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ВЛИЯНИЕ НА НИВОТО НА ЗАПЪЛВАНЕ НА СЪДА ПРИ РЕДИСТИЛАЦИЯ ВЪРХУ ХИМИЧНИЯ СЪСТАВ НА ПЛОДОВИ ДЕСТИЛАТИ

Б. Попович[1], Н. Никичевич[2], В. Тешевич[3], О. Митрович[1], М. Кандич[1], Н. Милетич[1]

[1]*Институт по овощарство, 32000 Чачак, Сърбия*
[2]*Факултет по земеделие, 11080 Земун, Сърбия*
[3]*Факултет по химия, 11000 Белград, Сърбия*
e-mail: popovicb@tfc.kg.ac.rs

EFFECT OF CHARGING LEVEL IN ALAMBIC AT REDISTILLATION ON CHEMICAL COMPOSITION OF FRUIT DISTILLATES

B. Popović[1], N. Nikićević[2], V. Tešević[3], O. Mitrović[1], M. Kandić[1], N. Miletić[1]

[1]*Fruit Research Institute, 32000 Čačak, Serbia*
[2]*Faculty of Agriculture, 11080 Zemun, Serbia*
[3]*Faculty of Chemistry, 11000 Belgrade, Serbia*

РЕЗЮМЕ

Статията изследва влиянието на нивото на запълване на съда при редистилация на сурови дестилати от сливи и ябълки върху химичния състав на получените междинни фракции на дестилатите. Нивото на запълване е 40, 50, 60, 70, 80, 90 и 100% от използваемия обем на казана. Редистилацията е направена при еднакъв режим използвайки подобна скорост на дестилация.

Установени са разликите в получените междинни фракции, зависещи от нивото на запълване при редистилация за дестилатни компоненти (естери, киселини, алдехиди и HCN) променящи се химически при дестилация. Нивото на запълване на съда не влияе значително върху разликите в съдържанието на по-висши алкохоли,

SUMMARY

The paper examines the influence of charging level of alambic at redistillation of raw distillates of plum and apple on chemical composition of obtained hearts of the distillates. The charging level was 40, 50, 60, 70, 80, 90 and 100% of usable boiler volume. Redistillation was done at identical regime using similar distillation rate.

Differences in the obtained mid-fractions (hearts), depending on the alambic charging level at redistillation was established for the distillate components (esters, acids, aldehydes and HCN) which change chemically at distillation.

Charging level of alambic did not significantly affect the differences in content of higher alcohols, furfural, methanol and benzaldehyde in obtained

фурфурал, метанол и бензалдехид при получените междинни фракции.

Ключови думи: дестилация, казан, сливова ракия, ябълкова ракия, химичен състав

mid-fractions.

Key words: distillation, alambic, plum brandy, apple brandy, chemical composition

INTRODUCTION

Traditional production of fruit spirits in Serbia is based on simple batch copper pot stills – so called alambic. Their volume mostly ranges from 80 to 2,000 liters, depending on producer capacities. Batch distillation in alambic of different volumes and shapes is also used worldwide for the production of renowned high quality spirits, such as cognac, calvados and malt whiskey (Nikićević and Tešević, 2010). Different shapes and capacities of distillation devices depend on their purpose and differ among countries (Leaute, 1990).

Application of alambic in production of fruit spirits necessarily involves double distillation. Distillation of fermented fruit mash gives first distillate (raw crude brandy) in which ethanol content mostly ranges between 25 and 30% v/v and 20 and 30% v/v in plum and apple brandies, respectively. In most cases, at first distillation, fractions are not separated. Second distillation (redistillation of raw crude brandy) is done on the same devices and involves separation of head, heart and tail. Only the heart is used for making fruit spirit intended for market.

Ethanol content in mid-fraction (heart) obtained through redistillation ranges among producers from 50 and 65% v/v (Paunović and Daničić, 1967; Nikićević and Tešević, 2010).

At redistillation of raw fruit brandy in alambic, it is recommended that boiler be charged by about 70% of its useful volume (Paunović and Daničić, 1967). However, this is not a strict rule, but rather a recommendation which many small producers mostly fail to observe. Therefore, the level of charging of boiler with raw brandy at redistillation varies widely from 40% to 100% of useful volume. This, among other things, induces differences in duration of distillation at the same heating intensity.

Given the fact that some brandy producers fully charge boiler (100%) at redistillation, and some with less than 70%, the objective of this paper was to establish the influence of level of charging boiler on the dynamics of distillation of major components, chemical composition and quality of middle distillate fractions (hearts) used for the production of final fruit brandies.

MATERIAL AND METHODS

Raw fruit distillates obtained directly from commercial fruit brandy producers were used for assessment of effect of level of charging alambic at redistillation on quality of middle distillate fraction. Raw distillates were obtained by distillation of fermented mash (plum and apple) on 100 Lalambic, without fraction separation. Ethanol content in raw plum and apple distillates was 26.6% v/v and 21.75% v/v, respectively. The chemical composition is shown in Tables 1 and 2. Redistillation of raw fruit distillates was done using a pilot batch copper pot still – alambic, 25 L boiler volume.

The level of charging was 40, 50, 60, 70, 80, 90 and 100% of useful boiler volume. The boiler was heated by gas burner, whereby the distillation rate was similar irrespective of the level of charging. Head (1% of raw fruit distillate), heart (ethanol content amounting to 60% v/v) and tail were obtained from the redistillation. After each distillation, all alambic parts which were in contact with raw fruit distillate and vapors were thoroughly rinsed with water.

Content of ethanol, higher alcohols, acids, esters, aldehydes, furfural, methanol, benzaldehyde and HCN in middle fractions obtained by redistillation was assessed using standard law regulation methods (Official Journal of SFRY 70/87). Volatile components content is the sum of higher alcohols, acids, esters, aldehides and furfural.

Statistical data processing was done using Statistica 7 (StatSoft, Inc., Tulsa, OK, USA).

RESULTS AND DISCUSSION

Chemical compositions of raw fruit distillates and middle fractions (hearts) obtained by redistillation in alambic (at the different charging levels) are shown in Tables 1 and 2 (redistillation of raw plum and apple brandies, respectively).

The data infer that similar distillation dynamics for a particular component, irrespective of the charging level in boiler at redistillation. Leaute (1990) provides no report on the charging level as a factor important for the behavior of particular compounds during distillation, but highlights a major influence of their boiling point, solubility in alcohol or water; and alcohol content in vapors during the distillation on the dynamics of the distillation.

Owing to the different distillation dynamics of particular components, middle fractions (hearts), obtained by respective redistillation regime, differ in composition from raw crude brandies, which was confirmed by Radovanović et al., 1963; Paunović, 1985; Leaute, 1990; Nikićević, 1992; Guan and Pieper, 1999 and other authors in the studies of double distillations or redistillation of fruit and wine distillates.

Table 1. Effect of charging level of alambic on chemical composition of middle fraction – heart (ethanol content 60.0% v/v) obtained at redistillation of raw plum brandy (ethanol content 26.6 %v/v)

Charging level in alambic (%)	Higher alcohols (mg/L a.a.)	Acids (mg/L a.a.)	Esters (mg/L a.a.)	Aldehydes (mg/L a.a.)	Furfural (mg/L a.a.)	Volatile components (mg/L a.a.)	Volatile components without acids (mg/L a.a.)	Methanol (g/L a.a.)	Benzaldehyde (mg/L a.a.)	HCN (mg/L a.a.)
Raw plum brandy (26.6 % v/v ethanol)										
-	1231	4038	2097	92	19	7477	3439	8,28	71	9,75
Middle fraction – heart obtained by redistillation (60.0% v/v ethanol)										
40	1123	795	1248	35	21	3222	2427	8.40	65	3.84
50	1156	875	1259	29	18	3337	2462	8.66	65	4.80
60	1317	644	1424	26	18	3429	2785	8.82	65	4.31
70	1215	653	1283	42	19	3212	2559	9.13	66	3.84
80	1221	582	1347	24	19	3193	2611	7.42	65	3.85
90	1138	665	1381	35	18	3237	2572	8.55	65	2.88
100	1138	859	1244	37	19	3297	2438	8.45	66	2.89
Min	1123	582	1244	24	18	3193	2427	7.42	65	2.88
Max	1317	875	1424	42	21	3429	2785	9.13	66	4.80
Me	1156	665	1283	35	19	3237	2559	8.55	65	3.84
Mx	1189	724	1312	33	19	3275	2551	8.49	65	3.77
SD	69	116	72	6	1	85	125	0.53	0	0.70
CV (%)	5.82	16.05	5.47	19.81	5.67	2.58	4.93	6.28	0.75	18.53

Table 2. Effect of charging level of alambic on chemical composition of middle fraction – heart (ethanol content 60.0% v/v) obtained at redistillation of raw apple brandy (ethanol content 26.6 %v/v).

Charging level in alambic (%)	Higher alcohols (mg/L a.a.)	Acids (mg/L a.a.)	Esters (mg/L a.a.)	Aldehydes (mg/L a.a.)	Furfural (mg/L a.a.)	Volatile components (mg/L a.a.)	Volatile components without acids (mg/L a.a.)	Methanol (g/L a.a.)
Raw apple brandy (21.75 % v/v ethanol)								
-	1765	8844	3512	66	8	14195	5351	6.41
Middle fraction – heart obtained by redistillation (60.0% v/v ethanol)								
40	1913	1103	1618	31	7	4672	3569	5.76
50	1867	1176	1555	35	7	4640	3464	4.83
60	1829	1123	1668	22	7	4649	3526	4.96
70	1721	963	1960	40	7	4691	3728	5.15
80	1865	946	2041	33	7	4902	3956	5.15
90	1823	1286	2122	37	7	5275	3989	5.15
100	1850	1189	1995	42	7	5083	3894	5.36
Min	1721	946	1555	22	7	4640	3464	4.83
Max	1913	1286	2122	42	7	5275	3989	5.76
Me	1850	1123	1960	35	7	4691	3728	5.15
Mx	1838	1112	1851	34	7	4843	3731	5.19
SD	60	123	230	7	0	251	216	0.30
CV (%)	3.24	11.03	12.43	19.33	0.00	5.18	5.78	5.78

Since head and tail are separated at redistillation, contents of acids, esters, aldehydes and total volatile components decrease substantially. The comparison of raw distillates and redistillation-obtained middle fractions inferred that the highest decrease in acids content ranged between 78.33 and 85.59% and 85.46 and 89.30% at plum and apple raw brandies redistillation.

In contrast, minor changes in methanol, higher alcohols and furfural contents occurred during redistillation. These changes may be such that their contents in middle fraction obtained by redistillation can be somewhat higher or lower than in raw fruit distillate. Therefore, purification of these compounds at redistillation in alambic is only minor, which means that owing to the properties of components above, their concentration in the obtained middle fraction cannot significantly change in comparison with raw brandy.

Decrease in benzaldehyde content at redistillation of raw crude plum brandy (7.04–8.45%) is in agreement with the results obtained by Paunović and Nikićević (1989) at similar redistillation regimes. The decrease in HCN at plum brandy redistillation ranged between 50.77 and 70.46%, depending on charging level of boiler, which is somewhat lower than in the study of Paunović and Nikićević (1989) at redistillation in copper pot still.

The behavior of some components at distillation is not governed only by their physical and chemical characteristics which are important for the distillation dynamics, but also by their participation in numerous chemical reactions. Depending on reaction type, the content of particular components may rise or fall, whereby the boiler can be considered as a reactor (Leaute, 1990). Duration of heating or distillation can also affect these reactions.

Level of charging boiler at redistillation of raw fruit distillates influenced the duration of distillation although the heating intensity was identical and distillation rate similar. At redistillation of raw plum brandy, distillation ranged from 3 hours and 18 minutes (40% charging level) to 6 hours and 53 minutes (100% charging level). The duration of distillation at redistillation of raw apple brandy ranged from 2 hours and 18 minutes (40% charging level) to 5 hours and 1 minute (100% charging level).

Depending on charging level in boiler, the following components varied most in middle fractions (hearts) obtained by redistillation: aldehydes (CV=19.33% and CV=19.81% in apple and plum brandies, resp.), acids (CV=11.03% and CV=16.05% in apple and plum brandies, resp.) and esters (CV= 12.43% and CV=5.47% in apple and plum brandies, resp.). According to Leaute (1990), during distillation, aldehydes, acids and esters participate in acetalization, esterification and hydrolisis. Nikićević and Tešević (2010) report that, at distillation, these compounds are subject to chemical changes, hence their total content change accordingly. Esters formation - esterification (etylacetates in particular) is more intensive at higher acidity of the distilling medium. This also brings about a higher variation coefficient of esters content in middle fractions obtained by redistillation of raw apple brandy than it is at redistillation of raw plum brandy, since raw apple brandy had double high acids (8844 mg/L a.a.) than raw plum brandy (4038 mg/L a.a.). Redistillation of apple brandy revealed a significant dependence (p=0.008143) between charging level in boiler and esters content in the obtained middle fraction (correlation coefficient r=0.88). It is apparent that the higher the charging level in boiler (raw apple brandy) the longer the redistillation, which results in longer esterification. Given the fact that esters are among major components in apple brandy as well as their contribution to total volatile components content, some statistically significant dependences between charging level in boiler and volatile components content (p=0.016871, correlation coefficient r=0.84) were established as well as between charging level in boiler and content of volatile components without acids (p=0.009929, correlation coefficient r=0.87). Charging level in boiler at redistillation influenced relatively high variation coefficient (CV=18.54%) in respect of HCN content in the obtained middle distillate fractions. HCN reacts on copper, whereby copper cyanides are formed. Statistically significant dependence (p=0.035049) was established between charging level in boiler and HCN content in the obtained middle fraction (negative correlation coefficient r=–0.79). The higher the charging level in boiler, the longer the redistillation, and extended time for chemical reaction between HCN and copper in copper pot still accordingly. This leads to a considerably lower HCN content in heart fractions obtained in fully charged boiler at identical redistillation regime. The other components (methanol, higher alcohols, furfural and benzaldehyde) turn into a distillate at a particular dynamics at redistillation, being rarely subject to any chemical changes. Variation coefficients of their contents in redistillation-obtained middle fractions are considerably lower, depending on the charging level in boiler, and range from CV=0.00% (furfural at redistillation of apple brandy) and CV=0.75% (benzaldehyde at redistillation of plum brandy) to CV=5.78% (methanol and sum of volatile components without acids at redistillation of apple brandy) and CV=6.28% (methanol at redistillation of plum brandy). No regularities in change of content of components above were established as related to the charging level in boiler at redistillation of raw fruit distillates.

CONCLUSIONS

Charging level of alambic (40–100% of boiler useful volume) at redistillation of raw plum and apple distillates:

- affects contents of esters, acids and aldehydes obtained in middle distillate fractions. Statistically significant dependence ($p=0.008143$) was established only between charging level at redistillation of raw apple brandy and esters content in the obtained distillates (correlation coefficient $r=0.88$).

- affects HCN content in middle distillate fractions obtained by redistillation of raw plum brandy. Statistically significant dependence ($p=0.035049$) was established between charging level in boiler and HCN content in the obtained distillates (correlation coefficient $r= -0.79$).

- does not induce significant differences in contents of higher alcohols, furfural, methanol and benzaldehyde in middle fractions (hearts) obtained by redistillation.

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