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Areas of energy advantage for flowsheets of separation modes for mixtures containing components with similar volatilities

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Objectives*. The conditions for the effective application of the sharp distillation technique (without a component distributed between the distillate and bottom flows) for the separation of quaternary zeotropic mixtures containing components with similar volatilities were determined. The area of energy advantage for the flowsheet based on the preliminary fractionation of the mixture, compared with the flowsheet, the first distillation column of which works based on the indirect separation mode, was identified for an ethyl acetate–benzene–toluene–butyl acetate system. Energy savings of up to 20% were achieved. The direct and indirect distillation modes can become competitive when the point of the original composition is located near single K-surfaces or in a region with a different ratio of distribution coefficients. Sharp distillation is not suitable for the separation of a mixture containing a pair of components exhibiting relative unity volatility with medium boiling points.*

Methods. *The mathematical modeling in the Aspen Plus V.10.0 software package was chosen as the research method. The simulation was based on the Wilson local composition equation. The relative errors in the description of the phase equilibrium did not exceed 3%.*

Results. *The structure of the vapor–liquid equilibrium diagram and diagram of surfaces of the unit component distribution coefficients were studied for the ethyl acetate–benzene–toluene–butyl acetate and acetone–toluene–butyl acetate–o-xylene systems. Flowsheets based on the sharp, indirect (both systems), or direct (second system) distillation modes were proposed. The distillation process was simulated, and the parameters of the column work were determined (the quality of the substances meets the State Standard requirements of the Russian Federation for minimal energy consumption).*

Conclusions. *Recommendations regarding the use of sharp distillation for the separation of quaternary mixtures containing components with similar volatilities were devised.*

Keywords: *distillation, sharp distillation, liquid–vapor equilibrium, components relative volatility, components distribution coefficients.*

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Области энергетического преимущества схем разделения смесей, содержащих компоненты с близкими летучестями

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Цели. *Для ректификации четырехкомпонентных зеотропных смесей, содержащих компоненты с близкими летучестями, определены условия эффективности применения промежуточного заданного разделения (при отсутствии компонента, распределенного между дистиллятным и кубовым потоками). На примере системы этилацетат–бензол–толуол–бутилацетат выделена область энергетического преимущества схемы, основанной на использовании предварительного фракционирования смеси, по сравнению со схемой, первая ректификационная колонна которой работает по второму заданному разделению. Экономия энергозатрат составляет до 20%. Реализация первого и второго заданного разделения может стать конкурентной при расположении точки исходного состава вблизи единичных K-поверхностей или в области с другим соотношением коэффициентов распределения. Промежуточное разделение не может быть рекомендовано для разделения смеси с близкой к единице относительной летучестью пары компонентов со средними температурами кипения.*

Методы. *В качестве метода исследования выбрано математическое моделирование в программном комплексе Aspen Plus V.10.0. Моделирование основывалось на уравнении локального состава Wilson. Относительные ошибки описания фазового равновесия не превышают 3%.*

Результаты. *Исследована структура диаграммы парожидкостного равновесия и диаграммы поверхностей единичных коэффициентов распределения компонентов для систем этилацетат–бензол–толуол–бутилацетат и ацетон–толуол–бутилацетат–о-ксилол. Предложены схемы, основанные на использовании промежуточного, второго (обе системы) или первого (вторая система) заданного разделения. Проведен расчет процесса ректификации и подобраны параметры работы колонн, обеспечивающие получение веществ, качество которых отвечает требованиям ГОСТ при минимальных энергозатратах.*

Выводы. *На основе проведенных исследований сформулированы рекомендации по использованию промежуточного разделения при ректификации четырехкомпонентных смесей, содержащих компоненты с близкими летучестями.*

Ключевые слова: *ректификация, промежуточное разделение, равновесие жидкость–пар, относительная летучесть компонентов, коэффициенты распределения компонентов.*

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INTRODUCTION

Choosing an energy-efficient version of the separation flowsheet is one of the key challenges in basic organic and petrochemical synthesis. This is primarily because the separation unit of the reaction mixture accounts for 60–80% of the total energy consumption [1–3]. Developing a separation flowsheet for multicomponent mixtures is a polyvariant task, since the same mixture can be separated using different modes (direct, indirect, or sharp distillation) or using special methods [1, 2, 4–8]. The formulation of practical recommendations for the use of a particular technique or method will significantly reduce the time expended at the pre-project development stage of the separation technology.

In [9], we evaluated the possibility of using sharp distillation (provided that there is no component distributed between the cube and the distillate) for the separation of quaternary non-ideal mixtures containing azeotropes and/or components with similar volatilities. Based on the analysis of the diagrams of surfaces of the unit component distribution coefficients, the areas of compositions are identified for which the use of the sharp distillation mode is not only possible but also potentially more energy-efficient than the direct or indirect distillation modes.

In this paper, a comparative analysis of the separation flowsheets of multicomponent zeotropic mixtures (containing components with similar volatilities) based on various types of separation modes is carried out. The conditions, under which sharp distillation is more energy-efficient than other separation modes, as well as the restrictions to its application, are determined.

The objects of research are quaternary systems: ethyl acetate (EA)–benzene (B)–toluene (T)–butyl acetate (BA) (a mixture of solvents produced by biodegradable polymers [10]) and acetone (A)–toluene (T)–butyl acetate (BA)–*o*-xylene (*o*-X) (a mixture of solvents produced by epoxy primers [11]). Both systems are zeotropic and contain pairs of components with similar volatiles: ethyl acetate–benzene and toluene–butyl acetate.

MATERIALS AND METHODS

Phase equilibrium modeling was performed in the AspenPlus V.10.0 software package using the Wilson equation:

$$\ln y_i = 1 - \ln\left(\sum_j A_{ij} x_j\right) - \sum_j \frac{A_{ji} x_j}{\Sigma_k A_{jk} x_k}$$

where $A_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + d_{ij} T + \frac{e_{ij}}{T^2}$, a_{ij}, a_{ji}, b_{ij} and b_{ji} are the parameters of the Wilson equation.

This equation has been proven to be instrumental in the study of the phase equilibrium of homogeneous systems, including the changes in the external conditions. This model is chosen to enable the simulation of the phase equilibrium and the distillation process at low pressures.

The parameters of the binary interaction and errors in the description of the phase equilibrium are given in Table 1.

RESULTS AND DISCUSSION

Based on the analysis of the phase equilibrium curves of the binary systems, ethyl acetate–benzene and toluene–butyl acetate [12–13], it was shown that the separation of ethyl acetate from benzene using conventional distillation is impossible under any condition. This fact restricts the use of direct distillation for the separation of the EA–B–T–BA mixture. The separation of toluene from BA without special methods is possible in a distillation column at a low pressure (the relative volatility of the components is increased by more than 1.5 times). Thus, for the separation of the EA–B–T–BA mixture at the first stage, it is possible to use a sharp distillation (at reduced pressure) specified separation technique; for the A–T–BA–*o*-X mixture, any technique can be utilized.

The efficiency of using a particular separation technique for mixtures of different compositions characterized by different ratios of component distribution coefficients was evaluated. To select the original compositions, diagrams of the unit surfaces of the component distribution coefficients were constructed (Fig. 1).

The area of compositions in which the distribution coefficients of two components are

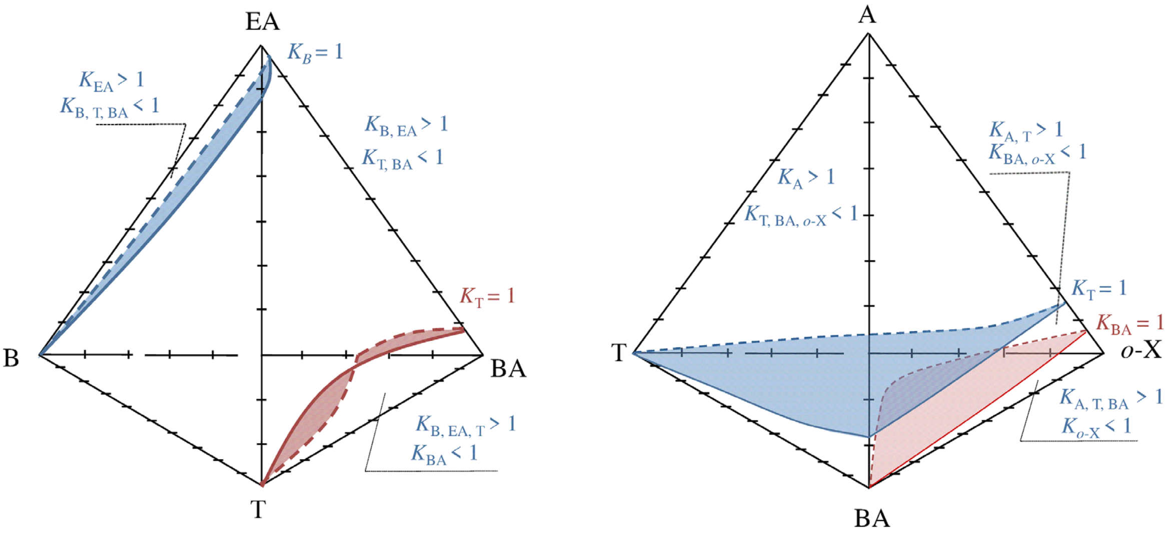
Table 1. Wilson equation parameters for the binary constituents of the benzene (B)–toluene (T)–ethyl acetate (EA)–butyl acetate (BA) and acetone (A)–toluene (T)–butyl acetate (BA)–*o*-xylene (*o*-X) systems

Binary system	a_{ij}	a_{ji}	b_{ij}	b_{ji}	Δ*T*, %	Δ*Y*, %
B–T	−1.5857	2.3275	634.7787	−913.6505	0.17	1.06
B–EA	8.2122	−11.6434	−2841.5425	4010.0664	0.07	0.31
B–BA	0	0	−19.0272	54.5272	0.20	1.12
T–A*	5.10951	−4.14947	−2010.08	1570.5	0.20	0.94
T–BA*	−2.0001	1.53945	951.97	−848.68	0.27	4.56
EA–BA	0	0	−5.6575	−15.65	0.37	1.67

Table 1. Continued

Binary system	a_{ij}	a_{ji}	b_{ij}	b_{ji}	ΔT, %	ΔY, %
A–T	0.8857	−0.8619	−461.065	247.597	0.57	1.47
A–BA	0	0	−0.1353	−87.2465	0.44	0.55
A–*o*-X	0	0	−163.265	−96.3392	0.00	0.10
T–*o*-X*	0	0	−151.016	126.916	–	–
BA–*o*-X**	0	0	245.808	−409.273	–	–

Note: *parameters are estimated from experimental data [12–14];
**parameters were evaluated using the UNIFAC model.



a b

Fig. 1. Diagrams of the unit *K*-surfaces of the systems: ethyl acetate (EA)–benzene (B)–toluene (T)–butyl acetate (BA) (a) and acetone (A)–toluene (T)–butyl acetate (BA)–*o*-xylene (*o*-X) (b) at 760 mm Hg.

characterized by a value greater than one, and the rest by less than one, is favorable for the implementation of sharp distillation. For the system shown in Fig. 1a, this area occupies a significant part of the composition simplex. For the system in Fig. 1b, this region is quite narrow, which is due to the proximity of the volatile components with intermediate boiling points (toluene and butyl acetate).

For the EA–B–T–BA system, the points of original compositions belonging to different secants are selected (secant 1 corresponds to the equimolar ratio of benzene, toluene, and butyl acetate; for secants 2, 3, and 4, the compositions are enriched with butyl acetate, benzene, and toluene, respectively). For each section, five compositions are considered, corresponding to sections 1–5 with constant concentrations of ethyl acetate: 0.05 (1), 0.25 (2), 0.45 (3), 0.65 (4), and 0.82 (5). The original composition of the mixture is represented by two digits, the first of which indicates the number of the secant, and the second—the section number. Composition **2.1** ($x_{EA} = 0.05$, $x_B = 0.05$, $x_T = 0.3$, $x_{BA} = 0.6$ mol. fractions) belongs to the area where only butyl acetate is a highly volatile component; the other components are highly volatile. Other compositions are characterized by the following ratio of distribution coefficients: $K_{EA} > 1$, $K_B > 1$, $K_T < 1$, $K_{BA} < 1$.

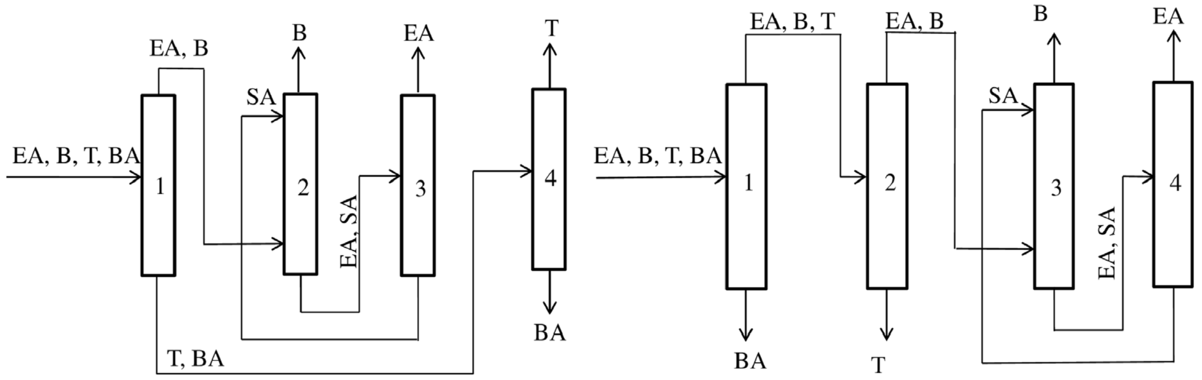
For the A–T–BA–*o*-K system, two original compositions, belonging to regions with different ratios of distribution coefficients, will be considered: equimolar ($K_A > 1$, $K_T > 1$, $K_{BA} > 1$, $K_{o\text{-X}} < 1$) and $x_A = 0.04$, $x_T = 0.32$, $x_{BA} = 0.32$, $x_{o\text{-X}} = 0.32$ mol. fractions ($K_A > 1$, $K_T > 1$, $K_{BA} < 1$, $K_{o\text{-X}} < 1$).

For each system, the separation flowsheets for different structures are proposed, the distillation process is simulated, and the parameters of the columns are selected to ensure the production of substances whose quality meets the requirements of GOST (benzene No. 5955-75; ethyl acetate, butyl acetate No. 8981-78; toluene No. 14710-78; acetone No. 2768-84; *o*-xylene No. 9410-78) with minimal energy consumption (the column reboiler duty is considered).

Ethyl acetate–benzene–toluene–butyl acetate system

Two flowsheets are proposed for the separation of the mixtures (Fig. 2).

The parameters of the columns (NTS: the number of theoretical stages; *P*: the pressure (mm Hg); F_{init}/F_{SA}: the ratio of the amounts of the initial mixture and the separating agent (SA); FS: the feed stage; *R*: the reflux ratio), as well as the energy consumption (*Q*) for both flowsheets and 20 original compositions, are shown in Tables 2–5.



a b

Fig. 2. Ethyl acetate (EA)–benzene (B)–toluene (T)–butyl acetate (BA) mixture separation flowsheets based on the sharp (a) and indirect (b) distillation modes (separating agent (SA): phenol).

Table 2. Parameters of the columns work of the separation flowsheets shown in Fig. 2 (for the original compositions from **1.1** to **1.5**)

Column	**NTS (F_{init}/F_{SA})**	***P***	**FS mix/SA**	***R***	***Q*, kW**	**NTS (F_{init}/F_{SA})**	***P***	**FS mix/SA**	***R***	***Q*, kW**
	Sharp distillation					**Indirect distillation**				
The original composition of the mixture is **1.1** (x_{EA} = 0.04, x_B = 0.32, x_T = 0.32, x_{BA} = 0.32 mol. fract.)										
1	34	760	14	2.7	1189.2	36	100	10	1.1	1551.0
2	24 (1/1)	760	13/6	1	766.6	34	760	18	1.7	850.1
3	36	760	6	4.8	222.0	24 (1/1)	760	13/6	1	766.6
4	32	110	10	3.5	1492.7	36	760	6	4.8	222.0
					∑*Q* = 3670.5					**∑*Q* = 3389.7**
The original composition of the mixture is **1.2** (x_{EA} = 0.25, x_B = 0.25, x_T = 0.25, x_{BA} = 0.25 mol. fract.)										
1	24	760	14	2	1346.9	24	100	9	1	1669.5
2	30 (1/1.7)	760	9/4	3	608.6	24	760	12	1.4	1064.2
3	22	760	9	3	987.4	30 (1/1.7)	760	9/4	3	608.6
4	24	110	12	3.8	1230.6	22	760	9	3	987.4
					∑*Q* = 4173.5					**∑*Q* = 4329.7**

Table 2. Continued

Column	NTS (F_{init}/F_{SA})	*P*	FS mix/SA	*R*	*Q*, kW	NTS (F_{init}/F_{SA})	*P*	FS mix/SA	*R*	*Q*, kW
	Sharp distillation					**Indirect distillation**				
The original composition of the mixture is **1.3** ($x_{EA} = 0.46$, $x_B = 0.18$, $x_T = 0.18$, $x_{BA} = 0.18$ mol. fract.)										
1	32	760	19	1.4	1413.6	28	100	8	0.4	1419.1
2	36 (1/3)	760	10/4	1.3	1417.2	32	760	21	1.2	1278.3
3	28	760	5	1.3	1172.5	36 (1/3)	760	10/4	1.3	1417.2
4	36	110	12	3.1	766.6	28	760	5	1.3	1172.5
					$\sum Q = 4769.9$					**$\sum Q = 5287.1$**
The original composition of the mixture is **1.4** ($x_{EA} = 0.64$, $x_B = 0.12$, $x_T = 0.12$, $x_{BA} = 0.12$ mol. fract.)										
1	36	760	23	1.3	1598.5	28	100	8	0.3	1417.1
2	36 (1/4)	760	10/4	1.3	1943.1	32	760	22	1.3	1582.6
3	32	760	5	1.6	1791.0	36 (1/4)	760	10/4	1.3	1943.1
4	32	110	11	3.5	559.7	32	760	5	1.6	1791.0
					$\sum Q = 5892.3$					**$\sum Q = 6733.8$**
The original composition of the mixture is **1.5** ($x_{EA} = 0.82$, $x_B = 0.06$, $x_T = 0.06$, $x_{BA} = 0.06$ mol. fract.)										
1	36	760	24	1.2	1751.0	24	100	8	0.2	1339.1
2	32 (1/5.5)	760	11/4	0.9	2885.0	32	760	21	1.3	1821.2
3	32	760	5	2.1	2708.6	32 (1/5.5)	760	11/4	0.9	2885.0
4	32	110	11	3.6	285.9	32	760	5	2.1	2708.6
					$\sum Q = 7630.5$					**$\sum Q = 8753.9$**

Note: the separating agent is phenol.

Table 3. Parameters of the columns work of the separation flowsheets shown in Fig. 2 (for the original compositions from **2.1** to **2.5**)

Column	NTS (F_{init}/F_{SA})	*P*	FS mix/SA	*R*	*Q*, kW	NTS (F_{init}/F_{SA})	*P*	FS mix/SA	*R*	*Q*, kW
	Sharp distillation					**Indirect distillation**				
The original composition of the mixture is **2.1** ($x_{EA} = 0.05$, $x_B = 0.05$, $x_T = 0.3$, $x_{BA} = 0.6$ mol. fract.)										
1	58	760	16	8	832.6	37	100	11	4.3	2296.7
2	33 (1/2)	760	11/6	0.5	175.7	36	760	15	4.6	509.8
3	28	760	6	1.3	125.9	33 (1/2)	760	11/6	0.5	175.7
4	37	110	12	6.1	2195.6	28	760	6	1.3	125.9
					$\sum Q = 3329.8$					**$\sum Q = 3108.1$**

Table 3. Continued

Column	NTS (F_{init}/F_{SA})	*P*	FS mix/SA	*R*	*Q*, kW	NTS (F_{init}/F_{SA})	*P*	FS mix/SA	*R*	*Q*, kW
	Sharp distillation					**Indirect distillation**				
The original composition of the mixture is **2.2** (x_{EA} = 0.25, x_B = 0.039, x_T = 0.237, x_{BA} = 0.474 mol. fract.)										
1	37	760	17	2.5	960.1	36	100	10	2.1	1900.8
2	32 (1/5)	760	11/5	0.5	882.2	33	760	20	1.9	767.9
3	33	760	5	2.1	818.2	32 (1/5)	760	11/5	0.5	882.2
4	40	110	12	5.7	1638.4	33	760	5	2.1	818.2
					$\sum Q$ = 4298.9					**$\sum Q$ = 4369.1**
The original composition of the mixture is **2.3** (x_{EA} = 0.45, x_B = 0.029, x_T = 0.173, x_{BA} = 0.348 mol. fract.)										
1	36	760	21	1.6	1176.5	33	100	9	1.2	1689.8
2	33 (1/5.5)	760	13/5	0.4	1550.1	28	760	18	1.6	1131.9
3	28	760	5	2.2	1525.1	33 (1/5.5)	760	13/5	0.4	1550.1
4	37	110	12	6.2	1283.6	28	760	5	2.2	1525.1
					$\sum Q$ = 5535.3					**$\sum Q$ = 5896.9**
The original composition of the mixture is **2.4** (x_{EA} = 0.65, x_B = 0.0184, x_T = 0.1108, x_{BA} = 0.2208 mol. fract.)										
1	37	760	25	1.4	1485.0	28	100	8	0.7	1519.8
2	32 (1/6.5)	760	12/5	0.5	2599.0	29		19	1.8	1686.3
3	33	760	5	2.6	2443.6	32 (1/6.5)	760	12/5	0.5	2599.0
4	37	110	12	6.1	810.9	33	760	5	2.6	2443.6
					$\sum Q$ = 7338.5					**$\sum Q$ = 8248.7**
The original composition of the mixture is **2.5** (x_{EA} = 0.85, x_B = 0.008, x_T = 0.048, x_{BA} = 0.094 mol. fract.)										
1	36	760	25	1.3	1786.6	29	100	9	0.2	1172.9
2	33 (1/8)	760	15/8	0.4	4075.4	32	760	21	1.8	2152.2
3	36	760	5	3.2	3689.0	33 (1/8)	760	15/8	0.4	4075.4
4	33	110	12	7	395.0	36	760	5	3.2	3689.0
					$\sum Q$ = 9946.0					**$\sum Q$ = 11089.5**

Note: the separating agent is phenol.

The stage numbering begins at the top of the column. To separate the pair of components: ethyl acetate–benzene, phenol, recommended in the literature [15], is used, which increases the volatility of benzene relative to that of ethyl acetate.

Figure 3 shows graphs of the dependence of the total energy consumption of the separation flowsheets on the concentration of EA in the original mixture (for secants 1 and 2). For the compositions located in the other two sections, similar graphs were not obtained because the energy consumption of the flowsheet based on the sharp distillation is lower than that of the flowsheets, the first column of which operates in the indirect distillation mode.

The graphs, shown in Fig. 3, were used to determine the coordinates of the intersection points

Table 4. Parameters of the columns work of the separation flowsheets shown in Fig. 2 (for the original compositions from **3.1** to **3.5**)

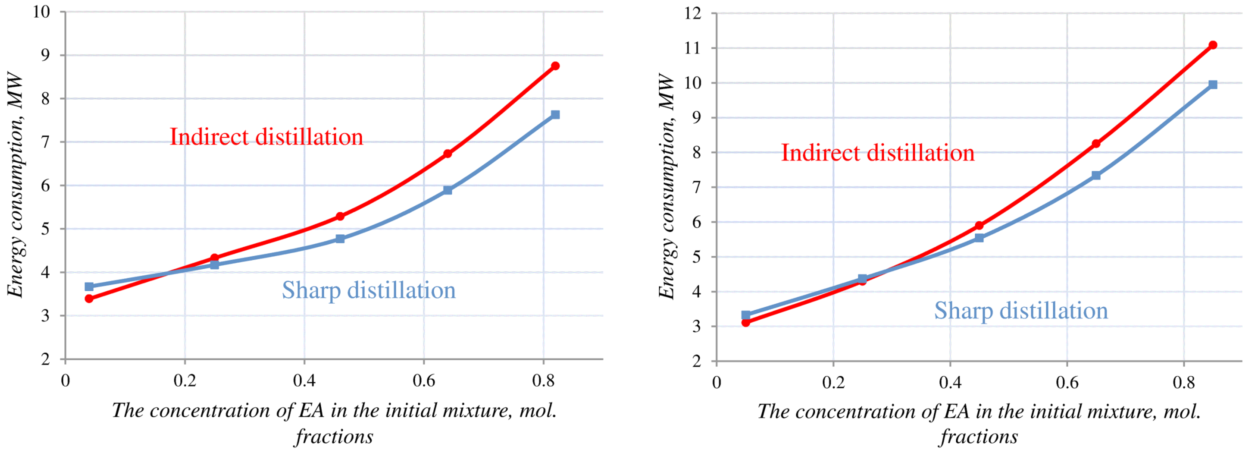
Column	NTS (F_{init}/F_{SA})	*P*	FS mix/SA	*R*	*Q*, kW	NTS (F_{init}/F_{SA})	*P*	FS mix/SA	*R*	*Q*, kW
	Sharp distillation					**Indirect distillation**				
The original composition of the mixture is **3.1** (x_{EA} = 0.05, x_B = 0.6, x_T = 0.05, x_{BA} = 0.3 mol. fract.)										
1	30	760	15	1.8	1616.23	30	100	7	1.4	1745.58
2	30 (1/1)	760	14/7	1.2	1123.41	36	760	23	1	1318.31
3	32	760	5	6.2	359.27	30 (1/1)	760	14/7	1.2	1123.41
4	47	110	14	18.3	859.27	32	760	5	6.2	359.31
					∑*Q* = 3958.18					**∑*Q* = 4546.61**
The original composition of the mixture is **3.2** (x_{EA} = 0.25, x_B = 0.474, x_T = 0.039, x_{BA} = 0.237 mol. fract.)										
1	30	760	15	1.4	1571.93	29	100	9	0.8	1629.03
2	22 (1/2.6)	760	10/6	2.4	1332.27	36	760	23	1	1606.97
3	24	760	5	4	1240.14	22 (1/2.6)	760	10/6	2.4	1332.27
4	47	110	14	18.5	671.34	24	760	5	4	1240.16
					∑*Q* = 4815.68					**∑*Q* = 5808.43**
The original composition of the mixture is **3.3** (x_{EA} = 0.45, x_B = 0.348, x_T = 0.029, x_{BA} = 0.173 mol. fract.)										
1	30	760	16	1.4	1745.25	28	100	9	0.6	1674.92
2	38 (1/2.4)	760	9/4	3.5	1218.12	33	760	21	1	1850.27
3	20	760	5	1.6	1275.53	38 (1/2.4)	760	9/4	3.5	1218.19
4	47	110	14	18.5	500.86	20	760	5	1.6	1275.58
					∑*Q* = 4739.76					**∑*Q* = 6018.96**
The original composition of the mixture is **3.4** (x_{EA} = 0.65, x_B = 0.2208, x_T = 0.0184, x_{BA} = 0.1108 mol. fract.)										
1	30	760	16	1.4	1901.95	28	100	10	0.5	1720.68
2	38 (1/4.4)	760	10/5	8.5	1616.26	34	760	21	1	2043.17
3	24	760	5	2.4	2326.96	38 (1/4.4)	760	10/5	8.5	1620.69
4	47	110	14	18.3	313.27	24	760	5	2.4	2327.07
					∑*Q* = 6158.44					**∑*Q* = 7711.61**
The original composition of the mixture is **3.5** (x_{EA} = 0.85, x_B = 0.094, x_T = 0.008, x_{BA} = 0.048 mol. fract.)										
1	30	760	17	1.5	2128.95	27	100	10	0.5	1756.05
2	38 (1/5)	760	10/4	29	2159.29	36	760	23	1.1	2239.51
3	23	760	5	2.2	2893.40	38 (1/5)	760	10/4	29	2164.64
4	47	110	14	16.4	137.03	23	760	5	2.2	2893.40
					∑*Q* = 7318.67					**∑*Q* = 9053.60**

Note: the separating agent is phenol.

Table 5. Parameters of the columns work of the separation flowsheets shown in Fig. 2 (for the original compositions from **4.1** to **4.5)**

Column	**NTS (F_{init}/F_{SA})**	P	**FS mix/SA**	R	Q, **kW**	**NTS (F_{init}/F_{SA})**	P	**FS mix/SA**	R	Q, **kW**
	Sharp distillation					**Indirect distillation**				
The original composition of the mixture is **4.1** (x_{EA} = 0.05, x_B = 0.3, x_T = 0.6, x_{BA} = 0.05 mol. fract.)										
1	36	760	17	4	1543.79	25	100	9	0.4	1406.04
2	29 (1/0.8)	760	13/5	1	503.63	32	760	15	2.1	1244.33
3	22	760	5	3.3	209.09	29 (1/0.8)	760	13/5	1.3	580.73
4	25	110	10	1.1	1094.80	22	760	5	3.3	212.09
					∑Q = 3351.31					**∑Q = 3443.19**
The original composition of the mixture is **4.2** (x_{EA} = 0.25, x_B = 0.237, x_T = 0.474, x_{BA} = 0.039 mol. fract.)										
1	32	760	16	3	1769.60	23	100	8	0.3	1405.04
2	33 (1/2.4)	760	9/4	3.1	767.02	29	760	14	1.7	1540.01
3	23	760	5	1.7	729.90	33 (1/2.4)	760	9/4	3.2	788.41
4	25	110	10	1.1	864.99	23	760	5	1.7	730.26
					∑Q = 4131.51					**∑Q = 4463.72**
The original composition of the mixture is **4.3** (x_{EA} = 0.45, x_B = 0.173, x_T = 0.348, x_{BA} = 0.029 mol. fract.)										
1	30	760	16	3	2270.55	22	100	7	0.2	1368.67
2	38 (1/3.2)	760	10/5	7.9	1182.36	24	760	13	1.2	1641.69
3	22	760	5	1.6	1276.29	35 (1/3.2)	760	10/5	7.5	1109.44
4	25	110	10	1.1	634.97	22	760	5	1.7	1287.29
					∑Q = 5364.17					**∑Q = 5407.09**
The original composition of the mixture is **4.4** (x_{EA} = 0.65, x_B = 0.1108, x_T = 0.2208, x_{BA} = 0.0184 mol. fract.)										
1	30	760	18	2.8	2621.59	20	100	6	0.2	1408.87
2	38 (1/6)	760	9/4	17	1533.78	23	760	13	1.3	2008.85
3	22	760	5	3.2	2825.41	38 (1/6)	760	9/4	17	1528.09
4	25	110	10	1.1	402.88	22	760	5	3.2	2817.44
					∑Q = 7383.66					**∑Q = 7763.25**
The original composition of the mixture is **4.5** (x_{EA} = 0.85, x_B = 0.048, x_T = 0.094, x_{BA} = 0.008 mol. fract.)										
1	30	760	18	2.6	2907.61	18	100	5	0.2	1376.49
2	40 (1/9.5)	760	11/5	50	1883.38	24	760	13	1.4	2339.91
3	24	760	5	4.9	5077.87	40 (1/9.5)	760	11/5	50	1887.00
4	25	110	10	1.1	171.47	24	760	5	4.9	5075.90
					∑Q = 10040.33					**∑Q = 10679.30**

Note: the separating agent is phenol.



a b

Fig. 3. Dependence of the energy consumption of the ethyl acetate–benzene–toluene–butyl acetate mixture separation flowsheets on the content of ethyl acetate (EA) in the initial mixture: (a) secant 1 (compositions **1.1**–**1.5**); (b) secant 2 (compositions **2.1**–**2.5**).

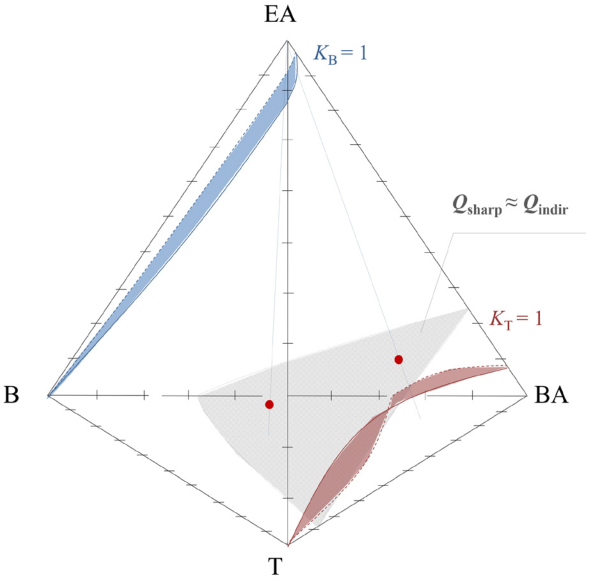


Fig. 4. Areas of energy advantage of the separation flowsheet based on the sharp distillation (above $Q_{sharp} \approx Q_{indir}$ surface) and indirect distillation (below $Q_{sharp} \approx Q_{indir}$ surface).

of the energy consumption dependences of the schemes on the content of ethyl acetate in the original mixture: for secant 1, x_{EA} = 0.17 mol. fractions; for secant 2, x_{EA} = 0.29 mol. fractions. Figure 4 shows a qualitative border (the surface is highlighted by hatching), where the energy consumptions of the considered separation schemes are almost identical.

The area of energy advantage of the flowsheet shown in Fig. 2a is located above the surface $Q_{sharp} \approx Q_{indir}$ diagram, and in Fig. 2b, it is located below $Q_{sharp} \approx Q_{indir}$ surface.

Acetone–toluene–butyl acetate–o-xylene system

For the separation of this mixture, five flowsheets of different structures are considered: the first column implements the direct (Figs. 5a, 5b), indirect (Figs. 5c, 5d), or sharp (Fig. 5e) distillation mode. The flowsheets in Figs. 5a and 5b and in Figs. 5c and 5d differ in the use of the direct and indirect distillation modes for the separation of the ternary mixture of toluene–butyl acetate–*o*-xylene (acetone–toluene–butyl acetate).

Preliminary calculations have shown that when separating toluene from a mixture of butyl acetate–*o*-xylene, it is impossible to achieve the required quality of toluene, even at a pressure of 50 mm Hg. This is because the volatility of toluene, in comparison with that of butyl acetate, in a ternary mixture is lower than that in a binary one.

The results of the simulation of the distillation process (parameters of the columns and energy consumption) for the other flowsheets are shown in Table 6.

The results obtained show that for the A–T–BA–*o*-X system, the use of sharp distillation for the separation of the original mixture is uneconomical (energy consumption is 20–30% higher compared to those for other separation modes).

CONCLUSIONS

If the original composition of a quaternary non-ideal zeotropic mixture, i–j–k–l ($T_i^0 < T_j^0 < T_k^0 < T_l^0$), belongs to a region for which the ratio, $K_i > 1, K_j > 1, K_k < 1, K_l < 1$, is observed, then we can recommend pre-fractionation

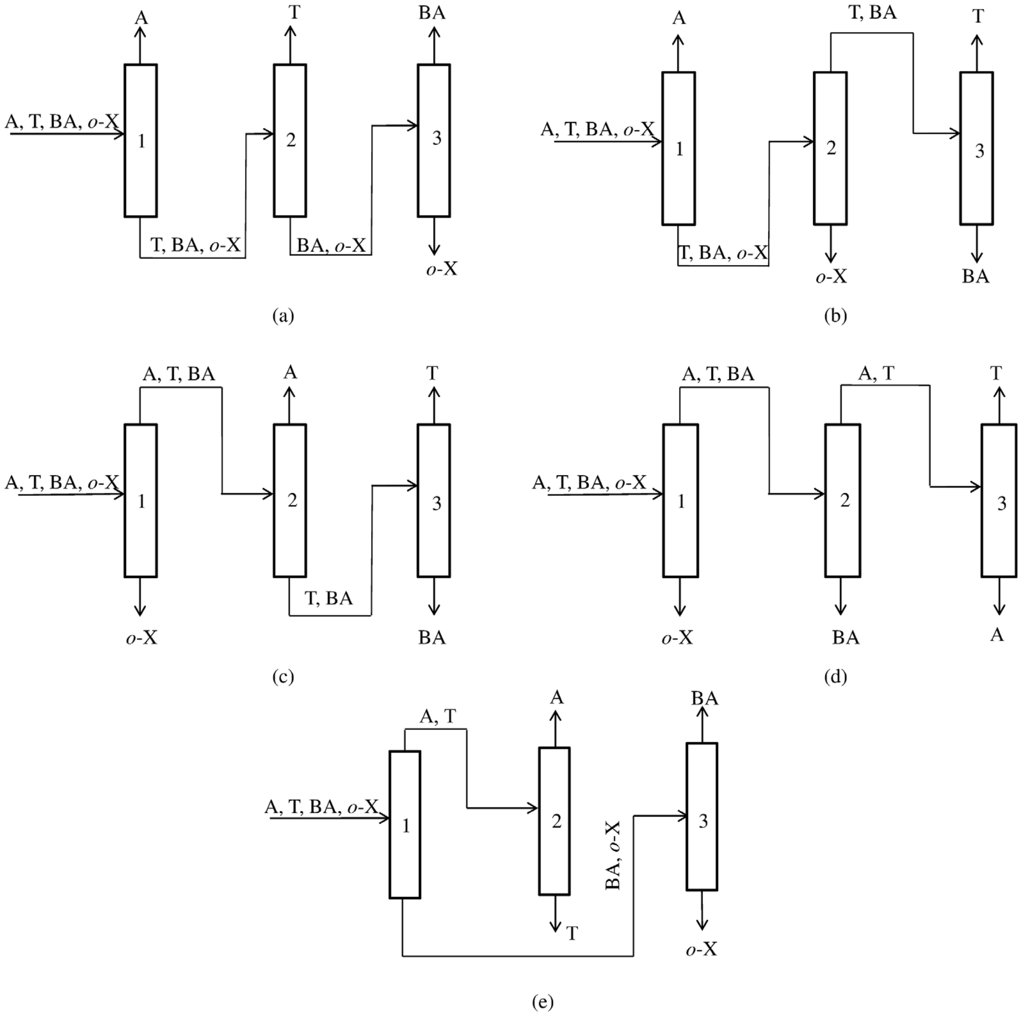


Fig. 5. Flowsheets of the separation of the mixture: acetone (A)–toluene (T)–butyl acetate (BA)–*o*-xylene (*o*-X), based on the direct (a)–(b), indirect (c)–(d) and sharp (e) distillation modes.

Table 6. Parameters of the columns work of the separation flowsheets shown in Fig. 5

Column	**NTS**	***P***	**FS**	***R***	***Q*, kW**	**NTS**	***P***	**FS**	***R***	***Q*, kW**
The original composition of $x_A = 0.25$, $x_T = 0.25$, $x_{BA} = 0.25$, $x_{o\text{-}X} = 0.25$ mol. fract.										
Direct distillation (Fig. 5b)						Sharp distillation (Fig. 5e)				
1	20	760	11	0.6	491.3	48	760	16	4.6	2832.3
2	33	760	16	2.3	1687.3	24	760	18	0.7	388.6
3	36	110	12	4.4	1397.2	40	760	24	4.8	1476.6
					$\sum Q = 3575.8$					**$\sum Q = 4697.5$**
Indirect distillation (Fig. 5c)						Indirect distillation (Fig. 5d)				
1	36	760	17	1.2	1868.0	36	760	17	1.2	1868.0
2	25	760	11	0.6	424.5	33	110	10	1.2	1208.5
3	40	110	13	4.5	1422.9	28	760	22	0.6	368.0
					$\sum Q = 3715.4$					**$\sum Q = 3444.5$**

Table 6. Continued

Column	**NTS**	***P***	**FS**	***R***	***Q*, kW**	**NTS**	***P***	**FS**	***R***	***Q*, kW**
The original composition of $x_A = 0.04$, $x_T = 0.32$, $x_{BA} = 0.32$, $x_{o\text{-}X} = 0.32$ mol. fract.										
Direct distillation (Fig. 5b)						Sharp distillation (Fig. 5e)				
1	20	760	9	3.6	213.7	80	760	24	8	3260.0
2	33	760	16	2.2	2090.1	24	760	13	1.6	110.5
3	36	110	12	3.1	1363.6	40	760	25	4.8	1889.5
					$\sum Q$ = 3667.4					**$\sum Q$ = 5260.0**
Indirect distillation (Fig. 5c)						Indirect distillation (Fig. 5d)				
1	38	760	18	1.8	2056.5	38	760	18	1.8	2056.5
2	25	760	11	3.2	177.3	33	110	11	2.7	1469.6
3	36	110	12	3.1	1363.7	24	760	13	1.6	110.6
					$\sum Q$ = 3597.5					**$\sum Q$ = 3636.7**

for the first stage of separation. The region with the specified ratio of distribution coefficients will occupy a large part of the volume of the composition simplex if the system is characterized by the presence of components with similar volatilities for pairs *i*–*j* and/or *k*–*l*. When a mixture of compositions belonging to this area are separated, the use of sharp distillation will be more energy-efficient (up to 20% energy savings) than the use of direct and indirect distillation modes. The latter modes can become competitive when the point of the original composition is located near the unit *K*-surfaces or in a region with a different ratio of distribution coefficients. These patterns are illustrated using the ethyl acetate–benzene–toluene–butyl acetate system as an example.

If the relative volatility of a pair of components with average boiling points (*j*–*k*) is close to one, the region of compositions with the ratio of distribution coefficients, $K_i > 1$, $K_j > 1$, $K_k < 1$, $K_l < 1$, will be small; consequently, sharp distillation would be unsuitable for separating the mixture, which is confirmed using the example of the acetone–toluene–butyl acetate–*o*-xylene system.

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