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Comparison of extractive distillation flowsheets for methanol–tetrahydrofuran–water mixtures

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Objectives. *Synthesis and comparative analysis of the extractive distillation flowsheets for aqueous mixtures of solvents utilized in pharmaceutical industries using the example of a methanol–tetrahydrofuran–water system with various compositions. The ternary system contains two minimally boiling azeotropes that exist in a vapor–liquid phase equilibrium. To evaluate the selective effect of glycerol, the phase equilibria of the methanol–tetrahydrofuran–water and methanol–tetrahydrofuran–water–glycerol systems at 101.32 kPa were studied.*

Methods. *The calculations were carried out in the Aspen Plus V.9.0 software package. The vapor–liquid equilibria were simulated using the non-random two-liquid (NRTL) equation with the binary interaction parameters of the software package database. To account for the non-ideal behavior of the vapor phase, the Redlich–Kwong equation of state was used. The calculations of the extractive distillation schemes were carried out at 101.32 kPa.*

Results. *The conceptual flowsheets of extractive distillation are proposed. The flowsheets consist of three (schemes I–III) or four (scheme IV) distillation columns operating at atmospheric pressure. In schemes I and II, the extractive distillation of the mixtures is carried out with tetrahydrofuran isolation occurring in the distillate stream. Further separation in the schemes differs in the order of glycerol isolation: in the third column for scheme I (traditional extractive distillation complex) or in the second column for scheme II (two-column extractive distillation complex + methanol/water separation column). Scheme III caters to the complete dehydration of the basic ternary mixtures, followed by the extractive distillation of the azeotropic methanol–tetrahydrofuran system, also with glycerol. Scheme IV includes a preconcentration column (for the partial removal of water) and a traditional extractive distillation complex.*

Conclusions. *According to the criterion of least energy consumption for separation (the total load of the reboilers of distillation columns), scheme I (a traditional complex of extractive distillation) is recommended. Additionally, the energy expended for the separation of the basic equimolar mixture using glycerol as the extractive agent was compared with that expended using another selective agent: 1,2-ethanediol. Glycerol is an effective extractive agent because it reduces energy consumption, in comparison with 1,2-ethanediol, by more than 5%.*

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Keywords: *extractive distillation, scheme, relative volatility, effective agent, methanol, tetrahydrofuran, water, glycerol.*

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Сравнение схем экстрактивной ректификации смесей метанол–тетрагидрофуран–вода

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Цели. *Синтез и сравнительный анализ схем экстрактивной ректификации водных смесей растворителей фармацевтических производств на примере системы метанол–тетрагидрофуран–вода различного состава. Трехкомпонентная система содержит два минимально кипящих азеотропа, которые присутствуют в диапазоне существования парожидкостного равновесия. Для оценки селективного действия глицерина исследованы фазовые равновесия систем метанол–тетрагидрофуран–вода и метанол–тетрагидрофуран–вода–глицерин при 101.32 кПа.*

Методы. *Вычислительный эксперимент выполнен на платформе Aspen Plus V.9.0. Проведены расчеты фазовых равновесий по уравнению NRTL (Non-Random Two-Liquid) с параметрами бинарного взаимодействия базы данных программного комплекса. Для учета неидеального поведения паровой фазы использовали уравнение состояния Редлиха–Квонга. Расчеты схем экстрактивной ректификации проведены при 101.32 кПа.*

Результаты. *Предложены принципиальные технологические схемы разделения (I–IV), состоящие из трех (I–III) или четырех (IV) ректификационных колонн, работающих при атмосферном давлении. В схемах I, II проводилась экстрактивная ректификация базовых смесей с различным содержанием воды для выделения в дистиллатном потоке тетрагидрофурана. Дальнейшее разделение в схемах различалось очередностью выделения глицерина: в третьей колонне схемы I (традиционный трехколонный комплекс экстрактивной ректификации) или во второй колонне схемы II (двухколонный комплекс экстрактивной ректификации + колонна разделения метанола и воды). В схеме III предусмотрено полное обезвоживание базовых трехкомпонентных смесей с последующей экстрактивной ректификацией азеотропной системы метанол–тетрагидрофуран также с глицерином. Схема IV состоит из колонны концентрирования (частичного удаления воды) и традиционного комплекса экстрактивной ректификации.*

Выводы. *По критерию наименьших энергозатрат на разделение (суммарная нагрузка кипятильников ректификационных колонн) рекомендована схема I (традиционный комплекс экстрактивной ректификации). Дополнительно проведено сравнение энергозатрат схемы I при разделении смеси эквимолярного состава с другим селективным веществом – этиленгликолем, предложенным ранее в качестве агента. Глицерин является эффективным экстрактивным агентом, поскольку обеспечивает снижение энергозатрат более чем на 5%.*

Ключевые слова: *экстрактивная ректификация, схема, относительная летучесть, эффективный агент, метанол, тетрагидрофуран, вода, глицерин.*

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INTRODUCTION

To separate ternary azeotropic mixtures containing water, special distillation methods including extractive distillation (ED) are used in industries [1–7]. The structures of schemes for the ED of different types of ternary systems are provided in [1, 8]. The task of synthesizing possible schemes for the ED process can be considered via two approaches: for a certain set of agents that differ in selective effect or for a specific agent, which uniquely determines the result of the ED when added to the basic mixture [9, 10].

It is known that the preliminary concentration of binary aqueous mixtures makes it possible to reduce the energy consumption of ED schemes [11–16]. In this regard, it is necessary to additionally evaluate the feasibility of the preliminary partial dehydration (concentration) of basic ternary mixtures.

In this study, ED schemes of methanol–tetrahydrofuran–water mixtures were considered. Their separation is of interest to the chemical industry [4, 17]. Glycerol was chosen as the separating agent since it is recommended for the ED of tetrahydrofuran–water mixtures [18–20], as well as for methanol–tetrahydrofuran–water mixtures [4, 21].

MATERIALS AND METHODS

The basic system contains two azeotropes (Fig. 1, Table 1). The properties of the substances required for the empirical selection of extractive agents are given in Table 2. Glycerol has the highest boiling point and vaporization enthalpy and does not form azeotropes with the substances to be separated.

The simulation of phase equilibria was carried out on the Aspen Plus V. 9.0 platform using the non-random two-liquid (NRTL) equation with the parameters of the software package database. The non-ideal behavior of the vapor phase was considered using the Redlich–Kwong equation of state.

The component relative volatility diagrams of the basic methanol (1)–tetrahydrofuran (2)–water (3) system are shown in Fig. 2. The relative volatilities for the azeotropic pairs were calculated according to the vapor–liquid equilibrium data.

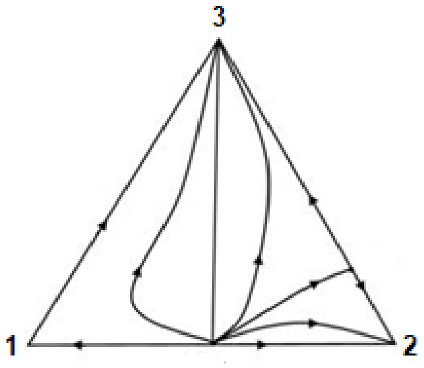


Fig. 1. Diagram of distillation lines in the methanol (1)–tetrahydrofuran (2)–water (3) system.

Table 1. Required properties of substances to be used as extractive agents

Substance	Normal boiling point, K	Vaporization molar enthalpy, kJ/mol
Methanol	337.85	37.6 ± 0.5
Tetrahydrofuran	339.15	32.0
Water	373.15	43.99
Glycerol	563.15	91.7 ± 0.9

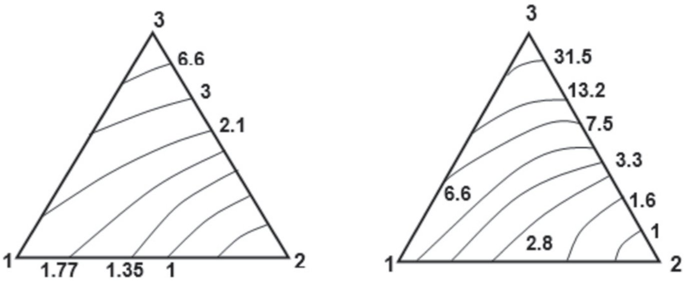
Table 2. Calculated azeotropic data at 101.32 kPa

Azeotropic system	Composition, mol. fract.			Temperature, K
	x_1	x_2	x_3	
Methanol–tetrahydrofuran	0.4910	0.5090	–	332.90
Tetrahydrofuran–water	–	0.8304	0.1696	336.59

RESULTS AND DISCUSSION

The volatility of tetrahydrofuran relative to that of methanol (α_{21}) increases with increasing water content in the basic mixtures, i.e., water exerts an extractive effect (Fig. 2a). The volatility of tetrahydrofuran relative to that of water (α_{23}) also increases in the ternary mixtures (Fig. 2b).

For comparison, the compositions of the basic mixtures (x^0_F) with different water contents located on secant $x_1 : x_2 = 1 : 1$ were chosen (Fig. 3). The relative volatilities in the presence of different amounts of the agent (4) are given in Table 3. The selective effects of water and glycerol are unidirectional. The concentration of tetrahydrofuran in the distillate is determined upon the ED of the basic mixtures. When separating basic mixtures with high water contents, a low concentration of the agent is required.



a b

Fig. 2. Diagrams of the relative volatilities of the components of the methanol (1)–tetrahydrofuran (2)–water (3) system at 101.32 kPa (a: α_{21}; b: α_{23}).

Notably, the glycerol amount had a different effect on the tetrahydrofuran volatility. For the basic compositions of $x^0_{F\text{-}I}$ and $x^0_{F\text{-}II}$, the values of α_{21} and α_{23} increased, and for the $x^0_{F\text{-}III}$ composition enriched with water, they decreased. In the latter case, it is important to accurately determine the smallest amount of the high-boiling point component, glycerol, which exerts sufficient extractive effect, since excessive consumption of the agent will result in a decrease in glycerol selectivity and an increase in the load of the ED column reboiler.

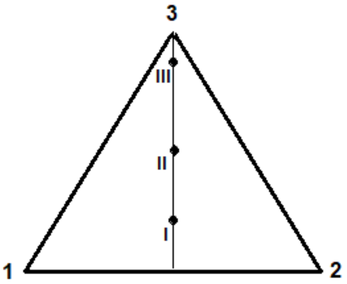


Fig. 3. Compositions (mol. fract.) of the basic methanol (1)–tetrahydrofuran (2)–water (3) mixture: I – $x^0_{F\text{-}I}$ (0.392; 0.408; 0.200); II – $x^0_{F\text{-}II}$ (0.333; 0.333; 0.334); III – $x^0_{F\text{-}III}$ (0.049; 0.051; 0.900).

The principal flowsheets of ED with glycerol are shown in Fig. 4. It is predicted that the azeotrope-forming component, tetrahydrofuran, will be obtained in the distillate of the ED column. Therefore, schemes I and II can be considered. Scheme I is traditional, with glycerol regeneration occurring in the last column. In scheme II, the heavy agent is separated in the second column.

Scheme III caters to the complete dehydration of the basic mixtures, after which the ED of the methanol–tetrahydrofuran mixture is carried out with glycerol. Thus, the ternary mixtures located to the left of secant $x_1 : x_2 = 1 : 1$ can be separated (Fig. 3).

Table 3. Relative volatilities of the components of the methanol (1)–tetrahydrofuran (2)–water (3)–glycerol (A) system at 101.32 kPa

$F_A : F$*	x_A	$x^0_{F\text{-}I}$		$x^0_{F\text{-}II}$		$x^0_{F\text{-}III}$	
		α_{21}	α_{23}	α_{21}	α_{23}	α_{21}	α_{23}
0 : 1	0	1.33	2.90	1.64	4.05	6.64	35.8
0.1 : 1	0.09	1.51	4.56	1.77	5.63	5.00	27.5
0.25 : 1	0.2	1.70	7.04	1.91	7.86	3.89	21.7
0.5 : 1	0.333	1.90	10.6	2.06	10.9	3.10	17.75
0.75 : 1	0.429	2.02	13.2	2.13	13.2	2.72	16.0
1 : 1	0.5	2.09	15.1	2.17	14.8	2.49	15.1
1.5 : 1	0.6	2.15	17.5	2.19	16.85	2.22	14.2

*F_A : F is the ratio of glycerol to the basic mixture (kmol).

In scheme IV, the preliminary concentration (partial dehydration) of the basic mixtures occurs, i.e., the separation option is intermediate for schemes I and III.

The operating parameters of the distillation columns were optimized by minimizing the reboiler duty in the distillation columns (*Q*) for the distillate composition of 0.995 mol. fraction. The variable parameter was the reflux number (*R*). At the first stage, we determined the lowest efficiencies for the ED columns (*N* is the number of theoretical stages) and the amount of glycerol (F_A), at which the required quality of product flows is achieved. The input levels of the feed flow (F) and agent (A) for the extractive columns were varied in the calculation experiment, i.e., the effect of the magnitude and position of the extractive part on the separation results was evaluated.

The calculation conditions comply with the data of [19]. Glycerol was introduced at a temperature (*T*) of 333.15 K to reduce the viscosity, and the feed flows of the columns were introduced at temperatures close to the boiling points of the separated mixtures.

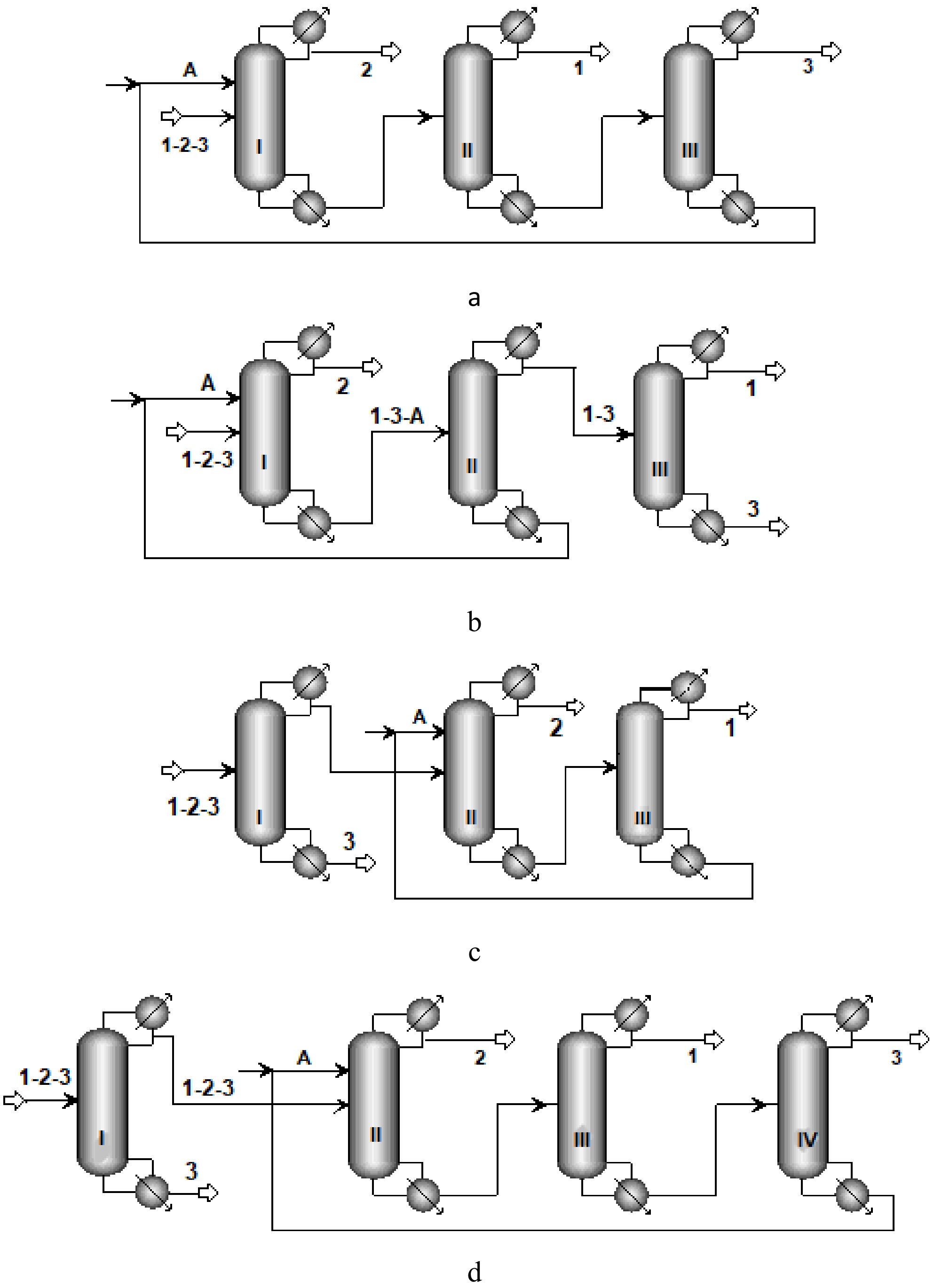


Fig. 4. Principal flowsheets for the extractive distillation of methanol (1)–tetrahydrofuran (2)–water (3) with glycerol (A) (a: scheme I; b: scheme II; c: scheme III; d: scheme IV).

The pressure of all the columns was 101.32 kPa. Tables 4–8 show the parameters of the distillate (D) and bottom (W) flows. The compositions are given sequentially for methanol, tetrahydrofuran, and water in mole fractions; the amount of flows (in kmol/h) and the reboiler duty (in kW) are determined. The flow rate (F) of the basic mixtures was 100 kmol/h.

Scheme I

The calculations were performed for the compositions of the basic methanol(1)–tetrahydrofuran (2)–water (3) mixtures: $x^0_{\text{F-I}}$ (0.392; 0.408; 0.2); $x^0_{\text{F-II}}$ (0.333; 0.333; 0.334); and $x^0_{\text{F-III}}$ (0.049; 0.051; 0.9).

An increase in the water content in the mixtures affects the energy consumption of the distillation columns of scheme I in different ways (Tables 4 and 5). The ED (column I) and methanol-isolation (column II) processes induced a significant reduction in the reboiler loads, while energy consumption, on the contrary, increased with glycerol recovery. The maximum contribution to the energy consumption was made by the methanol-isolation column (compositions $x^0_{\text{F-I}}$ and $x^0_{\text{F-II}}$) and by the agent recovery column ($x^0_{\text{F-III}}$). The total reboiler duty (kW) of the traditional ED flowsheet decreases in the following series: 4778 (x_1: 0.2 mol. fraction water);

Table 4. Static parameters and separation results for the extractive distillation column (schemes I and II)

Basic mixture	N, N_A/N_F	F_A	R	x_D	T_D	x_W	T_W	Q
$x^0_{\text{F-I}}$	30, 2/21	150	1.82	0.0050 0.9950 0 0	338.6	0.1865 0.0007 0.0956 0.7172	375.0	1753
$x^0_{\text{F-II}}$	40, 2/23	110	1.52	0.0050 0.9950 0 0	339.0	0.1855 0.0009 0.1920 0.6215	372.6	1158
$x^0_{\text{F-III}}$	30, 2/21	25	4	0.0039 0.9961 0 0	339.1	0.0407 0 0.7508 0.2085	374.2	442

Table 5. Static parameters and separation results for columns II and III (scheme I)

Basic mixture	No. col.	N, N_F	R	x_D	T_D	x_W	T_W	Q
$x^0_{\text{F-I}}$	II	25, 10	1.27	0.9951 0.0039 0.0010 0	337.3	0.0002 0 0.1174 0.8824	485.0	1966
	III	25, 10	0.12	0.0019 0 0.9950 0.0031	421.5	0 0 0.0004 0.9996	560.1	1059
$x^0_{\text{F-II}}$	II	30, 14	2.97	0.9950 0.0050 0 0	337.6	0 0 0.2361 0.7639	443.0	1783
	III	10, 5	0.2	0 0 0.9999 0.0001	383.5	0 0 0.0001 0.9999	560.8	1310
$x^0_{\text{F-III}}$	II	25, 10	5.66	0 0.9950 0.0050 0	337.5	0 0 0.7825 0.2175	381.0	338
	III	10, 5	0.05	0 0 0.9997 0.0003	390.1	0 0 0.0001 0.9999	560.4	1441

4251 (x_{II}: 0.334 mol. fraction water); 2221 (x_{III}: 0.9 mol. fraction water).

Scheme II

In the traditional ED flowsheet, direct separation is realized. Methanol is isolated in column I, and the agent is regenerated in the last column (direct separation) (Fig. 4). The recovery of the high-boiling point agent in column II, according to the second indirect separation, may reduce the total power consumption of the scheme. In scheme II, with indirect separation, glycerol is the first output; thereafter, the distillation of the zeotropic water–methanol mixture is carried out (indirect separation).

Scheme II was calculated for the basic mixtures of compositions $x^0_{F\text{-}I}$ (0.392; 0.408; 0.200) and $x^0_{F\text{-}III}$ (0.049; 0.051; 0.900). The calculation results for the ED column are given in Table 4; for columns II and III, the results are given in Table 6.

The maximum contribution to the total energy consumption is made by the agent recovery column (column II). The separation of glycerol from the mixtures with methanol and water is more energy-intensive than the recovery of the agent from the aqueous mixtures (column III, scheme I). Scheme II cannot be recommended for separating the basic methanol–tetrahydrofuran–water mixture with a low water content.

The positive effect of diluting the basic mixtures with water in all the columns was noted (Tables 4 and 6). The total energy consumption of scheme II is considerably low: $x^0_{F\text{-}I}$ = 5098, $x^0_{F\text{-}III}$ = 2545 kW.

Scheme III

This separation option caters to the complete dehydration of the basic mixture (Fig. 4). The calculations were carried out only for the equimolar composition, $x^0_{F\text{-}II}$, (Table 7).

Water increases the relative volatility of tetrahydrofuran. Therefore, its removal from mixtures leads to an increase in the glycerol amount: 150 kmol/h of agent per 66.6 kmol/h of methanol—tetrahydrofuran mixture (the ratio is 2.25 : 1) is required. However, in case of the ED of the ternary mixture of the same composition, this ratio is 110 kmol/h per 100 kmol/h (1.1 : 1). The total reboiler duty is 5325 kW, which is 20% higher than that in the case of scheme I (4251 kW). The complete dehydration of the basic mixture is impractical.

Thus, glycerol is not an effective agent for scheme III. The concept of an effective agent considers both the selectivity (effect on the vapor–liquid equilibrium) and the process parameters (reboiler duty) [22]. The energy consumption of the selective glycerol recovery column accounts for more than 51% of the total energy consumption of scheme II. If a more selective agent, with a lower boiling point and enthalpy of vaporization than glycerol (Table 1), which affects the energy consumption of the distillation columns, is used, scheme III may be viable. Such an agent may be, for example, dimethyl sulfoxide [9].

Scheme IV

The calculations of scheme IV were not performed. It can be considered as an intermediate separation option for schemes I and III, without preliminary concentration (partial removal of water) and with complete dehydration of the basic mixtures (Fig. 4). The preliminary concentration is impractical, because it will be inevitably accompanied by an

Table 6. Static parameters and separation results for columns II and III (scheme II)

Basic mixture	No. col.	N, N_F	R	x_D	T_D	x_W	T_W	Q
$x^0_{F\text{-}I}$	II	25, 10	0.5	0.6598 0.0024 0.3378 0	351.8	0 0 0.0003 0.9997	560.7	2813
	III	25, 10	2	0.995 0.0039 0.0011 0	337.7	0.0046 0 0.9954 0	372.3	532
$x^0_{F\text{-}III}$	II	25, 10	0.5	0.0514 0 0.9486 0	371.9	0 0 0.0001 0.9999	560.9	1921
	III	10, 5	2.53	0.9950 0 0.0050 0	337.9	0.0004 0 0.9996 0	373.1	182

Table 7. Static parameters and separation results for scheme III (basic mixture, $x^0_{\text{F-II}}$)

No. col.	N, N_A/N_F	F_A	R	x_D	T_D	x_W	T_W	Q
I	30, 15	–	1.89	0.4995 0.5 0.0005 0	332.9	0.0010 0.9990 0 0	373	1773
II	40, 2/26	150	1.87	0.0035 0.9965 0 0	339.1	0.1795 0.0006 0.0002 0.8197	379.3	810
III	20, 11	–	2	0.9964 0.0036 0 0	339.0	0.0008 0 0.0002 0.9990	374.2	2742

Table 8. Comparison of 1,2-ethanediol and glycerol for scheme I (basic mixture, $x^0_{\text{F-II}}$)

Agent	F_A	No. col.	N, N_A/N_F	R	Product purity		Q
					x	T	
1,2-Ethanediol*	400	I II III	45, 5/30 30,12 13, 6	2.2 1.9 2	$x_2 = 0.9980$ $x_1 = 0.9973$ $x_3 = 0.9991$ $x_A = 0.9999$	339.04 337.65 373.04 470.21	1928 1548 1628
Glycerol	120	I II III	40, 2/23 30, 14 10/5	1.88 3.96 0.1	$x_2 = 0.9980$ $x_1 = 0.9980$ $x_3 = 0.9999$ $x_A = 0.9999$	339.09 337.65 375.31 560.84	1306 2167 1360

* Data [19]: 1,2-ethanediol; in this study: glycerol.

increase in energy consumption due to the introduction of an additional column. A comparison of the energy consumptions for the separation in schemes I and III (Tables 4, 5, and 7) shows that, as the water content in the basic mixtures decreases, glycerol consumption increases due to a decrease in the relative volatility of tetrahydrofuran.

The ED of methanol–tetrahydrofuran–water mixtures can also be carried out using ethylene glycol as the extractive agent [4, 19]. For a correct comparison with the results of [19], additional calculations of scheme I were performed to obtain purer products (Table 8).

Using glycerol reduces the energy consumption of the complex by 5.6%. Therefore, glycerol is an effective agent for scheme I.

CONCLUSIONS

For the separation of mixtures of methanol, tetrahydrofuran, and water, a traditional ED scheme with glycerol is recommended. If it is necessary to separate mixtures with low water contents, a binary agent (water–glycerol) can be introduced into the ED column. In addition to increasing selectivity, this will ensure a decrease in the temperature in the ED column and, consequently, a decrease in the energy consumed for separation in the scheme.

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The authors declare no conflicts of interest.

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