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THE EFFECT OF DEPECTINIZATION IN APPLE WINE PRODUCTION ON THE WINES QUALITY WITH SPECIAL ATTENTION PAID TO METHANOL CONTENT

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Key words: depectinization, methanol, colloidal stability, pectinolytic enzymes.

It is demonstrated that to obtain a colloidally stable apple wine it is necessary to perform depectinization at least once, best in the pulp. A second or third depectinization is not advisable since the result is an increased methanol content on the finished product, and this is not necessary to ensure colloidal stability of wine. It is also shown that a full fermentation of sugar in the must gives wines of better quality than the application of partical additional fortification does.

INTRODUCTION

In countries with moderate climate the basic raw material in fruit wine production are apples which, however, contain fairly large amounts of pectins (ca 1%); this make it difficul to obtain clear and colloidally stable wine from this fruit. Hence the need for the so called depectinization process with the use of pectinolytic preparations. One must bear in mind, however, that these preparations contain numerous enzymes some of which are useful (polygalactouronase — PG, pectinotranseliminase — PTE) while others are not (pectimethylesterase — PME, oxidases), the former bringing about the desired decomposition of pectins, the latter having a potentially adverse affect on the final product [10].

In industrial practice depectinization is performed either in the fruit pulp, in the must or in young wines, and sometimes this process is repeated two or even three times in order to arrive at the desired clarity and colloidal stability of the wines.

Depectinization may on the one hand ensure colloidal stability of the wine but on the other it leads to a darkening of pulps and juices and may also cause turbidity and sedimantation of pectic acid or of its salts (pectates) as well as the formation of furfurals, especially if the process occurs in elevated temperatures [7].

The studies of Masior et al. [9] revealed that depectinization of apple pulp results in greater amounts of extracts from fruit and in reduced viscosity of musts but that the process also has an adverse effect on the wines obtained from such musts. The authors point out that depectinization increases the content of starch in apple musts and this makes it neccessary to remove the substance from the must or the wine prior to pasteurization. One must also bear in mind that the enzyme pectinmethylesterase, present in pectinolytic preparations, causes the splitting off of methanol from pectins.

Methanol content in wines varies depending on the kind of wine and the method of its production. The relevant studies were performed by, among others, Kiszkowskij and Skurichin [6] who found 20-100 mg methanol in 1 dm^3 of white grape wines and a much greater amount of 80-350 mg dm^3 in red wines. A higher methanol content in red wines as compared to that in white wines was also found by Lee [8] who additionally demonstrated that greater amounts of methanol (400-500 mg/dm^3) occurred in wines obtained by fermenting fruit pulp not subjected to previous heat treatment.

In Poland methanol in fruit wines was studied by Pacholczyk [11] who claims that the greatest bearing on methanol formation in wines is due to the kind of fruit and the way of fermentation. Among the wines studied by this author the highest methanol content was found in strawberry wine (0.17-0.23 cm^3/dm^3) and the lowest in currant and apple wines (0.08-0.10 cm^3/dm^3). The author also claims that a two-day fermentation in fruit pulp led to an enormous increase in methanol content in wines — in strawberry wines this increase was by ca. 70% and in apple wines by 140% — in relation to methanol content in wines obtained from fruit which were not subjected to this process.

It must be stressed that the quality standards valid today do not state the admissible methanol content in wines and only for meads they put the figure at 0.03% by volume [12].

OBJECTIVES AND SCOPE OF STUDY

The study was aimed at determining the effect of enzymatic processing applied in various stages of the technological process of fruit wine production (the wines being obtained by a full fermentation of the musts or by partial fortification) on selected features of the wine, especially on colloidal stability and methanol content. It was also intended to determine a way of depectinization of fruit pulp or must, possibly even of the wine, optimum from the point of view of rational utilization of pectinolytic preparations.

MATERIAL AND METHODS

Industrial apples of several varieties and various degrees of ripeness were used in the production of the wine.

Depectinization was performed with two different pectinolytic preparations: Pektopol P (Fruit-and-Vegetable Processing Enterprise "Pektowin" in Jasło, Poland) and Panzym Super (Bechringer Sohn, Federal Republic of Germany); their characteristic [2-4, 10, 15] is given in Table 1.

Table 1. Characteristic of pectinolytic preparations used in the study

	Pektopol P	Panzym Super
Dry mass (%)	54.3	97.4
Protein (N.6.25) (%)	10.5	23.1
Total pectinolytic activity (°PM)	72 460	728 200
Polygalacturonase activity ($°J_2PG$)	232.0	489.8
Pectinmethylesterase activity (°PME)	27.3	38.5
Ratio $°J_2PG/°PME$	8.5	12.7
Pectinotranseliminase activity (°PTE)	none	1.5

TECHNOLOGY

The apples were washed and broken up in a percussive thresher. The obtained pulp was divided into three parts, one of which was directly pressed on a POK-200 layer press, the other two being heated to a temperature optimal for the action of the pectinolytic preparation. The parameters of apple pulp depectinization and the must yields are presented in Table 2.

Table 2

Pectinolytic preparation	Dose g/kg	Temperature °C	Time h	Must yield %
Pektopol P	2.0	40	2	73.9
Panzym Super	0.018	55	2	70.1
No depectinization	—	—	—	66.0

The basic chemical composition (including methanol content) of the apple must obtained by pressing was determined; the results are shown in Table 3.

Table 3

Pectinolytic preparation	Extract	Total sugars as invertase g/dm³	Directly reducing sugars as invertase g/dm³	Titratable acidity as malic acid g/dm³	Methanol mg/dm³
Pectopol P	10.5	80.8	73.5	8.2	110.4
Panzym Super	10.7	82.6	74.9	7.3	76.8
No depectinization	11.5	87.8	79.7	8.4	7.2

The apple must were prepared for fermentation according to the following assumptions:

— alcohol content in wines — 14% vol.; in the case of wines made by the fortification method 3.5% vol. alcohol was obtained in the process of fermentation and the remainder was added in the form of rectified spirit;

— alcohol yield from sugar — 90%;

— sugar in the must constitutes 75% of the refractometrically determined extract;

— sulfuration of the musts — 50 mg SO_2/dm^3;

— diammonium phosphate addition to the musts — 0.3 g/dm^3;

— seed yeast addition — 5% of must volume;

— pectinolytic preparation addition to a part of the musts in the same amount as in the case of pulp depectinization;

— volume of the musts — 2 dm^3 each.

The prepared musts were inoculated with yeast of the Tokay brand and fermented at 20-22°C. In all, 30 musts were prepared according to different technological variants resulting in diverse combinations with regard to total and partial fermentation of the sugar and to enzymatic processing with pectinolytic preparations.

The obtained young apple wines were racked and bottled, with some of the wine samples subjected to additional enzymatic processing with pectinolytic preparations in doses analogous to those used in processing fruit pulp and musts.

The wines were pasteurized in tightly closed bottles at 75°C for 3 min and then cooled to 60°C, i.e. the temperature of heat processing (portweinization) which lasted for six weeks. The wines were then passed through a Seitz pressure filter containing diatomite.

The clear wines were analysed chemically — the main macrocomponents were assayed as well as some of the components appearing in wines in minute amounts.

ANALYTICAL METHODS

The characteristic of the obtained apple wines included determinations of the contents of the following components: alcohol, total extract, total reducing sugars and saccharose, sugarless extract, total and volatile acidity, ash, and sulphur dioxide (free, bounded and total) [2, 13]. Moreover the contents of methanol, glycerol, aldehydes, acetals and esters were assayed in the wines and their colloidal stability was tested.

RESULTS AND DISCUSSION

Table 1 gives the characteristics of the pectinolytic preparations used in the studies — the Polish liquid concentrate Pektopol P and the dry powdered preparation Panzym Super made in West Germany. As we can see, the preparations differ considerably as to dry mass and protein content as well as to the activities of the separate enzymes. Generally speaking, the Panzym Super preparation was qualitatively superior to Pektopol P which is indicated by the over ten times higher general pectinolytic activity of the former, the presence of pectinotranseliminase, absent in Pektopol P and useful in this case, and by the better ratio of the useful poligalacturonase activity to the undesirable pectinmethylesterase one. Due to the above differences the applied doses of Pektopol P were over 100 times higher than doses of Panzym Super.

The data concerning the pressing of apple pulp, both the one subjected to depectinization and the one that was not, are given in Table 2. Table 3, on the other hand, contains results of the analysis of the basic chemical composition of apple musts later used in wine production.

The data in Table 2 indicate that must yields from apple pulp depended on the applied enzymatic processing prior to its pressing and on the dose and kind of pectinolytic preparation.

The heat-enzymatic treatment of apple pulp led to an increase in juice yield from 66.0% to 70.1% in the case of Panzym Super application and to 73.9% when the Pektopol P preparation was used. It must be pointed out, however, that although depectinization brought about higher must yields in comparison to the yields in controls which were not subjected to this process, the musts nevertheless contained considerably less extract, sugars and acids which proves that depectinization does not serve to increase the amounts of extractive components obtained from apples.

The highest contents of extract, reducing and total sugars and titratable acidity were demonstrated by apple musts obtained from pulp that was not treated enzymatically, whereas the lowest levels of the above components were in the must obtained from pulp treated with Pektopol

T a b l e 4. Chemical composition of apple wines produced according to different technologies

Sample No.	Degree of must fermentation	Pectinolytic preparation	Depectinization stage: Pulp	Depectinization stage: Must	Depectinization stage: Wine	Total extract (g/dm^3)	Alcohol (% vol)	Directly reducing sugars as inverted (g/dm^3)	Total sugars as inverted (g/dm^3)	Sugarless extract (g/dm^3)	Total acidity as malic acid (g/dm^3)	Volatile acidity as acetic acid (g/dm^3)	Ash (g/dm^3)	Colloidal stability test	Methanol (mg/dm^3)	Glycerol (g/dm^3)	Aldehydes as acetic aldehyde (mg/dm^3)	Acetals as acetic aldehyde acetal (mg/dm^3)	Esters as ethyl acetate (mg/dm^3)
1			–	–	–	25.8	14.7	1.7	1.7	24.1	5.6	0.4	2.24	+	124.8	4.1	44.8	37.2	300.5
2	full	Pektopol P	–	–	+	26.6	14.3	3.0	3.0	23.6	5.1	0.4	2.28	–	224.0	3.9	49.4	40.9	309.4
3			–	+	+	27.1	11.1	3.8	3.8	23.3	5.9	0.5	2.50	–	259.2	3.7	48.0	43.4	333.3
4			–	+	–	27.6	14.0	4.0	4.0	23.6	5.9	0.4	2.38	–	235.2	4.1	47.1	42.1	317.4
5			+	–	–	26.6	14.4	2.9	2.9	23.7	6.3	0.6	2.45	–	237.6	4.2	51.7	45.8	337.8
6			+	+	–	26.1	14.5	2.5	2.5	23.6	6.5	0.6	2.54	–	247.2	4.0	55.5	48.3	296.1
7			+	+	+	26.1	14.2	2.7	2.7	23.4	6.2	0.4	2.71	–	259.2	3.9	60.1	54.5	335.1
8			+	–	+	28.7	13.7	5.2	5.2	23.5	6.4	0.4	2.48	–	271.2	3.8	55.9	50.8	331.6
9		Panzym Super	–	–	+	25.3	14.6	1.8	1.8	23.5	6.0	0.3	2.33	–	156.0	3.8	45.2	38.4	338.6
10			–	+	+	25.0	14.7	1.6	1.6	23.4	5.6	0.3	2.30	–	180.0	4.0	46.7	39.6	302.3
11			–	+	–	25.6	14.5	2.1	2.1	23.5	5.5	0.4	2.32	–	170.4	3.9	46.2	38.4	312.0
12			+	–	–	24.8	14.9	1.2	1.2	23.6	6.0	0.4	2.41	–	158.4	4.1	49.9	44.6	279.2
13			+	+	–	25.3	14.6	2.3	2.3	23.0	5.9	0.5	2.43	–	177.6	3.6	55.0	47.1	347.5
14			+	+	+	31.5	12.6	8.2	8.2	23.3	5.1	0.4	2.29	–	182.4	3.8	58.7	54.5	289.9
15			+	–	+	24.5	15.1	1.1	1.1	23.4	4.9	0.3	2.44	+	180.0	4.3	54.0	48.3	337.8

16	ferment up to 3.5% vol ethyl alcohol	Pektopol P	−	−	−	23.0	15.7	1.2	1.2	21.8	5.9	0.2	2.32	−	139.2	2.3	37.4	29.7	250.9
17			−	−	+	24.0	15.5	2.6	2.6	21.4	5.8	0.1	2.40	−	225.6	2.2	41.1	32.2	214.5
18			−	+	+	25.6	15.4	4.3	4.3	21.3	6.1	0.1	2.46	−	256.8	2.2	41.1	34.7	258.9
19			−	+	−	23.7	15.6	2.2	2.2	21.5	5.9	0.2	2.38	−	242.4	2.3	40.7	33.4	242.0
20			+	−	−	25.3	14.9	3.8	3.8	21.5	6.3	0.1	2.44	−	237.6	2.2	43.4	35.9	259.7
21			+	+	−	31.5	13.6	10.1	10.2	21.3	6.5	0.1	2.65	−	259.6	2.1	48.0	39.6	242.9
22			+	+	+	27.4	14.5	6.4	6.4	21.0	6.4	0.2	2.57	−	266.4	2.0	49.9	42.1	226.1
23			+	−	+	26.3	14.8	5.2	5.2	21.1	5.5	0.1	2.49	−	266.4	2.0	48.5	38.4	236.7
24	Panzym Super		−	−	+	23.0	15.7	1.7	1.7	21.3	5.2	0.1	2.27	−	156.0	2.2	39.3	31.0	257.9
25			−	+	+	23.0	15.6	1.8	1.8	21.2	5.7	0.1	2.38	−	182.4	2.1	39.7	39.6	219.0
26			−	+	−	23.2	15.7	2.4	2.4	20.8	5.7	0.1	2.30	−	175.2	1.9	39.3	32.2	251.8
27			+	−	−	24.0	16.7	1.4	1.4	22.6	5.1	0.1	2.35	−	156.0	2.5	43.4	34.7	223.4
28			+	+	−	27.4	15.1	5.8	5.8	21.6	5.4	0.1	2.40	−	182.4	2.1	45.7	37.2	248.2
29			+	+	+	23.7	15.4	2.2	2.2	21.5	5.2	0.1	2.41	−	185.8	2.2	49.9	40.9	247.3
30			+	−	+	25.8	15.0	4.2	4.2	21.6	5.6	0.1	2.42	−	182.4	2.3	45.3	37.2	256.2

P. This may be a result of different doses of pectinolytic preparations together with which certain amounts of extract components were introduced, but at the same time the preparations could have to some extent diluted the various must components.

There are very clear differences in methanol content between musts obtained from depectinized pulp and those from non-depectinized ones. This is due to the different levels of activity of the pectinmethylesterase enzyme in the preparations and to the doses in which the preparations were applied.

The characteristic of the chemical composition of the obtained apple wines is given in Table 4. We see that the content of total extract, directly-reducing and total sugars and of sugarless extract, in the studied wines depends primarily on the degre of must fermentation. Wines obtained as a result of total fermentation of the musts had a slightly higher content of total extract (24.8-31.5 g/dm^3) than the fortified wines in which the extract content ranged from 23.0 to 31.5 g/dm^3.

The sugarless extract content in the various wines depended not only on the degree of fermentation of the musts but also on depectinization and fortification. In the case of fortified wines the sugarless extract content was 20.8-22.6 g/dm^3 and was ca. 0.5-2.0 g/dm^3 lower than this content in wines obtained by full fermentation of sweetened musts. This is directly related to the level of glycerol content in wines which strictly depends on the degree of must fermentation. The fortified wines contained 1.9-2.5 g of glycerol in 1 dm^3 while the ones obtained by completely fermenting sweetened musts had 3.6-4.2 g of glycerol per dm^3.

Generally, the highest content of sugarless extract was in wines which were made without depectinization at any stage of production. In the case of the remaining wines it was found that the content of sugarless extract depended on repetitions of depectinization in the production process and on the dose of pectinolytic preparation introduced into the wine, the dependence being inversely proportional.

The ethyl alcohol content in the obtained wines is somewhat differentiated and this results mainly from the applied fortification but also from the fact that alcohol is a substrate of some reactions taking place during the maturing of wines, such as estrification, acetal formation, etc.

The obtained wines differed rather considerably as to methanol content. The maceration of pulp was found to greatly increase methanol content, both in the must and in the wine obtained from it, because it is freed from pectins by the action of pectinmethyl esterase added with the pectinolytic preparation and of the raw material's indigenous enzymes, and also by the acid reaction of the medium, particularly during heat treatment. If the pulp was not treated enzymatically, the methanol content was affected only by the endogenous enzyme of the raw material and by the acid reaction of the fruit medium.

The results of methanol content assays in the studied wines justify the conclusion that the level of this component in both the musts and the wines depends primarily on the activity of pectinmethylesterase present in pectinolytic preparations. This would explain the higherd (by ca. 40% or even up to 70%) amount of methanol in wines treated with the pectinolytic preparation Pektopol P than in wines processed with the Panzym Super preparation. Although in both the preparations the activity of pectinmethylesterase was more or less the same, the smaller amount of methanol in wines treated with Panzym Super was determined by the ca. 100 times smaller dose of this preparation compared to the Pektopol P dose. The increased methanol content in wines made of depectinized pulp may be explained by the higher content of pectin substances in fruit pulp than in the musts.

Studies have demonstrated that apple wines produced without processing with pectinolytic preparations are not stable colloidally and that even a single treatment with such preparations of either the pulp, the must or the young wine is enough to ensure full colloidal stability of apple wines. This fact indicates also the low activity of the apples' endogenous complex of pectinolytic enzymes.

Comparing the results of colloidal stability tests and methanol content in apple wines we see that a single depectinization suffices to obtain a colloidally stable wine with a relatively low methanol content. At the same time it should be stressed that repeating the enzymatic processing of pulp, musts and wines several times is pointless and that it leads to an increase of methanol content while boosting production costs at the same time.

The depectinization of apple pulp is not free from inconvenience since the pressing of depectinized apple pulp requires the application of a special type of presses or additions of draining agents. Moreover, the depectinization process, lasting several or a dozen or so hours, necessitates the storage of large quantities of pulped material in specially adapted reservoirs which poses serious organizational problems. Because of this the depectinization of apple pulp introduced to industrial practive in the 1960s was abandoned and the necessary pectins decomposition is achieved by depectinization of musts after their pressing. It is worth stressing that the Bucher-Guyer presses which are finding increasingly widespread application give very good results in pressing apple pulps but only when the pulps were not previously subjected to enzymatic treatment. Also important is the fact that the pomace obtained from pressing apples is at present the only raw material in Poland for the production of pectin preparations. Hence, the process of depectinization, necessary in the production of colloidally stable apple wine should take place in the must or in the young wine.

The assay of aldehyde content in the separate wine samples revealed that the relatively greatest amount of aldehydes occurs in wines made of depectinized pulp and that this content depends on the degree of fermenting the musts. The above dependences may be explained by the higher content of amino nitrogen in musts obtained from depectinized pulp, the substance being a substrate for the reaction of oxidative deamination of aminoacids which results in the formation of aldehydes [5, 6]. Aldehydes may also appear as side products during fermentation of sulfurated musts, hence the foreshortened fermentation of fortified wines significantly reduces the possibility of aldehyde formation at this stage of production and explains the higher aldehyde content in wines obtained by a full fermentation of the musts.

The content of esters in the studied wines depended on the degree of musts fermentation which is indicated by the fact that in fully fermented wines their content was higher by ca. 30-60% than in wines partly fortified with rectified spirit.

CONCLUSIONS

1. In order to produce colloidally stable apple wine it is necessary to apply depectinization at least once and it appears that it is most advisable to treat with pectinolytic preparations the apple must or the young wine. Repeating depectinization two or more times is unjustified both technologically and economically since it has no bearing on the clarity of the final product and increases methanol content.

2. The amount of methanol appearing in apple wine obtained by a technology including depectinization depends primarily on the activity of pectinmethylesterase contained in the pectinolytic preparation and also on the dose of this preparation.

3. In view of all the quality markers of the produced apple wines, it must be said that the traditional method of their production consisting in full fermentation of sweetened musts gives a product of better quality than the wines obtained by foreshortened fermentation and additional fortification with rectified spirit.

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WPŁYW ZABIEGU DEPENTYNIZACJI, STOSOWANEGO W PRODUKCJI WIN JABŁKOWYCH NA ICH JAKOŚĆ, ZE SZCZEGÓLNYM UWZGLĘDNIENIEM ZAWARTOŚCI METANOLU

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S t r e s z c z e n i e

Przeprowadzono badania nad wpływem zabiegu depektynizacji stosowanego w różnych etapach procesu technologicznego produkcji win jabłkowych otrzymywanych metodą pełnej fermentacji nastawów oraz częściowej ich fermentacji i dodatkowej alkoholizacji na niektóre cechy wina, a zwłaszcza stabilność koloidalną oraz zawartość metanolu. Ponadto, starano się ustalić optymalny sposób depektynizacji miazgi jabłkowej, moszczu lub wina, z jednej strony z punktu widzenia racjonalnego wykorzystania preparatów pektynolitycznych i z drugiej zapewnienia stabilności koloidalnej gotowego produktu.

Do produkcji wina użyto jabłek przemysłowych różnych odmian o zróżnicowanym stopniu dojrzałości, a proces depektynizacji prowadzono przy użyciu dwu różnych preparatów pektynolitycznych: Pektopolu P produkcji Zakładów Przemysłu Owocowo-Warzywnego w Jaśle oraz Panzymu Super produkcji Bechringer Sohn (RFN). Obydwa preparaty scharakteryzowano pod względem ogólnej aktywności pektynolitycznej, aktywności podstawowych enzymów pektynolitycznych oraz zawartości suchej masy i białka.

Z miazgi jabłkowej pozyskiwano moszcze w trzech wariantach: po depektynizacji preparatami Pektopolem P, Panzymem Super oraz bez stosowania tego zabiegu. Otrzymane moszcze przeanalizowano pod względem podstawowego składu chemicznego, a otrzymane z nich wina poddano szczegółowej charakterystyce jakościowej obejmującej następujące oznaczenia: ekstraktu ogółem i bezcukrowego, cukrów bezpośrednio-redukujących, ogółem i sacharozy, alkoholu etylowego, kwasowości ogólnej i lotnej, dwutlenku siarki form: wolnej, związanej i całkowitej, metanolu, popiołu, glicerolu aldehydów, acetali oraz estrów. Ponadto wina poddano próbie na stabilność koloidalną.

Uzyskane wyniki badań oraz ich analiza pozwalają na sformułowanie kilku ważnych dla praktyki winiarskiej wniosków, z których najważniejsze jest stwierdzenie,

że w celu otrzymania stabilnego kolidalnie wina jabłkowego wystarczające jest zastosowanie jednokrotnego zabiegu depektonizacji, najlepiej w miazdze, gdyż w tym przypadku osiąga się większe wydobycie moszczu, a także zadowalającą stabilność koloidalną gotowego produktu. Stosowanie dwu- lub trzykrotnego zabiegu depektynizacji nie powinno być stosowane, gdyż nie polepsza stabilności kolidalnej gotowego produktu, a przyczynia się do nagromadzenia w nim większych ilości metanolu.