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Energy Saving Schemes for Separation of Benzene-Cyclohexane-Toluene Mixture with Different Initial Compositions by Extractive Distillation

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Benzene is one of the important raw materials for organic synthesis. Extraction and extractive distillation (ED) are used to recover benzene from petroleum and coking coal products. Application of the systems with partially thermally coupled distillation columns (PTCDC) is one of the effective ways to reduce the energy consumption of ED.

In this paper, evaluation is considered of the energy efficiency of ED schemes with PTCDC (PTCEDS) to separate benzene (B)-cyclohexane (CH)-toluene (T) mixture with two different initial feed compositions and N-methylpyrrolidone (NMP) as entrainer. The mixture #1 is some equivalent of the product of catalytic dealkylation of the gasoline fraction of hydrocracking with B, CH, T concentrations 40, 20, 40 mass %, respectively, and mixture #2 is a some equivalent of product of the hydrocracking and hydropurification of vapor cracking gasoline with B, CH, T concentrations 50, 5, 45 mass %, respectively. Three conventional ED schemes and five ED schemes with PTCDC were considered. All 8 schemes were compared by the total boiler heat duties criterion under optimal values of operating parameters. Optimization was carried out by using sensitivity analysis and the SQP (sequential quadratic programming) optimization tools of Aspen Plus.

It was determined that the scheme where toluene is separated in the first column as the bottom product had the lowest energy consumption among the conventional schemes in all cases of the initial feed compositions. The best solution with PTCDC in the both cases is the scheme where CH is recovered in the first ED column as a distillate, B is a distillate of the main column and T is a bottom product of the complex column side stripper section. The power consumption reduces by 19.8% and 22% for mixture #1 and mixture #2, respectively, compared to the conventional ED schemes with two outlets columns.

1. Introduction

Benzene is an important raw material for organic synthesis. It is usually recovered from petroleum and coking coal products by extraction and extractive distillation (ED). ED is occurred by introducing an additional component, the so-called entrainer, as an independent additional feed into the column to facilitate a separation. An entrainer should desirable alter the relative volatility of the initial mixture azeotropic components. Sulfolane, dimethylformamide, N-methylpyrrolidone, N-formylmorpholine are used as the entrainers to recover benzene by extraction and ED (Stichlmair and Fair, 1998; Li et al., 2018). World production of benzene now exceeds 50 million tons per year (Market Publishers, Ltd., 2014). Therefore, the reduction of energy consumption in this process is an actual task. The traditional ways for energy saving in the ED are the search for high-selective entrainers (Galli et al., 2017), the determination of the unit's optimal operation parameters (You et al., 2015), and the definition of the optimal distillation sequence (Errico et al., 2013). Recently, the systems with partially thermally coupled distillation columns have been applied to reduce the energy consumption of ED. In some cases, PTCEDSs decrease the energy consumption in the column boilers up to 15-30% compared to the conventional extractive distillation (CED) schemes (Timoshenko et al., 2003; Kiss and Ignat, 2012; Anokhina et al., 2015b; Zhao et al., 2017).

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Early, Anokhina et al. (2015a, 2015b) considered the extractive distillation with N-methylpyrrolidone (NMP) of benzene (B), cyclohexane (CH) and toluene (T) mixture with the initial composition of components 78, 12, 10 mass %, respectively. This mixture is some equivalent of the crude benzene fraction. Let us denote this mixture as a referenced mixture. It was found, that implementation of PTCDC to separate the B–CH–T referenced mixture, leads to the decreasing of energy consumption in the column boilers up to 28.7 % compared to the conventional ED flowsheets.

The aim of this work is to identify ED flowsheet with the lowest energy consumption for two different other initial feed compositions: mixture #1 – the product of catalytic dealkylation of the gasoline fraction of hydrocracking with 40, 20, 40 mass % of B, CH, T, respectively, and mixture #2 – product of the hydrocracking and hydropurification of vapor cracking gasoline with 50, 5, 45 mass % of B, CH, T, respectively. All schemes were compared by the total boiler heat duties criterion (Q_Σ). Q_Σ value was determined for each scheme under the optimal values of operating parameters. Aspen Plus is used for the simulation of CED and PTCEDS schemes.

2. Design basis

The B–CH–T mixture contains a B–CH binary azeotrope with a minimum boiling point at benzene concentration 54 mol. %. The inversion of relative volatilities of the azeotrope-forming components is observed in the presence of NMP. Therefore, it is possible to separate CH in the distillate of extractive column.

Three different conventional schemes for this mixture separation by ED are presented in Figure 1.

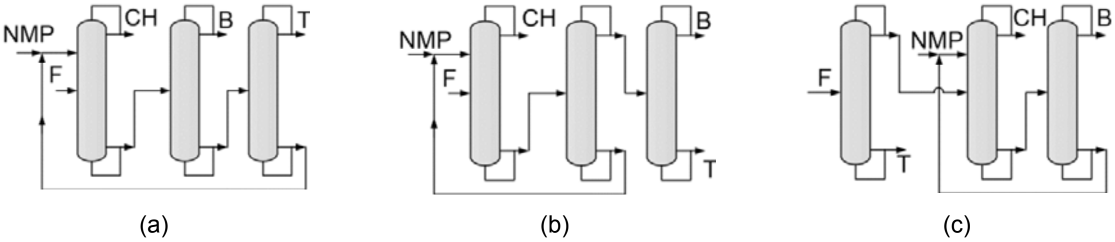
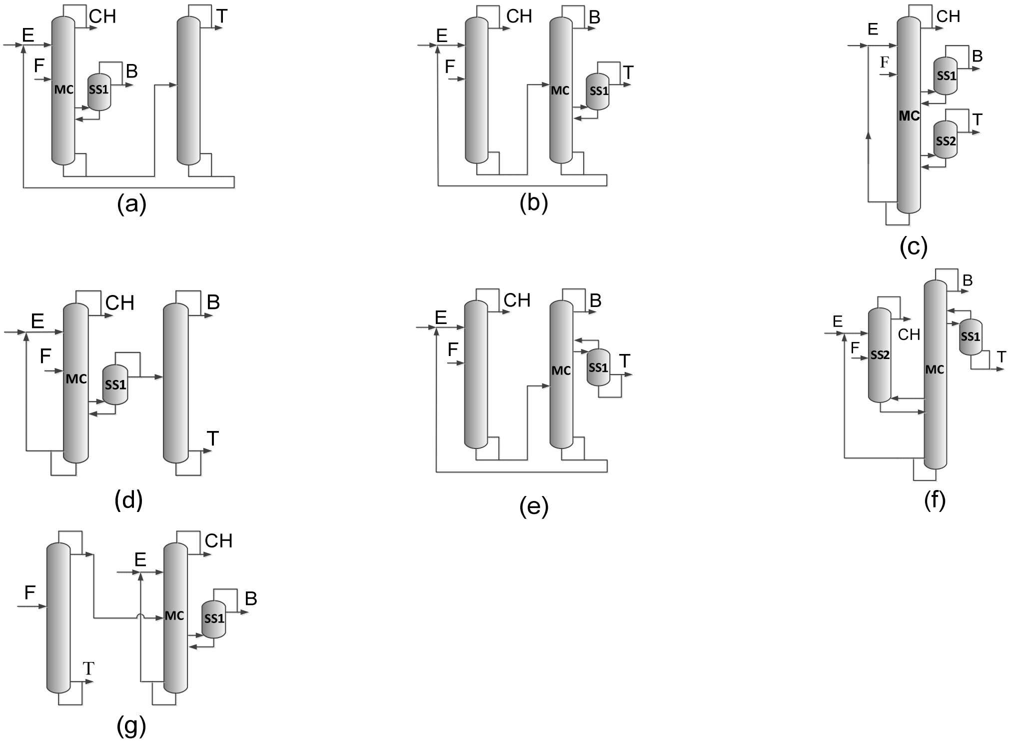


Figure 1: Conventional ED schemes for benzene-cyclohexane-toluene mixture separation with NMP: a) schema I, b) schema II, c) schema III, F – B-CH-T initial mixture, NMP – entrainer N-methylpyrrolidone

Seven new extractive distillation schemes with PTCDC (Figure 2) were generated by Anokhina et al. (2015b) on the base of these three CED schemes by using graph algorithm synthesis (Timoshenko et al., 2005). This approach is based on the representation of schemes in the form of graphs. Graph vertices correspond to the intersections separating the column sections. Nonoriented edges represent the oppositely directed flows of vapor and liquid inside a column and oriented edges represent the streams linking columns. The graph is transformed by combining of the two vertices which are connected by a single oriented edge. The scheme which is the base for synthesizing new technological solutions is called pre-image, and the resulting one - image. Thus, the CED flowsheets are used as the pre-images for the ED flowsheets with PTCDC. The schema I transformation gives three ED schemes with PTCDC: schema I.1 (Figure 2a), schema I.2 (Figure 2b) and schema I.3 (Figure 2c). Schema II produces also three ED schemes with PTCDC: schema II.1 (Figure 2d), schema II.2 (Figure 2e) and schema II.3 (Figure 2f). The schema III transformation produces only one schema III.1 ED with PTCDC (Figure 2g). As was found by Anokhina et al. (2015b), in the case of the B–CH–T referenced mixture separation the lowest total energy consumption of the boilers among all flowsheets is observed for the scheme II.3 (Figure 2f). However, the difference between the energy consumption of the schemes II.2 (Figure 2e) and II.3 is insignificant (~0.9%). The total energy consumption in the boilers of flowsheet I.3 is 9.5 % greater than in the schema II.3. It should be mentioned, that the flowsheets I.3 and II.3 are more complicated from the viewpoint of the apparatus design and the structure of vapor and liquid streams because these configurations contain two side sections thermally coupled with the main column. In this reason schemes I.3 and II.3 are not considered in this paper. Therefore, three CED flowsheets and five PTCEDS schemes were compared by the total heat duty of boilers criterion.

All 8 flowsheets were simulated under the next conditions: the initial mixture flow rate was 15,000 kg/h; the purities of products were assigned to B and CH as 99.90 mass %, for T as 99.75 mass %; the entrainer flow rate contained 99.99 mass % NMP; the entrainer temperature was fixed as 70 °C; the operating pressure was equal 101.3 kPa. NRTL model was used to predict the activity coefficients. Aspen Plus was used for the schemes simulation. The choice of the VLE model of B-CH-T-NMP system was discussed earlier by Anokhina et al. (2015a), where PRO-II was used for simulation. The same NRTL parameters were applied to predict the activity coefficients in all binary pairs except T-NMP. Aspen Plus built-in binary interaction NRTL parameters were used in the case of T-NMP system. Aspen Plus built-in Antoine equation coefficients were used for all components except NMP, for NMP Antoine parameters were applied from PRO-II database. The average relative deviation between experimental and calculated value of vapor composition and bubble point temperature for all binary mixtures did not exceed 3%. References to sources of experimental data are given in Anokhina et al. (2015a). If the Aspen Plus built-in Antoine equation coefficients are used for NMP, the average relative error of the bubble temperature in the system CH-NMP is 5.81%. The parameters of NRTL equation presented in the Table 1 were used to calculate the vapor-liquid equilibrium under the simulation of distillation schemes.



(a) (b) (c) (d) (e) (f) (g)

Figure 2: ED schemes with PTCDC for benzene-cyclohexane-toluene mixture separation with NMP: schema I.1 - (a), schema I.2 - (b), schema I.3 - (c), schema II.1 - (d), schema II.2 - (e), schema II.3 - (f), schema III.1 - (g). MC – main column, SS – side section

Table 1: NRTL binary interaction parameters, K

Component I	Component J	A(I,J)	A(J,I)	B(I,J)	B(J,I)	C(I,J)
Benzene	Cyclohexane	0.657505	-1.2279	-64.7939	400.999	0.3375
Benzene	Toluene	0	0	55.9156	-61.0122	0.3033
Benzene	NMP	0	0	663.349	-502.497	0.1771
Cyclohexane	Toluene	-0.102455	-0.776365	142.48	271.031	0.4299
Cyclohexane	NMP	0	0	523.919	323.62	0.2902
Toluene	NMP	-0.4766	1.5075	270.9658	-615.651	0.3

3. Optimal design of conventional ED schemes

The criterion of the summary power consumption in the boilers of the columns ($Q_{\Sigma CET}$) is used to identify the optimal operating parameters. Optimization variables include the entrainer flow rate (FE), the entrainer (N_E) and the feed (N_F) tray locations, reflux ratios (RR) and distillate flow rates (D). The total number of theoretical trays in the columns (Table 2) was assigned according to data Anokhina et al. (2015a). The optimal values of the operating parameters are identified by using the same procedure described in Anokhina et al. (2017).

Previously, the minimal and optimal values FE into the individual ED column were determined for several values of N_E/N_F by the Aspen Plus built-in sensitivity analysis module. The minimal FE is the minimal value of the entrainer flow rate at which the given product quality is possible to obtain in the distillate of ED column.

Table 2: The total number of theoretical trays in the columns of the conventional ED schemes

Schema	Column 1	Column 2	Column 3
Schema I	38	22	14
Schema II	38	14	22
Schema III	22	38	10

Later, the dependence of the N_F in the entrainer recovery column and additionally in the column 2 in the case of schema I on the entrainer flow rate at the certain intervals of FE values was investigated for all CED schemes. The minimal entrainer flow rate obtained for the individual ED column was chosen as the low variation interval boundary. A value somewhat greater than the maximum value of the optimal entrainer flow rate obtained for the individual ED column was set as the upper interval of the variation boundary. Furthermore, the optimal feed tray locations in the recovery columns (and additionally in the column 2 of schema I) were determined for several values of FE in the set interval. The calculations showed that the optimum values of the N_F in the entrainer recovery columns (and column 2 of schema I) in the set intervals of entrainer flow rate are practically unchanged. Thus, these values of the N_F were fixed as constant parameters in the procedure of optimizing the schema as a whole. N_F locations in the column 3 of the schema II and in the column 1 of schema III are independent of the entrainer flow rate. Thus, the N_F optimal position was determined before the optimization procedure of schemes as a whole by the sensitivity analysis and was later used as a fixed parameter.

Optimization of schemes was carried out by using sensitivity analysis and the SQP (sequential quadratic programming) optimization tools of Aspen Plus. The objective function is

$$\min\Phi = \sum_i Q_{rebi} \tag{1}$$

i – the number of column; i=1, 2, 3 in the case of schema I; i = 1, 2 in the case of schema II; i = 2, 3 in the case of schema III

The constraints are the purities of products.

The optimization procedure of the conventional ED schemes 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) by SQP method (RR and D are determined to all columns in the case of schema I, to columns 1 and 2 in the case of schema II, and in columns 2 and 3 in the case of schema III).

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

The results are presented of conventional ED schemes optimization for the separation of two investigated mixtures in Table 3.

Table 3: Optimal parameters and energy consumption of CED schemes for mixture #1 (mixture #2)

Schema	Column	N_E/N_F	RR	FE, kg/h	Q_{reb}, kW	$Q_{\Sigma CET}$, kW
Schema I	Column 1	4/19 (4/18)	2.5 (12.4)	15,033 (13,746)	1,509 (1,398)	6,695 (7,093)
	Column 2	–/12 (–/12)	4.2 (3.7)	–	3,656 (4,113)	
	Column 3	–/8 (–/8)	0.85 (0.7)	–	1,530 (1,582)	
Schema II	Column 1	5/18 (4/16)	1.9 (8.4)	16,611 (16,407)	1,397 (1,199)	6,534 (7,158)
	Column 2	– /8 (– /8)	0.39 (0.33)	–	2,485 (2,773)	
	Column 3	– /12 (– /12)	3.0 (2.8)	–	2,652 (3,186)	
Schema III	Column 1	– /13 (– /13)	2.4 (3.1)	–	3,250 (3,683)	5,804 (6,166)
	Column 2	5/18 (4/15)	1.2 (5.2)	14,301 (13,696)	1,082 (844)	
	Column 3	–/5 (–/5)	0.3 (0.23)	–	1,472 (1,639)	

It can be seen, that scheme III, where toluene is separated in the first column as the bottom product, has the lowest energy consumption among the three conventional schemes for separating both mixtures. Obviously, this is due to high concentration of toluene in the initial feed composition (40 mass % in the mixture #1 and 45 mass % in the mixture #2). The second place in terms of energy consumption is scheme II in the case of mixture #1 and scheme I in the case of mixture #2. However, it should be noted that the difference between the energy consumption of the schemes I and II is insignificant (about 2.4 % and 0.9 % for the separation of the mixtures #1 and #2, correspondently). The NMP flow rate has the least value in scheme III. The best solution among the CED schemes for the separation of referenced mixture, where the concentration of toluene is equal to10 mass %, is schema I.

4. Optimal design of PTCEDS schemes and schemes comparison

The optimization variables include the side outlet tray location (N_S), the value of flow rate directed to the side section (FS), reflux ratios in MC and reflux ratios in SS, distillate flow rates of MC, bottom flow rate of SS in the case of schema II.2 or distillate flow rate of SS to all others PTCDC. The entrainer flow rate, the entrainer and the feed tray locations were fixed for PTCEDS at the same values as optimal for CED pre-images. The total number of theoretical plates for the PTCEDS schemes is set the same value as for the conventional ED flowsheet. The number of plates of the main column of the schema I.1 is obtained by summing the number of plates of the extractive column and the stripper section of the column 2 of the schema I under the optimal design. The number of plates of the side section is equal to the number of plates of the rectifier section of the column 2 of the schema I under the optimal design. The number of plates of the main column and side section of all others PTCEDS schemes is obtained analogically. Optimization of the PTCEDS schemes was carried out by sensitivity analysis varying of N_S and the SQP method to determine the optimal value of FS, reflux ratios, distillate flow rates of MC and distillate (bottom) flow rates of SS. The obtained results for the separation of two investigated mixtures are presented in Table 4.

Table 4: Optimal parameters and energy consumption of PTCEDS schemes for mixture #1 (mixture #2)

Schema	Column		N_{total}	$N_E/N_F/N_S$	RR	FE, kg/h	FS, kg/h	Q_{reb}, kW	$Q_{\Sigma PTCDC}$, kW
Schema I.1	Column1	MC	48 (48)	4/19/37 (4/18/37)	3.17 (14.14)	15,033 (13,746)	19,000 (24,500)	4,119 (4,531)	5,649 (6,113)
		SS1	12(12)	–	2.28 (2.36)	–	–	–	
	Column 2		14 (14)	-/8/- (-/8/-)	0.85 (0.7)	–	–	1,530 (1,582)	
Schema I.2	Column1		38 (38)	4/19/- (4/18/-)	2.5 (12.4)	15,033 (13,746)	–	1,509 (1,398)	6,211 (6,575)
	Column2	MC	28 (28)	-/12/24 (-/12/24)	3.6 (3.18)	–	8,450 (9,100)	4,702 (5,177)	
		SS1	8(8)	–	0.7 (0.61)	–	–	–	
Schema II.1	Column1	MC	44 (44)	5/18/38 (4/16/38)	2.06 (8.9)	16,611 (16,407)	13,100 (15,500)	3,649 (3,737)	6,301 (6,923)
		SS1	8 (8)	–	0.16 (0.16)	–	–	–	
	Column 2		22 (22)	-/12/- (-/12/-)	3.0 (2.8)	–	–	2,652 (3,186)	
Schema II.2	Column1		38 (38)	5/18/- (4/16/-)	1.9 (8.4)	16,611 (16,407)	–	1,397 (1,199)	5,242 (5,585)
	Column2	MC	26 (26)	-/20/15 (-/20/15)	3.8 (3.44)	–	19,273 (22,722)	2,426 (2,699)	
		SS1	10 (10)	–	–	–	–	1,419 (1,687)	
Schema III.1	Column1		22 (22)	-/13/- (-/13/-)	2.4 (3.1)	–	–	3,250 (3,683)	5,651 (5,947)
	Column2	MC	43 (43)	5/18/37 (4/15/37)	1.06 (3.39)	14,301 (13,696)	6,270 (7,880)	2,401 (2,264)	
		SS1	5 (5)	–	0.11 (0.13)	–	–	–	

It can be seen that, for the both mixtures the scheme II.2 (Figure 3e) is the best solution among the five PTCEDS schemes. Their power consumption decreases by 19.8 and 22% in comparison with schema-preimage II for mixture #1 and mixture #2, respectively. It should be mentioned, that the similar results were obtained to referenced mixture by Anokhina et al. (2015b). Schemes I.1 and III.1 have approximately the same energy consumption and rank the second in terms of an energy efficiency. In the third place is schema I.2. Earlier, the criterion for the evaluation of the PTCEDS energy efficiency of ternary mixture separation was formulated by Anokhina et al. (2015b) as follows: PTCEDS with side-rectifier (side-stripper) is useful if the reflux ratio (vapor ratio) has a value equal to or greater than 1 in refining (stripping) section of the column of CED which is a preimage of side-rectifier (side-stripper) of PTCEDS. The vapor ratios in the column 3 of the scheme-preimage II are equal 4.4 and 4.7 in the cases of mixture #1 and mixture #2 separations, correspondingly. Therefore the energy saving by thermal coupling of the columns 2 and 3 in a scheme-preimage II in a one complex column with a stripping side section is significant (25.1% and 26.4 for mixture #1 and mixture #2 separations, correspondently). The reflux ratios in the column 2 of scheme II are equal 0.39 and 0.33 in the cases of mixture #1 and mixture #2 separations, respectively. Accordingly the energy saving by thermal coupling of the columns 1 and 2 in a scheme-preimage II into a one complex column with refining side section is smaller (about 6 %).

5. Conclusions

Thus, three CED flowsheets and five PTCEDS schemes were compared by the total energy consumption of reboilers criterion to separate B-CH-T mixture with two different initial feed compositions with NMP as entrainer. It was found, that for two initial feed compositions the scheme where T is separated in the first column as the bottom product has the lowest energy consumption among the three CED schemes. The best solution with PTCDC in the both cases is the scheme where CH is recovered at the first ED column as a distillate, B is a distillate of the main column and T is a bottom product of a side stripper section of complex column. The power consumption is reduced by 19.8% and 22% for mixture #1 and mixture #2, respectively, in comparison with CED schema-preimage.

Acknowledgments

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