Development of Resource-Saving Technologies in the Production of Organosilicon Enamels Basing on Rectification

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Abstract

A topological thermodynamic analysis was performed for a butanol-toluene mixture produced as a waste in the industry of paint-and-lacquer materials. Liquid-liquid equilibrium was experimentally studied in the system ethanol–toluene–chlorobenzene–water. Main pathways for separating a butanol-toluene mixture have been synthesized as flow graphs. A rectification analysis was performed for the system under study. Choosing a separating agent (benzene) has been performed. Variants were proposed for the technological schemes of the butanol-toluene mixture separation *via* combining simple and azeotropic distillation techniques.

Key words: distillation, resource-saving butanol-toluene mixture, liquid-liquid equilibrium, rectification analysis, chromatography, topological thermodynamic analysis, pentatope, schematic separation process diagram, azeotropic separating agent

INTRODUCTION

At the present time, in releasing the main products, the priority direction for most of the major chemical companies consists in developing environmentally safe resource-saving technologies those could cause reducing the amount of wastes formed, better isolating target components, obtaining additional marketable products, reducing raw material consumption rates.

The purpose of this research work consisted in developing a low-waste technology for separating a mixture of solvents generated in the production of the organosilicon enamels of KO-174, DA-1163 and DA-1164 brands. The latter are used in construction engineering as weatherproof decorative coatings for products made of concrete, asbestos cement, as well as for finishing the exterior and interior elements of buildings and structures.

The process of obtaining the KO-174 enamel consists of the following stages:

– Forming a reaction mixture by mixing tetraethoxysilane, bromoethyl and chlorobenzene;

– Obtaining the finyl paste *via* Grignard synthesis according to the following reactions
$C_6H_5Cl + Mg \rightarrow C_6H_5MgCl$
$C_6H_5MgCl + Si(OC_2H_5)_4 \rightarrow C_6H_5 Si(OC_2H_5)_3 + C_2H_5O MgCl$

– Obtaining silanol *via* hydrolyzing the finyl paste by adding hydrochloric acid, toluene and butanol;

– The separation of the silanol into solvent BTM (butanol-toluene mixture) and a F-9K resin;

– Obtaining a KO-85 lacquer *via* mixing a resin grades of F-9K with toluene, ethyl acetate, butyl acetate, a BMK-5 resin and acetone;

– The formation of a KO-174 enamel *via* mixing a KO-85 lacquer and titanium dioxide [1].

Thus, in the manufacture of organosilicon enamels, at the stage of solvent distillation there is a BTM mixture formed with the following composition (%): ethyl alcohol (EA) 72.4, water (W) 6.6, butyl alcohol (BA) 9.7, toluene (T) 6.8, chlorobenzene (CBz) 4.5. Each year, only at the AltaiChemProm Co. (Yarovoye City, Altai, Russia), about 1500 t of wastes undergo thermal destruction, which is accompanied by the loss of unreacted raw material, target product and by-components as well as by environmental pollution.

EXPERIMENTAL

The synthesis of schematic separation process diagrams (SSPD) is one of the main objectives in the design of resource-saving low-waste technologies. The synthesis tasks might be different depending on the properties of the original mixture, on the separating elements and complexes used, on the requirements for the quality of the products obtained. However, in any case, the SSPD should provide the separation of target components under technologically acceptable conditions with acceptable energy and capital cost [2].

The main method for separating the organic mixtures of complicated composition consists in the process of rectification.

The development of distillation flow sheets for imperfect polyazeotropic mixtures is based on studying the structures of liquid-vapour phase equilibrium diagrams called a topological thermodynamic analysis (TTA). The fundamentals thereof were developed by the L. A. Serafimov and V. T. Zharov scientific school [3, 4]. The topological thermodynamics analysis represents a field of knowledge, wherein there are general laws formulated those establish the relationship between the singular points of different types (between different dimension azeotropes and pure components) in the composition-property diagrams. In the case of the liquid-vapour phase equilibrium one deals with the laws of the formation of the phase portrait of diagrams reflecting the physicochemical properties of the objects under investigation by means of the methods of topological thermodynamics.

For the initial BTM, the number of possible binary, ternary and quaternary components (Z) can be determined by the following equation [4]:

$$Z = n!/r!(n - r)! \tag{1}$$

where n is the number of mixture components; r are the components under determination.

Table 1 demonstrates data concerning the composition of the five-component mixture. It can be seen that the system has 10 binary, 10 ternary, and five quaternary components, including azeotropic ones those could significantly complicate the process of separating the mixture into individual components. For the initial five-component system basing on the literature and our own experimental data there were revealed the presence of seven binary and five ternary azeotropes [5−8].

For the development of a low-waste technology for separating a BTM, it is worthwhile to establish the exact composition and the patterns of the distribution of components into the fractions in the process of rectification. This could be done *via* the rectification analysis that involves the distillation of the initial mixture on a periodically operating column with a relatively high efficiency, as well as analyzing the distribution of components into fractions.

The distillation of BTM was carried out at atmospheric pressure using a laboratory-scale rectification column with a height of the rectifying part equal to 1100 mm and 20 mm in diameter. As the packing, we used glass rings

TABLE 1

Components of the five-component mixture

Mixture components	Number of components (n)	Components under determining (r)	Number of possible components (Z)
Binary	5	2	10
Ternary	5	3	10
Quaternary	5	4	5

TABLE 2

Material balance of BTM distillation with respect to true boiling points

Fractions	Interval ofsampling the fractions, °C	Amount of fractions sampled		Fraction	Notes
		g	mass %		
I	74.3−74.4	19.10	9.55	EA−T−W	Heterogeneous azeotrope
II	74.4−76.5	10.05	5.03	Transient	EA−T−W
III	76.5−76.6	10.81	5.41	ЭС−Т	Homogeneous azeotrope
IV	76.6−77.3	4.87	2.44	Transient	EA−T−CBz−W
V	77.3−77.4	24.51	12.26	ЭС−Х6−В	Heterogeneous azeotrope
VI	77.4−78.0	7.42	3.71	Transient	EA−CBz−W
VII	78.0−78.5	89.01	44.81	EA−W	−
Vat residue	127.0	26.40	13.20	BA	−
Loss	−	7.20	3.60	−	−
Total	−	200.00	100.00	−	−

Note. Dash − no data.

those provide the overall efficiency equal to 30 theoretical plates with respect to benzene-dichloroethane mixture. The column was launched, then at a reflux ratio $R = 10$ there was taken a portion of distillate for analyzing.

The analytical control of the organic part was carried out using a Chromos GC-1000 chromatograph with a flame ionization detector. In the course of developing the analysis technique, as the stationary phase we have chosen Chromatron N-AW supplemented with 15 mass % of FFAP, hydrogen was used as the carrier gas, flow rate being 30 cm³/s. The temperature in the column was varied from 70 to 130 °C. The water content in the fractions was determined *via* titration with Fischer reagent according to the State Standard GOST 14870−77 [9]. Table 2 demonstrates the resulting material balance of distillation with respect to true boiling points (TBP) of BTM. It is obvious that none of the components of the system could not be isolated in pure state *via* usual rectification because of the presence of different dimensionality azeotropes with similar boiling points in the fractions. In this regard, there should be special separation methods considered.

The analysis of published data concerning the delamination for six binary and five ternary components of the BTM under investigation demonstrated [10, 11] that the EA−T−W and EA−CBz−W mixtures of at certain ratio values between the components can form stable heterogeneous systems, so of most interest

is studying the delamination of four-component EA−T−CBz−W mixture. For the experiment, we prepared a mixture of components at a EA/T/CBz/W mass ratio equal to 75.8 : 10.2 : 7.1 : 6.9, respectively. This composition corresponds to the distillate after the separation of butanol on a rectification column according to the distillation with respect to true boiling points of BTM components. The analysis of the layers formed was performed using a GC-1000 Chromos chromatograph according to the procedure described above. Data concerning the delamination in the system under investigation are presented in Table 3. One can see that the toluene with chlorobenzene are almost insoluble in ethyl alcohol and water, whereas at the concentration of these aromatic components in the mixture amounting to about 80 mass % and greater, stable heterogeneous system is formed. According to the fact,

TABLE 3

Data concerning the delamination in EA−(T−CBz)−W

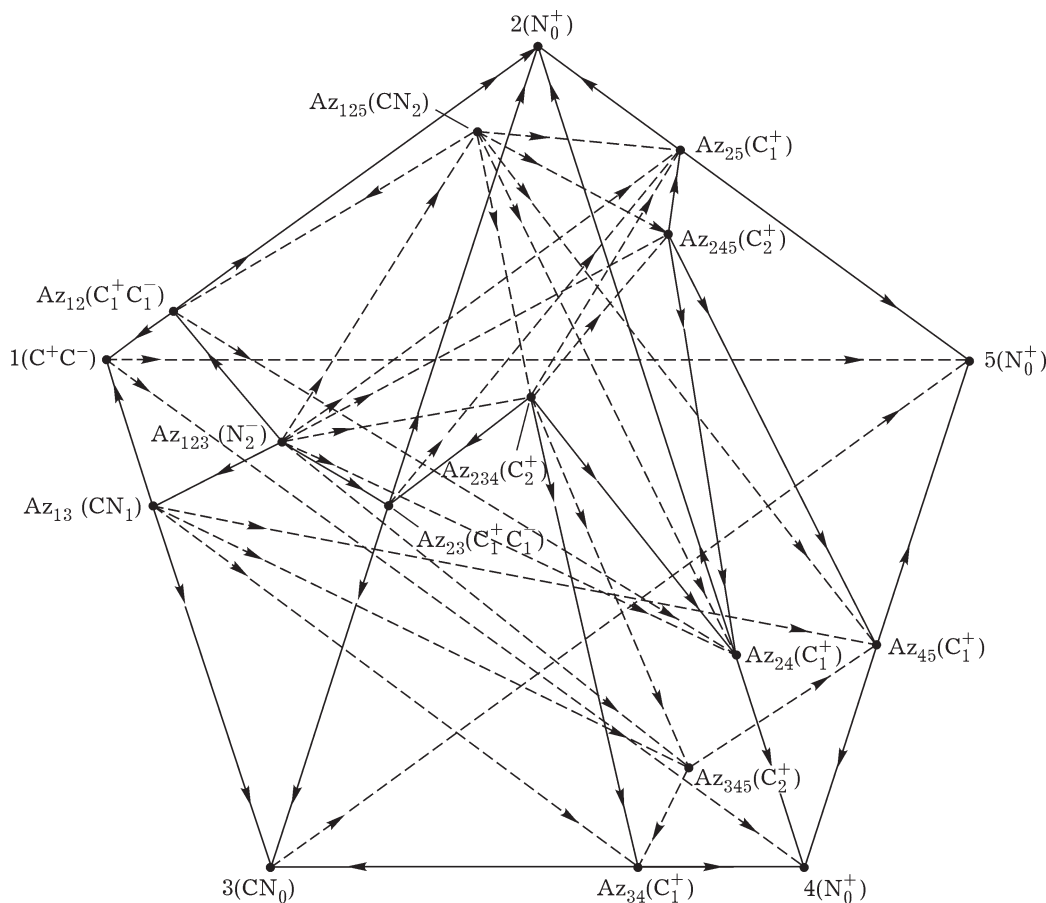| Content of component in the layer, mass %					
Organic layer			Aqueous layer		
EA	T + CBz	W	EA	T + CBz	W
34.8	63.8	1.4	60.9	18.5	20.6
12.2	84.7	3.1	56.6	10.6	32.8
12.8	86.3	0.9	61.3	5.1	33.6
6.7	88.6	4.7	52.7	3.1	44.2
5.1	89.5	5.4	41.1	0.9	58.0
5.5	92.9	1.6	43.4	0.7	55.9

Fig. 1. Structure of the phase diagram for the initial BTM. In brackets, the type of singular points is presented.

using a simple delamination one could separate toluene with chlorobenzene from ethyl alcohol and water.

Basing on data concerning the heterogeneous and azeotropic properties of the BTM components there can be TTA performed. The simplex under investigation represents a pentatope EA(1)−W(2)−T(3)−BA(4)−CBz(5) (Fig. 1). The concentration diagram of the simplex under study contains 17 singular points: one unstable node (N_2^-) Az_{123}; three stable nodes (N_0^+) − 2, 4, 5; seven unstable saddle points (C_2^-, C_1^-, C_0^-) − Az_{125}, Az_{13}, Az_{24}, Az_{25}, Az_{34}, Az_{45}, 3; six stable saddle (C_2^+, C_1^+, C_0^+) − Az_{245}, Az_{345}, Az_{234}, Az_{12}, Az_{23} and 1. The multidimensionality of the concentration space does not allow strongly fixing the position of the figurative point of the initial mixture composition. However, it is quite possible to determine the starting and finishing points of the bundle of dis-

tillation lines *via* decreasing the simplex dimensionality, for example, considering one of the tetrahedrons composing the pentatope EA−W−T−BA (Fig. 2).

In this system, there are ten singular points: four nodes corresponding to pure components five binary and two ternary azeotropes. The azeotropes Az_{12}, Az_{13}, Az_{234}, Az_{23}, Az_{24}, Az_{34} and the vertex 1 correspond to the «saddles». Vertices 2, 3 and 4 represent stable graph nodes (N_0^+), azeotrope Az_{123} represents an unstable node (N_0^-). Such a combination of singular points results in the formation of three distillation regions and twelve rectification regions. The point of the initial mixture composition belongs to the region of rectification $Az_{123}Az_{12}Az_{24}4$, wherein one could realize the following sequence of the mixture distillation into the individual components.

According to the first prescribed separation procedure, a target component Az_{123} goes into
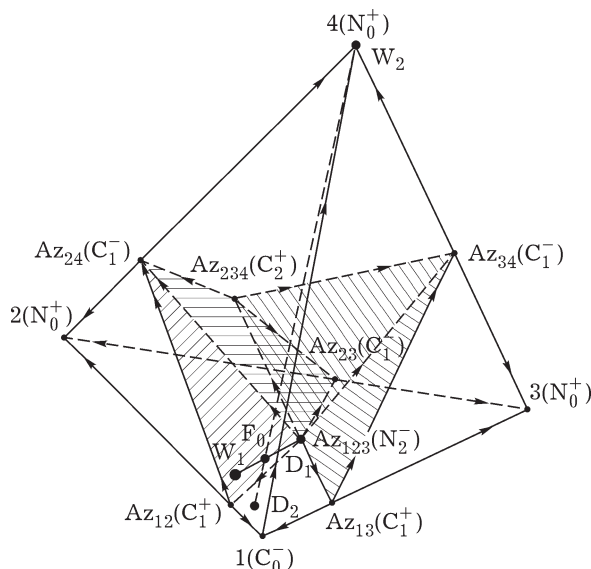
Fig. 2. Phase diagram for the mixture 1 (EA)−2 (W)−3 (T)−4 (BA).

the distillate. At the same time, a mixture 124 is obtained as the vat residue. The second prescribed mixture separation procedure allows separating BA(4) as the vat residue, whereas the distillate contains a mixture 123. In a similar manner, the other tetrahedral components of the five-component mixture are considered.

Thus, alternating the first and second prescribed separation procedures and taking into account the heterogeneity of the ternary component of the mixture under investigation, one could obtain the necessary components as products. Figure 3 illustrates the flow graphs of BTM separation we synthesized those are used for the synthesis of the SSPD for the mixture under investigation [2] with taking into account the following technological conditions and limitations:

1. The toluene, butyl alcohol and chlorobenzene are unreacted raw components, and in order to return them back to the stage of pre-
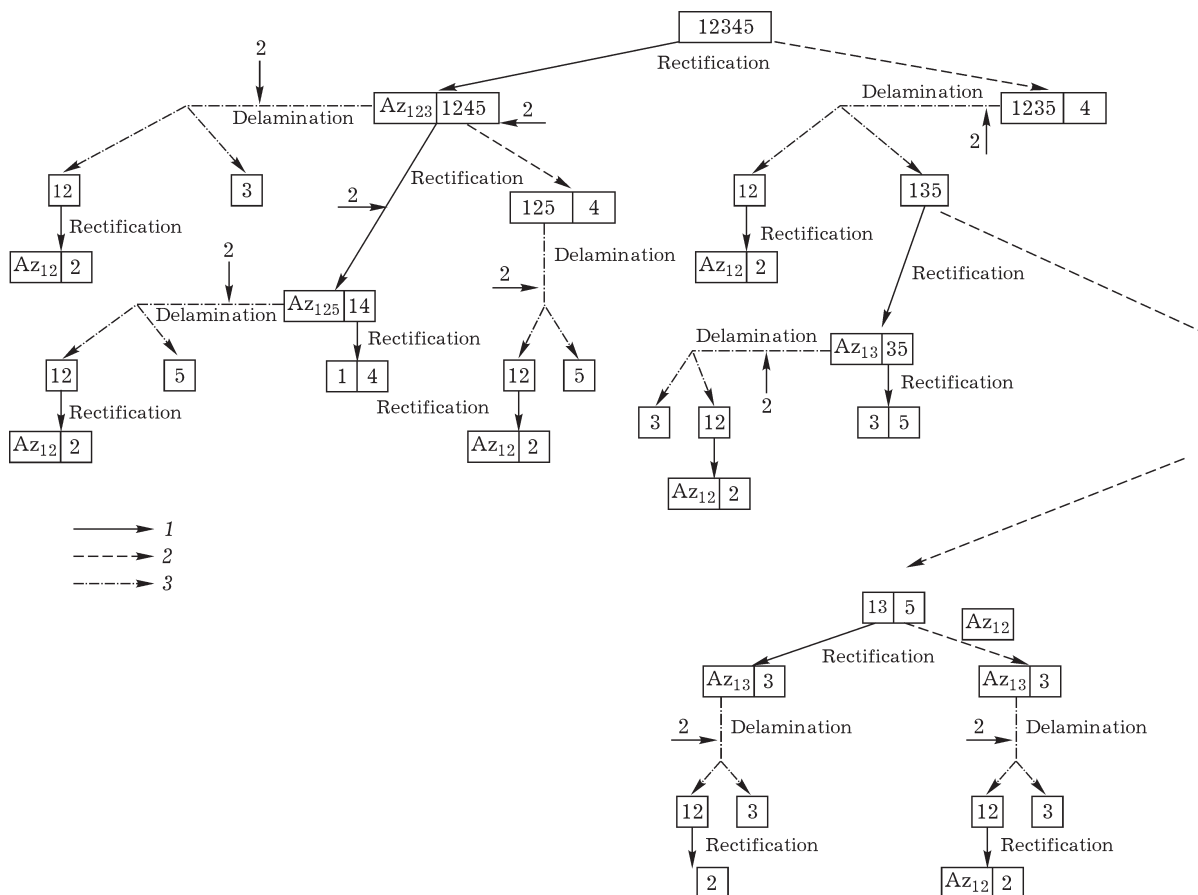

Fig. 3. Flow graphs for the separation of the mixture 1 (EA) − 2 (W) − 3 (T) − 4 (BA) − 5 (CBz): 1 − rectification (the first prescribed separation procedure), 2 − rectification (the second prescribed separation procedure), 3 − delamination.
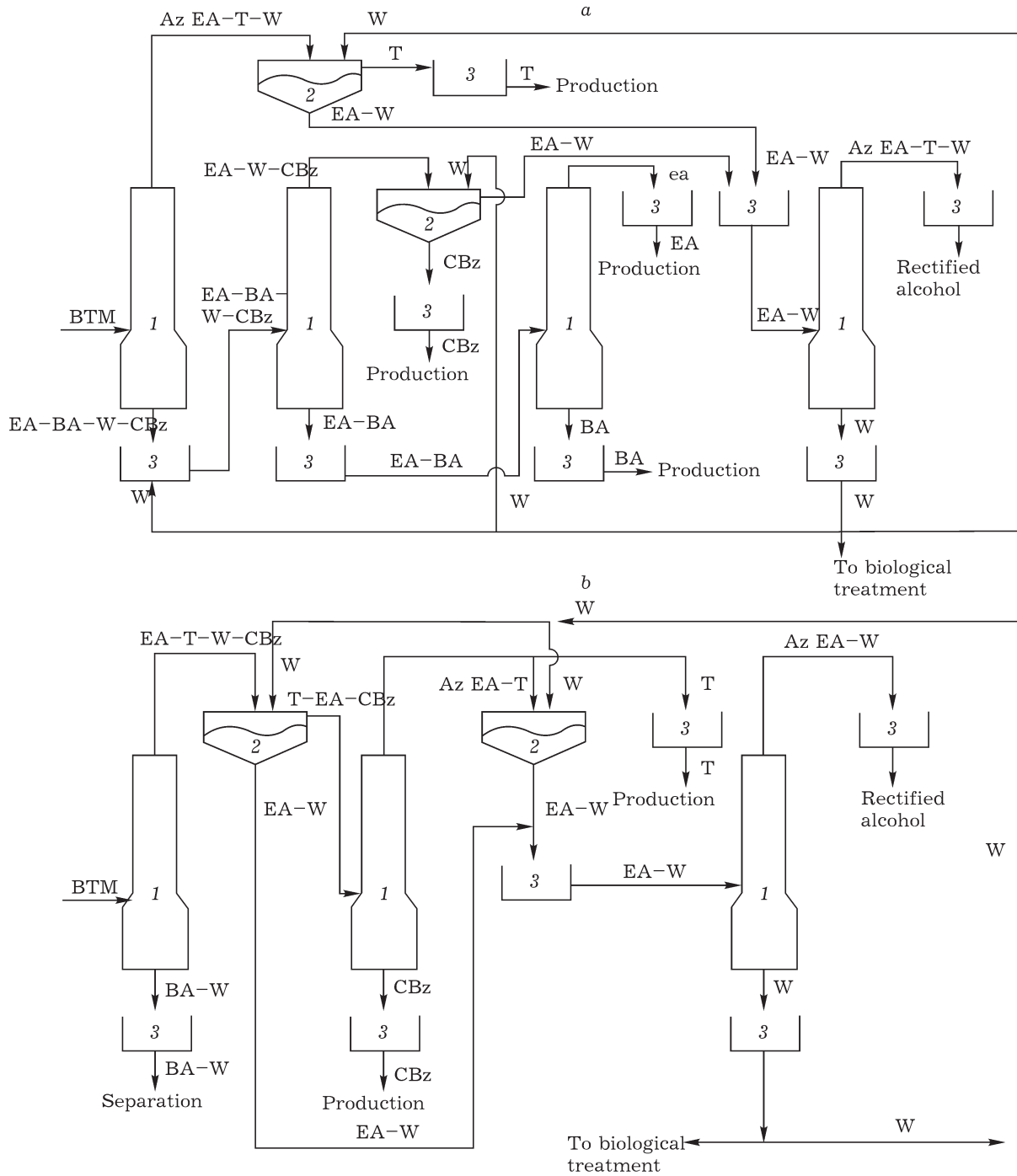
Fig. 4. Schematic separation process diagram for BTM: a − variant 1 (the first prescribed separation procedure), b − variant 2 (the second prescribed separation procedure); 1 − rectification column, 2 − delaminator, 3 − accumulating reservoir.

paring organosilicon enamels the content of impurities should not exceed 0.5 mass %.

2. The quality of ethyl alcohol as a by-product of enamel production should match the quality of rectified alcohol.

3. In the course of separation under the conditions of pilot production, there are small-scale material flows formed.

4. A minimal loss of the above mentioned components should be kept at all stages of the separation.

5. All the water contained in the initial mixture in the course of rectification is distilled in the form of heterogeneous azeotropes, which simplifies to a considerable extent the process of the BTM separation.

Initially, for the development we proposed two alternative SSPD variants (according to the first and the second prescribed separation procedures based on periodically operated columns) providing a decrease of the amount of wastes in the course of the reaction mixture separation, the regeneration of raw material components and obtaining additional commercial product (Fig. 4). However, in the course of the analysis of the material flows under formation, there could not be carrying out the delamination of EA−W−CBz intermediate fractions in the case of variant 1 and EA−W−T−CBz intermediate fractions in the case of variant 2. This is connected with the fact that the amount of water necessary in order to obtain a stable heterogeneous system is several dozen times greater than the initial volume of the mixture supplied to the delamination procedure. Thereby, the upper organic layer amounts to less than 3 % of the total amount, and it is impossible to separate this layer. In this regard, the further separation of the mentioned intermediate fractions is worthwhile to carry out *via* azeotropic rectification, wherefore we have experimentally chosen benzene as a separating agent [12]. The benzene allows separating ethanol and water from toluene and chlorobenzene in the form of a ternary heterogeneous azeotrope further fractioned in the rectification column under reduced pressure (down to 100 mm Hg) into a heterogeneous azeotrope EA−W−Bz and EA−W mixture.

CONCLUSIONS

1. A technique has been developed for the butanol-toluene mixture chromatographic analysis with the use of a Chromos GC-1000 chromatograph with temperature programming from 70 to 130 °C. As the liquid phase, FFAP was selected, supported on Chromaton N-AW, and Separon.

2. Experimental data have been obtained concerning the liquid-liquid equilibrium in the system ethyl alcohol−toluene−chlorobenzene−water those could be used as reference data.

3. A rectification analysis was performed for the system under study using a laboratory-scale distillation column.

4. Basing on the topological thermodynamic analysis, the initial mixture as presented in the form of pentatope containing 17 singular points, including seven binary azeotropes, five ternary azeotropes and five pure components.

5. Possible variants for separating the BTM were considered in the form of flow graphs according to the first and second prescribed separation procedures.

6. Choosing an azeotropic agent (benzene) has been made in order to separate ethyl alcohol−water−chlorobenzene mixture, and ethyl alcohol−water−butyl alcohol−chlorobenzene mixture, which provides the isolation (through a series of intermediate fractions) of the pure components by means of the initial separation of water and ethyl alcohol in the composition of a ternary azeotrope with benzene.

7. Basing on the result of studying the concentration spaces, flow graphs and distillation according to TBP there have been suggested two alternative variants for BTM separation into individual substances *via* combining both simple and azeotropic distillation. The implementation of these technological schemes at the enterprises would allow one to isolate starting ingredients from the initial five-component mixture of the production waste to bring them back to the stage of obtaining organosilicon enamels, as well as to reduce the amount of production wastes subject to thermal degradation, as well as to reduce the burden on the environment.

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