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CHANGES IN METHANOL CONTENT DURING FRACTIONAL DISTILLATION OF WATER-ETHANOL SOLUTIONS

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Young apple wine and water-ethanol model solutions with additions of methanol and other components were subjected to fractional distillation. During distillation, consecutive fractions were obtained according to volume, and the contents of methanol and ethanol were determined. The best conditions for the separation of methanol were found in solutions with a high ethanol concentration (over 43% vol.). In conditions of these experiments, distillation of 70% solutions makes possible a separation of about 24% of the total methanol content in the first fraction. The processes of heating and distillation contribute to methyl esters hydrolysis and methanol release. The amount of methanol released in this way depends mainly on the kind of ester and the pH of the solution, and amounts from 3 to 19% of the total content of methanol bound in ester.

The adverse effect of methanol (MeOH) on the human organism is well known. Its toxicity increases when it is consumed together with ethanol [7, 25]. The content of MeOH in fruit vodkas and distillates may be as high 16 g/dm³ of 100° solution [18]. The total removal of MeOH during distillation and rectification is very difficult since it passes through to all the fractions: the head, the distillate and the tail [1, 21, 23, 26]. This behaviour of MeOH during distillation is significantly affected by azeotropes [1, 2, 8]. The ultimate composition of the solution depends also on hydrolysis and synthesis of esters, and on transesterification [13, 24]. These transformations are favoured by elevated temperature, changes of the solution's pH during distillation, and rich chemical composition.

A very significant role in the separation of the solution's components is played by the technique and technology of distillation and rectification. Generally speaking, two techniques of distillation may be distinguished: the one based on the parallel current principle, and the other on the counter-current principle [10, 27]. If the distillate is collected in parts, the distillation is referred to as fractional; in fruit alcohol distillation it is also known as corrective [3, 6, 22]. Fractionation affects the quantitative proportions of aroma components in the successive distillate portions, and this makes possible alterations of the chemical composition of the main fraction. Most of the apparatuses used in fruit alcohol

production operate according to the principle of parallel current distillation with partial condensation. However, fruit mashes are better distilled in counter-current conditions [9, 17, 19, 26]. According to Majorow [12], a considerable proportion of MeOH may be separated in column distillers, but this is inadvisable given the risk of a loss of aroma in the distillate. Dellweg et al. [5] suggest to remove a large amount of the first fraction in order to reduce the content of MeOH, methyl acetate, and sulphur compounds. Wucherpennig and Bretthauer [26, 27] recommend a double distillation of fruit mashes, first in parallel current apparatus, and then according to the counter-current principle. Masiar et al. [14] reduced MeOH contents in grape wines by limited vacuum distillation of musts and young wines. Litchev and Goranov [11] introduced into wine distillation studies the coefficient of thermal conductivity which may be an important indicator in automation of distillation and rectification apparatuses. Also described are various methods of distilling water-ethanol solutions and of separating certain components from them [1, 15, 16, 20, 21, 26]. So far researchers did not take into account the effect of other components of the distilled solution on the amount of the separated MeOH, and the possibility of MeOH release from methyl esters.

The aim of this research was the preliminary determination of the per cent of total MeOH content removed during fractional distillation of model water-ethanol solutions and of young wine. Also determined were the amounts of MeOH released during distillation from methyl esters present in the solution.

MATERIAL AND METHODS

The experiments were performed with water-ethanol solutions supplemented with specific quantities of the following components: methanol, methyl formate, methyl acetate, ethyl acetate, acetic acid, methyl butyrate, methyl isobutyrate and methyl caproate. Fractionation of young wine with ethanol content adjusted to 10% vol and MeOH content to 0.1% vol was carried out for comparison. Periodic distillation of 100 cm³ samples was carried out according to the parallel and counter-current principle [10, 27]. The distilling apparatus consisted of a glass flask, condenser, receiver, and electric bath with autotransformer (parallel current) and of a column ($\varnothing = 45$ mm, $l = 300$ mm) filled with glass Raschig rings (counter-current). Distillation rate depended on ethanol content in the samples, ranging from 0.6 to 1.2 cm³/min. Successive 5 cm³ fractions were collected during distillation, and ethanol and methanol contents were determined in each. Ethanol was determined refractometrically, and MeOH by the colorimetric method with chromotropic acid [4] or in some samples (for control) by gas chromatography in a Pye Unicam model 104 apparatus [22]. The figures illustrate mean results from three parallel distillations.

RESULTS AND DISCUSSION

The changes in MeOH content during fractional distillation of model solutions and young wine are presented in Fig. 1. In both distillations, larger amounts of MeOH (by about 5%) passed to the first fraction when counter-current was applied. 39-45% of ethanol and 29-34% of MeOH was distilled off to the first fraction. The untypical changes of MeOH contents that can be seen in

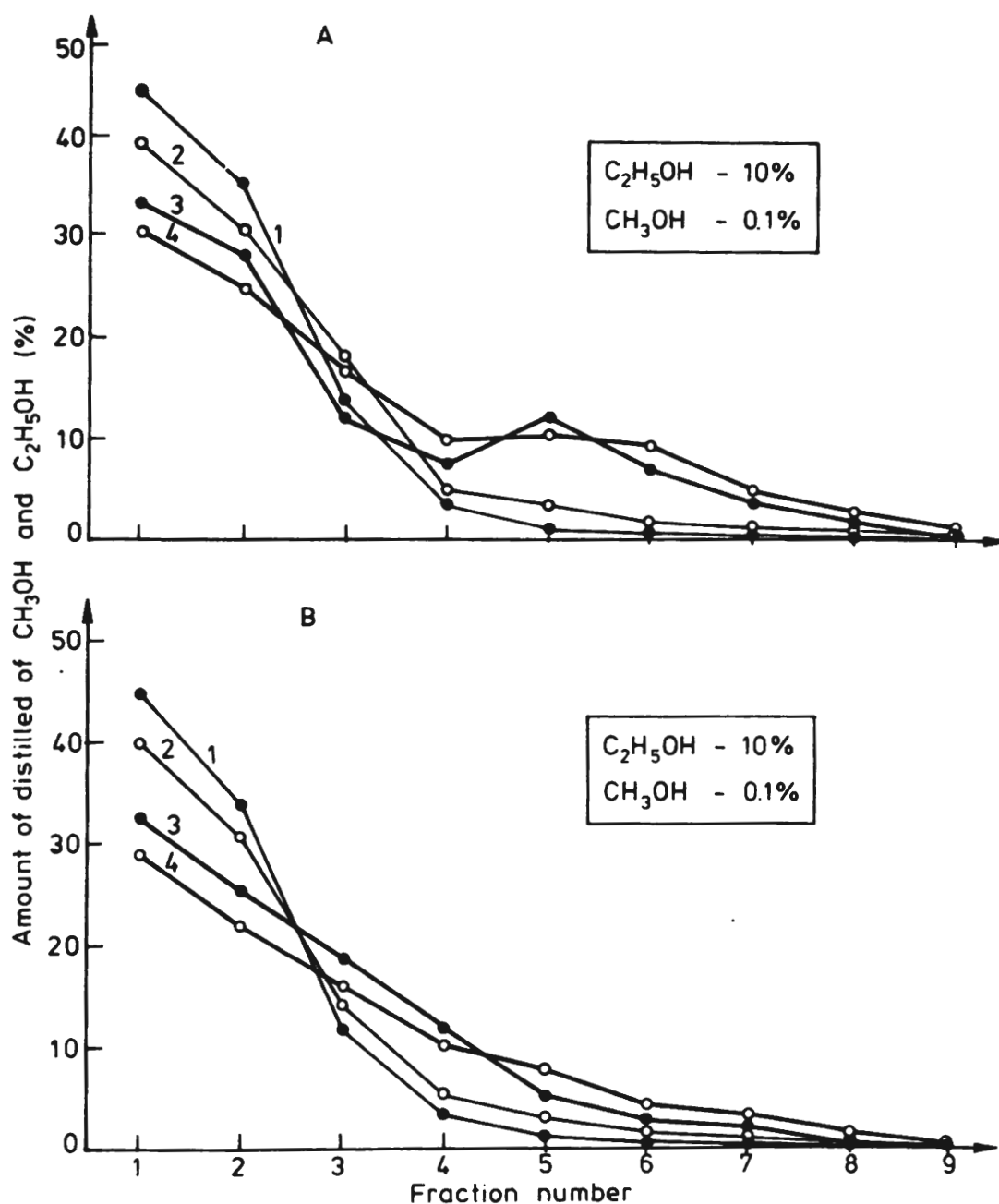


Fig. 1. Changes of methanol and ethanol during fractional distillation; A — young apple wine, B — model solution; 1 — ethanol — counter-current, 2 — ethanol — parallel current, 3 — methanol — counter-current, 4 — methanol — parallel current

diagram A (fractions 5 and 6), may be the result of methyl esters hydrolysis, and of the effect of azeotropic systems. Methyl alcohol forms two-components azeotropes with methyl acetate and ethyl acetate (boiling points: 54.0 and 62.2°C). A particularly high MeOH content (44%) is in the azeotropic system with ethyl acetate [8]. Two-component azeotropes with ethyl esters are also formed by ethanol and water, and some of them (water-methyl acetate, ethanol-methyl

isobutyrate, ethanol-methyl butyrate) have relatively low boiling points (56.5, 77 and 78°C) and may pass to the first and main fractions of the distillate. In the model three-component solution (Fig. 1B) there are fewer possibilities for azeotropization of components and quantitative changes during distillation than in a natural young wine solution. Unusual abrupt changes of concentrations of some components (esters and alcohols) in the course of distillations of fruit wines and distillates have already been described by Litchev and Goranov [11] and Tuszyński and Bachman [24].

Fig. 2 illustrates the effect of model solution components on the quantity of separated MeOH during fractional distillation using counter-current. The curves representing the amounts of MeOH separated in the successive fractions are similar for all the studied solutions. It may be concluded that in the applied distillation conditions the effect of ethyl acetate, methyl acetate, methyl formate and acetic acid on the amount of released MeOH was insignificant. The relatively largest amount of MeOH (37%) was released into the first fraction from the most complex (qualitatively) solution; in the case of the basic solution (water-ethanol-methanol) this amount was about 33% of the total MeOH content present in the initial sample.

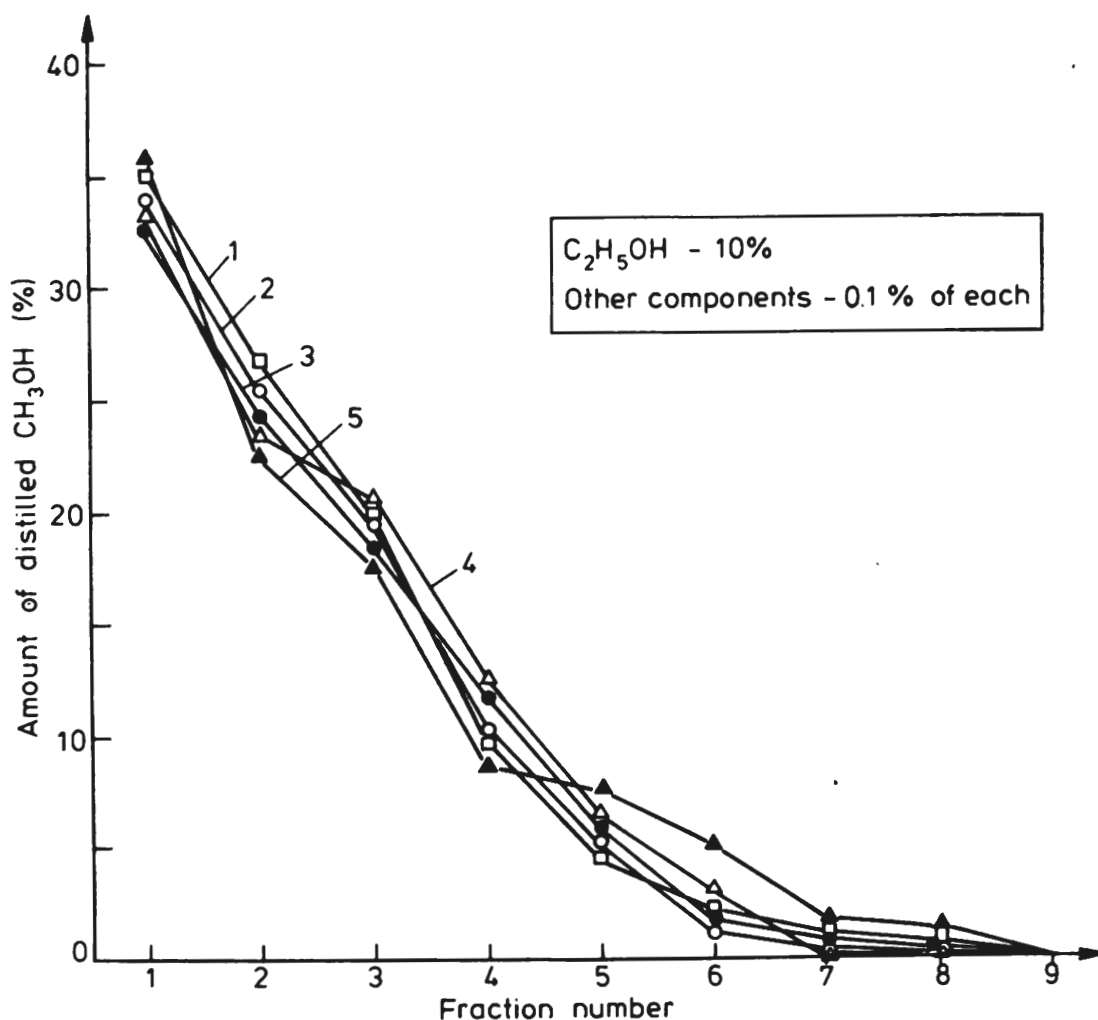


Fig. 2. The effect of model solutions components on the amount of methanol separated during fractional distillation according to the counter-current principle; 1— $C_2H_5OH + CH_3OH + CH_3COOC_2H_5$; 2— $C_2H_5OH + CH_3OH$; 3— $C_2H_5OH + CH_3OH - CH_3COOCH_3$; 4— $C_2H_5OH + CH_3HCOOCH_3$; 5— $C_2H_5OH + CH_3OH + CH_3COOCH_3 + CH_3COOC_2H_5 + HCOOCH_3 + CH_3COOH$

The removal of MeOH from qualitatively complex solutions is a difficult process, given that a considerable proportion of this component passes to the main and tail fractions. The presence of methyl esters in the distilled model solutions caused a slight increase of MeOH content in fractions 3 through 7. The observed changes are due to chemical-thermal hydrolysis of esters, illustrated in Fig. 5. One also has to reckon with the possibility that the increased content of MeOH in these fractions is to some extent due to the effect of azeotropic systems in the multi-component solution (Fig. 2). According to Augustynowicz [1, 2], MeOH and ethyl acetate play a positive role in the rectification of water-ethanol solutions by forming positive azeotropes with many other components of the solution.

The effect of the initial content of ethanol in the distilled sample on the amounts of MeOH and ethanol separated in the first fraction is presented in Fig. 3. Conditions for MeOH separation are better in solutions with higher ethanol contents. 19% of the methanol and 19% of the ethanol contained originally in the sample taken for distillation was separated into the first fraction from a solution containing about 43% vol of ethanol. Fractional distillation of a solution with initial ethanol concentration of 90% vol separated about 34% of the total MeOH content and a mere 10% of the total ethanol content into the first fraction.

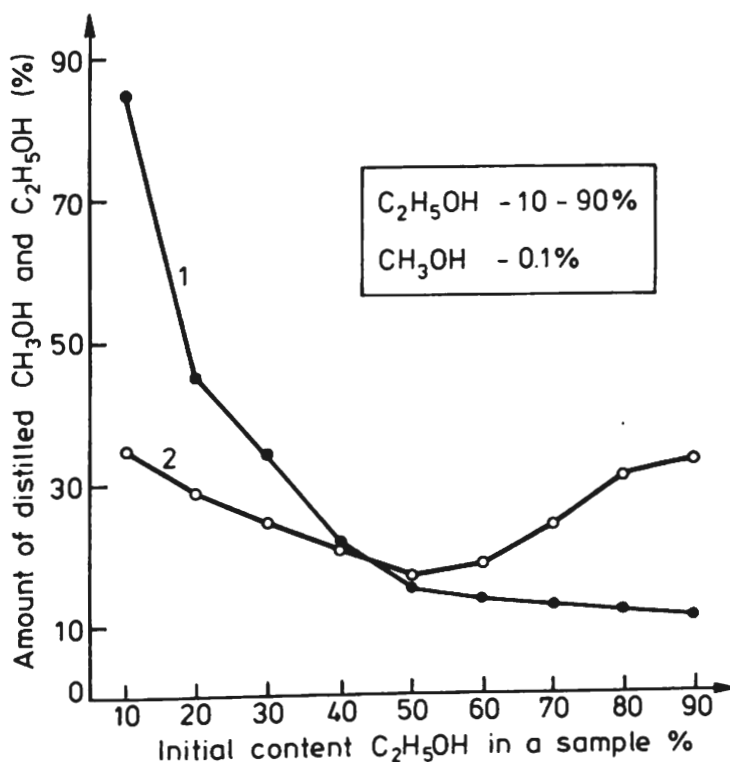


Fig. 3. The effect of initial ethanol content on the amount of methanol separated in the first fraction — counter-current principle; 1 — C₂H₅OH; 2 — CH₃OH

Analogous distillation of a 10% solution removed a similar amount of MeOH (35%) into the first fraction, but the amount of ethanol distilled off simultaneously was as high as 85%.

The quantitative proportions of components removed to the first fractions depend also on the technique of distillation and on the structure of the distiller.

However, both in the laboratory and in the industrial apparatuses the amounts of MeOH that are removed are similar and unsatisfactory. An almost complete removal of MeOH from solutions with a high ethanol concentration is possible using a special column (methanol column) for the elimination of this component [20]. Unfortunately, the cost of this apparatus and its energy consumption are too high to warrant its application in the production of spirits and fruit distillates.

Fig. 4 illustrates the effect of the time of heating a 40% solution prior to distillation on the amount of methanol and ethanol separated in the first fraction. Heating the solution in a system incorporating a reflux condenser increased the amount of released MeOH. 20-60 minutes of heating increased the amount of MeOH in the first fraction by 3-8%. The preheating of ethanol solutions with all the condensate returning to the column is aimed at condensing the first fractions, and thereby ensuring their better separation.

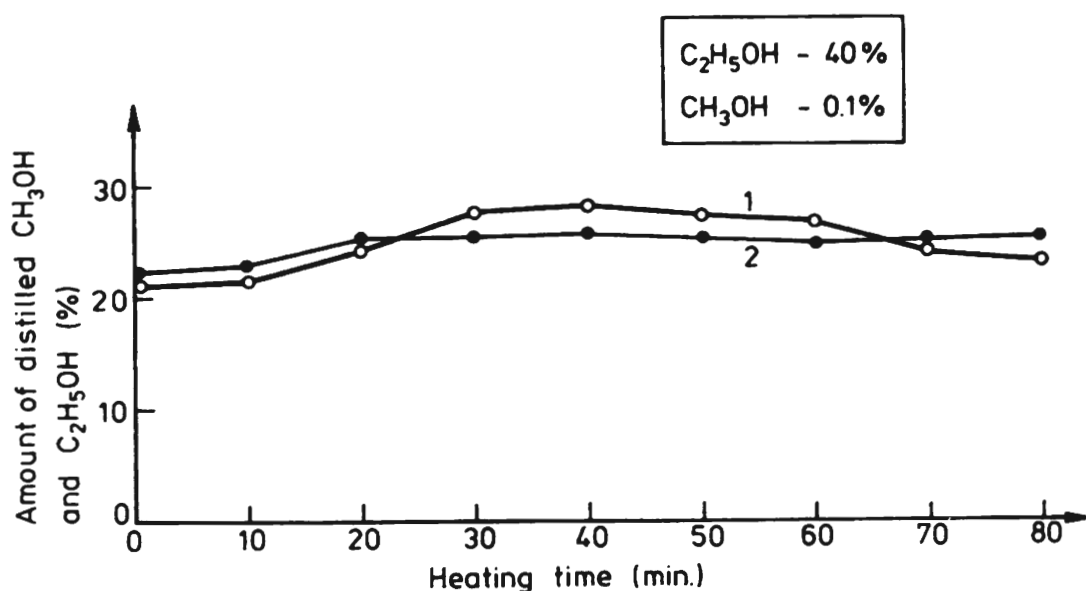


Fig. 4. The effect of heating time of sample before distillation on the amount of CH₃OH and C₂H₅OH separated in the first fraction — counter-current principle; 1 — CH₃OH; 2 — C₂H₅OH

The heating and fractional distillation of the model multi-component solution (Fig. 2) revealed that the total content of MeOH in the obtained fractions exceeds its initial content (positive methanol balance). The possibility of MeOH release from methyl esters was examined by distilling model water-ethanol solutions with additions of methyl formate, methyl acetate, methyl butyrate, methyl isobutyrate and methyl caproate. The experiments showed that MeOH is indeed released from the methyl esters present in the solution during distillation. The largest amounts of MeOH were released from methyl formate and methyl acetate (Fig. 5). The acid hydrolysis of esters usually has the character of nucleophilic dimolecular substitution, and is a reversible reaction [13]. High temperature and low pH of the solution increase the reaction rate. A decrease of the distilled solution's pH from 5.0 to 3.5 increased the amount of MeOH released from methyl acetate by 180 mg/dm³. Distillation of solutions with initial pH of 4.6-5.0 led to release of 0.5-3.0% of total MeOH bound in methyl ester.

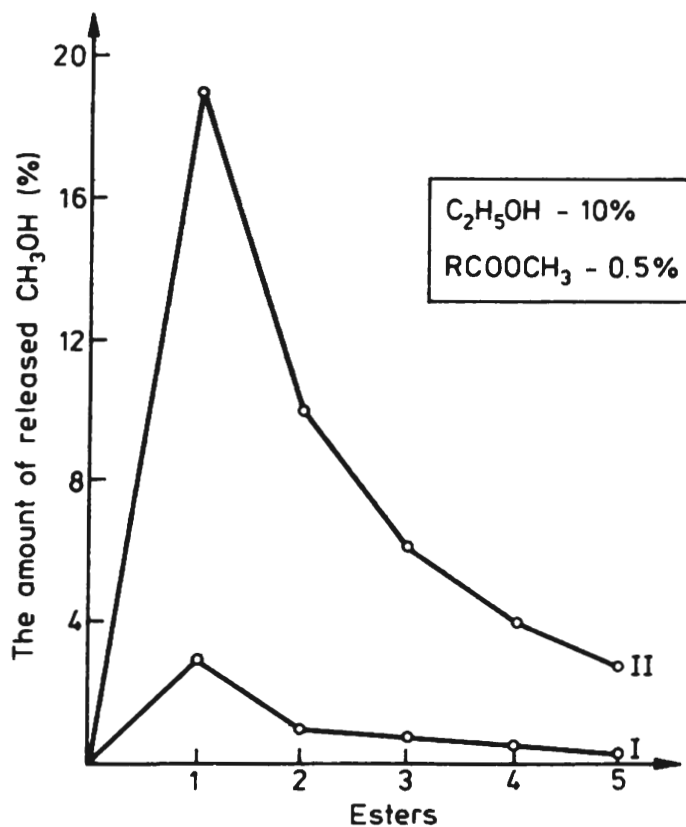


Fig. 5. Release of CH_3OH from esters during distillation — counter-current principle; I — pH 4.6-5.0; II — pH — 3.5; 1 — methyl formate, 2 — methyl acetate, 3 — methyl butyrate, 4 — methyl isoburate, 5 — methyl caproate

Distillation of a solution of pH 3.5 containing methyl formate led to the release of 317 mg/dm^3 , or 19% of total methyl bound in ester. Esters of higher fatty acids were hydrolysed to a lesser extent.

Although methyl esters may undergo hydrolysis with a simultaneous release of MeOH during heating and distillation of water-ethanol solutions, these processes have little effect on the final content of MeOH given the small amounts of these esters in wines and distillates. Certain amounts of MeOH may also be produced by transesterification, consisting in a transformation of methyl esters into ethyl esters. These transformations are favoured by elevated temperature and excess amounts of ethanol in the solution.

CONCLUSIONS

1. The MeOH contents in successive fractions obtained during distillation of water-ethanol solutions vary, depending on the initial ethanol concentration, the method of distillation, and on the qualitative composition of the solution. Fractional distillation of solutions with ethanol concentration in excess of 43% vol creates favourable conditions for the separation of MeOH in the first fraction.

2. Heating of alcohol solutions during their distillation promotes hydrolysis of methyl esters present in the solution and the release of MeOH from them. The amount of MeOH released in this way depends on the kind of methyl ester, the time and temperature of heating, and the pH of the solution.

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BADANIA ZMIAN ZAWARTOŚCI METANOLU PODCZAS FRAKCJONOWANEJ DESTYLACJI ROZTWORÓW WODNO-ETALONOWYCH*)

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Streszczenie

Przeprowadzono destylację frakcjonowaną młodego wina jabłkowego oraz modelowych roztworów wodno-etanolowych z dodatkiem metanolu (MeOH) i innych komponentów, głównie z grupy estrów. Podczas destylacji prób odbierano objętościowo kolejne frakcje, w których oznaczano zawartość MeOH i etanolu.

Stwierdzono, że zawartość MeOH w kolejno odbieranych frakcjach jest zróżnicowana i zależna od początkowego stężenia etanolu w próbce, sposobu destylacji oraz ilościowego i jakościowego składu roztworu. Z roztworów o złożonym składzie jakościowym oddzielanie MeOH jest trudniejsze; znaczna ilość tego składnika przechodzi również do frakcji środkowych i końcowych (rys. 1A i 2). Najkorzystniejsze warunki do oddzielania MeOH są w roztworach o mocy wyższej niż 43% obj. (rys. 3). Destylacja roztworu 70% w warunkach doświadczeń doprowadziła do wydzielenia w pierwszej frakcji ok. 24% całkowitej ilości MeOH, obecnego w próbce wyjściowej (rys. 3).

Wygrzewanie roztworów etanolowych podczas ich destylacji powoduje również hydrolizę estrów metylowych i uwalnianie MeOH. Ilość uwalnianego w ten sposób MeOH jest uzależniona od rodzaju estru, czasu i temperatury wygrzewania oraz pH roztworu. Destylacja 10% roztworu o pH 3,5 z 0,5% dodatkiem octanu metylu spowodowała uwolnienie 200 mg/dm³ MeOH, a ilość ta stanowiła 10% całkowitej zawartości MeOH związanego w tym estrze (rys. 5).

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