

POSSIBILITIES FOR METHANOL CONTENT REDUCTION IN PLUM BRANDY

N. Nikićević¹ and V. Tešević²

Abstract: Several methods for reducing the methanol content of plum brandies were tried: possibilities for its reduced forming during fruit must alcohol fermentation, and employing effective and rational methods in order to decrease the already existing amount of methanol by applying demethanolization column. Apart from numerous valued components, plum brandy also contains some undesirable ingredients, among which methanol has a special place. It appears during hydrolysis of pectin substances under the influence of the specific pectolytic enzymes, pectin-methyl-esterase in particular. A certain amount still has to be present in natural brandies in order to maintain the authentic fruit origin.

Reduction of the existing methanol amounts by applying demethanolization column was most effective and came to 43-77% in comparison to the starting amount.

Key words: plum brandy, methanol, pectin matter, pH, alcohol fermentation, demethanolization.

I n t r o d u c t i o n

Plum brandy, as a distillate of *Prunus* crop plum fermented must, apart from the main elements – ethanol and water, contains numerous ingredients the amount of which varies within an average of 0.5–1.0 % depending on the raw material content, the way in which alcohol fermentation is carried out and the manner in which distillation is conducted. Apart from numerous valued components it contains, plum brandy can also contain some undesirable ingredients which may be harmful. This refers, first of all, to HCN, ethyl-carbamate and methanol.

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Methanol is a regular ingredient in all natural fruit brandies and its content is directly correlated to pectins, it derives from after hydrolysis is carried out. However, certain amounts of methanol must be present in fermented plum must distillates, in respect of the fact that its presence in them is considered to be a proof and indicator of authentic, natural, fruit origin.

Decreasing of the methanol content in fruit brandies and other strong alcohol beverages is the problem that has been studied in different parts of the world, and the most important works are as follows:

1. Using fraction distillation to reduce methanol content in fruit brandies and mush (Nikova, 1954)
2. Separation of methyl alcohol from fruit brandy (Rankov, G., Popov, A., Lovchev, A. 1955)
3. Using complex installation for distillation of fruit husks and distillates to reduce methanol content (Boičkov, 1955)
4. Using demethanoliation column to eliminate methanol from grapa and fruit distillates (Meloni, 1958)
5. Continuous heating of must prior to fermentation to decrease methanol in fruit brandy (Daskalov, Lj. (1964)
6. Heat treatment of fresh unfermented fruit husks (Radovanović, and Paunović, 1965) (Paunović, 1967)
7. Reduction of methanol content by separation of fruit must parts during alcohol fermentation (Paunović, 1967)
8. Using demethanoliation column to eliminate methanol from Italian grapa (Tarantola, 1971)
9. Methanol content in fruit wine materials and alcohols and ways to reduce it. (Gitenshtein, B. M., Maltabar, V.M. 1971)
10. Heat treatment of fresh fruit husks (Tanner, 1972) (Tanner and Brunner, 1982)
11. Reduction of the methanol content by inactivating pectinesterasis ferment in Moldavia plum by airing (Gitestain, 1974)
12. Application of clear apple juice vacuum distillation to reduce methanol content (Kaldare et al. 1975)
13. Elimination of methanol from grape brandies by rectification column in continuous flow) *Revue Suisse de Viticulture, Arboriculture et Horticulture*, 7(5), 182,1975
14. Removing of methanol from alcohol-water mixtures by CuO oxidation treatment (Nogaideli et al.1976)
15. Heat treatment of mirabel husks (Jouret et al. 1979)
16. Reduction of methanol content in fruit brandies by anionic recuperation and polyphenol substances (Pieper et.al. 1979)

17. Elimination of higher alcohols and methanol from alcohols by natural crimean ceolites (Taran, 1983)
18. Dynamics of metanol formation in manufacture of plum brandy (Bikfalvi, I., Flanek, A. 1987)
19. Complex studies of various possibilities for methanol content reduction in fruit brandies (Bindler and Laugel, 1989)
20. Elimination of methanol content by using demethanoliation column within the operation of complex installation for continuous production of grape brandies (Cogat, Gueraïn and Guigon, 1992)
21. Possibilities for the reduction of methanol levels in pear brandies (Bindler, F., Laugel, P. 1993)
22. Possibilities of methanol reduction in Barlett pear distillates using traditional production methods (Ludwig, A. 1995)
23. Method for reducing the methanol content of brandy (Mikitenko, P., Pont, J., Barbat Du Closel, R. 2000)

Material and Methods

The research in this paper referred to the possibilities for the reduction of methanol content in plum brandies from the varieties: Požegača, Stanley and Džanarika. The research was aimed in two directions:

1. Finding the most convenient method which will be used to reduce methanol amount during the proces of plum must fermentation, and
2. Researching and finding the most rational and the most effective method for reducing, during demetanolization rectification, methanol amounts already present in plum brandy.

The experiments related to lesser forming of methanol during alcohol fermentation were carried out with three varieties of Prunus crop plums: Požegača, Stanley, and Džanarika delivered from "Srbijanka" Co.-Valjevo and "Podgorka" Co.-Osečina, while for the experiments on the reduction of methanol content by demethanolization the plum brandy from "Podgorka" Co.-Osečina, Ostružanj-Podgorina Region, was used.

Methanol was determined by gas chromatography method (Tanner et al., 1982) using a Varian 3400 gas chromatograph equipped with a flame ionization detector (FID) and a split/splitless injector. The separation was achieved using a J&W Scientific DB-5 fused silica capillary column, 30 m x 0.25 mm i.d., 0.25 µm film thickness. GC oven temperature was programmed from 30°C (6 min) to 220°C at a rate of 4.3°C/min. Hydrogen was used as a carrier gas; flow rate: 1 ml/min at 210°C. Injector temperature: 250°C; detector temperature: 280°C. Injection mode: split.

Results and Discussion

Possibilities for methanol content reduction forming during fruit must alcohol fermentation

In the first part of this paper, the research was conducted by monitoring with attention the following influential factors:

- a) influence of fruit must pH
- b) influence of alcohol fermentation causing agent
- c) influence of “waiting time” of fermented must before distillation

a) Influence of fruit must pH

Among many compounds, constituent elements of plum are organic acids which are of great importance for alcohol fermentation chemical processes. Plum fruit doesn't contain higher amounts of acids and its pH is over 3.5, in most cases. In order to obtain as pure fermentation as possible, as well as better storing of fermented must until distillation starts, in some countries (Switzerland, Germany) strong mineral or organic acids are added to fruit must. For that reason, a number of experiments were carried out to inhibit the growth of undesirable microflora, as well as the influence of pectolitic enzymes which cause forming of methanol in plum brandy. Having in mind the fact that the optimal conditions for these enzymes to produce effect are the temperature of 45 °C and pH 4.5, a number of tests were carried out in which alcohol fermentation process was observed at lowered pH value and the temperature of 20 °C.

Fermentation in all the experiment variants took place in laboratory conditions at room temperature. After completed fermentation, in all variants distillation of fermented must was carried out on a simple apparatus, Sharante type, up to 20% vol, in distillation mass, without fraction separation. Redistillation of raw weak brandy up to 50% vol, was carried out on the same apparatus, also without fraction separation.

The obtained results of redistilled samples have shown obvious influence of plum must acidification during fermentation on the methanol content. The lowest amount of it was found in fermentation variants with pH 2.5. The reduction of methanol content, compared to control, is shown in figure 1.

This varying of the results occurs due to the fact that in certain variants the different conditions for pectolitic enzymes activity existed. Less favorable conditions had those variants with must fermentation at pH value of 2.5, when the highest reduction of methanol content was achieved, while the most favorable conditions for their activity had variants with must fermentation at pH value of 4.0-4.5, in which cases the lowest methanol reduction occurred.

After completed fermentation, the samples with original pH control, as well as the samples with reduced acidity, had dark brown surface in fermentation vessels, while lower part had natural red color of the starting raw material. In the experiment variants with increased acidity (pH 2.5) both surface and the inside of must had the same, fresh rouge color. Increased acidity contributed neither to decreasing of pectolytic nor to oxidizing enzymes activity. This helps to achieve preservation of plum primary aromatic matter from oxidation changes. By must acidification, higher viscosity was achieved due to the reduced degree of pectin matter disintegration. After completed fermentation, the variants with acidified must had higher consistency than control.

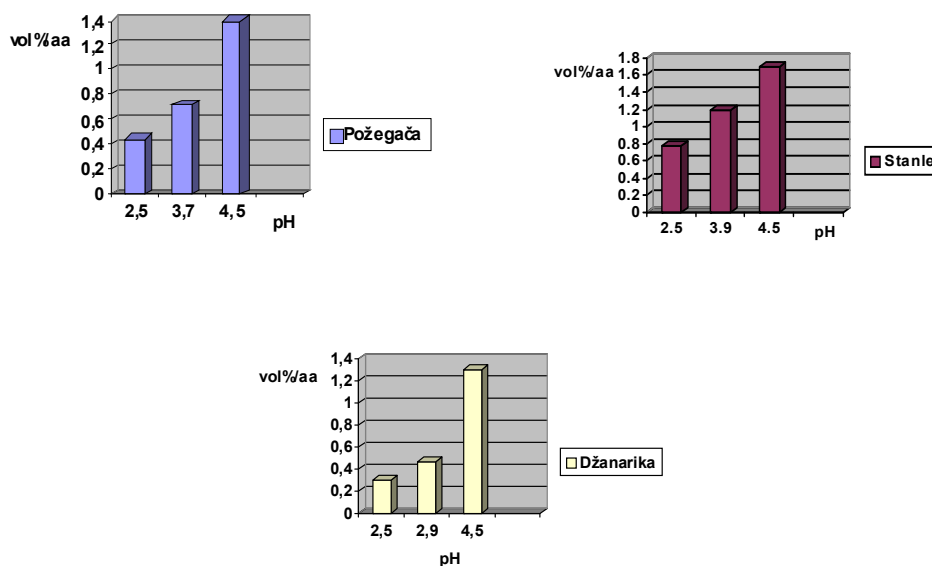
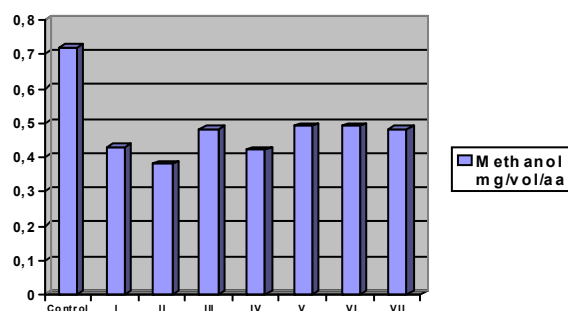


Fig.1. - Influence of fruit must pH to methanol content plum brandies

b) Influence of alcohol fermentation causing agent

Having in mind that alcohol fermentation causing agents influence the creation of plum brandy's chemical composition, as well as forming of secondary components during fermentation, it was interesting to check what direction that influence would take concerning methanol. For that reason, the experiment was

carried out, where 6 types of yeast (I-VII) were added, in identical quantities, to fermenting substrate with previously increased acidity by adding 10% H₂SO₄. All parameters during fermentation were uniform so as to determine the influence of yeast types only. The results of the experiment are shown in figure 2.



- I- Baking yeast
- II- DI-GO dry active yeast "Podravka" Koprivnica
- III- Regina dry active yeast "Kolinska" Ljubljana
- IV- Dry active yeast made in Japan
- V- Dry active yeast DP "Toma Kostić" Leskovac
- VI- Dry active yeast "Crnagoracoop" Podgorica
- VII- Dry active yeast PKB Belgrade

Fig. 2. - Influence of alcohol fermentation causing agent to methanol content in plum brandies

The results have shown that in all experiment variants the methanol amount was lower compared to control sample. There are several reasons for such different methanol content in distillates obtained by fermentation of must with autochthonous microflora and baking yeast, as well as its selected types:

1. One of the possible reasons is that within autochthonous microflora, bacterial activity was also prominent, some kinds of which, living in plums, could influence increased pectin substance hydrolysis, which means increased forming of methanol.

2. We are of the opinion that in variants with must fermentation under the influence of baking yeast, i.e. its selected types, lower methanol content was the direct result of reciprocal enzymes rivalry, during which some of them could have influenced pectolytic enzymes reduced activity. On the other hand, in variants with baking, i.e. selected yeasts, alcohol fermentation was completed in a shorter period of time than in variant with microflora. For that reason, pectin substance hydrolysis lasted a considerably shorter time, which caused incomplete deesterification of pectin macromolecule and reduced methanol formation in distillates.

3. According to Kotomini and Pisarniceva, certain types of saccaromyces yeasts are capable of forming polygalacturonasa-pectin-esterasa fermentation complex. All this leads to the conclusion that by selecting the type of yeast which does not form pectinesterasis, contribution can be made to the reduction of methanol occurrence.

c) Influence of fermented must storage time length prior to distillation

It has been proved in practice that the best time to carry out distillation of fermented plum must is as soon as fermentation is completed. However, for certain reasons it happens that fermented must is distilled several months later. In such a case, a range of chemical and biochemical transformations and changes might occur, which can have negative influence on the quality of the final distillate. Under the influence of air oxygen, microbiological rotting occurs on must surface in open fermentation vessels. The aim of the research in this part of the study was to find out how the length of waiting and storage of fermented must influence methanol and other components content in plum brandy, all in connection with fermenting must pH influence. For that purpose, the experiments of must fermentation were set with three plum varieties: Požegača, Stanley and Džanarika at original pH values, fermented must being distilled immediately after completed fermentation (8 days), after 30 days and after 60 days, following must surface conservation with Na-benzoate. The results of methanol content plum brandies achieved were as follows (figure 3).

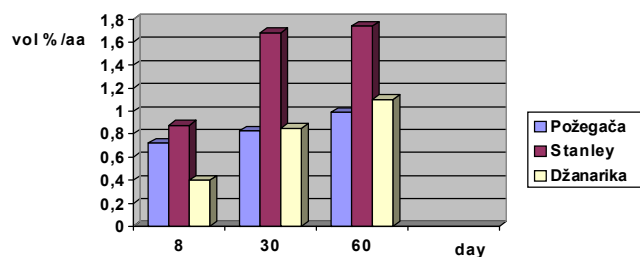
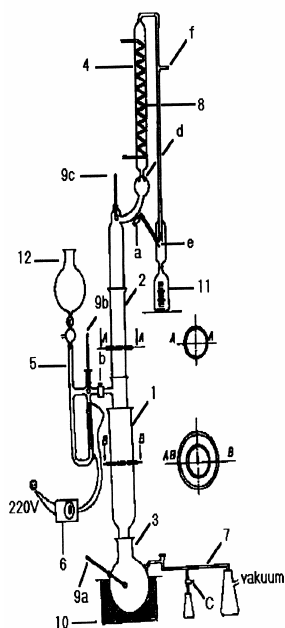


Fig. 3. - Influence of fermented must "waiting time" prior to distillation on methanol content in plum brandies

It can be concluded that during storage of fermented must before distillation in all experiment variants changes occur but of different intensity. It is evident that methanol content increases.

**Decreasing of methanol content during rectification by
using laboratory demethanolization column**

Laboratory demethanolization column (figure 4) is gauged in such a manner to enable singling out of methanol from plum brandy in parts (discontinuous work) and at continuous flow of starting substance (continuous work). Concentration of methanol and ethanol vapours occurs in higher parts of the column. After these vapours have been circling for a certain period of time, commences separation of the first lot fraction in the amount of 2-3% from the starting amount allotted for demethanolization. A certain reflux ratio is being adjusted on that occasion (most frequently 1:5 or 1:10). Separation of the first lot results in a considerable reduction of methanol content, but of other undesirable ingredients as well (esters and aldehydes) in final distillate. Plum brandy from the Požegača variety was used as the starting material for demethanolization process. Distillation of fermented husks, without separation of the first lot fractions and the last one, was carried out on a simple distillation apparatus, of Sharhant type, to the complete alcohol exhaustion. Redistillation of raw mild brandy was carried out on the same apparatus to 53 %vol. in the mass, without the last lot fraction separation, but with separation of the first lot amount 2%.



- 1,2. Rectification column
- 3. Glass vessel
- 4. Rectification head condenser
- 5. Preheater vessel
- 6. Variable Transformer
- 7. Vessel out
- 8. Rectification head
- 9a. Vessel thermometer
- 9b. Preheater thermometer
- 9c. Rectification head thermometer
- 10. Heater
- a,b,c. Special taps
- d,e. Dropper

After strengthening the sample with ethanol to 65%, adjusting methanol to the amount of 1% vol/aa, demethanolization process commenced in the following experiment variants:

Variant I: Discontinuous rectification

Rectification of 500 ml plum brandy was carried out with the first lot fraction separation in the amount of 20 ml (4%) after achieving the temperature optimum of 71.5 °C (arithmetical mean value of the boiling point temperatures sum, for ethanol 78.3 °C and methanol 64.8 °C). This temperature can be seen and monitored on the thermometer (9c) located on the top of the column. This variant was separately repeated three times for each strength.

Variant II: Continuous rectification

In this variant, working conditions at continuous rectification, most frequently seen in industrial plants, were simulated. 500 ml of plum brandy was poured into glass vessel and slowly heated. From the glass vessel preheater the same brandy, heated up to 70 °C, flowed into the central part of the column. After achieving the corresponding temperature (71.5 °C) in the upper part of the column, taps b and c were opened, so that the amount of the sample flowing into the column was equal to the amount of brandy taken out from the glass vessel. Thus, continuous flow in the column was simulated. At the same time, the rectification head tap was opened, which enabled fraction separation of the first lot in the amount of 3x20 ml (4%), i.e. 60 ml. During the course of this variant, the total of 1500 ml of plum brandy passed through the column, and the same amount was drawn out from the glass vessel. Concentration and circulation of ethanol and methanol vapours, as well as distillate fractions sampling, took about 7 hours altogether. With heating regime as well as with adjusting of tap opening, the achieved dripping ratio in places d and e was from 5:1 to 8:1.

Variant III: Discontinuous fraction rectification

In this variant, everything was carried out in the same manner as in the first one, but this time five fractions of 20 ml each (4%) were separated each time from the top part of the column. The same amount of distillate was taken from the glass vessel. Separation of fractions commenced only after achieving the temperature optimum. The methanol content reduction is given in table 1.

Table 1.

Variant	Methanol content reduction (%)
I	45
II	65
III	75

Conclusion

The results show that decrease in methanol forming was most prominent during must fermentation at pH 2.5.

Methanol content increase in all three plum varieties, in all variants, correlates with the length of storage, i.e., the longer the waiting period prior to distillation, the higher methanol content. That was one more evidence that pectin substance hydrolysis continues, although with reduced intensity, during storage period of fermented must prior to distillation.

By selecting the type of yeast which does not form pectinesterasis, contribution can be made to the reduction of methanol occurrence.

The experiment results from demethanolization column show that methanol amount decrease in plum brandy ranged, depending on experiment variant, from 45%-75% of the starting amount in control sample.

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MOGUĆNOSTI SMANJIVANJA SADRŽAJA METANOLA U RAKIJI ŠLJIVOVICI

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R e z i m e

Predmet ovog istraživanja bio je pronalaženje različitih mogućnosti za smanjivanje količine metanola u rakiji šljivovici. Pored velikog broja drugih komponenti rakija šljivovica sadrži i neke neželjene sastojke, među kojima metanol zauzima specijalno mesto. Metanol nastaje tokom hidrolize jedinjenja pektinskog tipa, a pod uticajem pektolitickog enzima, pektin-metil-esteraze. Odredjeno prisustvo metanola predstavlja dokaz autentičnog voćnog porekla rakije.

Istraživanja u ovom radu su se odnosila na mogućnosti snižavanja sadržaja metanola u rakijama šljivovicama od sorti požegača, stenli i džanarika a tekla su u dva pravca:

1. Na iznalaženju najpogodnijeg postupka za manje nastajanje metanola tokom alkoholne fermentacije kljuka šljive (uticaj pH kljuka, uticaj vremena čekanja pre destilacije i uticaj različitih izazivača vrenja).

2. Ispitivanje i pronalaženje najracionalnijeg načina za smanjivanje već postojećih količina metanola u šljivovici tokom izvodjenja demetanolizacione rektifikacije.

Eksperimenti vezani za smanjenje formiranja metanola tokom alkoholne fermentacije su radjeni sa tri sorte šljiva: požegača, stenli i džanarika, dobijenih od preduzeća "Srbijanka" Co.-Valjevo i "Podgorka" Co.-Osečina, dok su eksperimenti redukcije metanola pomoću demetanolizacione kolone izvodjeni sa rakijom šljivovicom iz "Podgorka" Co.-Osečina, region Ostružanj-Podgorina. Količina metanola je određivana metodom gasne hromatografije uz primenu kapilarne kolone.

Dobijeni rezultati pokazuju da je najveće smanjenje u formiranju metanola tokom fermentacije kljuka pri pH 2.5.

Povećanje sadržaja metanola u sve tri sorte i svim varijantama je u direktnoj korelaciji sa vremenom koje protekne pre destilacije kljuka. Ovo je dokaz više da se hidroliza pektinskih supstanci nastavlja sa smanjenim intenzitetom tokom vremena čekanja pre destilacije.

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Odabrani tipovi kvasaca koji ne proizvode pektinesterze mogu biti odabrani za smanjenje količine metanola.

Eksperimentalni rezultati sa kolonom za demetanolizaciju pokazuju da je smanjenje zavisno od eksperimentalne varijante moguće od 45%-75% u odnosu na količinu u kontrolnom uzorku.

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