



Benzene Purification from Thiophene by Extractive Distillation with Dimethylformamide

Andrey V. Timoshenko*, Elena A. Anokhina, Alexander Yu. Akishin,
Anna V. Remizova

Moscow Technological University, Lomonosov Institute of Fine Chemical Technology, 86, Vernadskogo Ave., 119571,
Moscow, Russia
timoshenkoav@yandex.ru

Thiophene (T) is the one of the main sulfur-containing impurities in the composition of crude benzene by coke production. The effective way to remove the main amount of thiophene from crude benzene is an extractive distillation (ED) with dimethylformamide (DMF) when the relative volatility of the benzene-thiophene pair increases from 1.13 to 1.8–2.18. The aim of this work is to investigate the possibility to increase benzene yield from the initial fraction and to reduce ED heat demand of B-T mixture with DMF as entrainer by using an extractive distillation system with partially thermally coupled distillation columns (PTCEDS). To achieve the goal, the conventional extractive distillation (CED) and the PTCEDS were subjected to parametric optimization. The total energy consumption in the column reboilers (Q_{reb}) was selected as a criterion. It was found that the same yield of benzene is achieved in PTCEDS at lower heat demand in the columns' boilers than in CED. With an increase in the yield of benzene, energy savings are increased compared to conventional ED. Also, the production of the thiophene fraction in the side section of the PTCEDS requires a significantly smaller reflux ratio (1.0 – 2.28) than in the recovery column of the CED (7.17 – 73.13).

1. Introduction

Benzene is an important intermediate in the organic synthesis. In industry, benzene (B) is produced by coking coal, vapor cracking and reforming of petroleum feedstock, hydrodealkylation of aromatic fractions. In the production of benzene, there is both the problem for aromatics recovery from pyrolysis gasoline (Abushwireb et al., 2009) and the problem of purifying crude benzene from impurities. Thiophene (T) is the one of the main sulfur-containing impurities in the composition of crude benzene by coke production. Relative volatility of benzene to thiophene is close to 1. Extractive distillation (ED) is one of the most effective methods for the separation of compounds with close boiling points and azeotropic mixtures (Liu et al., 2017; Zhao, T. et al., 2017). Currently, dimethylformamide (DMF) is used as an entrainer (E) to remove the main amount of thiophene from crude benzene by ED (Zaretskii, 2004). The relative volatility of the benzene-thiophene pair increases from 1.13 to 1.8–2.18 in the presence of DMF. Recently, the mixtures of DMF and N-methylpyrrolidone with an ionic liquid were proposed as the entrainers for the separation of the B-T mixture by ED (Han et al., 2015; Dai et al., 2015). However, the high cost of ionic liquids can be an obstacle to the widespread industrial application of such mixed entrainers. The conventional extractive distillation (CED) flowsheet for the separation of B–T mixture includes an extractive column (EC) and an entrainer recovery column (RC). Benzene with concentration 99.78 mass % is the distillate of EC, and thiophene fraction with concentration of T 10–12 mass % is the distillate of RC. The distillate of RC is designated as “thiophene fraction” because practically all thiophene, contained in the input feed of crude benzene, is isolated in this stream. The thiophene fraction contains a large amount of benzene, it provides a sufficient amount of distillate for the stable operation of the column. In this case, 93% of benzene is recovered from the initial fraction. The level of benzene yield can be increased if its losses with a thiophene fraction are reduced. However, as follows from the literature data, this leads to DMF consumption and reflux ratios increasing, which leads to an increase in energy consumption for separation. Recently, the systems with partially thermally coupled distillation columns (PTCEDS) have been applied to reduce the energy consumption of ED (Timoshenko et al.,

2003; Gutiérrez-Guerra et al., 2009; Kiss and Ignat, 2012; Anokhina et al., 2013; Errico et al., 2013; Zhao Y. et al., 2017). PTCEDS is a single complex column that consists of a main column (MC) and a refining side section (SS) in the case of binary mixture separation by ED with a heavy boiling entrainer. Earlier, the criterion for the evaluation of the PTCEDS energy efficiency of binary mixture separation was formulated by Anokhina and Timoshenko (2015) as follows: PTCEDS is useful if the reflux ratio in the RC of CED has value equal to or greater than 1. Since in the case of separation of the B-T mixture the reflux ratio in the RC of the CED is greater than 1, then it is expected that the application of the PTCEDS will be effective.

The aim of this work is to investigate the possibility to increase benzene yield from the initial fraction and to reduce ED energy consumption of B-T mixture with DMF as entrainer by using a PTCEDS. To achieve the goal, the CED and the PTCEDS were subjected to parametric optimization. The total energy consumption in the column reboilers (Q_{reb}) was selected as a criterion. Aspen Plus was used for the flowsheets simulation.

2. Basis of design

The CED flowsheet for the separation of B-T mixture is presented in Figure 1a. PTCEDS (Figure 1b) was generated by the transformation of CED schema applying a graph algorithm (Timoshenko et al., 2005).

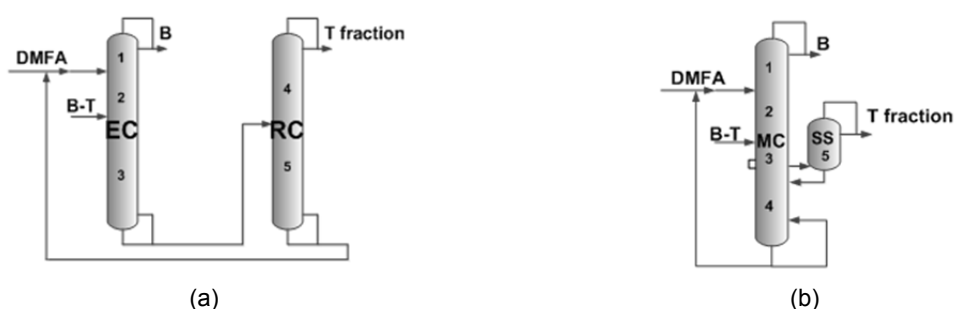


Figure 1: Conventional ED flowsheet (a) and PTCEDS (b) for benzene-thiophene mixture separation. MC – main column, SS – side section, EC – extractive distillation column, RC – entrainer recovery column, 1–5 – column's sections

CED and PTCEDS were simulated under the next conditions: the input stream of crude benzene with a value of 10,000 kg/h has a concentration of B and T 99 mass % and 1 mass %, respectively; the temperature of initial feed is 75 °C; the purity of B has been assigned as 99.78 mass %, concentration of DMF in thiophene fraction $\leq 0,01$ mass %, the entrainer flow rate contains 99.99 mass % DMF; the operating pressure is equal 101.3 kPa, the pressure drop per tray is adopted equal to 0.3 kPa. The WILS-VOL model with parameters published by Zaretskii et al. (1989) was used to predict the activity coefficients (Table 1). Built-in Aspen Plus Antoine equation coefficients were used for all components. The average relative deviation between experimental and calculated value of vapor composition and temperature for all binary mixtures do not exceed 3%.

Table 1: WILS-VOL binary interaction parameters, K

Component I	Component J	A(I,J)	A(J,I)	B(I,J)	B(J,I)	C(I,J)	C(J,I)	D(I,J)	D(J,I)	E(I,J)	E(J,I)
Benzene	Thiophene	0	0	2.7696	-11.3301	0	0	0	0	0	0
Benzene	DMF	0	0	39.3784	-203.7908	0	0	0	0	0	0
Thiophene	DMF	0	0	-56.6505	-52.9745	0	0	0	0	0	0

3. Results and discussion

3.1 Design of optimal CED

The criterion of the summary energy consumption in the reboilers of the columns ($Q_{\Sigma CET}$) is used to identify the optimal operating parameters. Optimization variables include: the number of theoretical trays in the columns (N_{total}), the location of feed plates of the B-T mixture (N_F) and entrainer (N_E), the temperature (T_E) and flow rate of entrainer (F_E), distillate streams (D) and reflux ratios (RR).

Due to the concentration of benzene in the thiophene fraction (the distillate of an entrainer recovery column) several cases have been considered: in the base case benzene concentration is equal 90 mass %, in the case #1 – 80 mass %, in the case #2 – 70 mass %, in the case #3 – 60 mass %, in the case #4 – 50 mass %.

Initially, the base case was investigated.

At the first stage, the acceptable value of the total number of theoretical plates in the extractive column and entrainer recovery column at a fixed flow rate of DMF 30,000 kg/h and a fixed entrainer temperature 80 °C was determined. The criterion of energy consumption in the column reboilers (Q_{reb}) was used. Figure 2a, b shows the dependence of the energy consumption in the reboilers of EC and RC on the number of plates. The energy consumption in the reboiler of the EC increases slightly (about 2–3 % per each 5 plates) with the number of plates decreasing from 70 to 55. With a further reduce the number of trays, Q_{reb} increasing becomes more visible. The change is 5.3 % by decreasing the number of plates from 55 to 50. Therefore, for all further calculations, the number of theoretical plates in the extractive column is set equal to 55. Similarly, the energy consumption in the reboiler of the RC increases slightly (about 2–3 % per each 2 plates) with the number of plates decreasing from 32 to 26. With a further reduction in the number of plates, the increasing of Q_{reb} becomes more apparent. It increases by 4.52 % from 26 to 24 plates and by 5.8 % from 24 to 22 plates. Therefore, for all further calculations, we set the number of theoretical plates in the RC equal to 26. The optimal initial feed tray locations were identified by using sensitivity analysis for each column with assigned N_{total} . For extractive distillation columns, the optimal entrainer feed plates were also determined.

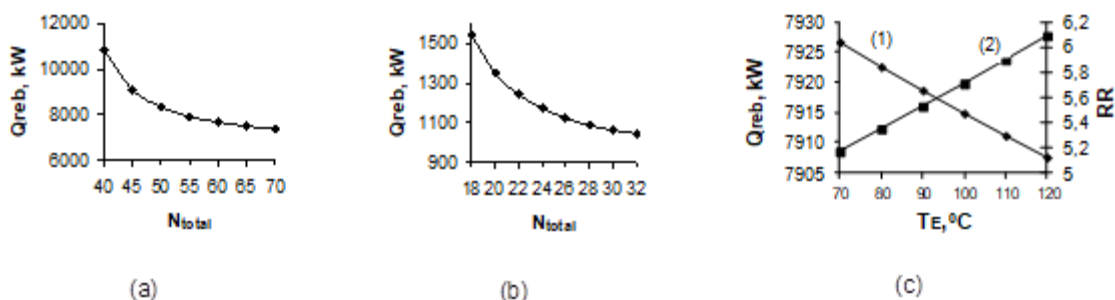


Figure 2: The dependence of the energy consumption in the reboilers of the extractive column (a) and recovery column (b) on the number of plates; (c) the dependence of the EC energy consumption in the reboiler (1) and reflux ratio (2) on the DMF temperature

At the second stage, the dependence was investigated of energy consumption in the reboiler of EC on the entrainer temperature at a fixed flow rate of DMF 30,000 kg/h and previously identified the total number of theoretical plates, as described above. The optimal initial and entrainer feed tray locations were determined at each temperature by using sensitivity analysis. Figure 2(c) shows the dependence of the energy consumption in the reboiler and the reflux ratio of the extractive column on the DMF temperature. The energy consumption in the reboiler of the EC decreases slightly (~ 0.2 %) by increasing the DMF temperature from 70 to 120 °C. The reflux ratio in this case increases from 5.2 to 6.1 (17.8 %). Thus, the entrainer feed temperature 80 °C was chosen. Its value is close to boiling point of the distillate of EC. In this research, we do not take into account the amount of heat that can be recovered by the entrainer cooling. Considering this fact, the temperature may vary: Q_{reb} of the EC decreases by DMF temperature rising (Figure 2(c)), but at the same time the heat recovery by the entrainer cooling is reduced.

At the third stage, the optimal value of FE in the individual ED column for the several values of N_E and N_F was determined by Aspen Plus optimization tool SQP (sequential quadratic programming). The objective function is Q_{reb} in EC, the constraints are the concentration of B in distillate of the EC 99.78 mass % and $(X_T/X_B) = 0.12$ in the bottom product of EC. Then, the dependence was investigated of N_F in entrainer recovery column on the entrainer flow rate at certain intervals of FE values. The lower variation interval boundary was assigned as 10,000 kg/h. A value somewhat larger than the maximum value of the "optimal entrainer flow rate to individual EC" was established as the upper interval of the variation boundary. Furthermore, calculations of the flowsheet were performed, and the optimal feed tray locations in the recovery column were determined for several values of FE from the performed interval by using sensitivity analysis. The calculations showed that the optimum N_F in the entrainer recovery column at the selected entrainer flow rate intervals is unchanged and equal 11. Thus, this value of N_F was fixed in the optimization procedure of scheme as a whole.

Optimization of the conventional ED scheme as a whole was carried out by using sensitivity analysis and the SQP (sequential quadratic programming) optimization tools from Aspen Plus. The objective function is the total energy consumption in the column reboilers ($Q_{\Sigma CET}$), the constraints are the purity of products.

The optimization procedure of the conventional ED scheme is summarized below:

- 1) Guess the entrainer (N_E) and the feed (N_F) tray locations in the extractive column.
- 2) Find the optimal values of continuous variables (FE, RR and D) in extractive and entrainer recovery columns by using SQP method.

3) Go back to step 1, vary N_E and N_F in the extractive column by using the sensitivity analysis and for each position of N_E/N_F repeat step 2. Repeat steps 1, 2 until $Q_{\Sigma CET}$ is minimized.

The optimal value of CED operating parameters in the cases #1–4 of benzene concentration in the distillate of RC was determinate analogously. The total number of plates in EC and RC and entrainer temperature were taken to be the same as the values chosen for the base case. The results are presented for conventional ED flowsheet optimization for all investigated cases in Table 2.

Table 2: Optimal parameters and energy consumption of CED depend on benzene concentration in the thiophene fraction (the distillate of RC)

	Base case	Case #1	Case #2	Case #3	Case #4
Extractive column					
N_{total}	55	55	55	55	55
N_E/N_F	7/29	7/26	7/23	7/22	7/20
FE, kg/h	18,702	23,540	27,592	32,571	38,115
RR_{EC}	5.87	6.18	6.55	6.92	7.42
D_{EC} , kg/h	9,240	9,602	9,736	9,802	9,842
Q_{cond} , kW	-6,951	-7,552	-8,058	-8,508	-9,079
Q_{reb} , kW	7,873	8,742	9,468	10,180	11,038
Recovery column					
N_{total}	26	26	26	26	26
N_F	11	11	11	11	12
RR_{RC}	7.17	18.05	32.10	51.36	73.13
D_{RC} , kg/h	759.9	398.0	264.2	197.7	158.2
Q_{cond} , kW	-677	-823	-944	-1,113	-1,255
Q_{reb} , kW	750	815	914	1,065	1,192
$Q_{\Sigma CET}$, kW	8,623	9,557	10,382	11,245	12,230
benzene yield (φ_B), %	93.1	96.8	98.1	98.8	99.2

The optimal position of the entrainer feed plate (N_E) is equal 7 in all cases, but the optimum position of the initial mixture feed plate (N_F) rises in the column as benzene yield increases. This is due to the fact that the higher the yield of benzene, the lower the concentration of benzene in the bottom stream of EC. The lower concentration of benzene in the bottom stream of the EC should be obtained with the minimal reboiler duty, the higher must be an initial feed location in EC.

It can be seen, that benzene yield rises from 93.1 % to 99.2 % when the concentration of benzene in the distillate of entrainer recovery column decreases from 90 mass % to 50 mass %. However, at the same time, the total energy consumption in the reboilers increases in 1.4 times. Obviously, this is due to rising 2.04 times the optimal value of the DMF flow rate, and reflux ratios increasing in the EC and in the RC in 1.3 and 10 times, correspondingly. The reflux ratio in the RC significantly rises because the total concentration of benzene and thiophene in the feed stream of this column decreases from 3.9 mass % up to 0.4 mass % by increasing the flow rate of DMF and also due to decreasing of the distillate of this column in 4.8 times.

Since in the case of separation of the B-T mixture the reflux ratio in the RC of the CED is significantly greater than 1, then, according to the criterion for the evaluation of the PTCEDS energy efficiency of binary mixture separation which was formulated by Anokhina and Timoshenko (2015) it is expected that the application of the PTCEDS will be effective.

3.2 Design of optimal PTCEDS

The optimized parameters for PTCEDS are: the location of side stream (N_S) to side section, the value of flow rate directed to the side section (FS), the reflux ratios in the MC and in the SS, the flow rate of distillates in the MC and in the SS. The minimum energy consumption in the reboiler of the main column (Q_{PTCEDS}) is the criterion. The total number of theoretical plates for the PTCEDS is set the same as the optimal value for the CED. According to the synthesis algorithm of the PTCEDS's (Timoshenko et al., 2005), the number of plates in the main column (N_{MC}) is obtained by summing the number of plates in the extractive column of the CED flowsheet and in the stripper section of the recovery column under the optimal design. The number of plates in the side section (N_{SS}) is equal to the number of plates in the rectifier section of the recovery column of the CED flowsheet under the optimal design. Additional fixed parameters for PTCEDS are: the location of feed plates of the B-T initial mixture and entrainer, the temperature and flow rate of DMF, which are taken to be the same as the optimal values for CED.

Optimization of the PTCEDSs was carried out by using sensitivity analysis to varying of N_S and the SQP method to determine the optimal value of FS, reflux ratios, distillate flow rates in the MC and of the SS. The optimization results for PTCEDS for all investigated cases are presented in Table 3.

As can be seen from Tables 2 and 3, the same degree of benzene recovery in the PTCEDS is achieved at lower energy consumption in the reboilers of columns and substantially lower reflux ratios in the SS compared to the RC of the CED. With an increase in the benzene yield, a more significant decrease in the reflux ratio in SS is observed compared to the RC of the CED: at a yield of 93%, the reflux ratios in these apparatuses differ by a factor of 7, and at the 99% yield by a factor of 32. At the same time, as the yield of benzene increases, the energy saving, DQ, increases from 9.7% with a yield of 93% to 20.8% with a yield of 99% (Table 4). Where

$$DQ = \frac{Q_{\Sigma CED} - Q_{PTCEDS}}{Q_{\Sigma CED}} \cdot 100\% \quad (1)$$

Table 3: Optimal parameters and energy consumption of PTCEDS depend on benzene concentration in the thiophene fraction (the distillate of SS)

	Base case	Case #1	Case #2	Case #3	Case #4
N_{MC}	70	70	70	70	69
N_{SS}	11	11	11	11	12
$N_E/N_F/N_S$	7/29/65	7/26/65	7/23/65	7/22/65	7/20/64
RR_{MC}	5.5	5.55	5.74	5.8	6.07
RR_{SS}	1.0	1.17	1.43	1.85	2.28
D_{MC} , kg/h	9,238	9,598	9,734	9,801	9,841
D_{SS} , kg/h	762.1	401.7	266.5	199.2	159.0
FS, kg/h	1,291	710	518	444	396.8
Q_{condMC} , kW	-6,549	-6,888	-7,185	-7,298	-7,620
Q_{condSS} , kW	-169.0	-94.8	-70.1	-61.0	-55.9
Q_{PTCEDS} , kW	7,717	8,237	8,720	9,083	9,687
benzene yield, %	93.1	96.8	98.1	98.8	99.2

Table 4: The dependences of composition of the feed stream and reflux ratio in the RC of CED and in the SS of PTCEDS on the benzene concentration in the thiophene fraction

	The sum of the concentrations of B and T in the feed of the RC of the CED, mass %	The sum of the concentrations of B and T in the flow rate directed to SS, mass %	RR_{RC}	RR_{SS}	RR_{RC} / RR_{SS}	DQ, %
Base case	3.9	94.6	7.17	1.0	7.17	9.7
Case #1	1.7	67.0	18.05	1.17	15.4	13.8
Case #2	1.0	60.0	32.1	1.43	22.4	16.0
Case #3	0.6	52.0	51.36	1.85	27.8	19.2
Case #4	0.4	46.0	73.13	2.28	32.1	20.8

It was found, that the separation of the thiophene fraction of identical composition in the SS of the PTCEDS is carried out at substantially lower reflux ratio values than in the RC of the CED. This is due to the fact that the stream that enters the side section of the PTCEDS has a higher concentration of B and T than a stream entering the RC of the CED. Therefore, the more composition of these streams differs, the greater the decrease of reflux ratios and, accordingly, of the energy consumptions (Table 4). It has also been determined that the energy efficiency of PTCEDS application increases with benzene concentration decreasing in the thiophene fraction.

4. Conclusions

It was found that the same yield of benzene is achieved in PTCEDS at lower power consumptions in the columns' boilers than in CED, the higher the yield of benzene, the more energy is saved. For example, with a

benzene yield of 93%, it is 9.7%, and when the yield is 99%, it is 20.8%. Also, the production of the thiophene fraction in the side section of the PTCEDS requires a significantly smaller reflux ratio (1.0 – 2.28) than in the RC of the CED (7.17 – 73.13). The obtained data confirm the criterion of energy saving effectiveness of the application of PTCEDS for the separation of binary azeotropic mixtures, formulated in the work (Anokhina and Timoshenko, 2015): PTCEDS is useful if the reflux ratio in the RC of CED has value equal to or greater than 1. In the all investigated cases of separation of the B-T mixture the reflux ratio in the RC of the CED is significantly greater than 1 and energy effectiveness of PTCEDS is equal 9.7–20.8 %. Thus, the criterion developed for the separation of binary azeotropic mixtures can be extended to extractive distillation of mixtures of components with close relative volatilities. Since the reduction in heat consumption in distillation entails a decrease in the flow of vapor along the height of the apparatus, this, even with the same number of plates, makes it possible to reduce the diameter of the column and, thereby, decrease capital cost.

Acknowledgments

The work was supported by the Russian Foundation for Basic Research, project No. 17-03-00347

References

- Abushwreb F., Elakrami H., Emtir M., 2009, The effect of solvent selection on energy-integrated extractive distillation for aromatics recovery from pyrolysis gasoline: Simulation and optimization, *Chemical Engineering Transactions*, 18, 243-248.
- Anokhina E.A., Shleynikova E.L., Timoshenko A.V., 2013, Energy efficiency of complexes with partially coupled thermally and material flows for extractive distillation of methyl acetate - chloroform mixture depending on entrainer, *Vestnik MITHT (Fine Chemical Technologies)*, 8 (2), 18–25 (in Russ.).
- Anokhina E., Timoshenko A., 2015, Criterion of the energy effectiveness of extractive distillation in the partially thermally coupled columns, *Chemical Engineering Research and Design*, 99, 165-175.
- Dai Ch., Dong Y., Han J., Lei Zh., 2015, Separation of benzene and thiophene with a mixture of N-methyl-2-pyrrolidinone (NMP) and ionic liquid as entrainer. *Fluid Phase Equilibria*, 388, 142–150.
- Errico M., Rong B.-G., Tola G., Spano M., 2013, Optimal synthesis of distillation systems for bioethanol separation. Part 2. Extractive distillation with complex columns, *Industrial and Engineering Chemistry Research*, 52, 1620–1626.
- Gutiérrez-Guerra R., Segovia Hernández J.G., Hernández S., 2009, Reducing energy consumption and CO₂ emissions in extractive distillation, *Chemical Engineering Research and Design*, 87, 145–152.
- Han J., Lei Zh., Dong Y. Dai Ch. and Chen B., 2015, Process Intensification on the Separation of Benzene and Thiophene by Extractive Distillation, *AIChE Journal*, 61 (12), 4470–4480.
- Kiss A.A., Ignat R.M., 2012, Innovative single step bioethanol dehydration in an extractive dividing-wall column, *Separation and Purification Technology*, 98, 290–297.
- Liu X.-Y., Shang D.-J., Liu Z.-Y., 2017, Comparison of extractive and pressure-swing distillation for separation of tetrahydrofuran-water mixture, *Chemical Engineering Transactions*, 61, 1423–1428.
- Timoshenko A.V., Anokhina E.A., Timofeev V.S., 2003, Russia Patent 2207896, A way for separation of the acetone-chloroform azeotropic composition mixture by extractive distillation (in Russ.)
- Timoshenko A.V., Anokhina E.A., Ivanova L.V., 2005, Extractive distillation systems involving complex columns with partially coupled heat and material flows, *Theoretical Foundation of Chemical Engineering*, 39, 463–470.
- Zaretskii M.I., Mozzuhin A.S., Pershina L.A., Taytz S.Z., Golub V.B., Chartov E.M., 1989, Evaluation of process parameters for production of the thiophene fraction and isolation of pure thiophene by extractive rectification, *Coke & Chemistry (USSR)*, 2, 35–41 (in Russ.).
- Zaretskii M.I., 2004, Cleaning of coke-chemical benzene from thiophene. Preparation of pure thiophene from thiophene fraction by extractive rectification. Calculation of industrial plant, *Coke & Chemistry*, 6, 20–23 (in Russ.).
- Zhao T., Li M., Yang J., Ma K., Zhu Z., Wang Y., 2017, Separation of acetone/isopropyl ether/water ternary mixture via hybrid azeotropic-extractive distillation, *Chemical Engineering Transactions*, 61, 1423–1428.
- Zhao Y., Jia H., Geng X., Wen G., Zhu Zh., Wang Y., 2017, Comparison of Conventional Extractive Distillation and Heat Integrated Extractive Distillation for Separating Tetrahydrofuran/Ethanol/Water, *Chemical Engineering Transactions*, 61, 751–756.