Regimes of extractive distillation in ethanol production
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Regimes of extractive distillation in ethanol production

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Abstract

The influence of operating conditions to the effectiveness of extractive distillation process was investigated by using the method of gas chromatography. The experiment took place on an industrial vacuum plant of purification ethanol from impurities formed during fermentation. It is obtained that the concentration of different micro impurities at the selection zones depends on the temperature and the volumetric flow rate of extractive solvent. It gives us an opportunity to affect of ethanol purification from the various volatility impurities. Proposed method allows us to choose the extractive distillation regime that guarantees the necessary quality of ethanol. The values of operating conditions of extractive distillation for the best total purification from the attendant micro impurities are estimated.

Keywords: distillation process, industrial vacuum plant, extractive solvent, impurities

1. Introduction

One method of production of alimentary ethyl alcohol is based on the distillation of alcohol-water solution obtained in the fermentation of food grains. In this process, in addition to the increase of concentration of alcohol, purification from various impurities occurs which were formed during fermentation and which are harmful (e.g., methyl, propyl, and other higher alcohols, various ethers, acids, aldehydes, etc.). According to the volatility with respect to ethanol, these impurities are subdivided into volatile, low-volatile, and intermediate ones. It is especially difficult to separate the latter class of impurities because they form azeotropic solutions with ethanol.

The existing methods of distillation column computation enable to calculate the concentration of ethyl alcohol along the column height to a good approximation. As a rule, these methods assume that the mixture to be separated contains only ethyl alcohol and water while the impurities (which total content is less than 1%) do not affect the separation (Tsigankov, 2002; Yarovenko, 2002). Zones of concentrations of impurities where their samples should be taken from are determined empirically. In practice, the desired purification is achieved by using several distillation columns in series. Presently, vacuum distillation apparatus are gaining acceptance due to economic reasons and because they provide effective mass transfer.

The intensity of ethanol purification from every impurity must be different. It is important to remove the impurities which worsen of ethanol quality very strong.

To separate a volatile and a part of intermediate impurities, a special distillation column of preliminary purification is used (Tsigankov, 2002). In order to make it more efficient, one uses a principle of extractive distillation (Ainshtein, 2003; Kogan, 1971) consisting in the extractive solvent (water) feed on one of the plates in the concentration part of the column. This enables to lower the concentration of ethanol and to shift the equilibrium for some impurities to the transition from liquid to the vapor phase. Extractive distillation considerably enhances the capabilities for the creating or destruction of zones of concentration of various impurities along the column and their separation from ethanol. The process flowsheet of industrial units for ethanol production is shown in Fig. 1.

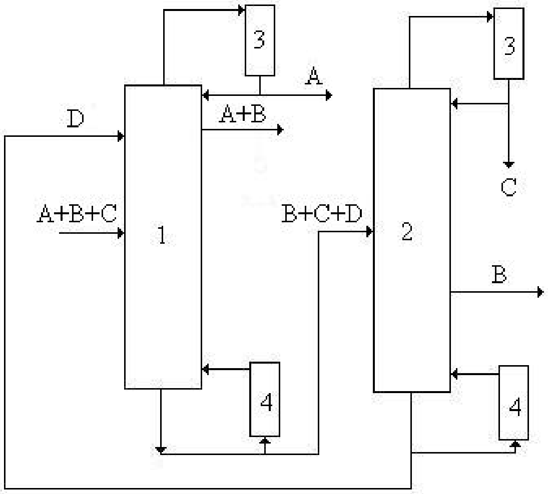

Figure 1: The process flowsheet of extractive distillation for ethanol production: 1 – preliminary purification column, 2 – concentration column, 3 – condensers, 4 – boilers

Unrefined ethanol alcohol (C) containing volatile (A) and intermediate (B) impurities feed on the preliminary purification column 1. As rule volatile impurities (A) are concentrated in top part of the column and separated from its condenser 3. The water (extractive solvent D) feed on one of the plates in the concentration part of the column. Impurities (A) and (B) are concentrated near the plate in the entering water. Selection of liquid phase from this zone give possibility to decrease the concentrations of the impurities (B) in product (C) directed to concentration column 2 for the following purification. Separated water in column 2 is returned to preliminary purification column 1 for the secondary using.

It is essential that many problems connected with purification of ethanol are common for chemical engineering. In this case we deal with the problem of using the new technique for separation of multicomponent and polyazeotropic mixtures.

Among the process parameters which define the efficiency of extractive distillation are the volumetric feed rate and the temperature of input water. This paper deals with the results of experimental definition of the process parameters for ethanol distillation in columns operating at a low pressure when we have the best purification from impurities.

2. Conditions of the experiments

The effect of the parameters on the purification degree of ethanol was studied on a commercial distillation column of the ethanol production plant Joint-Stock Company "Topaz" Distillery by measuring amounts of impurities in the products of distillation using highly effective gas chromatograph.

The diameter of the preliminary purification column is 1200 mm. It has 39 bubblecap plants for heat and mass transfer between phases. The column works in continuous running and has the stabilizing systems for pressure in barometrical condenser and for pressure of secondary vapor. The reflux ratio for concentration part of the column is 50.

Unrefined water-ethanol mixture feed on the plate number 23 of the column. An overhead distillate contained volatile impurities are separated from a condenser and follows to secondary distillation column for processing and repeated using. The product are directed to a concentration column for continue of a rectification. In our case the process of extractive distillation consists of feeding of the heating water to plate number 32 and in selection the water-ethanol mixture together with large quantity of impurities from plate number 33 (side cut distillate).

The unrefined water-ethanol mixture is characterized by volumetric flow rate Q_f, temperature t_f, ethanol concentration in the feed x_f, and concentrations of impurities formed during fermentation α_{fi}. Here subscript i indicates on specific impurity. The water (extractive solvent) is characterized by volumetric flow rate Q_h and average temperature t_h. Namely these parameters must be select for the best ethanol purification.

The overhead and side cut distillates are characterized by volumetric flow rates Q_d and Q_p, ethanol concentrations x_d and x_p, and impurities concentrations α_{di} and α_{pi}. A qualitative and quantitative allowance of impurities in these flows depends on effectiveness of the extractive distillery process.

Specificity of the column operation does not allow direct measure a volumetric flow rate of the product produced on the column Q_w. It may be calculate from equation of material balance of column

$$Q_w = Q_f + Q_h - Q_d - Q_p. \tag{1}$$

The impurities concentrations in product α_{wi} can not be measured because the sensibility of the gas chromatographic method is insufficient. One can calculate its values from the equations of material balance of column for every impurity

$$\frac{\alpha_{\mathrm{wi}}}{\alpha_{\mathrm{fi}}} = \frac{x_{\mathrm{f}} Q_{\mathrm{f}} - \left(\alpha_{\mathrm{di}}/\alpha_{\mathrm{fi}}\right) x_{\mathrm{d}} Q_{\mathrm{d}} - \left(\alpha_{\mathrm{pi}}/\alpha_{\mathrm{fi}}\right) x_{\mathrm{p}} Q_{\mathrm{p}}}{x_{\mathrm{w}} \left(Q_{\mathrm{f}} + Q_{\mathrm{h}} - Q_{\mathrm{d}} - Q_{\mathrm{p}}\right)}. \tag{2}$$

During of experiments the technological parameters of column are retained as a constant. In this time output of rectification plant is invariable.

The original gas chromatographic method of determination of quantitative impurities allowance in ethanol-water mixes was used (Vyazmina, 2002). Selection, identification and determination of the impurities concentrations was carried out by using gas chromatograph HP 6890 with the flame-ionization detector and the capillary column 50m× 0.32mm having motionless phase HP-FFAP. The treatment of experimental dates and analysis on its base technological regimes of column was used only for impurities which concentrations in unrefined water-ethanol feed have been defined.

3. Influence of volumetric flow rate of extractive solvent on the column efficiently

The results of experimental determination of the relative concentrations of some impurities presented in unpurified ethanol (in converting on absolute alcohol) in the overhead and side cut distillates on the volumetric flow rate of the extractive solvent are shown in Fig. 2.

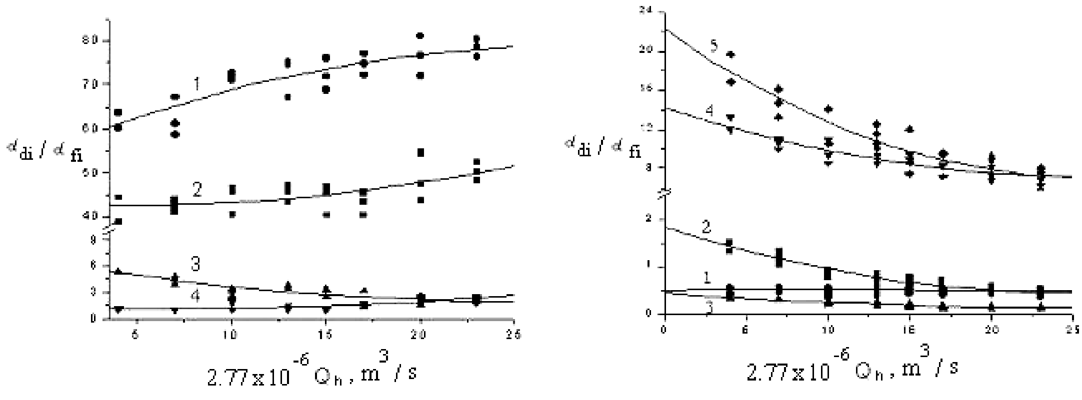

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Figure 2: Dependence of the relative concentrations of impurities in the overhead distillate α_{di}/α_{fi} (a) and in side cut distillate α_{pi}/α_{fi} (b) on the volumetric flow rate of extractive solvent (water) used for the extractive distillation, Q_h. Impurities: 1 – ethyl acetate, 2 - acetaldehyde, 3 - methanol 4 - i-amyl acetate, 5 - ethyl octanoate. No ethyl octanoate was found in the overhead distillate

For subsequent calculations, it is convenient to express the experimental data from Fig. 2 in the form of empirical formulas. This may be performed by their interpolation with polynomials within the range under study. Because all dependences are monotonous, let us use the second-order polynomials for the interpolation

$$Y_i = A_i X^2 + B_i X + C_i, \tag{3}$$

where Y_i are either α_{di}/α_{fi} or α_{pi}/α_{fi}, X is the value of Q_h; A_i, B_i, and C_i are empiric constants which are defined both by the particular impurity in the overhead and side cut distillates.

For the interpolation of experimental data by polynomials (3) it is necessary to obtain the values of empirical constants. The technique of least squares was used for this purpose (Blox, 1971). In each case, the problem of calculation of the coefficients reduces to the solution of the set of ordinary linear equations

$$\begin{aligned} A_i\sum_{j=1}^{n} X_j^4 + B_i\sum_{j=1}^{n} X_j^3 + C_i\sum_{j=1}^{n} X_j^2 &= \sum_{j=1}^{n} Y_{ij} X_j^2 , \\ A_i\sum_{j=1}^{n} X_j^3 + B_i\sum_{j=1}^{n} X_j^2 + C_i\sum_{j=1}^{n} X_j &= \sum_{j=1}^{n} Y_{ij} X_j , \\ A_i\sum_{j=1}^{n} X_j^2 + B_i\sum_{j=1}^{n} X_j + C_i n &= \sum_{j=1}^{n} Y_{ij} , \end{aligned} \tag{4}$$

where n is the number of experimental points used for the interpolation. The interpolation was performed using the method of successive approximations. If the calculation results have experimental points, deviating from interpolation date more than for ±5%, these points were discarded, and the calculations were repeated from the beginning. The results of fitting the experimental data shown in Fig. 2 are resumed in Table. 1.

Table 1: The values of empiric constants A_i, B_i, and C_i for various impurities

i	Impurity	Overhead distillate		
		A_{di}	B_{di}	C_{di}
1.	Ethyl acetate	55.57	1.73	-0.04
2.	Acetaldehyde	44.88	-0.18	0.03
3.	Methanol	6.62	-0.37	0.006
4.	I-amyl acetate	1.28	-0.045	0.004
5.	Ethyl octanoate	-	-	-

i	Impurity	Side cut distillate		
		A_{pi}	B_{pi}	C_{pi}
1.	Ethyl acetate	0.499	0.003	-
2.	Acetaldehyde	1.88	-0.11	0.002
3.	Methanol	0.454	-0.03	-
4.	I-amyl acetate	14.25	-0.24	0.01
5.	Ethyl octanoate	22.29	-1.68	0.034

By using expression (3) with the coefficients given in Table 1 and relationship (2) one is able to calculate the corresponding dependence of the relative concentration of each impurity in the product obtained in the column, α_{wi}/α_{fi}, on the volumetric flow rate of the extractive solvent (water) feed, Q_h. The corresponding plots for each impurity indicated above are shown in Fig. 3 for typical for a real mode of operation of the preliminary purification column parameters: $Q_f = 6.94\times10^{-4}$ m^3/s, $Q_d = 3.0\times10^{-6}$ m^3/s; Q_p=1.73×10^{-5} m^3/s; x_f=x_w=0,33; x_d=0,95; x_p=0,88.

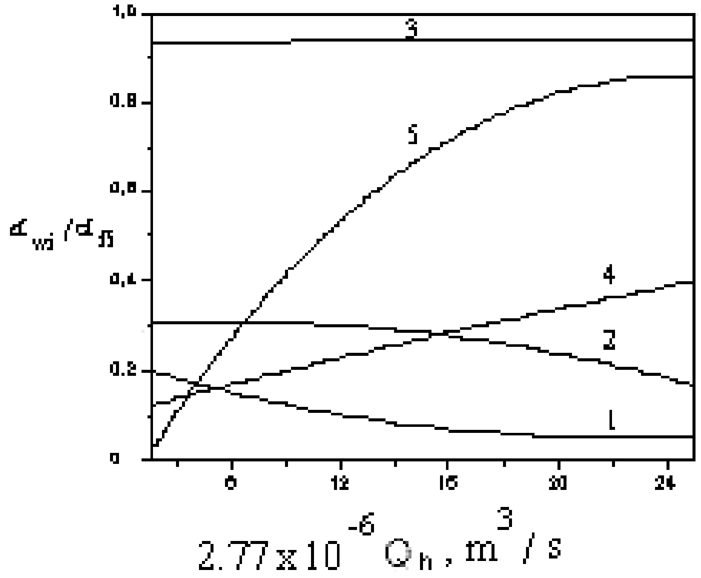

Figure 3: Dependence of relative concentrations of impurities in the product, α_{wi}/α_{fi}, on the volumetric flow rate of extractive solvent, Q_h. For notation see Fig. 2.

The values of process parameter Q_h, for each impurity should be chosen in such a way that its α_{wi}/α_{fi} is minimum value. However, in the case of multicomponent mixture the concentration of *i*-th impurity is minimum value for its own Q_h, different for different impurities. As can be seen from Fig. 3, at increasing volumetric flow rate of the extractive solvent, concentrations of some impurities decrease (with respect to absolute alcohol) whereas they increases for other impurities. Thus, the choice of process parameter Q_h is not simple and requires some validation.

Let us consider a column of preliminary purification as a single apparatus. As a parameter characterizing efficiency of purification of a particular substance it is natural to consider the ratio of total impurity content in the product to the total impurity content in the initial aqueous-alcoholic mixture

$$I = \sum_{i=1}^{m} k_{\mathrm{i}} \left(\alpha_{\mathrm{wi}} / \alpha_{\mathrm{fi}} \right) \Bigg/ \left(m \sum_{i=1}^{m} k_{\mathrm{i}} \right), \tag{5}$$

where *m* is the number of impurities, which are removed in this column and $k_{\mathrm{i}} = \alpha_{\mathrm{fi}} / \alpha_{\mathrm{f1}}$. In the example under study $m = 5$. The coefficient k_{i} shows how much the amount of *i*-th impurity in the initial aqueous-alcoholic mixture is higher than the concentration of one of them, for example, of the first. Values of coefficients k_i for the impurities in the unpurified ethanol used in the experiments are given below in Table 2. This coefficient is a normalizing factor which shows the effect of purification from *i*-th impurity on the efficiency column on the whole. Then, the sum in the denominator of (5) depends only on the impurity composition of the unpurified ethanol and do not depend on the operating mode of extractive distillation.

Table 2: The values of k_i and γ_i for various impurities

i	Impurity	k_i	γ_i
1.	Ethyl acetate	1	1
2.	Acetaldehyde	0.165	1
3.	Methanol	0.00145	0.1
4.	I-amyl acetate	0.0732	0.3
5.	Ethyl octanoate	0.243	0.3

The results of calculation of the *I* dependence on Q_h according to the data given in Tables 1 and 2, are presented by curve 1 in Fig. 4. As follows, in a separately taken column of preliminary purification a slight decrease of the total (with respect to all impurities) degree of purification is observed if the volumetric flow rate of extractive solvent increases. In this case, the highest purification efficiency for this column is achieved without using extractive distillation.

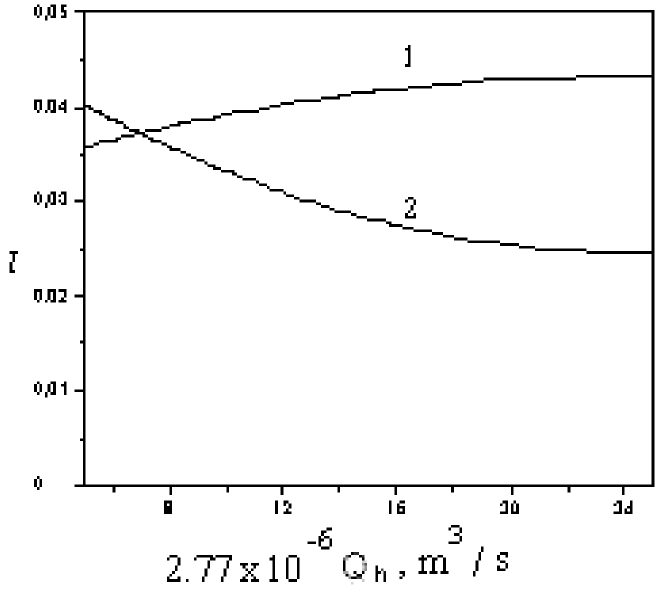

Figure 4: Dependence of *I* on Q_h. Curve 1: for a single column, 2: for the whole unit.

The industrial purification of ethanol is performed in multicolumn distillation units, when there is no need to reach its maximum purification from all impurities in the first column. One should selectively address the problem of purification from each impurity, by taking account its effect on the qualitative characteristics of the finished product and the possibility to remove it in the next columns. In this case, instead k_i of one should use in (5) a different coefficient, $\tilde{k}_i = \gamma_i k_i$, where γ_i is the weighted factor of the purification required for the *i*-th impurity, this factor varying from 0 to 1. The values of γ_i, obtained by expert evaluation, for the above-mentioned impurities is given in Table 2.

The results of calculation of the dependence I on Q_h with the account taken on the correction for the selectivity of purification from different impurities are shown by curve 2 in Fig. 4. From this Figure it follows that by choosing the column operating mode with taking account the possibility of further ethanol purification in the other columns, one may achieve a significant enhancement (doubling) of the total degree of extraction with respect to all impurities by simply increasing the volumetric flow rate of extractive solvent supplied for extractive distillation. The best result is obtained when the volumetric flow rate is about 10% from the volumetric flow rate of aqueous-alcoholic mixture given as column feed. The further increase only slightly affects the efficiency of column.

4. Temperature mode selection of extractive distillation

The ratios of the impurity concentrations in the distillate and in the water-ethanol side cut distillate to the corresponding quantities in the initial unrefined mixture were studied versus temperature by using the gas chromatography method.

The first group of impurities (A) includes: acetic aldehyde, acetic methyl ester, butyric aldehyde, and acetic ethyl ester. All of them have a higher volatility than ethanol in its water solutions of any concentration. According to the current conception of the distillation process, these impurities should be concentrated in the overhead distillate mainly. It is apparent from Fig. 5 that their concentrations in overhead distillate exceed their initial values by 25-70 times. However, in water-alcohol solution, solely butyric aldehyde is concentrated in insignificant quantity in side cut distillate.

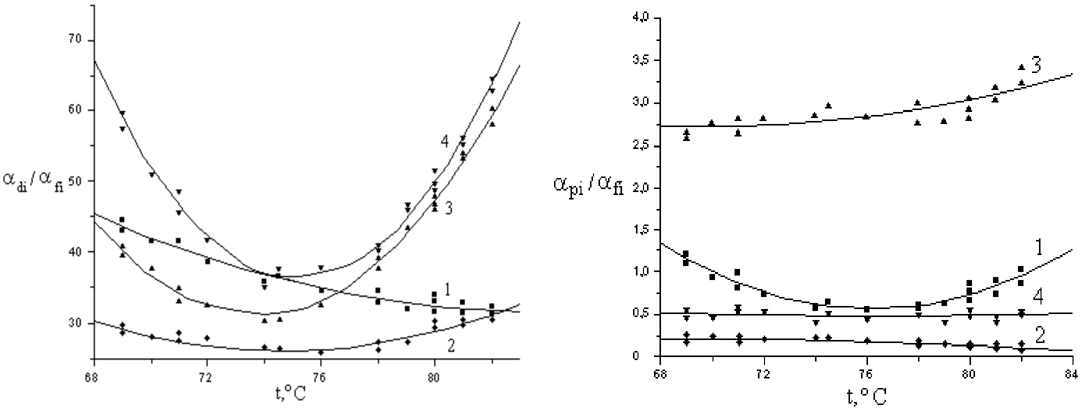

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Figure 5: Relative concentrations of the impurities of group A in the overhead (a) and in the side cut (b) distillates versus the temperature of the extractive solvent: 1 - acetic aldehyde; 2 - acetic methyl ester; 3 - butyric aldehyde; 4 - acetic ethyl ester

The second group (B) consists of the following impurities: isopropyl alcohol, diacetyl, acetic-acid isobutyl ester, and crotonaldehyde. All of them form azeotropic mixtures with ethanol in its water solutions, with the volatility of isopropanol being close to that of ethanol at any concentration of the latter. As seen in Fig. 6, isopropyl alcohol is not virtually concentrated in the preliminary distillation column, whereas the other impurities are well concentrated not only in the overhead distillate but also in the side cut distillate. All temperature dependences of the relative impurity concentrations in the water-alcohol solution have a minimum between 75°C and 77°C.

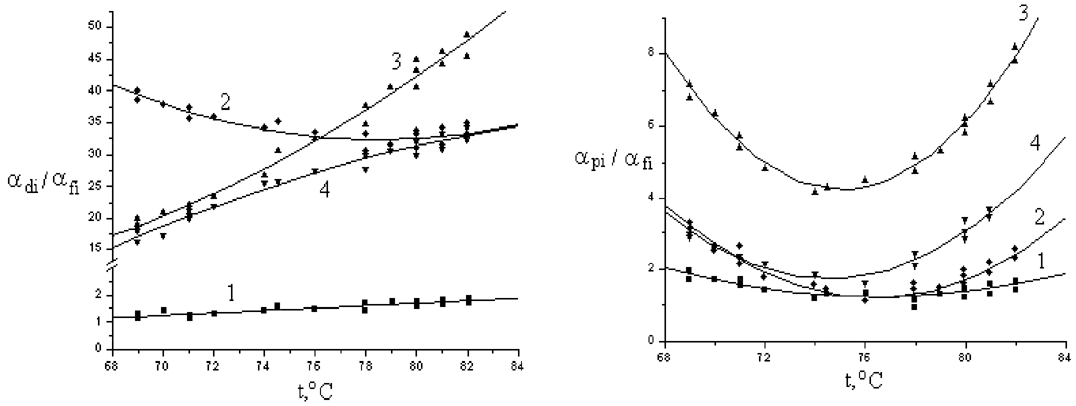

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Figure 6: Relative concentrations of the impurities of group B in the overhead (a) and in the side cut (b) distillates versus the temperature of the extractive solvent: 1 - isopropyl alcohol; 2 - diacetyl; 3 - acetic-acid isobutyl ester; 4 - crotonaldehyde

The relative concentrations of the impurities of groups A and B in the product of the preliminary distillation column are plotted in Fig. 7 against temperature. It is apparent that the concentrations of the more volatile substances from group A decrease by an order of magnitude and even more, whereas the degree of purification of the azeotropes and the less volatile substances from group B in the column is much lesser. Note that isopropanol cannot practically be separated from ethanol in a vacuum preliminary distillation column.

It follows from the results shown in Fig. 7 that the temperature dependences have a maximum or minimum between 72°C and 80°C, with different impurities having different positions of the extreme. This is caused by the fact that the impurities in the overhead and side cut distillates are concentrated differently.

In order to select the water temperature (water is used as the extractive solvent), t_h, at which the highest degree of purification of ethanol from impurities is achieved, it is convenient to represent the data plotted in Fig. 7 in the form of empirical formulas. This can be done by interpolating the data with polynomial relations (3) on the temperature interval in question using the technique described. However, it should be taken into account that the Y_i are now the ratios α_{wi}/α_{fi} and X is now t_h, with the A_i, B_i, and C_i being empirical constants corresponding to each of the impurities in the overhead and in the side cut distillates.

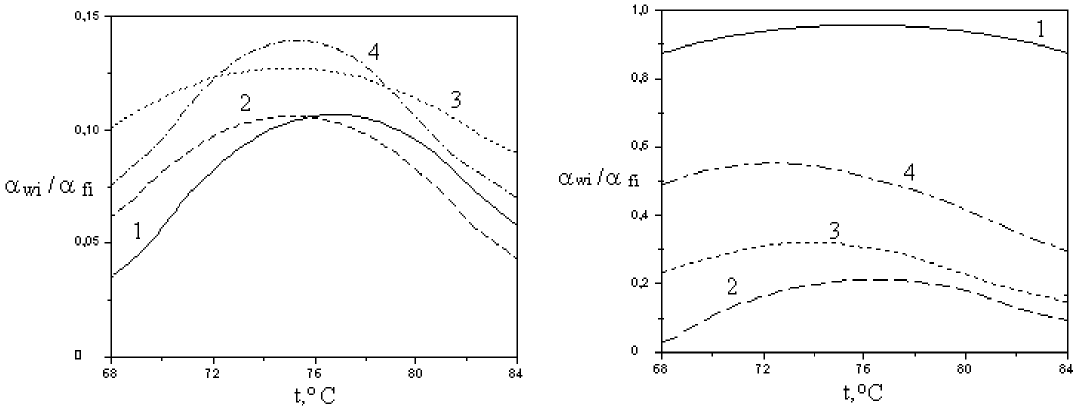

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Figure 7: Relative concentrations of impurities from groups A (a) and B (b) in the product obtained in the preliminary distillation column against the temperature of the extractive solvent. The numbers labelling the curves are explained in Fig. 5 and Fig. 6, respectively

From the viewpoint of the distillation technology, the technological parameter t_h for each impurity should ideally be chosen so that the ratio α_{wi}/α_{fi} is minimum. However, the minima of α_{wi}/α_{fi} will be attained at different temperatures t_h for each i-th impurity when separating a multicomponent mixture.

As in the case considered in the previous section, we take I defined by (5) as the quantity characterizing the quality of purification of the initial mixture in the column. Here, we have $m = 8$.

Fig. 8 depicts the calculation results, obtained by the above technique, for the ratio of the total concentration of impurities in the product to their total content in the initial water-alcohol mixture versus the temperature of the extractive solvent. Just as earlier in formula (5), we use the coefficient $\tilde{k}_i = \gamma_i k_i$ instead of k_i, with γ_i, taking values from 0 to 1, being the indicator of the required quality of purification from each of the impurities.

Curve 1 corresponds to the highest degree of purification of ethanol from all its main 16 impurities, curve 2 corresponds to the highest degree of purification from all impurities except those to be removed in the further columns, and curve 3 corresponds to the highest degree of purification from impurities of groups A and B only. From analysing together the data presented in Figs. 5–8 it may be concluded that the extractive solvent should be fed into the preliminary rectification column at temperatures higher than 80°C for all its modes of operation considered.

A hydraulic calculation was carried out to determine the residual vapour pressure over the extractive solvent feed plate; the data on the ethanol concentration along the height of the vacuum preliminary distillation column were taken into account. The liquid-vapour phase transition temperature was calculated for water at that pressure, based on the solution of the Clapeyron–Clausius equation. This temperature was found to be approximately equal to 76°C. At lower temperatures, the extractive solvent enters the column as liquid and at higher temperatures, as vapour.

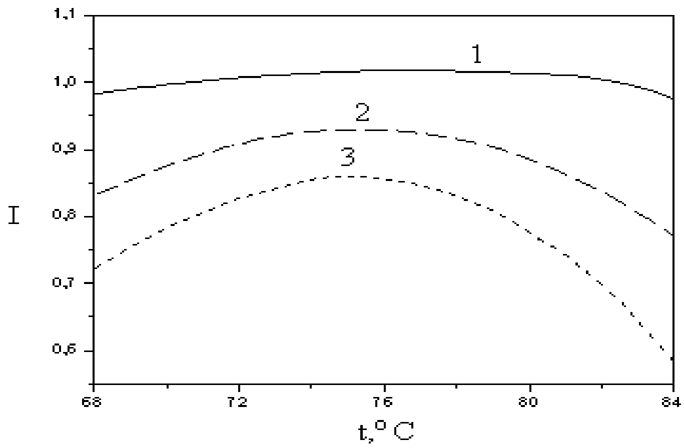

Figure 8: Ratio of the total concentration of impurities in the product leaving the preliminary distillation column to their concentration in the initial mixture versus the extractive solvent temperature for different modes of exploitation of the preliminary distillation column

As the temperature of the extractive solvent, fed to the column as liquid, increases due to mixing up with the water-alcohol mixture in an appropriate plate, the liquid evaporates more and more quickly. This favours the vapour phase composition approaching its equilibrium. As a result, the driving force of the separation in the part of the distillation column above the extractive solvent feed plate gradually diminishes, and hence the concentration of ethanol and accompanying impurities (which are more volatile than water) in the distillate and water-alcohol solution also decreases. As the extractive solvent temperature attains the liquid-vapour phase transition temperature and further increases, the larger and larger portion of the extractive solvent gets into the vapour phase above the plate, and hence the concentration of more volatile components there is reduced. Consequently, the driving force of the process is raised, thus favouring the concentration of impurities in the column part above the plate.

In reality, the above mechanism is much more complicated, since the volatility of impurities changes as the concentration of ethanol in the water solution in the extractive solvent feed plate decreases.

5. Nomenclature

A, B, C - empirical constants in (3);
I - function introduced of the formula (5);
k - coefficient in the formula (5);
$\tilde{k}$ - modified coefficient in the formula (5);
m - number of investigated impurities;
n - number of experimental points used for the interpolation;
Q - volumetric flow rate, m^3/s;
t - temperature, ^0C;
X - variable in (3), may be Q_h or t_h;
x - ethanol concentration, % vol.;
Y - function introduced in the form (3), may be α_{di}/α_{fi}, α_{pi}/α_{fi}, or α_{wi}/α_{fi}.

Greek Letters

α - impurity concentration, % vol.;
γ - index of the quality of purification.

Subscripts

d -overhead distillate;
f - unrefined water-ethanol mixture;
i - number of specific impurity;
h - extractive solvent (water);
p - side cut distillate;
w - product produced on the column.

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