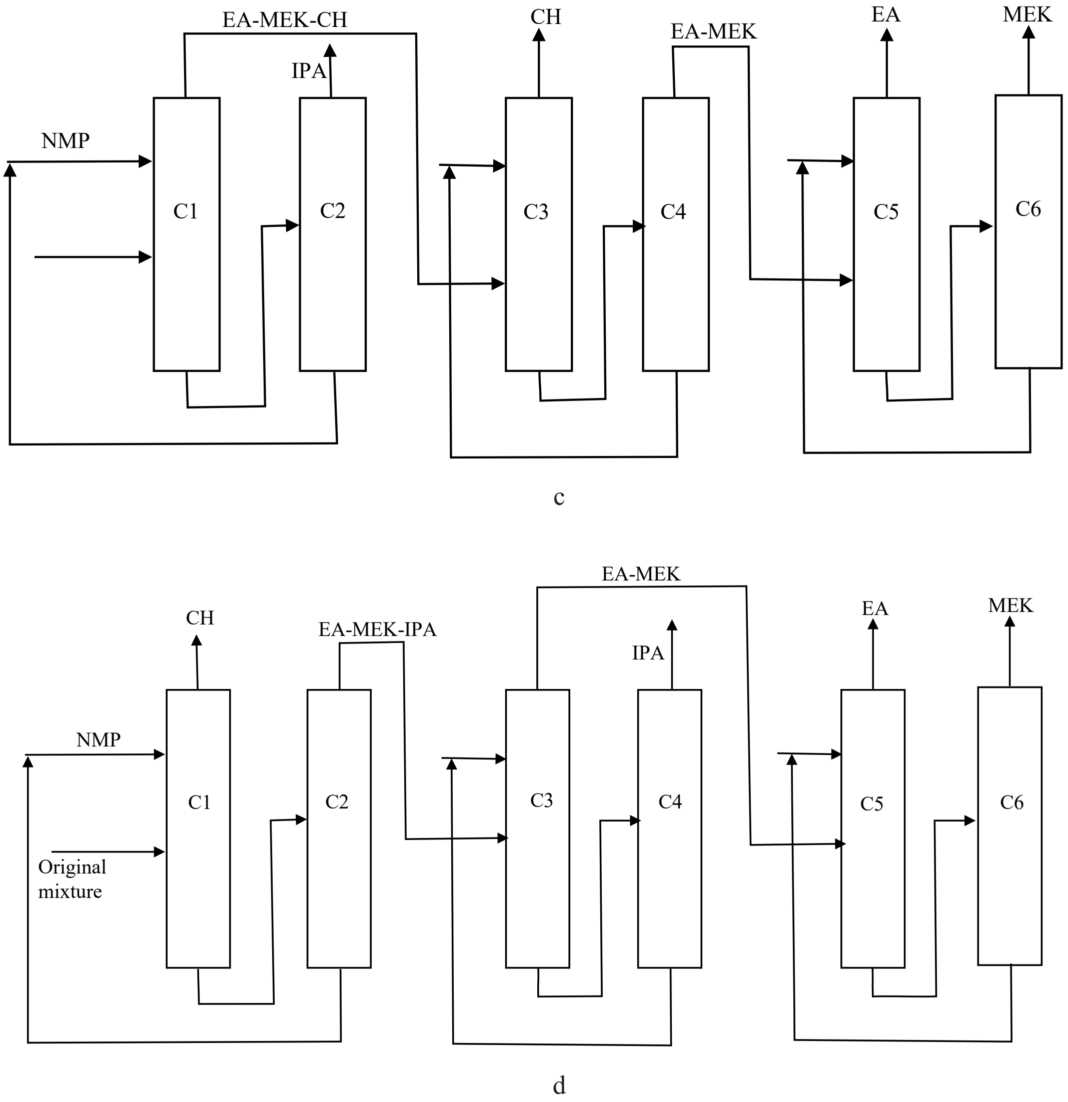


Fig. 3. Separation flowsheets for mixtures: (a) acetone (A)–chloroform (CHL)–ethanol (E) (isopropanol (IPA))–water (W);
(b) chloroform (CHL)–ethanol (E)–cyclohexane (CH)–water (W);
(c)–(d) ethyl acetate (EA)–methyl ethyl ketone (MEK)–cyclohexane (CH)–isopropanol (IPA) (EG is ethylene glycol, DMSO is dimethyl sulfoxide, NMP is *N*-methylpyrrolidone. C1–C6 are distillation columns;
R_{f1} and R_f are flows of equilibrium liquid phases from the decanter).

When separating quaternary systems containing more than three binary azeotropes, it is possible to use different agents at different stages of ED separation [40, 41]. For ED ternary aqueous mixtures of organic solvents, it is usually recommended to use dimethyl sulfoxide (DMSO), glycerin, or diols [48–53]. For the separation of a mixture of methanol (M)–*tert*-butyl alcohol (TBA)–methyl *tert*-butyl ether (MTBE)–water (W) industrial solvents, DMSO, and ethylene glycol (EG) are considered. The flowsheet shown in Fig. 5 provides for the introduction of a single DMSO or EG agent into the ED columns (columns C1, C4), as well as the use of these agents in different ED columns.

The component separation sequence in the flowsheet is determined by the nature of the SA's effect on the relative volatility of substances in the derived five-component system. According to the data of the M(1)–MTBE(2)–TBA(3)–W(4)-SA VLE systems, the relative volatility of the α_{ij} components was calculated at 101.32 kPa, depending on the amounts of injected SA. In the presence of both agents, concentration of the organic solvents mixture in the distillate of the ED column is predicted. For example, when the flow rate is $F{:}F_{SA}$ = 1:1 (kmol/kmol) we have the ratio of values α_{ij}: α_{12} (0.95) < α_{34} (1.2) < α_{13} (3.0) < α_{23} (3.2) < α_{14} (3.8) < α_{24} (4.0), for EG, and α_{12} (0.55) < α_{13} (1.2) < α_{34} (2.5) < α_{23} (2.8) < < α_{14} (3.0) < α_{24} (6.8), for DMSO. An increase in the

Table 2. Operation parameters and energy consumption (Q) of the distillation columns for the flowsheets presented in Fig. 3 (the amount of the original mixture is 100 kmol/h, the original composition of the mixture corresponds to the azeotropic, for the chloroform–ethanol–cyclohexane –water system, an equimolar composition was analyzed)

Column (P^*, kPa)	Stages number	$\mathrm{FS}_{\mathrm{orig(SA)}}$**	R***	Q, kW	Column (P^*, kPa)	Stages number	$\mathrm{FS}_{\mathrm{orig(SA)}}$**	R***	Q, kW
Flowsheet (a) in Fig. 3 for a system with ethanol, the SA amount in C1 (water) is 180 kmol/h; in C2 (ethylene glycol) – 100 kmol/h					Flowsheet (a) in Fig. 3 for a system with isopropyl alcohol, the SA amount in C1 (water) is 180 kmol/h; in C2 (ethylene glycol) – 100 kmol/h				
C1	30	19 (9)	0.9	488.6	C1	30	16 (10)	0.8	489.4
C2	20	12 (3)	0.5	1172.3	C2	20	17 (5)	2.8	2081.3
C3	35	23	8.6	4262.7	C3	25	16	6.6	2403.0
C4	7	4	0.1	2849.1	C4	7	4	0.2	2848.5
Total energy consumption				8772.7	Total energy consumption				7821.9
Flowsheet (b) in Fig. 3: the SA amount in C1 (water) is 110 kmol/h; in C2 (DMSO) – 70 kmol/h; in C4 (ethylene glycol) – 170 kmol/h									
C1	10	7 (3)	0.2	512.1	C4	16	10 (3)	0.6	869.9
C2	14	8 (4)	0.4	469.5	C5	13	6	0.4	2704.2
C3	11	5	0.4	466.2	Total energy consumption				5021.9
Flowsheet (c) in Fig. 3: the SA amount (*N*-methylpyrrolidone) in C1 is 300 kmol/h; in C3 – 194 kmol/h (cyclohexanol); in C5 – 57.93 kmol/h					Flowsheet (d) in Fig. 3: the SA amount (*N*-methylpyrrolidone) in C1 is 200 kmol/h; in C3 – 212.7 kmol/h (cyclohexanol); in C5 – 57.93 kmol/h				
C1 (50)	30	19 (5)	1.4	2327.6	C1	29	16 (5)	1.6	2685.4
C2	16	5	0.8	2050.5	C2	15	6	1.0	962.7
C3 (50)	20	11 (3)	3.9	1793.5	C3 (50)	37	26 (5)	1.2	1791.0
C4	13	5	0.7	1199.8	C4	12	5	0.8	1173.9
C5 (50)	29	14 (6)	0.4	324.6	C5 (50)	29	14 (6)	0.4	324.6
C6	17	8	0.6	408.5	C6	17	8	0.6	408.5
Total energy consumption				8104.5	Total energy consumption				6046.1

* The pressure in the columns is 101.32 kPa, except for the values given in parentheses;

** $\mathrm{FS}_{\mathrm{orig(SA)}}$ is a feed stage of original mixture (separating agent);

*** Reflux ratio.

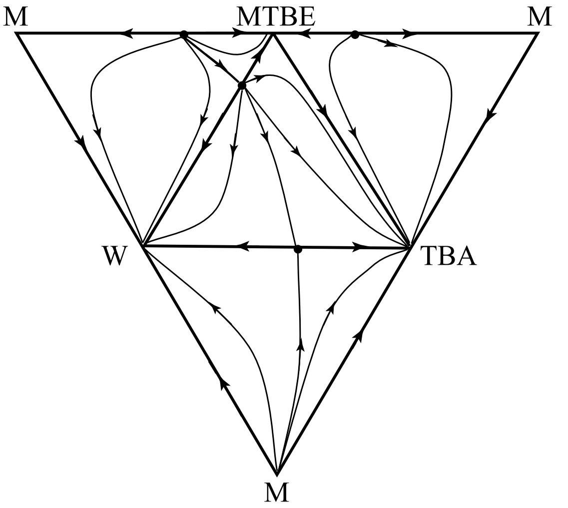


Fig. 4. Phase diagram of methanol (M)–*tert*-butyl alcohol (TBA)–methyl-*tert*-butyl ether (MTBE)–water (W) system at atmospheric pressure.

consumption of agents affects α_{ij} differently: in the case of EG, α_{12}, α_{34} increase and α_{23}, α_{24} decrease, and the values of α_{13} and α_{14} increase to $F{:}F_{SA} \approx 1{:}1$ and then go down. In the case of DMSO, a similar effect is observed for other pairs of components: α_{12}, α_{14}, and α_{34} increase, α_{13} and α_{23} decrease, and α_{24} first increases, then decreases. The complex nature of the influence of agents on α_{ij} leads to inversions of the relative volatility of the components when the flow rate of agents changes. The purpose of the ED of the quaternary mixture is the dehydration of organic solvents, achieved at different costs of EG and DMSO (Tables 3–6).

Then, ED is used to separate the azeotropic M−MTBE mixture (column C4, Fig. 5). With the introduction of EG, methanol is predicted to be obtained in the distillate of the ED column, and MTBE—in the case of DMSO introduction. For the ratio $F{:}F_{SA} = 1{:}1$ (kmol/kmol), the relative volatility values are: $\alpha_{12} = 1.4$ for EG and $\alpha_{21} = 2.3$ for DMSO.

Since both EG and DMSO can be used in ED, it is possible to compare four variants of ED, differing in sets of agents for columns C1 and C4: 1) EG, EG, 2) DMSO, DMSO, 3) EG, DMSO, and 4) DMSO, EG. The calculation results of static parameters for the operation of the flowsheet columns necessary for this comparison are given in Tables 3–6. Accepted designations of the parameters of the columns: N is the total efficiency, theoretical stages (t.s.); N_F/N_{SA} are the numbers of the stages of the feed of the initial mixture and SA, respectively, t.s.; R is the reflux ratio; F_{SA} is the amount of SA, kmol/h; Q is the energy consumption in the column boilers, MW; t_D and t_w are the temperatures of the distillate and the bottom product, respectively, °C. The total energy consumption for separation (the duty of the column boilers) and the total number of theoretical stages in the distillation columns of the ED flowsheet, given in Table 7, show that the separation of the M–TBA−MTBE–W mixture can be carried out with a single agent—DMSO.

In general, based on the analysis of the SPED of four- and five-component systems and the assessment of the effect of SA on the relative volatility of the azeotropic components of the MCS, basic technological flowsheets for separating mixtures have been developed and static parameters of the apparatus operation have been determined (column efficiency,

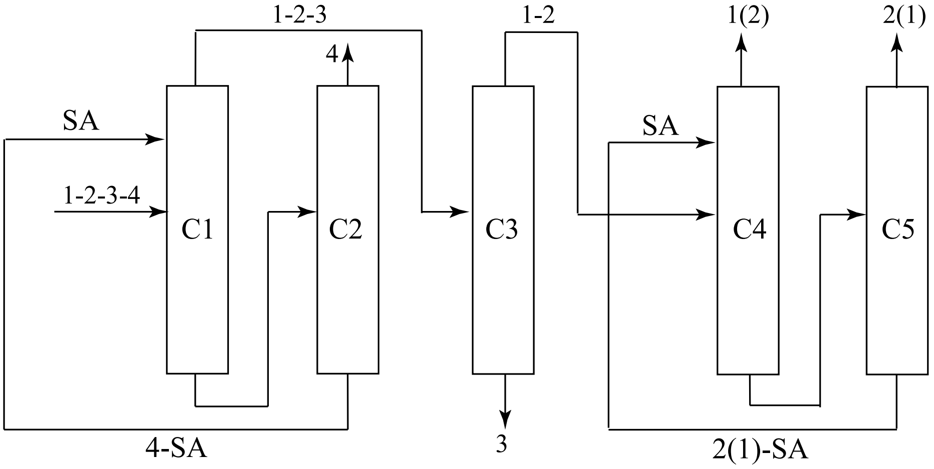


Fig. 5. Principal technological flowsheet for the M (1)–MTBE (2)–TBA (3)–W (4) mixture separation with dimethylsulfoxide or ethylene glycol as SA: C1 and C4 are the ED columns, C2 and C5 are the SA recovery columns, and C3 is the TBA isolation column.

Table 3. Column operation parameters and separation results for ED flowsheet with ethylene glycol

Col.	P, kPa	F_{SA}	N	N_F/N_{SA}	R	Distillate composition, mol. fr.					Bottom composition, mol. fr.					Q, MW	t_D, °C	t_w, °C
						M	W	MTBE	TBA	SA	M	W	MTBE	TBA	SA			
1	101.32	375	50	41/4	1.35	0.50	0.0005	0.25	0.2495	–	–	0.05	–	0.0001	0.949	3.57	60.3	178.3
2	101.32	–	20	–	2.8	–	0.998	–	0.002	–	0.0001	–	–	–	0.9999	1.20	97.6	–
3	101.32	–	40	–	4	0.666	0.002	0.33	0.002	–	0.0025	0.0005	–	0.997	–	2.79	53.15	82.45
4	101.32	350	52	29/4	4.9	0.9967	–	0.0033	–	–	–	–	0.054	–	0.946	4.28	64.3	170.2
5	101.32	–	20	–	5	0.0046	0.0018	0.993	0.0006	–	–	0.0001	–	–	0.9999	1.27	54.7	197.1

Table 4. Column operation parameters and separation results for ED flowsheet with dimethylsulfoxide

Col.	P, kPa	F_{SA}	N	N_F/N_{SA}	R	Distillate composition, mol. fr.					Bottom composition, mol. fr.					Q, MW	t_D, °C	t_w, °C
						M	W	MTBE	TBA	SA	M	W	MTBE	TBA	SA			
1	101.32	50	49	31/4	1.15	0.5	–	0.25	0.25	–	следы traces	0.286	–	–	0.714	1.24	60.35	148.6
2	80	–	15	–	3	0.0004	0.9996	–	–	–	–	–	–	–	0.9999	0.99	93.4	151.8
3	101.32	–	40	–	4	0.6664	0.0001	0.333	0.0005	–	0.0015	–	–	0.9985	–	2.79	53.15	82.8
4	101.32	130	37	28/3	4.4	0.006	–	0.994	–	–	0.0002	0.0001	0.0537	–	0.946	1.33	54.8	123.3
5	80	–	14	–	1	0.0043	0.0018	0.993	0.0009	–	0.0001	–	–	–	0.9999	1.13	58.4	181.8

Table 5. Column operation parameters and separation results for ED flowsheet with ethylene glycol and dimethylsulfoxide

Col.	P, kPa	F_{SA}	N	N_F/N_{SA}	R	Distillate composition, mol. fr.					Bottom composition, mol. fr.					Q, MW	t_D, °C	t_w, °C
						M	W	MTBE	TBA	SA	M	W	MTBE	TBA	SA			
1	101.32	375	50	41/4	1.35	0.5	0.0005	0.25	0.2495	–	–	0.05	0	0.001	0.949	3.57	60.3	178.3
2	101.32	–	20	–	2.8	–	0.998	–	0.002	–	–	–	–	–	0.9999	1.20	97.6	197.1
3	101.32	–	40	–	4	0.666	0.0006	0.3332	0.0002	–	0.0025	0.0001	–	0.997	–	2.79	53.15	82.45
4	101.32	130	37	28/3	4.4	0.006	–	0.994	–	–	0.234	–	0.0007	0.0002	0.7651	1.33	54.8	123.3
5	80	–	14	–	1	0.996	0.0001	0.0032	0.0007	–	0.0001	–	–	–	0.9999	1.13	58.4	151.8

Table 6. Column operation parameters and separation results for ED flowsheet with dimethylsulfoxide and ethylene glycol

Col.	P, kPa	F_{SA}	N	N_F/N_{SA}	R	Distillate composition, mol. fr.					Bottom composition, mol. fr.					Q, MW	t_D, °C	t_w, °C
						M	W	MTBE	TBA	SA	M	W	MTBE	TBA	SA			
1	101.32	50	49	34/4	1.15	0.5	–	0.25	0.25	–	0.0001	0.2859	–	–	0.714	1.24	60.35	148.6
2	80	–	15	–	3	0.0004	0.9996	–	–	–	–	–	–	0.0001	0.9999	0.99	93.4	151.8
3	101.32	–	40	–	4	0.666	0.0001	0.333	0.0005	–	0.0010	–	–	0.9990	–	2.79	53.15	82.5
4	101.32	350	52	29/4	4.9	0.9966	–	0.0034	–	–	0.0002	–	0.0537	–	0.946	4.28	64.3	170.2
5	101.32	–	20	–	5	0.004	0.001	0.993	0.0015	–	0.0001	–	–	–	0.9999	1.27	54.7	197.1

reflux ratios, feed level of the initial mixture and SA, and agent consumption), providing energy savings of up to 30% while ensuring the required product quality. Table 8 summarizes the studied systems and methods on which the separation flowsheet of mixtures of different compositions is based.

CONCLUSIONS

The revealed features of the formation of phase equilibrium diagrams and the peculiarities of the distillation separation of different complexity mixtures are used to improve the methodology of synthesis of separation flowsheets and the choice of energy-efficient separation modes of multicomponent mixtures.

The main methodology provisions relate to the following issues:

– to define the boundaries of the system under study and to form an experimental base (collecting background information, conducting a full-scale experiment) necessary to solve the task;

– to justify a choice of a phase equilibrium model and to obtain a set of model parameters reproducing the properties of the system with a relative error not exceeding 3–5%. In some cases, this range can be changed: when studying a system containing components with similar properties, the description accuracy should be increased to 1.0–1.5%; when modeling a system with more than two liquid phases, the relative error values may be 6–7%;

– to study the composition space of the phase diagram (to analyze the boundary space of the second dimension with determination of the number of nodal points (stable and unstable), saddle points (with nonzero Poincare index), the number of distillation regions, closed contours forming one-dimensional boundaries of the separating manifold of dimension ($n - 2$), and one-dimensional binodals; to determine the internal structure of the simplex (to predict the presence of an internal singular point, the structure of internal separatric hyper (surfaces), and the structure of splitting areas);

– to assess the possibility of using at the first stage special modes of distillation (direct and indirect sequences) or the MCS fractionation due to sharp distillation with favorable ratios of the coefficients of distribution of components between phases (the first apparatus is a column) or due to splitting (the first apparatus is a decanter). The implementation of these techniques is possible in the absence of internal separatric surfaces or a favorable mutual arrangement of binodal and separatric manifolds;

– when it is impossible to implement one of the listed above techniques, the special methods based on the addition of SA should been used. It is necessary to choose the SA (individual or binary) and predict separation products based on new techniques developed by the authors [31];

– to synthesize and structural optimize the flowsheets representing a combination of various functional complexes, in particular, several ED complexes with one or different agents;

Table 7. Comparison of ED flowsheets with different sets of agents

ED mode	Separating agent, kmol/h		ΣN, t.s.	ΣQ_i, $i = 1–5$, MW
	Column 1	Column 4		
Mode 1	375 EG	350 EG	182	13.11
Mode 2	50 DMSO	130 DMSO	155	7.47
Mode 3	50 DMSO	350 EG	176	10.58
Mode 4	375 EG	130 DMSO	161	10.01

Note: 100 kmol/h of M–TBA–MTBE–W mixture; DMSO is dimethyl sulfoxide, EG is ethylene glycol.

Table 8. Investigated multicomponent systems and methods of different composition mixtures separation

No.	System	Production	Separation flowsheet (method)	Lit.
1	Ethyl acetate–Benzene–Toluene–Butyl acetate	Mixture of solvents for biodegradable polymer production	Alternative variants (direct, indirect, sharp separation sequence)	[35, 37]
2	Acetone–Toluene–Butyl acetate–o-Xylene	Mixture of solvents for epoxy primer production	The advantage of sharp separation sequence in the first stage of separation	[35, 37]
3	Acetone–Methanol–Ethanol–Propanol-2	Model mixture		[37]
4	Methanol–Methyl acetate–Acetic acid–Acetic anhydride	Reaction mixture for acetic anhydride production		[37, 38]
5	Methyl-2-hydroxybutyrate–Methoxypropyl acetate–Ethyl lactate–Ethylethoxypropionate	Mixture of solvents for liquid crystal display production		–
6	Acetone–Chloroform–Ethanol–Water	Mixture of solvents for vitamin C production	Autoextractive-heteroazeotropic distillation, (SA – water)	[47]
7	Acetone–Chloroform–Propanol-2–Water			
8	Ethanol–Water–Toluene–Butyl acetate–Ethylcellosol	Solvents in the flexography process	Extractive distillation using sulfolane, EG, DMSO	[33]
9	Acetone–Water–Isopropylbenzene–Alpha-methylstyrol–Phenol	Phenol production by cumulus method	Optimization of the extractive distillation block (SA – DEG)	–
10	1,2-Dichloroethane–Chloroform–cis-Dichloroethylene	Chloroform production		
11	Diethyl ether–Hexane–Ethyl acetate–Ethanol (Water)	Solvents for dihydroquercetin production	The composition of solvents is recommended (a mixture of organic substances in the absence of water)	[39]

Table 8. Continued

No.	System	Production	Separation flowsheet (method)	Lit.
12	Methanol–Ethanol–Acetonitrile–Water (SA – glycerin, DMSO)	Model mixture	Alternative variants of flowsheets containing two ED complexes with different SA	[40]
13	Methanol–Tetrahydrofuran–Acetonitrile–Water (SA – DMSO, glycerin)	Tetrahydrofuran production		–
14	Methanol–*tert*-Butanol–Methyltretbutyl ether–Water (SA – DMSO)	Methyltretbutyl ether production		–
15	Acetone–Methanol–Tetrahydrofuran–Chloroform (SA – DMSO, NMP, TBA)	Model mixture		[41]
16	Ethyl Acetate–Methylethyl ketone–Cyclohexane–Propanol-2 (SA – NMP)	Model mixture	Alternative ED flowsheets of different structures	–

Note: EG is ethylene glycol, DMSO is dimethyl sulfoxide, NMP is *N*-methylpyrrolidone, TBA is tributylamine, DEG is diethylene glycol

– to conduct a local full-scale experiment in order to verify individual results (features of phase equilibrium, including in the presence of SA, and modes of operation of distillation columns).

The improving of the procedure for the synthesis of flowsheets for the distillation separation of multicomponent mixtures was based on original methods for studying the of the MCS phase diagram structures, the selection of additional substances (optimization at the level of the physicochemical subsystem of technology development), a variety of separation flowsheets structures (structural optimization of flowsheets): new results of a computational experiment obtained by varying the apparatus parameters, in particular, column efficiency, feed stages, and reflux ratios (parametric optimization); and new results of a full-scale experiment that allowed establishing the presence of previously unknown ternary, quaternary azeotropes, confirming the adequacy of mathematical modeling of liquid–vapor and liquid–liquid phase equilibria, and calculating the selectivity of SA in the MCS ED.

Various initial MCS fractionation methods were considered, which allow already at the first stage dividing the mixture into smaller constituents, the separation features of which are well known. Thus, it becomes possible to use well-known features and specific parameters of the separation flowsheets of binary and ternary mixtures, which are presented in the literature, including the article authors' works, and to solve the tasks set. It is shown that the reduction of energy consumption of flowsheets (up to 30% while ensuring the required quality of products) is associated with the implementation of a sharp distillation mode as an alternative to the limit modes (direct and indirect sequences), the use of the initial mixture pre-splitting, and the choice of SA in the processes of heteroazeotropic ED, including binary, showing in some cases the positive synergistic effect on increasing the SA selectivity.

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Authors' contributions

A.K. Frolkova – development of approaches to the synthesis of energy-efficient flowsheets of multicomponent mixtures separation, and writing the paper;

A.V. Frolkova – calculation of phase equilibrium, development of separation flowsheets, and parametric optimization of flowsheets;

V.M. Raeva – calculation of phase equilibrium, development of separation flowsheets, and parametric optimization of flowsheets;

V.I. Zhuchkov – conducting experimental studies on the selection of extractive agents.

The authors declare no conflicts of interest.

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