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THE RELATIONSHIP BETWEEN THE STRUCTURE OF PHASE EQUILIBRIUM DIAGRAM AND THE STRUCTURE OF FLOWSHEET DIAGRAMS OF MULTIPHASE QUATERNARY MIXTURES SEPARATION*

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In this work the structures of phase equilibrium diagrams of multiphase four-component systems n-hexane (n-heptane, n-octane) – cyclohexane – furfural – water were investigated. The systems are characterized by the existence of areas of three-phase separation. On the basis of the obtained data the synthesis of feasible variants of separation schemes was carried out, rational modes of functioning of each column were found, the energetically favorable variant was chosen. It was found that the use of preliminary phase separation in systems with n-hexane and n-octane is power-efficient, and the profit in case of the octane system (equimolar mixture) in comparison with the application of the first predetermined separation at the first stage is more than 25%. Certain difficulties (the high values of columns effectiveness: 60 and 40 theoretical plates) upon the separation of the hexane and heptane systems are due to the similar volatilities of n-hexane (n-heptane) and cyclohexane in the vicinity of the point of pure alkane.

Keywords: *phase diagram structure, limited solubility, azeotrope, mathematical simulation, three-phase delamination region, separation flowsheet.*

Introduction

Separation of multicomponent azeotropic mixtures is carried out in most cases by methods based on the principle of redistribution of concentration fields (PRCF) [1]. One of methods for the implementation of this principle is the use of a combination of rectification and spontaneous phase separation in unhomogeneous separation complexes. In many cases this method provides considerable economy of energy consumption at the stage of isolation and purification of target products.

By now literature has accumulated a large amount of data on the phase equilibria of mixtures undergoing phase separation [2–4] and on the separation of binary and ternary mixtures [5–7]. As a rule, the latter are characterized by the existence of areas of two-phase separation limited in ternary systems by closed- and open-type binodals. The authors of work [8] studied the structure of the phase equilibrium diagram of a quaternary system including the area of equilibrium of three liquid phases. Analysis of three-phase separation evolution in the concentration tetrahedron was carried out. The critical node corresponding to the transition from the three-phase area to the two-phase one was found. In work of [9] the phase equilibrium in a quaternary system water – acetonitrile –

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cyclohexene – cyclohexanone and its binary and ternary components was studied with the use of experimental and calculation methods. Parameters of the NRTL equation adequately describing liquid – vapor, liquid – liquid – vapor and liquid – liquid – liquid equilibria were determined. On the basis of the obtained model evolution of the three-phase separation area in the concentration tetrahedron was studied, and its transformation into the two-phase area via the critical node was shown.

This article is devoted to studying the interrelation of the structure of the phase diagrams of quaternary systems: *n*-hexane (Hx) – cyclohexane (CHx) – furfural (F) – water (W), *n*-heptane (Hp) – cyclohexane (CHx) – furfural (F) – water (W), *n*-octane (O) – cyclohexane (CHx) – furfural (F) – water (W) with the structure of the separation complex for mixtures of different composition.

Calculation and Theoretical Part

The sequence of isolation of components or fractions from a multi-component mixture of a preset composition is uniquely determined by the structure of the phase equilibrium diagram. Works [10, 11] published previously are devoted to studying vapor-liquid equilibrium, liquid-liquid equilibrium and solubility for three-component systems considered in this article, namely: *n*-hexane – furfural – water, *n*-heptane – furfural – water, *n*-octane – furfural – water and cyclohexane – furfural – water. It was found that the specified three-component systems contain an extensive area of equilibrium of three liquid phases in addition to areas of two-phase separation.

It follows from the reference information [10, 12] that quaternary systems are characterized by the existence of azeotropes:

– *n*-hexane – cyclohexane – furfural – water system contains three binary heteroazeotropes;

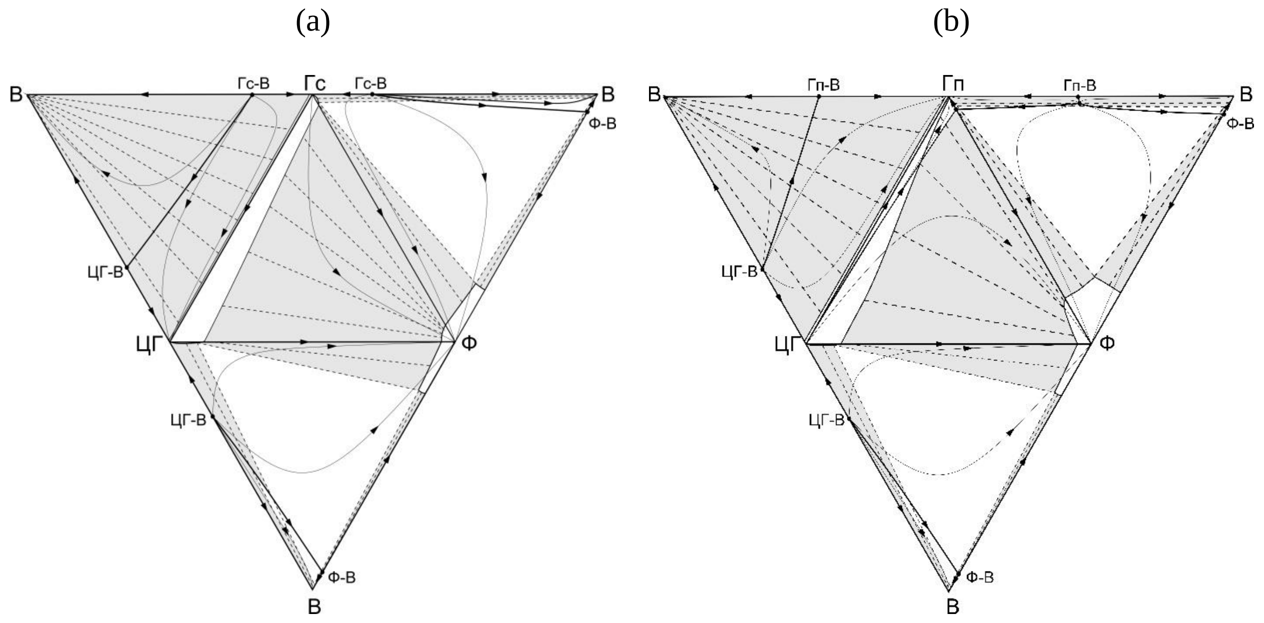
– *n*-heptane (*n*-octane) – cyclohexane – furfural – water systems contain four binary and one three-component heteroazeotrope.

Analysis of the ratio of the boiling points of the azeotropes and pure components made it possible to determine the types of singular points, the number of distillation areas, as well as to find separatrix manifolds. The types and Poincare's indexes of all the singular points of the studied systems with respect to the tetrahedron border and the volume of the concentration simplex are presented in Table 1. The algebraic sum of the indexes of the singular points with respect to the border and to the tetrahedron is equal to 2 and 0, respectively, which is fully in accordance with the azeotropy rule [13].

Table 1. Test of accordance with the azeotropy rule
with respect to the tetrahedron border and the tetrahedron volume

Singular point	With respect to the border		With respect to the volume	
	Type	Poincare's index	Type	Poincare's index
n-Hexane (Hx) – cyclohexane (CHx) – furfural (F) – water (W) systems				
Hx	CN_1	0	–	–
CHx	CN_1	0	–	–
F	N_1^{stab}	+1	N_1^{stab}	+1
W	N_1^{stab}	+1	N_1^{unstab}	+1
CHx – W	N_2^{unstab}	+1	N_2^{unstab}	–1
CHx – W	CN_2	0	–	–
F – W	C_2	–1	C_2	–1
		$\sum_{i} = 2$		$\sum_{i} = 0$
n-Heptane (Hp) (n-octane (O)) – cyclohexane (CHx) – furfural (F) – water (W) systems				
Hp (O)	N_1^{stab}	+1	N_1^{stab}	+1
CHx	CN_1	0	–	–
F	N_1^{stab}	+1	N_1^{stab}	+1
W	N_1^{stab}	+1	N_1^{stab}	+1
Hp (O) – F	C_2	–1	C_2	–1
Hp(O) – W	C_2	–1	C_2	–1
CHx – W	N_2^{unstab}	+1	N_2^{unstab}	–1
F – W	C_2	–1	C_2	–1
Hp (O) – F – W	N_3^{unstab}	+1	C_3	+1
		$\sum_{i} = 2$		$\sum_{i} = 0$

Thus, it can be concluded that the structure of the phase diagram is thermodynamically true. Figure 1 shows developments of the boundary surface of the tetrahedron with the positions of the singular points and phase separation areas.


(a)

(b)

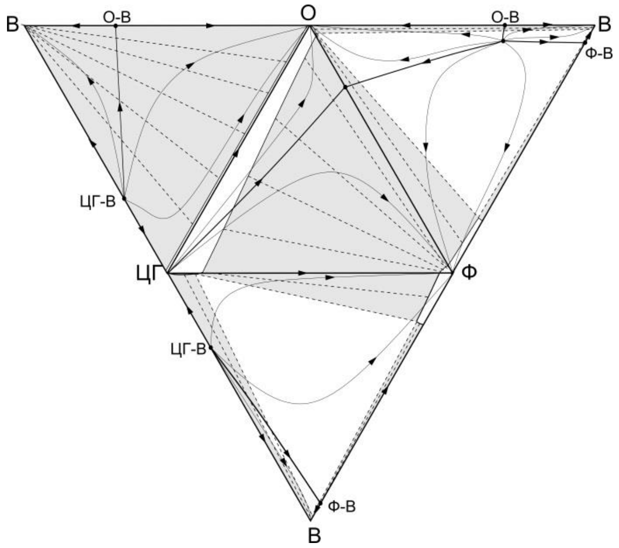

(c)

Figure 1. Development of the tetrahedrons of the systems:
a) *n*-hexane – cyclohexane – furfural – water,
b) *n*-heptane – cyclohexane – furfural – water, c) *n*-octane – cyclohexane – furfural – water
(The areas of two-phase separation are painted.)
[Гс means Hx; Гп means Hp; ЦГ means CHx; О means O; В means W; Ф means F]

Thermodynamic-topological analysis of the vapor-liquid equilibrium diagrams of the quaternary systems allowed revealing the following regularities:

– *n*-Hexane – cyclohexane – furfural – water system has two areas of distillation created by bunches of distillation lines beginning in the binary heteroazeotrope *n*-hexane – water and ending in the points of pure components (water, furfural).

– *n*-Heptane (*n*-octane) – cyclohexane – furfural – water systems have three areas of distillation created by bunches of distillation lines beginning in the binary heteroazeotrope cyclohexane – water and ending in the points of pure components (*n*-heptane (*n*-octane), water, furfural).

The distillation areas are separated from each other by separatrix manifolds, the structure of which is presented in Figure 2.

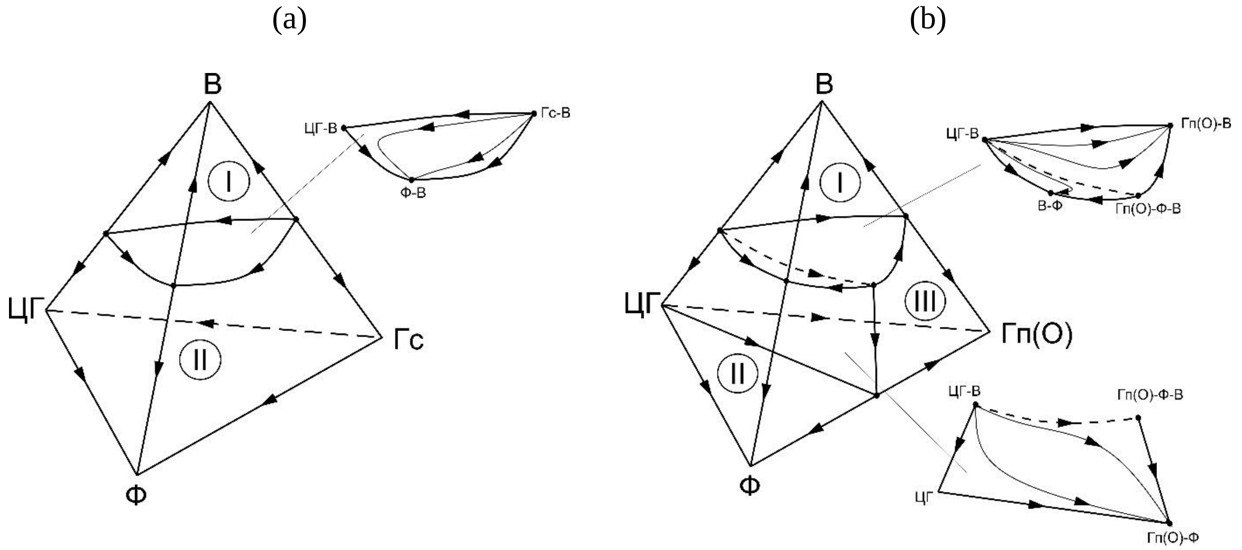

(a) (b)

Figure 2. The structures of the phase diagrams and of the separatrix manifolds of quaternary systems: a) *n*-hexane – cyclohexane – furfural – water,
b) *n*-heptane (*n*-octane) – cyclohexane – furfural – water
(I, II, III are designations of the distillation areas).
[Гс means Hx; Гп means Hp; ЦГ means CHx; O means O; В means W; Ф means F]

One of the most effective methods of studying the physical and chemical properties of mixtures and separation processes is mathematical modeling and computing experiment. Modeling of the phase equilibria was carried out with use of Aspen Plus software system and NRTL equation of local compositions. The reason for this choice of equation is that it allows well describing both homogeneous mixtures and mixtures with limited mutual solubility of components [14]. When modeling liquid – vapor and liquid – liquid equilibria we used parameters of the NRTL equation both contained in the Aspen Plus database and estimated by us according to experimental data (Table 2).

Table 2. Parameters of binary interaction of the NRTL equation

Binary component	Parameters of binary interaction				
	A_{ij}	A_{ji}	B_{ij} (K)	B_{ji} (K)	C_{ij}
n-hexane – cyclohexane	0	0	–100.144	143.411	0.3061
n-hexane – furfural	–2.9757	–0.7813	1529.096	707.3496	0.2
n-hexane – water	0	0	1512	3040	0.2
n-heptane – cyclohexane	0	0	–13.636	31.3555	0.3024
n-heptane – furfural	–3.00422	–0.26458	1676.164	514.9026	0.248851
n-heptane – water	–9.8652	10.5468	4795.66	440.7775	0.2
n-octane – cyclohexane	0	0	–333.132	482.9905	0.2288
n-octane – furfural	0	0	581.0572	692.2884	0.2
n-octane – water	–12.035	1.2166	5381.434	2997.701	0.2
cyclohexane – furfural	–1.3399	–3.8477	700.5334	1870.461	0.2
cyclohexane – water	–10.4585	13.1428	4954.897	–1066.98	0.2
furfural – water	112.6	52.8289	–4050	–2890	0.2

The adequacy of the mathematical model was checked by comparison of the obtained calculation data on the azeotropy and compositions of the equilibrium layers with the experimental data (Tables 3, 4). Modeling of vapor-liquid equilibrium was carried out at a pressure of 101.3 kPa, and modeling of liquid-liquid-liquid equilibrium, at 20 °C.

Table 3. Comparison of experimental and calculation data on the compositions and boiling points of binary and ternary azeotropes at 101.3 kPa

Component	Temperature, °C		Azeotrope composition, mol fractions	
	exp. [10, 12]	calc.	exp. [10, 12]	calc.
Binary azeotropes				
n-hexane – water	61.6	61.43	0.79	0.7898
			0.21	0.2102
n-heptane – water	80.1	79.32	0.546	0.5453
			0.454	0.4547
n-octane – water	90.4	89.57	0.329	0.3194
			0.671	0.6806
cyclohexane – water	69.5	69.49	0.7	0.699
			0.3	0.301
n-heptane – furfural	98.3	98.16	0.945	0.9499
			0.055	0.0501
n-octane – furfural	120.3	118.59	0.775	0.7526
			0.225	0.2474
furfural – water	97.9	98.45	0.092	0.0796
			0.908	0.9204
Ternary azeotropes				
n-heptane– furfural – water	79.7	79.31	0.535	0.54
			0.030	0.007
			0.435	0.443
n-octane – furfural – water	90.2	88.73	0.273	0.2883
			0.054	0.0752
			0.673	0.6365

Note. The boiling points of the pure substances determined by Antoine's equation at pressure of 101.3 kPa, °C: *n*-hexane – 68.7, *n*-heptane – 98.4, *n*-octane – 125.7, cyclohexane – 80.78, furfural – 161.4, water – 100.

Table 4. Compositions of conjugate liquid phases of studied three-component systems at T=20°C, P=101.3 kPa

Component	Hydrocarbon layer, mol fractions		Aqueous layer, mol fractions		Furfural layer, mol fractions	
	exp.	calc.	exp.	calc.	exp.	calc.
n-Hexane – furfural – water system						
n-hexane	0.964	0.959	traces	traces	0.01	0.051
furfural	0.036	0.039	0.016	0.016	0.791	0.810
water	traces	0.003	0.984	0.984	0.198	0.138
n-Heptane – furfural – water system						
n-heptane	0.965	0.974	traces	traces	0.009	0.067
furfural	0.035	0.025	0.016	0.015	0.809	0.800
water	traces	traces	0.984	0.985	0.182	0.134
n-Octane – furfural – water system						
n-octane	0.966	0.963	traces	traces	0.008	0.025
furfural	0.034	0.036	0.016	0.016	0.815	0.829
water	traces	0.001	0.984	0.984	0.177	0.147

Using the parameters available in Aspen Plus software system satisfactorily describes the liquid-liquid-liquid equilibrium in the three-component system *n*-heptane – furfural – water, but does not model the existence of real binary (*n*-heptane – furfural) and ternary (*n*-heptane – furfural – water) heteroazeotropes [10]. In order to improve the description we carried out separately an assessment of the NRTL equation parameters according to experimental data on vapor-liquid equilibrium (VPE) for *n*-heptane – furfural component. When modeling with the parameters estimated according to VPE, the structure of the phase diagram of *n*-heptane – furfural – water system is reproduced (azeotropy, phase separation). However, divergence (0.9% rel.) between the experimental and calculated compositions of the hydrocarbonic layer in this triple system is observed. Note that such an error of description is not critical, because the relative positioning of the separatrix and phase separation simplex is favorable from the viewpoint of PRCF realization. Calculated compositions of equilibrium liquid layers certainly belong to different areas of rectification differing in the compositions of product (vat) flows.

Thus, using the obtained mathematical model of phase equilibrium enables conducting systematic research of various versions of separation schemes and picking up rational modes of functioning for each column. Synthesis of possible separation schemes for mixtures of different composition is presented below. The existence of phase separation areas covering almost all the concentration simplex allows to use stripping columns [15] at different stages, which considerably decreases energy consumption.

n-Hexane – cyclohexane – furfural – water system

Analysis of the structure of the system phase diagram showed the existence of two distillation areas and three rectification subareas (Figure 2a). Each of them can correspond to a certain set of schematic diagrams of separation (depending on the composition of the original mixture F0). The schemes include complexes based on a combination of rectification and spontaneous phase separation, and also separate columns. Figure 3 presents schemes for the separation of the original mixtures belonging to different rectification subareas.

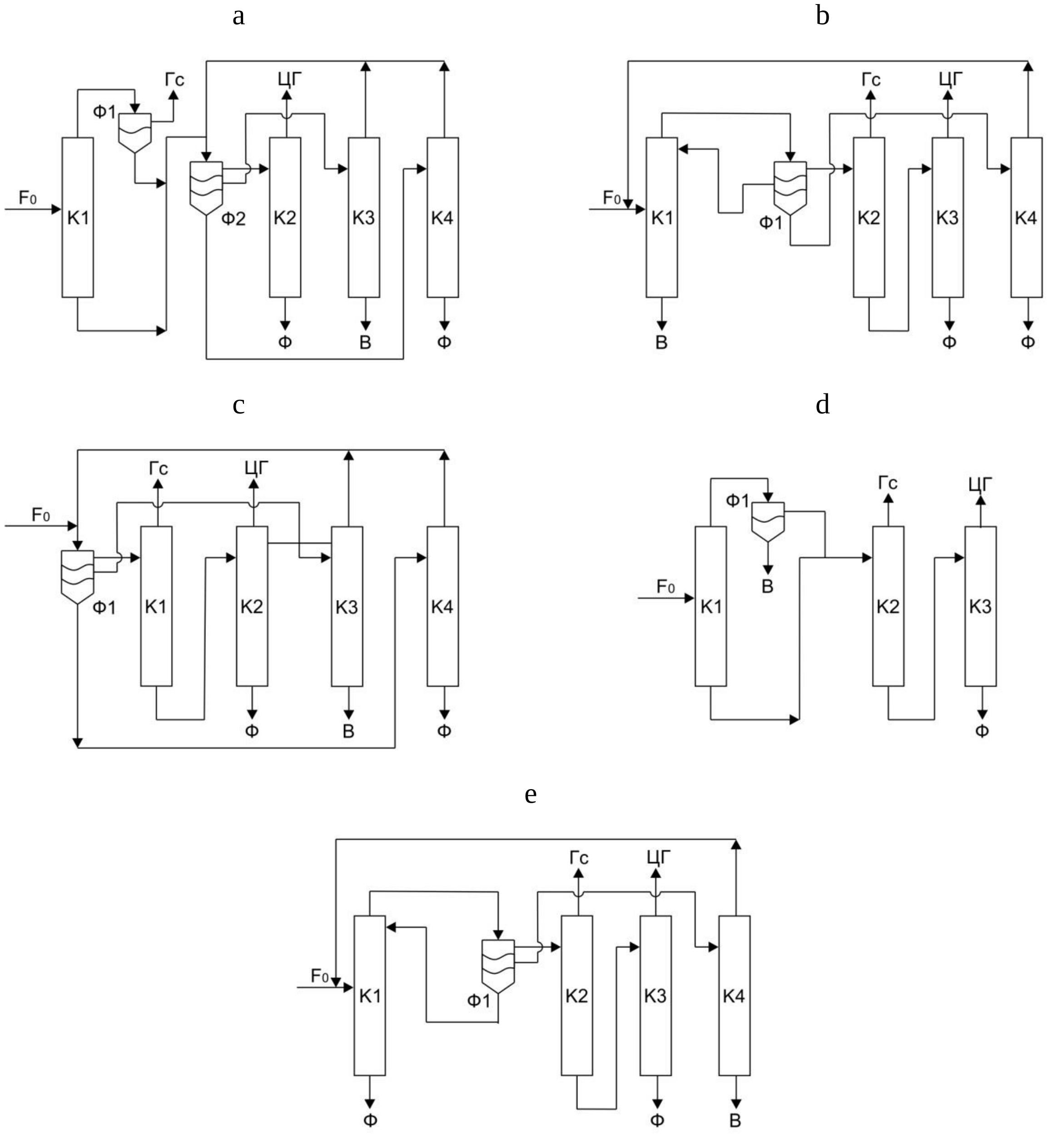


Figure 3. Process flow diagrams for the separation of *n*-hexane – cyclohexane – furfural – water mixture with the use of functional complexes
(C1–C4 are rectification columns; F1, F2 are Florentine vessels).
[Гс means Hx; ЦГ means CHx; В means W; Ф means F; К means C; Ф1, Ф2 means F1, F2]

The scheme variants differ in the application of the first or second preset separation in the columns, and also in the use of the phase separation phenomenon at the first stage of separation (Table 5). When developing the schematic diagrams, it was accepted that, if the quality of the layer formed in the Florentine vessel when separating *n*-hexane – water mixture conforms to the requirements of TU 2631-003-05807999-98 (Figure 3a, d), this layer is considered as a product stream (organic layer).

Table 5. Conformity of the structure of the separation schemes to the composition of the original *n*-hexane – cyclohexane – furfural – water mixture

Relation of the original mixture		Operating mode of the first column		Use of phase separation phenomenon
Distillation area	Rectification subarea	First preset separation	Second preset separation	
I	I-1	3a	3b	3c
II	II-1		3e	
	II-2	3d		

It can be seen that *n*-hexane – cyclohexane – furfural – water mixture of any composition can be separated with the use of four (three) columns and one (two) Florentine vessels. The operability of the presented schemes was confirmed by calculating the rectification process. For this purpose we calculated the mass balance of the scheme for three original mixtures relating to different rectification subareas. (The number of independent variables for the calculation of the mass balance [16] was determined, their values were set.) Besides, static parameters of the rectification columns operation that provide products of the preset quality meeting the requirements of the state standard specification/requirements specification were found. Table 6 shows static parameters of the columns operation and total energy consumption for the separation (the sum of loadings of column reboilers) when separating a mixture of equimolar composition (related to subarea II-1). The rectification columns operate at a pressure of 101.3 kPa, the Florentine vessels, at a temperature of 20 °C.

Table 6. Operating parameters of the columns and energy consumption for the separation of *n*-hexane – cyclohexane – furfural – water mixture of equimolar composition

Scheme number (Figure 3)	Column number	Column operation parameters				Q_{reb}, mW	∑Q, mW
		$N_{t.p.}$	N_{feed}	R	D/W		
3a	1	60	40	5.8	0.463	3.675	2.708
	2	40	39	0.7	9.398	0.72	
	3	10	1	–	0.525	0.229	
	4	16	1	–	0.325	0.212	

3e	1	10	1	–	3.542	0.848	2.973
	2	60	41	6.76	0.96	2.037	
	3	32	28	0.72	25.99	0.622	
	4	16	1	–	0.363	0.164	
3c	1	60	40	6.77	0.877	2.11	2.511
	2	32	28	0.87	6.933	0.828	
	3	16	1	–	0.521	0.211	
	4	12	1	–	0.332	0.221	

Designations: $N_{t.p.}$ – the number of theoretical plates in the column; N_{feed} – feed plate of the column; R – reflux ratio; D/W – ratio of the distillate flow to the vat flow; $Q_{reb.}$ – column reboiler loading; $\sum Q$ – total energy consumption for the separation.

It can be seen from Table 6 that the scheme with the use of preliminary three-phase separation of the mixture at the first stage is most power-efficient. As shown by the computing experiment, such tendency is observed when separating a mixture of any composition. Note that when separating a mixture which is in rectification subarea II-2, it is possible to use three rectification columns (Figure 3d). However, although the investment cost is lower as compared to the other separation variants (3c, e), this scheme is more power-intensive.

n-Heptane (n-octane) – cyclohexane – furfural – water systems

n-Heptane (*n*-octane) – cyclohexane – furfural – water systems are characterized by the existence of three distillation areas and five rectification subareas (Figure 2b). Figure 4 presents process flow diagrams for the separation of mixtures corresponding to different rectification subareas (Table 7). Besides, in case of the cyclohexane – water component of these systems the quality of the layers formed in the Florentine vessel conforms to the requirements of the state standard specification/requirements specification (Figures 4a, d, e, f).

Table 7. Conformity of the structure of the separation schemes to the composition of the original mixture *n*-heptane (*n*-octane) – cyclohexane – furfural – water

Relation of the original mixture		Operating mode of the first column		Use of phase separation phenomenon
Distillation area	Rectification subarea	First preset separation	Second preset separation	
I	I-1	4a	4b	4c
II	II-1		4e	
	II-2	4d		
III	III-1	4a	4f	
	III-2	4d		

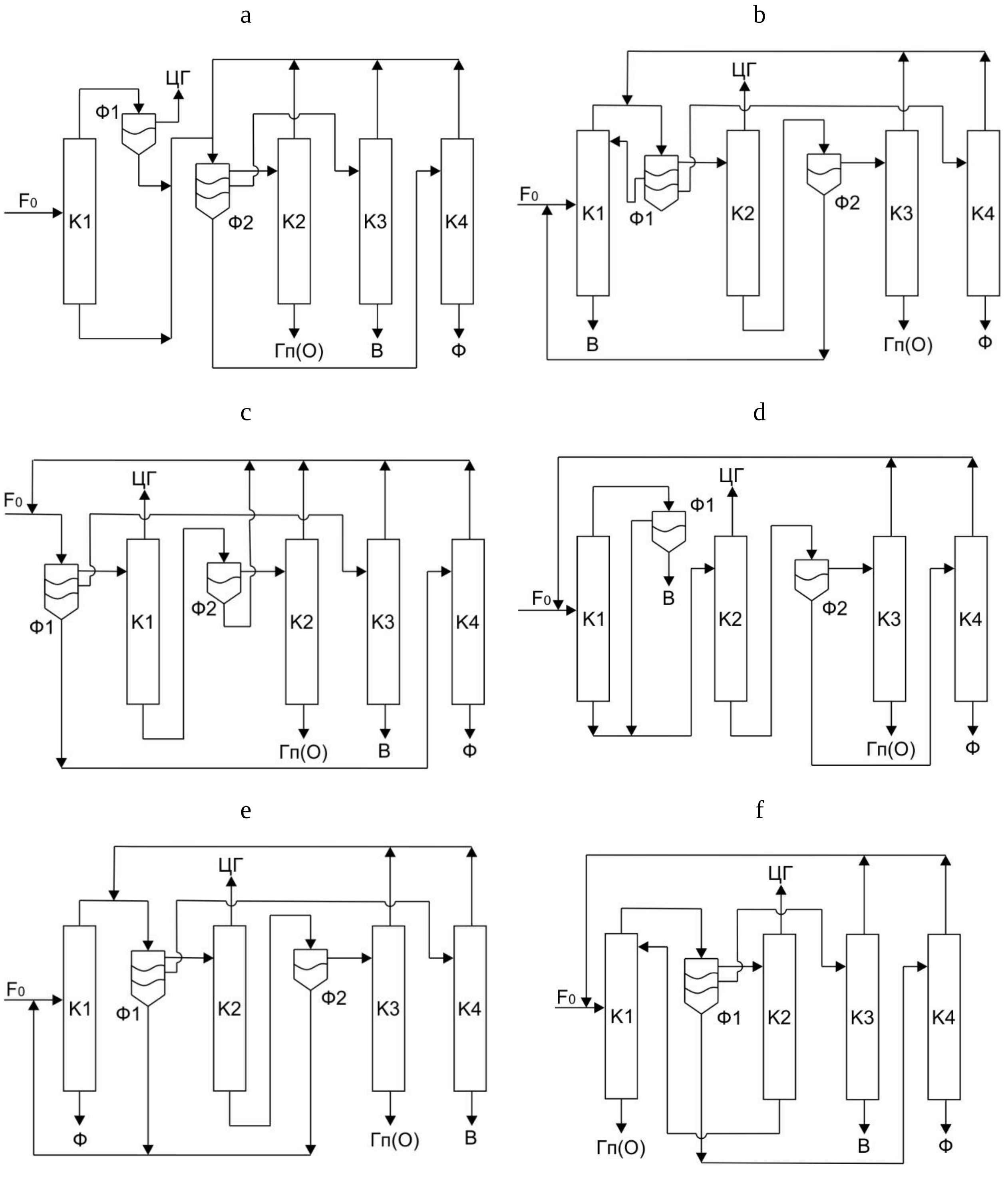


Figure 4. Process flow diagrams for the separation of *n*-heptane (*n*-octane) – cyclohexane – furfural – water mixture with the use of functional complexes (C1–C4 are rectification columns; F1, F2 are Florentine vessels).

[Гп means Hp; ЦГ means CHx; O means O; B means W; Ф means F; К means C; Ф1, Ф2 means F1, F2]

As we can see, *n*-heptane (*n*-octane) – cyclohexane – furfural – water mixture of any composition can be separated with the use of four columns and one (two) Florentine vessels. As in the previous case, the operability of the presented schemes was confirmed by calculating the rectification process. For this purpose we calculated the mass balance of the scheme for five original mixtures and found static operation parameters of the rectification columns. Table 8 presents the static operation parameters of the columns and the total energy consumption for the separation of mixtures of equimolar composition. The rectification columns operate at a pressure of 101.3 kPa, the Florentine vessels, at a temperature of 20 °C.

Table 8. Operating parameters of the columns and energy consumption for the separation of *n*-heptane (*n*-octane) – cyclohexane – furfural – water mixtures of equimolar composition

Scheme number (Figure 4)	Column number	Column operation parameters				Q_{reb}, mW	∑Q, mW
		$N_{t.p.}$	N_{feed}	R	D/W		
n-Heptane – cyclohexane – furfural – water system							
4a	1	60	25	4.85	0.557	1.934	4.511
	2	40	16	6.55	1.28	2.17	
	3	16	1	–	0.37	0.163	
	4	12	1	–	0.269	0.244	
4e	1	16	1	–	3.34	0.925	5.727
	2	60	25	5.56	0.332	1.91	
	3	40	16	5.35	1.67	2.65	
	4	16	1	–	0.260	0.242	
4c	1	60	25	5.43	0.316	1.893	5.161
	2	40	16	5.28	2.0	2.864	
	3	16	1	–	0.372	0.163	
	4	16	1	–	0.261	0.241	
n-Octane – cyclohexane – furfural – water system							
4a	1	32	14	1.92	0.577	0.982	1.708
	2	11	1	–	0.155	0.268	
	3	13	1	–	0.575	0.197	
	4	11	1	–	0.318	0.261	
4e	1	4	1	–	3.29	0.762	1.928
	2	32	23	1.5	0.666	0.571	
	3	9	1	–	0.415	0.380	
	4	15	1	–	0.525	0.215	
4c	1	32	20	1.46	0.777	0.559	1.327
	2	11	1	–	0.196	0.287	
	3	14	1	–	0.552	0.222	
	4	11	1	–	0.32	0.259	

Designations – see Table 6.

It can be seen from Table 8 that the scheme with the use of the first preset separation at the first stage of separation is most power effective for separating *n*-heptane – cyclohexane – furfural – water mixture. The scheme with the use of preliminary three-phase separation of the mixture at the first stage is least power-intensive for separating *n*-octane – cyclohexane – furfural – water mixture.

Conclusion

We studied the features of the separation of quaternary systems, one of the components of which belongs to the alkane homologous series. The separation complexes were based on a combination of rectification and phase separation. It was found that the use of preliminary phase separation in systems with *n*-hexane and *n*-octane is power effective, and the saving in case of the octane system (equimolar mixture) as compared to the application of the first preset separation at the first stage is more than 25%. Certain difficulties (high values of the columns effectiveness: 60 and 40 theoretical plates) upon the separation of the hexane and heptane systems are due to the close values of *n*-hexane (*n*-heptane) and cyclohexane volatilities in the vicinity of the pure alkane point. In addition, the *n*-heptane – cyclohexane binary component is characterized by the existence of a tangential zeotrope.

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