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Separation of water – formic acid – acetic acid mixtures in the presence of sulfolane

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In this paper, extractive distillation flowsheets for water–formic acid–acetic acid mixtures were designed. Flowsheets not involving preliminary dehydration were considered, and the relative volatilities of the components in the presence of sulfolane were analyzed. The result of extractive distillation depends on the amount of sulfolane. The structure of the flowsheet is determined by the results of the basic ternary mixture extractive distillation. In three-column flowsheets (schemes I, II), water is isolated in the distillate of the extractive distillation column. In the second column, distillation of the formic acid–acetic acid–sulfolane mixture is carried out, yielding formic acid (90 wt %) and acetic acid (80 wt %). The recycled flow is returned to the first column. Dilution of the formic acid–acetic acid–sulfolane mixture with sulfolane (second column of flowsheet II) allows for acids of higher quality (main substance content equal to or more than 98.5 wt %) to be obtained. Flowsheet III includes four columns and two recycling stages. First, the water–formic acid mixture is isolated in the distillate of the extractive distillation column. Then, water and formic acid are separated in a two-column complex by extractive distillation, also with sulfolane. We were carrying out calculations for column working pressure 101.32 and 13.33 kPa. To prevent thermal decomposition of sulfolane, working pressure for regeneration columns was always 13.33 kPa. The extractive distillation column of the basic three-component mixture is the main factor contributing to the total energy consumption for separation (in all schemes).

Keywords: *formic acid, acetic acid, water, sulfolane, extractive distillation, separation flowsheet.*

Разделение смеси вода – муравьиная кислота – уксусная кислота в присутствии сульфолана

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При экстрактивной ректификации (ЭР) водных смесей низших карбоновых кислот (муравьиной и уксусной), в зависимости от выбора селективного агента, возможно выделение в дистиллате воды или смеси вода – муравьиная кислота. Однако обычно задача выделения всех практически чистых компонентов не рассматривается. Здесь предлагаются схемы выделения муравьиной (МК) и уксусной (УК) кислот из водной смеси экстрактивной ректификацией (ЭР) с сульфоланом, не предусматривающие предварительное обезвоживание. Анализ рядов относительных летучестей компонентов в присутствии сульфолана показал, что в зависимости от количества вводимого агента возможны три варианта организации ЭР. В схемах, состоящих из трех колонн, в дистиллате колонны ЭР базовой смеси вода–МК–УК выделяют воду, в последней колонне схемы УК отделяют от агента, возвращаемого в первую колонну схемы. Во второй колонне схемы I проводят ректификацию смеси МК–УК–сульфолан с получением МК (90% масс.) и УК (80% масс.), в схеме II смесь МК–УК разбавляют сульфоланом, что позволяет получать кислоты более высокого качества: МК (УК) с содержанием основного вещества не менее 98.5% масс. Схема III состоит из двух двухколонных комплексов ЭР: сначала выделяют смесь воды и муравьиной кислоты, которую затем разделяют ЭР также с сульфоланом. Расчеты схем проведены для рабочих давлений колонн 101.32 и 13.33 кПа. Для предотвращения термического разложения сульфолана колонны регенерации всегда работают при давлении 13.33 кПа. Максимальный вклад в суммарные энергозатраты на разделение во всех схемах вносит колонна ЭР базовой трехкомпонентной смеси.

Ключевые слова: муравьиная кислота, уксусная кислота, вода, сульфолан, экстрактивная ректификация, схема разделения.

Introduction

It is often necessary to separate aqueous mixtures of carboxylic acids with low molecular weights (C_1 – C_4) for the purposes of fine organic synthesis and in pulp manufacturing [1–3]. For example, the oxidation of C_9 – C_{20} paraffins results in a mixture of C_1 – C_6 carboxylic acids (wt %): formic acid (FA) – 35–40, acetic acid (AA) – 30–35, propionic and butyric acids – 20–30, valeric and caproic acids – up to 2–6. Having removed the C_4 – C_6 acids, the next step is to separate the water–FA–AA mixture of different compositions.

The use of reactive distillation has been proposed, namely esterification with low molecular weight alcohols, in order to purify waste waters [4–7]. The latter, when resulting from the liquid-phase oxidation of solid paraffins, contain on average 8–10 wt % of C_1 – C_4 carboxylic acids [2]. Reactive distillation experimental tests have been carried out for the undiluted solutions of acids [7]. In the column distillate, it is possible to obtain a mixture of esters (methyl formate–methyl acetate) by reactive distillation, using water–FA–AA mixtures with 10:80:10 and 30:60:10 wt %. The methanol:AA ratio is 2.4:1 (mol/mol) and the reflux ratio is 10. The bottom product contains water and acetic acid.

Results of extractive distillation in industrial conditions have also been published [8, 9]. In these experiments, the periodic operation mode was used at a pressure of 101.32 kPa. Water–FA–AA mixtures with 40:32:28 wt %, with various added agents, were analyzed.

When pelargonic acid was introduced, the distillate composition of water–FA–AA mixture was 75:14:11 wt %, and the bottom product of the column contained an FA–AA–agent mixture with the ratio of 12:15:73 wt % [8]. The addition of an acetylsalicylic acid/heptanoic acid mixture (50:50 wt %) led to the following composition of the distillate and bottom product: 78:18:4 wt % and 10:14:76 wt %, respectively [9].

Extractive distillation in the presence of *N*-methyl-2-pyrrolidone was performed for the mixture water–FA–AA–admixtures. The ratio of the components was 27.8:5.5:64.7:2 wt %, and atmospheric pressure (1.013 bar) was applied. The bottom product in this case also contained mostly acetic acid and added agent; water–FA–AA–agent = 0.1:2.0:28.6:69.6 wt %. The distillate contained water and formic acid, with no more than 0.2 wt % total admixtures [10]. The regeneration of *N*-methyl-2-pyrrolidone in the industrial setting was performed at 0.3 bar (60 theoretical plates; $R \approx 1$). This produced rather pure *N*-methyl-2-pyrrolidone; 0.1:0.4:4.7:94.9 wt %. The distillate of the regeneration column was as follows: water–FA–AA = 0.4:7.6:92.0 wt %.

Another goal, was set in [11], namely the generation of almost pure water by extractive distillation of basic mixtures with *N*-methyl-2-pyrrolidone. Extractive distillation was performed for mixtures containing formic acid at 10–80 wt % with an increment of 10 wt %. The pressure was 101.3 kPa and *N*-methyl-2-pyrrolidone was used at

a 2:1 (mol/mol) ratio with feed. The result showed that extractive distillation with *N*-methyl-2-pyrrolidone could be done for mixtures containing: 10 wt % formic acid and more than 50 wt % water; 20 (30) wt % formic acid and more than 40 wt % water. The rate of agent was selected, without any further reasoning, as the economically stipulated limit, with anything above it leading to a dramatically higher consumption of energy used for separation. This is why it is recommended to use Pressure Swing Distillation (PSD) for mixtures that contain less than 30 wt % water [11].

Thus, the choice of the additive for extractive distillation of the basic three-component mixture dictates the need to further separate water–FA or FA–AA mixtures, for instance, by extraction [12, 13] or extractive distillation.

In order to choose the selective solvents in an industrial setting (based on vapor–liquid equilibrium (VLE) data from Othmer Still), the influence of various chemical substances on the VLE for water–FA [14–20] and FA–AA [21, 22] mixtures has been investigated.

The increase in the volatility of water (W) compared to FA at atmospheric pressure has been observed in the presence of individual or mixed solvents, of different compositions. They can be based on:

- sulfolane or adiponitrile with added acetophenone, acetylsalicylic acid, sulfones, etc. ($3.2 \leq \alpha_{W/FA} \leq 5$) [14];
- cyclohexanone or isophorone with added aliphatic monocarboxylic acids and acetophenone ($2 \leq \alpha_{W/FA} \leq 3$) [15];
- ethylene carbonate or propylene carbonate with added carboxylic acids (various structures) and isophorone ($2.5 \leq \alpha_{W/FA} \leq 2.9$) [16];
- dicarboxylic acids with added monocarboxylic acids, 2-hydroxyacetone and other substances with a high boiling point ($2.8 \leq \alpha_{W/FA} \leq 3.1$) [17];
- sulfolane, adiponitrile, dimethylformamide, *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, acetophenone and their mixtures with other organic substances ($3 \leq \alpha_{W/FA} \leq 11$) [18].

Batch extractive distillation for water–FA mixtures shows that the distillate may contain almost pure water if the following agents are used: heptanoic and azelaic acids (ratio 80:20 wt %); heptanoic, azelaic acids and 2-hydroxyacetone (ratio 67:16:17 wt %) [17]; sulfolane [14]; adiponitrile [18]; *N*-formylmorpholine [19]. The use of isophorone leads to the accumulation of FA in the distillate (89 wt %) [15].

According to experimental data, the choice of a selective agent for extractive distillation of FA–AA mixtures is rather complicated [8, 9, 21–23]. Certain binary extractive agents have been suggested, in which acetylsalicylic acid is paired with an organic solvent: amyl acetate, ethylene carbonate, propylene carbonate, diisobutyl ketone, 2-(4-)hydroxyacetophenone, methyl

(ethyl, butyl) benzoates, cyclohexanone, and aromatic nitro compounds. The majority of these substances have been found to be not selective enough, with the highest values of $1.5 \leq \alpha_{FA/AA} \leq 2.2$ observed for the mixed agents which contain carboxylic acids, nitrobenzene or acetophenone [8].

This work focuses on extractive distillation of the three-component water–FA–AA mixture with sulfolane (S). The latter is an industrial solvent, which fits the standard requirements for extractive agents [24, 25], and sulfolane was previously suggested for extractive distillation of water–FA [18], water–AA [26] mixtures. The use of sulfolane allows for the expectation that separation of water from carboxylic acids will occur.

Methods

Calculations were conducted using Aspen ONE Engineering V9.0 software. The NRTL equation was utilized to simulate VLE. The nonideal behavior of the vapor phase was taken into account by the NRTL-HOC model.

Results and Discussion

The VLE simulation for the water–FA–AA mixture corresponds to the existing data [27, 28]: at pressure of 101.32 kPa and lower than 26.66 kPa the curvature of the separatrix is different (Fig. 1). The selection of 13.33 kPa pressure is determined by the need to prevent the decomposition of the agent [25].

According to the data from [11], the highest energy consumption (for PSD) is observed when water–FA–AA mixtures contain 10–20 wt % FA. To evaluate the

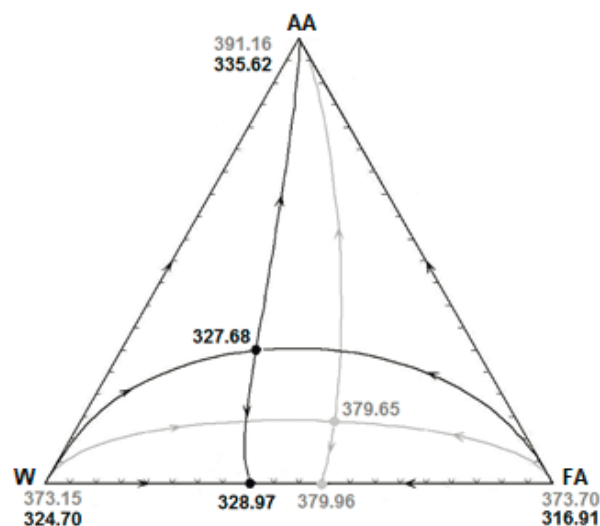


Fig. 1. The diagram of the vapor–liquid equilibrium (VLE) for the water (W)–formic acid (FA)–acetic acid (AA) system.

———— 13.33 kPa - - - - - 101.32 kPa

feasability of extractive distillation with sulfolane, we have selected the equimolar mixture (water:FA:AA = 14.5:37.0:48.5 wt %). This mixture has been considered in previous publications, and the separation options take into account the changes in separatrix position and shape with changing pressure [11, 27, 28].

We have calculated the relative volatilities α_{W-FA} , α_{W-AA} , α_{FA-AA} for the basic equimolar mixture and for the

derived system, water-FA-AA-S, with various amounts of sulfolane (S). Two different pressure values were used (Tables 1, 2). Since the α_{FA-AA} values are the lowest, it is predicted that a water-enriched distillate will be obtained at extractive distillation of the equimolar water-FA-AA mixture. The calculations for extractive distillation of this mixture are presented in Table 3 (column I). The distillate contains almost pure water.

Table 1. The relative volatilities of the substances and selectivity of sulfolane at 101.32 kPa

F_S	α_{W-FA}	α_{W-AA}	α_{FA-AA}	S_{W-FA}	S_{W-AA}	S_{FA-AA}
0	1.17	1.26	1.08	—	—	—
50	1.99	2.90	1.46	1.70	2.30	1.35
100	2.67	4.23	1.585	2.28	3.35	1.47
150	3.25	5.29	1.63	2.77	4.19	1.51
200	3.73	6.14	1.65	3.19	4.87	1.53
250	4.14	6.82	1.65	3.54	5.41	1.53
300	4.48	7.37	1.64	3.84	5.84	1.53
350	4.77	7.81	1.64	4.07	6.19	1.52
400	5.00	8.16	1.63	4.27	6.47	1.51
450	5.20	8.45	1.62	4.44	6.695	1.51
500	5.37	8.68	1.62	4.56	6.88	1.50

Table 2. The relative volatilities of the substances and selectivity of sulfolane at 13.33 kPa

F_S	α_{W-FA}	α_{W-AA}	α_{FA-AA}	S_{W-FA}	S_{W-AA}	S_{FA-AA}
0	0.86	0.955	1.115	—	—	—
50	1.68	2.53	1.50	1.96	2.645	1.36
100	2.44	3.99	1.64	2.845	4.18	1.40
150	3.14	5.31	1.695	3.66	5.57	1.52
200	3.77	6.50	1.72	4.41	6.81	1.54
250	4.35	7.54	1.73	5.10	7.90	1.55
300	4.86	8.45	1.74	5.67	8.85	1.56
350	5.31	9.24	1.74	6.20	9.67	1.56
400	5.71	9.92	1.74	6.67	10.4	1.56
450	6.071	10.5	1.73	7.09	11.0	1.555
500	6.389	11.05	1.73	7.46	11.6	1.55

We have considered the separation of 100 kmol/h of the water-FA-AA equimolar mixture at two different pressure values. To prevent reagent decomposition, the columns whose bottom products contain almost pure sulfolane, work at reduced pressure.

Extractive distillation flowsheets for the basic water-FA-AA mixture are shown in Fig. 2. Flowsheets I, II result in the production of water in the distillate, flowsheet III results in the water-FA mixture in the distillate.

According to empirically substantiated guidelines, $S \geq 2$ for selective agents in extractive distillation of binary mixtures. The sulfolane selectivity relative

to water for the basic three-component mixture is determined as follows:

$$S_{W-FA} = \frac{\alpha_{W-FA}^{(S)}}{\alpha_{W-FA}}, \quad S_{W-AA} = \frac{\alpha_{W-AA}^{(S)}}{\alpha_{W-AA}}$$

abovementioned condition of the amount of sulfolane being less than 100 kmol/h (Tables 1, 2).

The calculations for extractive distillation are shown in Table 3 (column I). The lowest amount of the agent which allows for the separation of almost pure water (99.5 wt %) is 150 and 170 kmol/h at atmospheric and

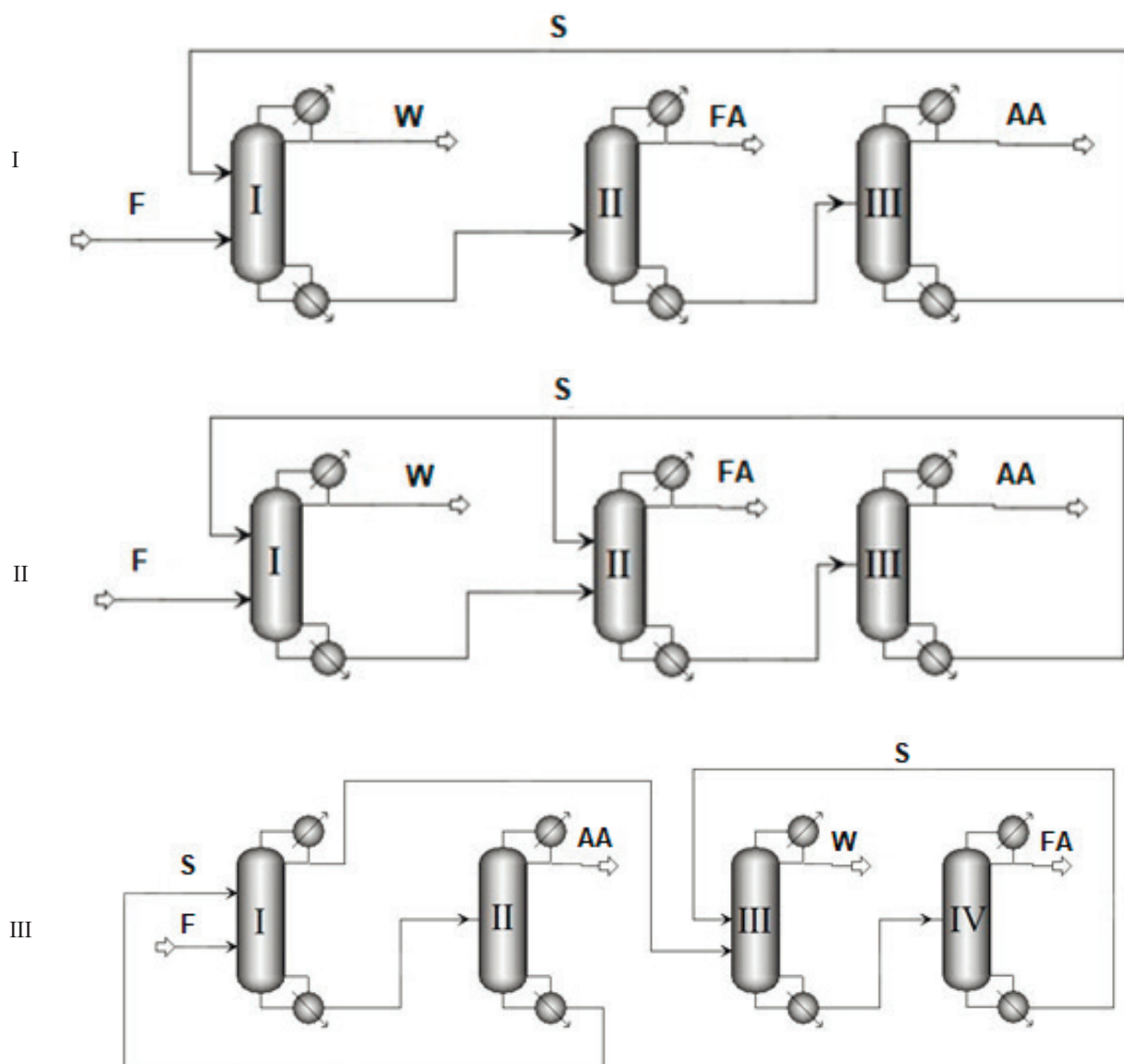


Fig. 2. Principal flowsheets of extractive distillation.

Flowsheets **I, II**: I – extractive distillation column; flowsheet **III**: I, III – extractive distillation columns.

F – basic mixture: water (W)–formic acid (FA)–acetic acid (AA).

reduced pressure, respectively. Further sequential selection of carboxylic acids is possible (flowsheet **I**, Fig. 2).

Table 4 shows the quality of acids where the content of the main component is no less than 86.5 wt % for formic acid (GOST 1706-78, mark B) and no less than 80 wt % for acetic acid (GOST 19814-74, 3rd grade).

Sulfolane is not selective in the separation of binary mixtures of carboxylic acids. For example, at 101.32 kPa, α_{FA-AA} is 1.49 (addition of 50 kmol agent) and 1.45 (addition of 400 kmol agent) when the amount of FA–AA is 100 kmol. The selectivity of the agent

$$S_{FA-AA} = \frac{\alpha_{FA-AA}^{(S)}}{\alpha_{FA-AA}}$$

is close to 1 at both pressure values and is almost independent of the amount of the agent.

Flowsheet **II** suggests the additional introduction of sulfolane into column II (flowsheet **II**, Fig. 2). Dilution with this agent leads to the weakening of interactions between the molecules of the acids [29], thus helping to separate them. Upon the addition of 120 kmol sulfolane to the FA–AA–S mixture (bottom flow of the extractive distillation column), the selectivity S_{FA-AA} is 0.987 (101.32 kPa) and 0.977 (13.33 kPa), indicating the absence of auto-extractive distillation.

Calculations for flowsheet **II** are shown in Table 5. Dilution of the FA–AA–S mixture with sulfolane gives purer acids (compared with data in Table 4) – no less than 98.5 wt % of the main component (formic acid, GOST 1706-78, mark A; acetic acid, GOST

Table 3. Static parameters for distillation columns in flowsheet I

Column		I	II	III	I	II	III
Pressure, kPa		101.32	101.32	13.33	13.33	13.33	13.33
$N, N_s/N_F$		40, 5/25	50, 18	5, 4	40, 3/12	50, 8	5, 4
R		1	6.6	0.01	0.05	8	0.05
Feed flow F, kmol/h		100	216.7	183.4	100	236.7	203.4
Feed flow composition, mol. fract.	W	0.3330	0.0003	0	0.333	0.0002	0
	FA	0.3330	0.1534	0.0140	0.333	0.1405	0.0126
	AA	0.3340	0.1541	0.1681	0.334	0.1411	0.1516
	S	–	0.6922	0.8179	–	0.7182	0.8358
Feed temperature T_F , K		379.86	437.78	397.45	327.49	373.36	400.98
Sulfolane flow F_s , kmol/h		150	–	–	170	–	–
Sulfolane temperature T_s , K		353.15	–	–	303.15	–	–
Distillate flow D, kmol/h		33.3	33.3	33.4	33.3	33.3	33.4
Distillate composition, mol. fract.	W	0.9983	0.0017	0	0.9984	0.0017	0
	FA	0.0017	0.9210	0.0742	0.0016	0.9216	0.0736
	AA	0	0.0773	0.8491	0	0.0767	0.8487
	S	0	0	0.0767	0	0	0.0777
Distillate temperature T_D , K		373.21	374.54	336.51	324.73	317.89	336.56
Bottom product flow W, kmol/h		216.7	183.4	150	236.7	203.4	170
Its composition, mol. fract.	W	0.0003	0	0	0.0002	0	0
	FA	0.1534	0.0140	0.0007	0.1405	0.0126	0.0006
	AA	0.1541	0.1681	0.0164	0.1411	0.1516	0.0147
	S	0.6922	0.8179	0.9829	0.7182	0.8358	0.9847
Bottom flow temperature T_W , K		437.78	469.42	460.93	373.36	400.98	462.64
Reboiler duty Q, MW		1.62	1.85	0.98	1.17	2.10	1.05
ΣQ , MW		4.45			4.32		

Abbreviations (here and throughout): N – total number of theoretical plates in the column; N_s – number of the plate where sulfolane is introduced; N_F – number of the theoretical plate with feed (numbering starts from the top of the column); R – reflux ratio.

Table 4. The quality of the obtained products

Scheme	I		II		III	
Pressure, kPa	101.32	13.33	101.32	13.33	101.32	13.33
W, wt %	99.58	99.54	99.58	99.59	99.63	99.51
FA, wt %	90.06	90.14	98.53	98.60	98.53	98.62
AA, wt %	80.14	80.03	99.17	99.21	99.00	99.02

Table 5. Static parameters for distillation columns in flowsheet II

Column		I	II	III	I	II	III
Pressure, kPa		101.32	101.32	13.33	13.33	13.33	13.33
$N, N_s/N_F$		40, 5/25	45, 5/26	15, 10	40, 3/12	45, 5/21	15, 10
R		1	5	1.3	0.05	3	1.4
Feed flow F, kmol/h		100	216.7	303.4	100	236.7	323.4
Feed flow composition, mol. fract.	W	0.3330	0.0003	0	0.333	0.0002	0
	FA	0.3330	0.1534	0.0012	0.333	0.1405	0.0011
	AA	0.3340	0.1541	0.1089	0.334	0.1411	0.1022
	S	–	0.6922	0.8899	–	0.7182	0.8967
Feed temperature T_F , K		379.86	437.78	415.28	327.49	373.36	417.30
Sulfolane flow F_s , kmol/h		150	120	–	170	120	–
Sulfolane temperature T_s , K		353.15	353.15	–	303.15	303.15	–

Table 5. Continued

Column		I	II	III	I	II	III
Distillate flow D, kmol/h		33.3	33.3	33.4	33.3	33.3	33.4
Distillate composition, mol. fract.	W	0.9983	0.0017	0	0.9984	0.0016	0
	FA	0.0017	0.9875	0.0108	0.0016	0.9882	0.0097
	AA	0	0.0108	0.9892	0	0.0102	0.9903
	S	0	0	0	0	0	0
Distillate temperature T_D , K		373.21	373.85	335.30	324.73	317.10	335.33
Bottom product flow W, kmol/h		216.7	303.4	270	236.7	323.4	290
Bottom flow composition, mol. fract.	W	0.0003	0	0	0.0002	0	0
	FA	0.1534	0.0012	0	0.1405	0.0011	0
	AA	0.1541	0.1089	0.0004	0.1411	0.1022	0.0004
	S	0.6922	0.8899	0.9996	0.7182	0.8967	0.9996
Bottom flow temperature T_W , K		437.78	491.17	479.82	373.36	417.30	479.84
Reboiler duty Q, MW		1.62	2.77	1.49	1.17	2.01	1.55
ΣQ , MW		5.88			4.73		

19814-74, “synthetic acetic acid”, 2nd grade). Evidently, the generation of purer products requires more energy.

Flowsheet III (Fig. 2) uses a variant of extractive distillation where water–FA is separated in the

first column, thus eliminating the need to separate carboxylic acids at any further steps.

Energy consumption of the extractive distillation column for the basic mixture at 101.32 kPa (Table 6) is

Table 6. Static parameters for distillation columns in flowsheet III

Column		I	II	III	IV
Pressure, kPa		101.32	13.33	101.32	13.33
N, N_S/N_F		40, 5/28	30, 20	30, 5/10	20, 10
R		3	0.8	1	1
Feed flow F, kmol/h		100	133.4	66.6	133.3
Feed flow composition, mol. fract.	W	0.3333	0	0.5000	0.0004
	FA	0.333	0.0032	0.4935	0.2462
	AA	0.334	0.2472	0.0065	0.0032
	S	–	0.7496	0	0.7502
Feed temperature T_F , K		379.86	387.68	379.87	369.76
Sulfolane flow F_S , kmol/h		100	–	100	–
Sulfolane temperature T_S , K		353.15	–	353.15	–
Distillate flow D, kmol/h		66.6	33.4	33.3	33.3
Distillate composition, mol. fract.	W	0.5000	0	0.9986	0.0014
	FA	0.4935	0.0130	0.0014	0.9856
	AA	0.0065	0.9870	0.0000	0.0130
	S	0	0	0	0
Distillate temperature T_D , K		379.87	335.24	373.21	317.11
Bottom product flow W, kmol/h		133.4	100	133.3	100
Bottom flow composition, mol. fract.	W	0	0	0.0004	0
	FA	0.0032	0	0.2462	0
	AA	0.2472	0.0010	0.0032	0.0001
	S	0.7496	0.9990	0.7502	0.9999
Bottom flow temperature T_W , K		456.92	478.97	439.42	480.32
Reboiler duty Q, MW		3.19	0.89	1.32	1.03
ΣQ , MW		6.43			

twice as high as the values for flowsheets **I** and **II**. At 13.33 kPa the total energy consumption in flowsheet **III**, with unchanging static parameters of the columns ($N, N_s/N_F$), remains largely unchanged: $\Sigma Q = 6.5$ MW, Q for columns **I–IV** is 3.08; 0.94; 1.19; and 1.29 MW, respectively.

Conclusions

Sulfolane can be used to separate water – formic acid – acetic acid mixtures. The rate of the agent determines the results of the extractive distillation for the basic mixture. When less sulfolane is used, the distillate contains water and formic acid (flowsheet **III**). When more sulfolane is used, the distillate contains only water (flowsheets **I, II**).

The highest energy consumption is observed for those distillation columns where acids are distributed in various product flows: water – FA (distillate), AA – bottom product (column **I** in flowsheet **III**) and FA – distillate, AA – bottom product (column **II** in flowsheets **I, II**). The energy consumption of the extractive distillation column for the basic mixture in flowsheet **III** is twice as high as the values for schemes **I** and **II**, thus

making flowsheet **III** inefficient.

The dilution of the formic acid–acetic acid mixture with sulfolane for distillation (column **II**, flowsheet **II**) allows for the production of acids of higher quality and purity. Flowsheet **I** is recommended for the production of “mark B” formic acid (GOST 1706-78) and 3rd grade acetic acid (GOST 19814-74). Yet higher quality of acids can be achieved in flowsheet **II** – “mark A” formic acid and 2nd grade acetic acid. The operation distillation columns **I, II** is recommended, with the working pressure in flowsheet **I** set at 101.32 kPa, and in flowsheet **II** – at 13.33 kPa.

It is necessary to search for ways to lower energy consumption during the separation of aqueous mixtures with formic and acetic acids. This necessity determines the next steps in research, in particular, finding selective agents for the extractive distillation of formic acid–acetic acid mixtures.

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References:

1. Kushner T.M., Tatiyevskaya G.I., Serafimov L.A., L'vov S.V. Isolation of lower carboxylic acids from the fraction of straight-run gasoline oxide. *Khimicheskaya promyshlennost' = Chemical Industry*. 1969;1:20-23 (in Russ.).
2. Frolov G.M., Shaburov M.A. Acetic acid production. Moscow: Lesnaya promyshlennost' Publ., 1978. 240 p. (in Russ.).
3. Muurinen E.I., Solo J.K. Solvent recovery in peroxyacid pulping. In: *Proceed. of the First European Congress on Chemical Engineering*. Florence, Italy. May 4-7, 1997; 1:543-552.
4. Painer D., Lux S., Graftschafter A., Toth A., Siebenhofen M. Isolation of carboxylic acids from biobased feedstock. *Chem. Ing. Tech.* 2017;89(1-2):161-171. <https://doi.org/10.1002/cite.201600090>
5. Patil K.D., Kulkarni B.D. Review of recovery methods for acetic acid from industrial waste streams by reactive distillation. *J. Water Pollut. Purif. Res.* 2014;1(2):13-18. <https://www.researchgate.net/publication/263327618>
6. Saha B., Chopade S., Mahajan S. Recovery of dilute acetic acid through esterification in a reactive distillation column. *Catal. Today*. 2000;60(1):147-157. [http://dx.doi.org/10.1016/S0920-5861\(00\)00326-6](http://dx.doi.org/10.1016/S0920-5861(00)00326-6)
7. Painer D., Lux S., Siebenhofen M. Recovery of formic acid and acetic acid from waste water using reactive distillation. *Separation Science and Technology*. 2015;50(18):2930-2936. <https://doi.org/10.1080/01496395.2015.1085407>
8. Berg L. Separation of formic acid from acetic acid by extractive distillation: pat. 4,692,219 US; filed 12/03/1986; publ. 09/08/1987.
9. Berg L. Separation of formic acid from acetic acid by extractive distillation with acetyl salicylic acid: pat. 4,909,907 US; filed 01/17/1989; publ. 03/20/1990.
10. Cohen L.R. Method for separating carboxylic acids from mixtures with non-acids: pat. 4,576,683 US; filed 06/06/1984; publ. 03/18/1986.
11. Muurinen E. A review and distillation study related to peroxyacid pulping. *Organosolv pulping*. Oulu, Finland: Publ. House Oulu Yliopisto, 2000. 314 p. <http://herkules.oulu.fi/isbn9514256611/isbn9514256611.pdf>
12. Sprakel L.M.J., Schuur B. Solvent developments for liquid-liquid extraction of carboxylic acids in perspective. *Separation and Purification Technology*. 2019; 211:935-957. <https://doi.org/10.1016/j.seppur.2018.10.023>
13. Behrooz M., Vahedpour M., Shardi Manaheji M. Separation of formic acid from aqueous solutions by liquid extraction technique at different temperatures. *Phys. Chem. Res.* 2019;7(1):201-215. <https://dx.doi.org/10.22036/pcr.2019.154646.1557>
14. Berg L., Yeh An-I. Dehydration of formic acid by extractive distillation: pat. 4,642,166 US; filed 02/10/1986; publ. 02/10/1987.
15. Berg L., Kraig M., Szabados R. J. Dehydration of formic acid by extractive distillation: pat. 5,173,156 US; filed 12/09/1991; publ. 12/22/1992.
16. Berg L. Dehydration of formic acid by extractive distillation: pat. 4,786,370 US; filed 01/04/1988; publ. 11/22/1988.
17. Berg L. Dehydration of formic acid by extractive distillation with dicarboxylic acids; pat. 4,877,490 US; filed 01/23/1989; publ. 10/31/1989.
18. Berg L., Yeh An-I. Dehydration of impure formic acid by extractive distillation; pat. 4,735,690 US; filed 04/28/1986; publ. 04/05/1988.
19. Buelow H., Hohenschutz H., Schmidt J.E., Sachsze W. Purification of formic acid by extractive distillation; pat. 4,076,594 US; filed 10/04/1976; publ. 02/28/1978.
20. Prajapati Chintan, Bhatt R.P. Separation of azeotropic

mixture of formic acid – water by using Li-Br as a salt by extractive distillation. *IJARIE*. 2016;2(3):607-612 (available from <http://www.ijarie.com>).

21. Berg L. Separation of formic acid from acetic acid by extractive distillation: pat. 54,692,219. US; filed 03/12/1986; publ. 08/09/1987.

22. Berg L. Separation of formic acid from acetic acid by extractive distillation; pat. 5,227,029 US; filed 01/29/1993; publ. 07/13/1993.

23. Berg L. Separation of formic acid from acetic acid by extract separation of formic acid from acetic acid by extractive distillation; pat. 4,909,907 US; filed 01/17/1989; publ. 03/20/1990.

24. Kirk-Othmer Encyclopedia of Chemical Technology. V. 8. Online ISBN: 9780471238966 Copyright © 1999-2014 by John Wiley and Sons, Inc.

25. Gayle A.A., Somov V.Ye., Varshavskiy O.M.,

Semenov L.V. Sulfolan: Properties and use as a selective solvent. Saint-Petersburg: Khimizdat Publ., 1998. 144 p. (in Russ.).

26. Berg L. Dehydration of acetic acid by extractive distillation; pat. 5,167,774 US; filed 02/06/1992; publ. 12/01/1992.

27. Raeva V.M. Features of the behavior of azeotropic mixtures and their separation with varying pressure: thesis ... Cand. of Sci. (Engineering). Moscow, 1998. 168 p. (in Russ.).

28. Raeva V.M., Frolkova A.K. Separation of azeotropic mixtures using pressure-based complexes. *Russian Journal of General Chemistry*. 1998;XLII(6):76-88 (in Russ.).

29. Bates R.G., Pawlak Z. Solvent effects on acid-base behavior: Five uncharged acids in water-sulfolane solvents. *J. Solution Chem.* 1976;5(3):213-222. <https://doi.org/10.1007/BF00654338>

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