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Comparison of alternative methods for methyl acetate + methanol + acetic acid + acetic anhydride mixture separation

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Objectives. The paper is a comparative analysis of methyl acetate + methanol + acetic acid + acetic anhydride industrial mixture separation flowsheets based on the use of special distillation methods (extractive distillation and pressure-swing distillation). The results obtained illustrate the variability of the structure of the technological separation flowsheet.

Methods. Mathematical modeling using the software package Aspen Plus V. 10.0 was chosen as the research method. The simulation was based on the local composition equation NRTL and the Hayden–O’Connell equation of state. The relative uncertainties of phase equilibrium description do not exceed 3%.

Results. The vapor–liquid diagram of the quaternary mixture of methyl acetate + methanol + acetic acid + acetic anhydride was studied using thermodynamic topological analysis. It was shown that the system contains one binary azeotrope and is characterized by one distillation region. Although the structure is not complex, there is a possibility of using several methods for mixture separation: pressure-swing distillation, and extractive distillation with different entrainers. Twelve flowsheets with different structure were proposed, and 29 variants of separation were compared.

Conclusions. It was shown that the most perspective structure for the separation of a methyl acetate + methanol + acetic acid + acetic anhydride mixture is a combination of distributed sequence separation and extractive distillation.

Keywords: azeotrope, extractive distillation, pressure-swing distillation, separation flowsheet.

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Сравнение альтернативных методов разделения смеси метилацетат – метанол – уксусная кислота – уксусный ангидрид

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Цели. Целью работы является сравнительный анализ технологических схем разделения промышленной смеси метилацетат – метанол – уксусная кислота – уксусный ангидрид, основанных на использовании специальных методов разделения: экстрактивная ректификация и варьирование давления. Полученные результаты иллюстрируют вариативность структуры технологической схемы разделения.

Методы. В качестве метода исследования выбрано математическое моделирование в программном комплексе Aspen Plus V. 10.0. Моделирование основывалось на уравнении локального состава NRTL и уравнении состояния Хейдена–О'Коннелла. Относительные ошибки описания фазового равновесия не превышают 3%.

Результаты. С помощью термодинамико-топологического анализа изучена диаграмма парожидкостного равновесия четырехкомпонентной системы метилацетат – метанол – уксусная кислота – уксусный ангидрид. Показано, что система содержит один бинарный азеотроп и характеризуется одной областью дистилляции. Несмотря на то, что структура не является сложной, существует возможность использования нескольких методов разделения смеси: ректификация с варьированием давления, экстрактивная ректификация с различными разделяющими агентами. Предложено 12 технологических схем различной структуры и проведен сравнительный анализ 29 вариантов разделения.

Заключение. Показано, что наиболее эффективным для разделения смеси метилацетат – метанол – уксусная кислота – уксусный ангидрид является сочетание промежуточного режима разделения смеси и экстрактивной ректификации.

Ключевые слова: метилацетат, азеотроп, экстрактивная ректификация, варьирование давления, схема разделения.

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Introduction

Distillation is the most widely used method for the separation of liquid mixtures. The possibility of separation depends on the presence of azeotropes (minimum-boiling, maximum-boiling, homogeneous and heterogeneous). The existence of azeotropes might limit recovery or even make separation unfeasible, unless a special distillation method (for example, pressure-swing distillation [1], extractive distillation [2, 3], heteroazeotropic [4] distillation, or a combination of different methods [5–9]) is applied. Each method has its advantages and disadvantages. For example, pressure-swing distillation does not require the addition of a new component (solvent or entrainer), which could contaminate the product. However, this method is limited to systems, in which pressure has a significant effect on the azeotrope's composition. Extractive distillation is a process, in which an entrainer (a new component) favorably changes the relative volatility of azeotrope-forming components.

If the multicomponent azeotropic mixture has to be separated, a set of flowsheets with different structures may be proposed for this purpose [10]. Each flowsheet will be characterized by its sequence of components separation (direct, indirect, or distributed sequence), and also by the use of special methods. The pressure choice in distillation columns in the pressure-swing distillation complex will affect the change of the azeotrope's composition and hence the amount of recycle flows. The same azeotropic mixture can be separated by extractive distillation with different solvents: heavy [11–14], light [15], or mixed [16] entrainers. Thus, each flowsheet will be characterized by its energy consumption. It is not always possible to say in advance what flowsheet design is optimal.

This study illustrates the variability of separation flowsheets using the example of industrial mixture forming in the production of methyl acetate via acetic anhydride esterification with methanol [17]. The comparison of 29 separation variants revealed the optimal

structure of the flowsheet. Mathematical modeling (Aspen simulation) and thermodynamical topological analysis [10] were used in this work.

Mathematical modeling and thermodynamic topological analysis of phase diagram

The object of this study is a quaternary mixture containing methyl acetate (MA), methanol (M), acetic acid (AA) and acetic anhydride (AAh). The composition (x) and amount (F) of the mixture coming from the synthesis stage were taken from [17]: $x_{MA} = 0.391$, $x_M = 0.157$, $x_{AA} = 0.178$, $x_{AAh} = 0.274$ mol. frac; $F = 775$ kmol/h. All

binary constituents are well studied. There is the information about vapor–liquid equilibrium (VLE) and azeotropic data at different pressures [13, 18–20]. This information is sufficient to verify the adequacy of mathematical modeling. The presence of associating compounds in the mixture determined the choice of the property model. The non-random two-liquid (NRTL) thermodynamic model [21] and the Hayden–O’Connell equation of state [22] were applied to calculate VLE. The parameters were taken from the NIST database. The relative uncertainties of VLE and description of azeotropic characteristics are given in Table 1.

Table 1. Relative uncertainties of VLE in binary constituents and description of azeotropic (Az) characteristics in a methyl acetate (MA) + methanol (M) + acetic acid (AA) + acetic anhydride (AAh) system

Constituent	Vapor–liquid equilibrium					
	MA+M	MA+AA	MA+AAh	M+AA	M+AAh	AA+AAh
for y_1 , %	1.33	1.10	1.60	3.46	0.29	2.97
for T , %	0.05	0.95	0.73	0.49	0.49	0.29
Methyl acetate + methanol azeotrope						
Pressure, kPa	26.3	53.7	80.0	140.8	395.2	787.3
for x_{MA}^{Az} , %	1.98	1.39	0.55	2.58	2.49	3.54
for T^{Az} , %	1.58	0.59	0.34	0.56	2.35	2.67

The vapor–liquid equilibrium diagram is characterized by a rather simple structure (Fig. 1): the system contains one binary azeotrope MA+M, which is an unstable node, and all distillation lines are directed to AAh (maximum boiling point – stable node).

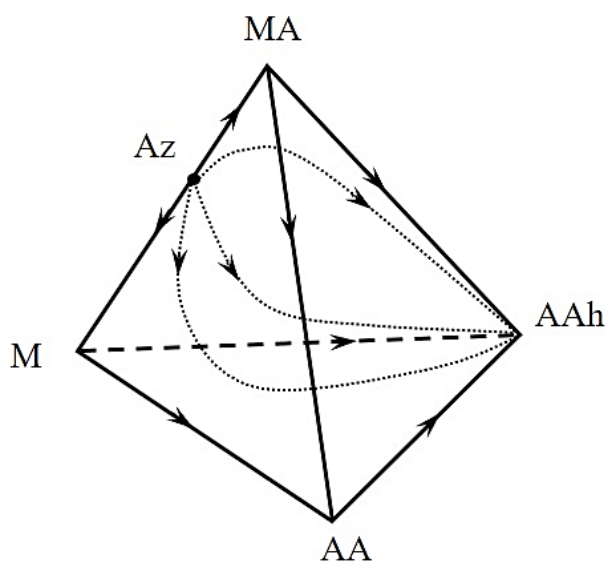


Fig. 1. VLE diagram of a methyl acetate (MA) + methanol (M) + acetic acid (AA) + acetic anhydride (AAh) system.

Other points are of a saddle type. The composition tetrahedron contains one distillation region. In this way, it is possible to realize separation of the mixture via direct (distillate flow will contain a mixture of MA+M of azeotropic composition), indirect (bottom flow will contain AAh), or distributed (MA+M at the top of the column and AA+AAh at the bottom) sequence.

The change in pressure has a significant effect on the methyl acetate + methanol azeotrope’s composition (Fig. 2). So, it is possible to use pressure swing distillation to separate this mixture.

Additionally, extractive distillation can be used for the separation of an azeotropic binary mixture. Ethylene glycol (EG) and dimethyl sulfoxide (DMSO) [23] were recommended as selective solvents. The study of methyl acetate + methanol’s relative volatility in the presence of these entrainers showed that it is more profitable to carry out the process of extractive distillation at a pressure of 50.7 kPa (an increase in the volatility by 2 and 1.5 times for EG and DMSO are observed respectively) [6].

It is possible to separate MA from the quaternary MA+M+AA+AAh, ternary MA+M+AA, or binary MA+M mixture. Table 2 shows the effect of the entrainer concentration on MA+M’s relative volatility at a pressure of 50.7 kPa.

The data obtained show (Table 2) that the relative volatility increases with the increase of entrainer

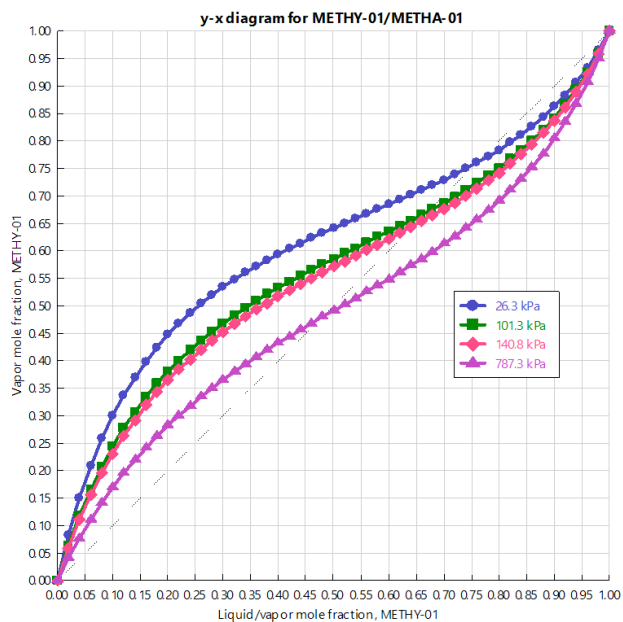


Fig. 2. VLE diagram of methyl acetate + methanol binary system at different pressures.

concentration. The coefficients in the case of extractive distillation of the binary mixture are higher, and in the case of the ternary and quaternary system they are lower due to the mixture’s dilution.

Design of separation flowsheet

The design of separation flowsheets was based on the use of direct (separation of methyl acetate + methanol azeotrope as a distillate product), indirect (separation of acetic anhydride as a bottom product), and distributed (distillate flow containing methyl acetate + methanol, bottom flow containing acetic acid + acetic anhydride) sequence and different special methods: extractive distillation (ED) with EG (or DMSO) or pressure-swing distillation (PSD) (26.34–787.30 kPa). Twelve flowsheets with different structures were designed to separate the quaternary mixture (Figs 3–5).

Taking into account the different ranges of pressure (26.34–101.32; 53.70–101.32; 101.32–395.17; 101.32–787.30 kPa) and extractive agents (EG and DMSO) 29 cases were considered. Material balances were calculated, and the column working conditions were determined using simulation in AspenPlus (Table 3).

Table 2. Effect of entrainer concentration on the relative volatility of methyl acetate + methanol mixture components at 50.7 kPa

Initial mixture	Entrainer concentration, mole frac.			
	0.2	0.4	0.6	0.8
Ethylene glycol				
MA+M+AA+AAh	1.50	1.82	2.38	3.38
MA+M+AA	1.82	2.45	3.42	4.46
MA+M	1.84	2.93	4.56	6.48
Dimethyl sulfoxide				
MA+M+AA+AAh	1.64	2.18	2.86	3.31
MA+M+AA	1.70	2.39	3.22	3.46
MA+M	1.72	2.60	3.60	4.27

Table 3. Column working conditions and energy consumption

Column (F / F _{EA})	P, kPa	Number of stages	Feed stage (EA stage)	Reflux ratio	Q, MW	Column (F / F _{EA})	P, kPa	Number of stages	Feed stage (EA stage)	Reflux ratio	Q, MW
Figure 3 (a)											
1	23.34	28	10	3	36.1	1	53.70	29	10	1.5	49.5
2	101.32	30	16	3.5	47.0	2	101.32	30	16	3.5	80.1
3	101.32	27	10	2	3.9	3	101.32	27	10	2	3.9
4	101.32	50	26	5	5.4	4	101.32	50	26	5	5.4
1	101.32	30	15	3	41.6	1	101.32	30	16	3.5	34.0
2	395.17	30	20	5	54.6	2	787.30	30	20	4	24.3
3	101.32	27	10	2	3.9	3	101.32	27	10	2	3.9
4	101.32	50	26	5	5.4	4	101.32	50	26	5	5.4

Table 3. Continued

Column (F/F _{EA})	P, kPa	Number of stages	Feed stage (EA stage)	Reflux ratio	Q, MW	Column (F/F _{EA})	P, kPa	Number of stages	Feed stage (EA stage)	Reflux ratio	Q, MW
Figure 3 (b)											
1	23.34	28	10	3	36.1	1	53.70	29	10	1.5	49.5
2	101.32	30	16	3.5	47.0	2	101.32	30	16	3.5	80.9
3	101.32	33	18	3.5	10.3	3	101.32	33	18	3.5	10.3
4	101.32	15	6	1.5	3.1	4	101.32	15	6	1.5	3.1
1	101.32	30	15	3	41.6	1	101.32	30	16	3.5	34.0
2	395.17	30	20	5	54.6	2	787.30	30	20	4	24.3
3	101.32	33	18	3.5	10.3	3	101.32	33	18	3.5	10.3
4	101.32	15	6	1.5	3.1	4	101.32	15	6	1.5	3.1
Figure 3 (c), EA = EG						Figure 3 (d), EA = EG					
1	50.66	30	14(4)	4	7.4	1	50.66	30	14(4)	4	7.4
2	101.32	24	12	1	13.7	2	101.32	24	12	1	13.7
3	101.32	30	6	3	5.1	3	101.32	33	18	3.5	10.3
4	101.32	50	26	5	5.4	4	101.32	15	6	1.5	3.1
Figure 4 (a), EA = EG						Figure 4 (a), EA = DMSO					
1	101.32	49	27	4.5	18.0	1	101.32	49	27	4.5	18.0
2	50.66	29	20(4)	2.5	4.3	2	50.66	28	20(4)	2	5.3
3	101.32	14	8	0.5	4.7	3	30.40	12	6	1.5	3.9
4	101.32	15	6	3	2.4	4	101.32	15	6	3	2.4
5	101.32	50	26	5	5.4	5	101.32	50	26	5	5.4
Figure 4 (b), EA = EG						Figure 4 (b), EA = DMSO					
1	101.32	49	27	4.5	18.0	1	101.32	49	27	4.5	18.0
2	50.66	29	20(4)	2.5	4.3	2	50.66	28	20(4)	2	5.3
3	101.32	14	8	0.5	4.7	3	30.40	12	6	1.5	3.9
4	101.32	38	20	4.5	8.8	4	101.32	38	20	4.5	8.8
5	101.32	19	10	1.5	1.4	5	101.32	19	10	1.5	1.4
Figure 4 (c)											
1	101.32	30	15	3	20.7	1	101.32	30	15	3	20.7
2	101.32	14	5	0.5	5.4	2	101.32	14	5	0.5	5.4
3	23.34	28	20	3	41.4	3	101.32	30	16	3	45.2
4	101.32	30	15	5	37	4	395.17	30	17	4	39.5
Figure 4 (c)						Figure 4 (d)					
1	101.32	30	15	3	20.7	1	101.32	30	17	3	20.7
2	101.32	14	5	0.5	5.4	2	101.32	40	24	3.5	42.8
3	101.32	29	22	3	28.7	3	23.34	29	20	2	41.8
4	787.30	30	20	4	24.3	4	101.32	18	10	0.5	4.0
Figure 4 (d)											
1	101.32	30	17	3	20.7	1	101.32	30	17	3	20.7
2	101.32	34	20	3.5	67.3	2	395.17	30	15	3.5	39.7
3	53.70	28	15	2	47.8	3	101.32	29	16	5	41.8
4	101.32	18	10	0.5	4.0	4	101.32	18	10	0.5	4.0

Table 3. Continued

Column (F/F _{EA})	P, kPa	Number of stages	Feed stage (EA stage)	Reflux ratio	Q, MW	Column (F/F _{EA})	P, kPa	Number of stages	Feed stage (EA stage)	Reflux ratio	Q, MW
Figure 4 (d)						Figure 5 (a), EA = EG					
1	101.32	30	17	3	20.7	1	101.32	30	15	3	20.7
2	787.30	30	15	2.5	23.9	2	101.32	14	5	0.5	5.4
3	101.32	36	24	4	21.7	3	50.66	25	16(4)	2.5	5.6
4	101.32	18	10	0.5	4.0	4	101.32	15	9	0.5	4.8
Figure 5 (a), EA = DMSO						Figure 5 (b), EA = EG					
1	101.32	30	15	3	20.7	1	101.32	30	15	3	20.7
2	101.32	14	5	0.5	5.4	2	50.66	29	17(4)	2.5	6.4
3	50.66	35	22(4)	2.5	6.1	3	101.32	17	7	0.5	5.0
4	30.40	15	4	2	4.7	4	101.32	29	10	4.5	5.3
Figure 5 (c)											
1	101.32	23	10	1	8.6	1	101.32	23	10	1	5.6
2	101.32	49	26	5	5.4	2	101.32	49	26	5	5.4
3	23.34	28	20	3	41.4	3	101.32	30	16	3	41.2
4	101.32	30	15	5	37	4	395.17	30	17	4	38.5
Figure 5 (c)						Figure 5 (d), EA = EG					
1	101.32	23	10	1	8.6	1	101.32	23	10	1	8.2
2	101.32	49	26	5	5.4	2	101.32	49	26	5	5.4
3	101.32	29	22	3	28.7	3	50.66	25	16(4)	2.5	5.8
4	787.30	30	20	4	24.3	4	101.32	15	9	0.5	5.1
Figure 5 (d), EA = DMSO											
1	101.32	23	10	1	8.2						
2	101.32	49	26	5	5.4						
3	50.66	35	22(4)	2.5	8.2						
4	30.40	15	4	2	4.6						

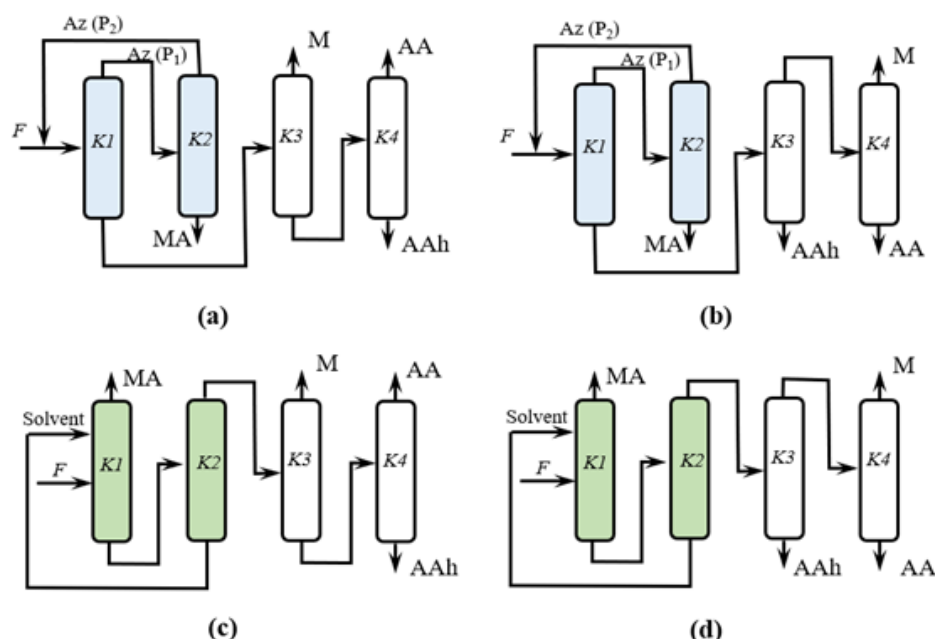


Fig. 3. Flowsheets for methyl acetate (MA) + methanol (M) + acetic acid (AA) + acetic anhydride (AAh) quaternary mixture separation:
 (a), (b) – Direct sequence in K1 + PSD; (c), (d) – ED.

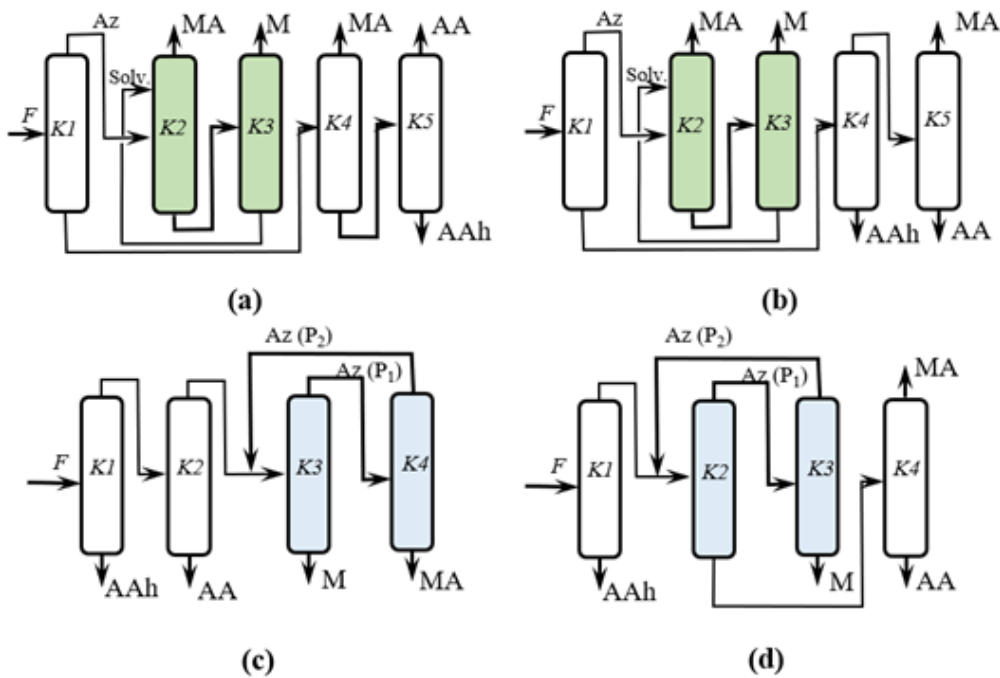


Fig. 4. Separation flowsheets for methyl acetate (MA) + methanol (M) + acetic acid (AA) + acetic anhydride (AAh) quaternary mixture separation:

(a), (b) – Direct sequence in KI + ED; (c), (d) – Indirect sequence in KI + PSD.

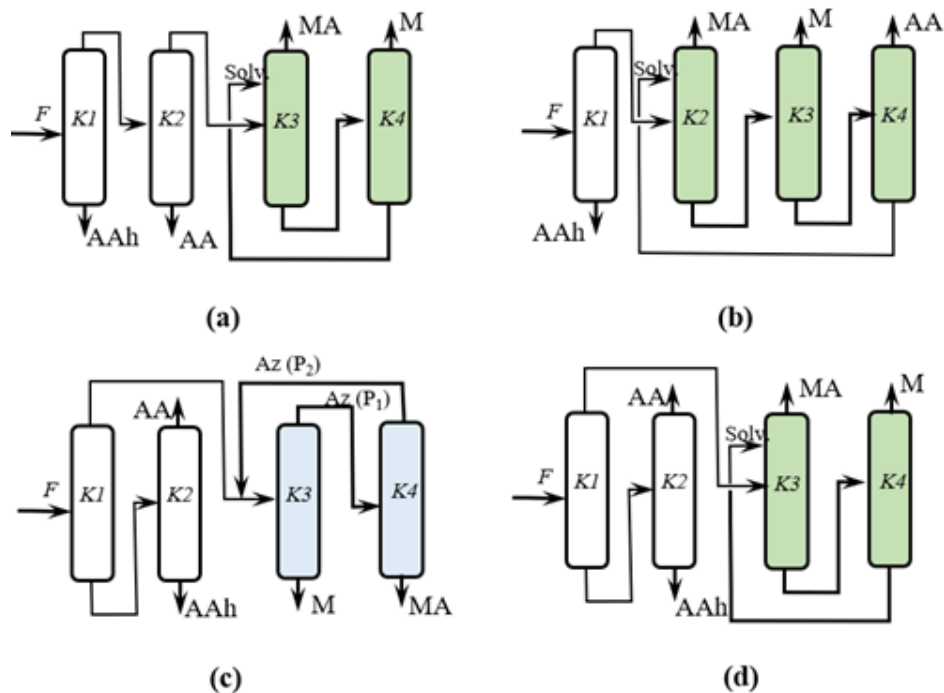


Fig. 5. Separation flowsheets for methyl acetate (MA) + methanol (M) + acetic acid (AA) + acetic anhydride (AAh) quaternary mixture separation:

(a), (b) – Indirect sequence in KI + ED; (c) – Distributed sequence in KI + PSD;
(d) – Distributed sequence in KI + ED.

The comparison of the amount of recycle flow and energy consumption is given in Table 4 and in histograms

presented in Fig. 6 (for pressure-swing distillation) and in Fig. 7 (for extractive distillation).

Table 4. Comparison of energy consumption

Figure	Method of separation	Pressure, kPa (EA)	Δx_1^{Az} , mole frac.	Recycle amount, kmol/h	Q, MW
3 (a)	Pressure-swing distillation (K1-K2) + Direct dist. (K3)	26.34-101.32	0.0872	863.2	92.5
		53.70-101.32	0.0453	1941.9	139.6
		101.32-395.17	0.1130	899.9	105.6
		101.32-787.30	0.1766	575.8	67.6
3 (b)	Pressure-swing distillation (K1-K2) + Indirect dist. (K3)	26.34-101.32	0.0872	863.2	96.5
		53.70-101.32	0.0453	1941.9	144.2
		101.32-395.17	0.1130	899.9	109.6
		101.32-787.30	0.1766	575.8	71.7
3 (c)	ED (K1-K2) + Direct dist. (K3)	50.66-101.32 (EG)	-	775.0	31.6
3 (d)	ED (K1-K2) + Indirect dist. (K3)	50.66-101.32 (EG)	-	775.0	34.5
4 (a)	Direct dict. + ED (K2-K3) + Direct dist.	50.66-101.32 (EG)	-	543.8	34.9
		50.66-30.40 (DMSO)	-	543.8	35.1
4 (b)	Direct dict. + ED (K2-K3) + Indirect dist.	50.66-101.32 (EG)	-	543.8	37.3
		50.66-30.40 (DMSO)	-	543.8	37.5
4 (c)	Indirect dist. + Pressure-swing distillation (K3-K4)	26.34-101.32	0.0872	863.2	104.5
		101.32-395.17	0.1130	899.9	111.0
		101.32-787.30	0.1766	575.8	79.1
4 (d)	Indirect dist. + Pressure-swing distillation (K2-K4)	101.32-26.34	0.0872	927.1	109.3
		101.32-53.70	0.0453	1784.6	139.8
		395.17-101.32	0.1130	593.7	107.2
		787.30-101.32	0.1766	336.1	70.3
5 (a)	Indirect dist. + ED (K3-K4)	50.66-101.32 (EG)	-	637.1	36.5
		50.66-30.40 (DMSO)	-	637.1	36.9
5 (b)	Indirect dist. + ED (K2-K3-K4)	50.66-101.32 (EG)	-	562.7	37.4
5 (c)	Distr. dist. (K1) + Pressure-swing distillation (K3-K4)	26.34-101.32	0.0872	863.2	92.4
		101.32-395.17	0.1130	899.9	90.7
		101.32-787.30	0.1766	575.8	67.0
5 (d)	Distr. dist. (K1) + ED (K3-K4)	50.66-101.32 (EG)	-	637.1	24.5
		50.66-30.40 (DMSO)	-	637.1	26.3

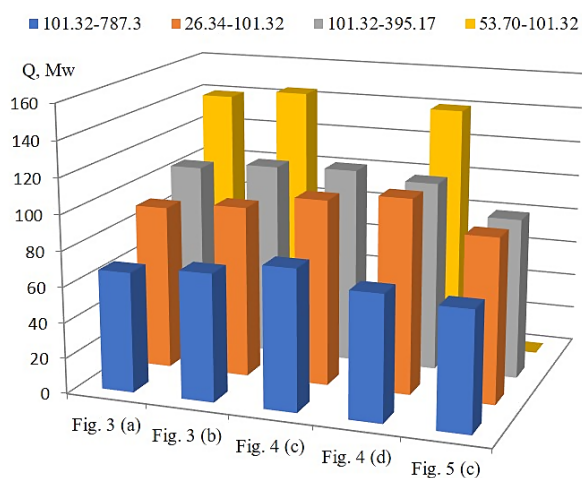


Fig. 6. Histogram showing the comparison of energy consumption in flowsheets based on the pressure-swing distillation.

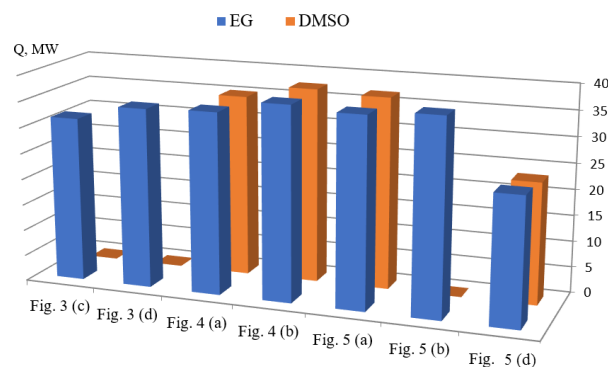


Fig. 7. Histogram showing the comparison of energy consumption in flowsheets based on the extractive distillation.

Conclusions

The amount of recycle flow depends on the mixture composition (feed to the pressure-swing distillation complex) and on the difference between azeotropic composition at chosen pressures. The results of Tables 3 and 4 show that the smaller this difference, the greater the amount of the recycle and hence energy consumption (for example, flowsheet in Fig. 3(a): $Q_{101.32-395.17} > Q_{101.32-787.30}$). It should be noted that an increase (decrease) in the value of the azeotrope composition changed by k times will result in a change in the value of the recycle and energy consumption by $k \pm 15\%$ times.

Direct distillation is preferable in comparison with indirect distillation (for example, $Q_{\text{Fig.3(a)}} > Q_{\text{Fig.3(b)}}$; energy saving varies from 13 to 31%).

The use of extractive distillation allows energy consumption to be reduced by 47–63% in comparison

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