

## **Influence Of Operating Conditions To The Effectiveness Of Extractive Distillation Columns**

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The influence of operating conditions to the effectiveness of extractive distillation process was investigated. The experiment took place on an industrial vacuum plant of purification ethanol. It is obtained that the concentration of different impurities at the selection zones depends on the volumetric flow rate of extractive solvent. It gives an opportunity to affect of ethanol purification from the various volatility impurities. Proposed method allows 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.

### **1. Introduction**

One method of production of ethyl alcohol is based on the distillation of alcohol-water solution obtained in the fermentation. In this process, in addition to the increase of concentration of alcohol, purification from impurities occurs which were formed during fermentation and which are harmful (e.g., methyl, propyl, and other alcohols, ethers, acids, aldehydes, etc.). According to the volatility to ethanol, these impurities are subdivided into volatile, low-volatile, and intermediate ones. It is 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 P.S. and Tsigankov S.P., 2002). In practice, the desired purification is achieved by using several distillation columns in series.

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 P.S. and Tsigankov S.P., 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

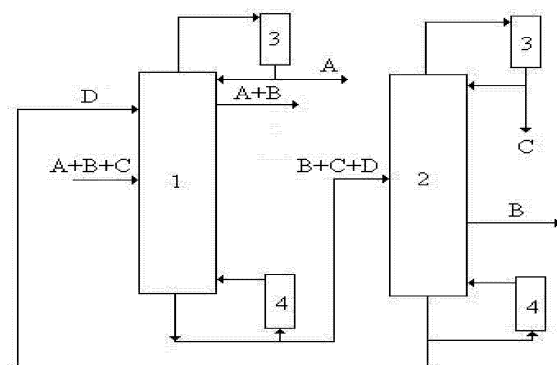


Fig. 1. The process flowsheet of extractive distillation for ethanol production: 1 – preliminary purification column, 2 – concentration column, 3 – condensers, 4 – boilers

phase. Extractive distillation considerably enhances the capabilities for the creating of zones of concentration of impurities along the column and their separation from ethanol. The process flowsheet of industrial units for ethanol production is shown in Fig. 1. Unrefined ethanol alcohol (C) containing volatile (A) and intermediate (B) impurities feed on the preliminary 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. Water from column 2 is returned to column 1. 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.

## 2. Conditions Of The Experiments

The effect of the parameters on the purification degree was studied on a commercial distillation column of the ethanol production plant by measuring amounts of impurities in the products of distillation using highly effective gas chromatograph. The diameter of the column is 1200 mm. It has 39 bubblecap plants. 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. An overhead distillate contained volatile impurities are separated from a condenser. The product are directed to a concentration column for continue of a rectification. The process of extractive distillation consists of feeding of the water to plate number 32 and in selection the ethanol mixture together with impurities from plate number 33 (side cut distillate). The unrefined water-ethanol mixture is characterized by volumetric flow rate  $Q_f$ , ethanol concentration in the feed  $x_f$ , and concentrations of impurities  $\alpha_{fi}$ . Here subscript  $i$  indicates on specific impurity. The water (extractive solvent) is characterized by volumetric flow rate  $Q_h$ . 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  $\alpha_{di}$  and  $\alpha_{pi}$ . 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

$$Q_w = Q_f + Q_h - Q_d - Q_p \quad (1)$$

The impurities concentrations in product  $\alpha_{wi}$  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

$$\frac{\alpha_{wi}}{\alpha_{fi}} = \frac{x_f Q_f - (\alpha_{di}/\alpha_{fi}) x_d Q_d - (\alpha_{pi}/\alpha_{fi}) x_p Q_p}{x_w (Q_f + Q_h - Q_d - Q_p)} \quad (2)$$

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 mixes was used (Vyazmina and Savchuk, 2002). Selection and determination of the impurities concentrations was carried out by using gas chromatograph with the flame-ionization detector and the capillary column  $50\text{m} \times 0.32\text{ mm}$  having motionless phase HP-FFAP.

### 3. Influence Of Volumetric Flow Rate Of Extractive Solvent On The Column Efficiency

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. 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

$$Y_i = A_i X^2 + B_i X + C_i, \quad (3)$$

where  $Y_i$  are either  $\alpha_{di}/\alpha_{fi}$  or  $\alpha_{pi}/\alpha_{fi}$ ,  $X$  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. In each case, the problem of calculation of the coefficients reduces to the solution of the set of ordinary linear equations

$$\begin{aligned}
 A_1 \sum_{j=1}^n X_j^4 + B_1 \sum_{j=1}^n X_j^3 + C_1 \sum_{j=1}^n X_j^2 &= \sum_{j=1}^n Y_{ij} X_j^2 \\
 A_1 \sum_{j=1}^n X_j^3 + B_1 \sum_{j=1}^n X_j^2 + C_1 \sum_{j=1}^n X_j &= \sum_{j=1}^n Y_{ij} X_j \\
 A_1 \sum_{j=1}^n X_j^2 + B_1 \sum_{j=1}^n X_j + C_1 n &= \sum_{j=1}^n Y_{ij}
 \end{aligned}
 \tag{4}$$

where  $n$  is the number of points used for the interpolation. If the calculation results have experimental points, deviating from interpolation date more than for  $\pm 5\%$ , these points were discarded, and the calculations were repeated. The results of fitting the experimental data shown in Fig. 2 are resumed in Table. 1.

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,  $\alpha_{wi}/\alpha_{fi}$ , on the volumetric flow rate of the extractive solvent feed,  $Q_h$ . The corresponding plots are shown in Fig. 3 for typical for a real mode of operation of the preliminary purification column parameters:  $Q_f = 6.94 \times 10^{-4} \text{ m}^3/\text{s}$ ,  $Q_d = 3.0 \times 10^{-6} \text{ m}^3/\text{s}$ ;  $Q_p = 1.73 \times 10^{-5} \text{ m}^3/\text{s}$ ;  $x_f = x_w = 0,33$ ;  $x_d = 0,95$ ;  $x_p = 0,88$ .

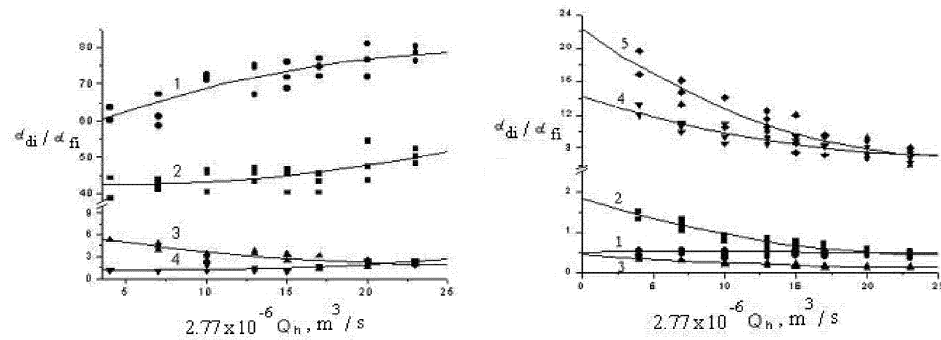


Fig. 2. Dependence of the relative concentrations of impurities in the overhead distillate  $\alpha_{di}/\alpha_{fi}$  (left) and in side cut distillate  $\alpha_{pi}/\alpha_{fi}$  (right) on the volumetric flow rate of extractive solvent (water) used for the extractive distillation,  $Q_h$ . Impurities: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

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

$i$	Impurity	Overhead distillate			Side cut distillate		
		$A_{di}$	$B_{di}$	$C_{di}$	$A_{pi}$	$B_{pi}$	$C_{pi}$
1.	Ethyl acetate	55.57	1.73	-0.04	0.499	0.003	-
2.	Acetaldehyde	44.88	-0.18	0.03	1.88	-0.11	0.002
3.	Methanol	6.62	-0.37	0.006	0.454	-0.03	-
4.	I-amyl acetate	1.28	-0.045	0.004	14.25	-0.24	0.01
5.	Ethyl octanoate	-	-	-	22.29	-1.68	0.034

The values of process parameter  $Q_h$ , for each impurity should be chosen in such a way that its  $\alpha_{wi}/\alpha_{fi}$  is minimum value. However, in the case of multicomponent mixture the concentration of  $i$ -th impurity is minimum value for its own  $Q_h$ . As can be seen from Fig. 3, at increasing  $Q_h$ , concentrations of some impurities decrease whereas they increase for other impurities. Thus, the choice of process parameter  $Q_h$  is not simple.

Let us consider a column 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 mixture

$$I = \sum_{i=1}^m k_i (\alpha_{wi} / \alpha_{fi}) / \left( m \sum_{i=1}^m k_i \right), \quad (5)$$

where  $m$  is the number of impurities, which are removed in this column and  $k_i = \alpha_{fi} / \alpha_{fi}$ . In the example under study  $m = 5$ . The coefficient  $k_i$  shows how much the amount of  $i$ -th impurity in the initial mixture is higher than the concentration of one of the first. Values of coefficients  $k_i$  used in the experiments are given in Table 2. This coefficient is a normalizing factor which shows the effect of purification from  $i$ -th impurity on the efficiency column.

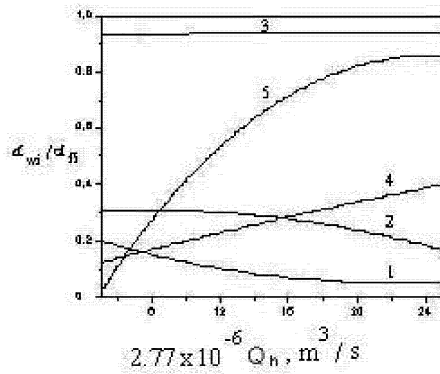


Fig. 3. Dependence of relative concentrations of impurities in the product,  $\alpha_{wi}/\alpha_{fi}$ , on the volumetric flow rate of extractive solvent,  $Q_h$ . For notation see Fig. 2.

Table 2. The values of  $k_i$  and  $\gamma_i$  for various impurities

$i$	Impurity	$k_i$	$\gamma_i$
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

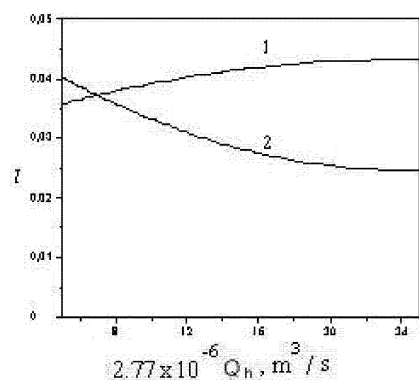


Fig. 4. Dependence of  $I$  on  $Q_h$ . Curve 1: for a single column, 2: for the whole unit.

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 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.

The purification of ethanol is performed in multicolumn distillation units, when there is no need to reach its maximum purification 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 coefficient  $\tilde{k}_i = \gamma_i k_i$ , where  $\gamma_i$  is the weighted factor required for the  $i$ -th impurity, this factor varying from 0 to 1. The values  $\gamma_i$ , obtained by expert evaluation, are 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 are shown by curve 2 in Fig. 4. It follows that by choosing the column operating mode with taking account the possibility of further purification, one may achieve a significant enhancement of the total degree of extraction with respect to all impurities by simply increasing the volumetric flow rate of extractive solvent. 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.

## References

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