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THE EFFECT OF THE DISTILLATION SYSTEMS ON THE QUALITY OF APPLE DISTILLATES

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT

Apple distillates are a common drink in Western European regions and considered as a high quality product. There are many factors that will influence the production and the quality of apple distillates.
The aim of this work was to produce apple distillates by column devices with different rectification index (1, 1.75 and 2.6) and by *alambic* device (classic process and double distillation). Distillates were analyzed to determine chemical composition, aroma profile and sensory properties.
Apple distillates produced by column process had significant higher ethanol content, but lower aldehydes, higher alcohols, esters and monoterpenes. All samples had very low concentration of methanol and furfural. Apple distillates produced by column process had significant higher grades of sensory properties.

Key words: *apple distillate, distillation, quality*

INTRODUCTION

Alcoholic beverages are complex mixtures mainly comprised of ethanol, water and a large number of minor compounds that may be present in the raw materials or formed during the distinct stages of the manufacturing process such as: alcohols, acids, esters, aldehydes, polyphenols, metals, aminoacids, etc. (Rodríguez Madrera & Suárez Vales, 2007).
Production of apple distillates (also called cider brandy or calvados in France or applejack in USA) is mentioned as far back as the 8th century. Cider brandy is a common drink in Western European regions where, because of peculiar climatic characteristics, grape-vine cultivars are not viable. In these countries, cider brandy is considered a high quality product and a factor of important economic repercussion. There are many factors that will influence the production and the quality of apple distillates. These include the type of cultivar, geographical origin, processing of the apples, fermentation, distillation processes and maturation of the distillate in oak barrels to produce the final aged brandy (Mangas et al., 1996). Apple distillate aroma depends more on technological parameters (Askew & Lisle, 1971) in addition to maturation in wood barrels (Onishi et al., 1977; Profumo et al., 1988), than on the raw material, since volatile compounds are formed during fermentation, distillation and aging from their precursors. However, the process of distillation is one of the most important factors to consider (Leaute, 1950). For instance, the extended length of heating in double distillation systems produces cider brandies with higher contents in furfural due to degradation of residual sugars (Rodriguez Madrera et al., 2003), thus imparting a caramel aroma.
Distillation is usually carried out in a traditional alembic pot still or in modern column still (single continuous distillation). The usual arguments for and against the two processes are that the column process gives the fresh and clean apple flavour but with less complexity. On the other hand, a traditional practice in the production process gives the distillate complexity and renders it suitable for longer aging (Guan and Pieper, 1998; Picinelli et al., 2005) as well as increase consumer approval of products.

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In this work distillates were produced by distillation of fermented apple pulp in column devices with different rectification index (1, 1.75 and 2.6) and by simple *alambic* device (classic process and double distillation). Produced apple distillates were analyzed to determine chemical composition, aroma profile and sensory properties.

MATERIALS AND METHODS

Preparation of apple distillates

Preparations of apple distillates were carried out in Zvečevo d.d. food industry Požega. Apple pulp (*Golden Delicious* varieties) was prepared and then treated with SO_2 (50 mg/L), as recommended by Nikićević and Tešević (2010). Fermentation was carried out in a fermenter at temperatures between 18-20°C with selected yeast *Feromol-Bouqet 125* (*S. cerevisiae*, LSA Pascal Biotech). The duration of fermentation was 12 days.

After fermentation samples were distilled in industrial copper clip distillation device, according to the distillation protocol:

Apple distillate (AD1): Column process with rectification index 1

Apple distillate (AD2): Column process with rectification index 1.75

Apple distillate (AD3): Column process with rectification index 2.60

Apple distillate (AD4): Classic process of distillation in *Alambic*

Apple distillate (AD5): Double distillation in *Alambic*

Chemical analysis of distillates

Chemical analysis of distillates (ethanol, extract, SO_2, aldehydes, higher alcohols, total acids, esters, methanol and furfural) was conducted according to standard AOAC (1995) procedures.

Analyses of aroma substances

Gas chromatography analyses were performed by gas chromatograph (Hewlett-Packard, type 5890) with a split/splitless injector and an FID detector. For analysis of distillates a Stabilwax (Restec); 30 m; i.d.=0,25 µm capillary column was used. Initial oven temperature was kept at 35°C for 7 min, then raised at 10°C/min to 80°C followed by 25°C/min to 200°C, and kept for 4 min at 200°C. Qualitative analysis was done by comparing the standard retention times (analytical grade from *Merck KGaA Darmstad,* Germany) with the corresponding peaks of samples. The quantification was carried out by comparing the peak areas to those of the Merck standards.

Sensory analyses

A sensory analysis of samples was performed according to the method of positive scoring factor according to the German DLG model (Koch, 1986).

This model was based on 4 sensorial experiences: colour, clearness, odour and taste, which are marked with grades 0 to 5, including 0, while the average grade is multiplied by the significance factor.

Sensory assessment was conducted in two repetition cycles by ten sensory testing experts.

RESULTS AND DISCUSSION

Chemical analyses

Chemical composition of apple distillates (AD) is presented in Table 1 and was in accordance with results reported by Rodriguez Madrera et al. (2006) and Versini et al. (2009).

Distillates had ethanol content ranging from 61.60% to 71.5%, where AD produced by column process had significant higher ethanol content: AD1, 69.91%; AD2, 69.7%; AD3 71.5%; AD4, 63.27% and AD5, 61.6%.

The content of total extract in distillates was in range 14.0-68.0 mg/L where AD4 had the highest value of 68.0 mg/L, followed by AD5 (58.0 mg/L), AD1 (41.0

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mg/L), AD2 (34.0 mg/L) and AD3 (14.0 mg/L).

The presence of free SO_2 in distillates ranging from 3.85 to 4.55 mg/L is the result of addition of 50 mg/L SO_2 during production process. SO_2 is important for the protection of pulp from degradation processes and non-controlled fermentation (Nikićević and Tešević, 2010).

Adehydes content were in range from 280.00 to 374.00 mg/L and higher alcohols from 1830.71 to 2845.57 mg/L, where AD produced by *alambic* process had higher level of adehydes and higher alcohols. As regards the higher alcohols quantities, it should be noted that their concentration in AD4 and AD5 is clearly higher than the minimum value accepted by the European Community Council Regulation of 2000 mg/L of a.a. These alcohols, except for 2-butanol, are formed from amino acids during the fermentation of apple pulp therefore their level in the final distillate depend on several factors such as raw material, yeast strains and fermentation conditions (Suarez Valles et al., 2005; Rodriguez Madrera et al., 2006).

The content of total acids and esters shows higher values for the AD produced by *alambic* process compared with the AD produced by column process. As from the literature referred both to distillates (Genovese et al., 2003), and to fermented products like beer (Meilgaard, 1975), these compounds are responsible for a so-called sweet alcoholic-floral-basic aroma on which interact other sensory active substances typical of the beverages.

Methanol is not a yeast fermentation product, but this volatile is cleaved from pectins, and its concentration depends on several factors as apple variety and ripening state (Suarez Valles et al., 2005). In this respect, the results obtained for AD shows values clearly below the maximum content of 12 g/L established by *Regulation,* 2009.

Differences of furfural content are not noted between the AD. Furfural formation in distillation is basically due to the presence of pentose residue in the mash as well as to a possible amadori decomposition product via 1,2-enolisation (Versini et al., 2009). The five AD presented furfural values ranging from 0.001 to 0.003 mg/L.

Table 1 Chemical composition of apple distillates

	AD1	AD2	AD3	AD4	AD5
Ethanol (% vol.)	69.91	69.70	71.50	63.27	61.60
Extract (mg/L)	41.0	34.0	14.0	68.0	51.0
SO_2 (mg/L)	4.54	3.95	3.85	4.55	4.04
Aldehydes (mg/L a.a.)	280.00	305.00	307.00	374.00	370.00
Higher alcohols (mg/L a.a.)	1955.14	1830.71	1880.27	2845.57	2837.39
Total acids (mg/L)	217.60	185.00	184.20	384.20	447.00
Esters (mg/L a.a.)	768.23	828.23	591.00	997.80	933.10
Methanol (g/L a.a.)	0.02	0.02	0.01	0.04	0.04
Furfural (mg/L a.a.)	0.002	0.001	0.001	0.002	0.003

AD1: distillate by column process with rectification index 1; AD2: distillate by column process with rectification index 1.75; AD3: distillate by column process with rectification index 2.60; AD4: distillate by classic process of distillation in *Alambic*; AD5: distillate by double distillation in *Alambic*

Analyses of aroma substances

Table 2 shows the average contents (mg/L) of the volatile components of apple distillates (AD). Among the different substances that determine the specific flavour of distillate spirits, volatile compounds are the most important.

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Analysis of these substances allows characterization of the product. Beech and Carr (1977) showed that cider brandies present differences in relation to the levels of low-temperature boiling compounds. On the other hand, typical aromatic compounds (alcohols, esters, allyl derivatives, etc.) have been associated with apple-like odours (Williams et al., 1977; Mangas et al., 1996). Scheirer et al. (1978) investigated the changes in aroma composition during apple-brandy production. Quantitative determinations of 97 aroma components have shown that the aroma of unaged apple brandy is characterised by components produced as a result of the yeast fermentation and technological steps such as mashing and heating rather than by the genuine apple aroma components.

Distillation enhanced the concentration of ethyl esters and many of the higher alcohols (Scheirer et al., 1978). Generally, AD produced by *alembic* process had higher concentration of esters. Ethyl acetate content was in range 44.31-57.49, where AD4 had the highest level of 57.49 mg/L, followed by AD5 57.27 mg/L, AD1 56.57 mg/L, AD2 54.2 mg/L and AD3 44.31 mg/L. Ethyl acetate is the main ester in many fresh distillates, the aroma of which is described as glue/varnish (Rodriguez Madrera et al., 2006). The levels of this compound in distillates are related to the quality of the raw materials used. It may be formed during fermentation or during distillation by esterification of acetic acid with ethanol. Its low boiling point (77°C) and minor solubility in water (10%) make it a typical product of first fractions during distillation (Rodriguez Madrera et al., 2006).

Other esters were in lower concentration: isoamyl acetate 24.96-27.35; acetaldehyde 12.22-28.68; ethyl octanoate 12.69-19.18; ethyl decanoate 10.91-11.74; 2-phenylethyl acetate 1.87-2.84; ethyl hexanoate 0-2.84 and ethyl lactate 0-4.10. The ethyl esters of fatty acids from hexanoate to ethyl decanoate related to a ripe fruits aroma (Salo, 1970) were at medium to low level which is in accordance with Versini et al. (2009). Ethyl lactate is present with rather low values in AD, a fact that indicates a reduced presence of lactic or malo-lactic fermentation in the apple pulp (Versini et al., 2009).

2-phenylethanol was of fermentative origin according to Williams (1975) and Schreier et al. (1978). Its presence in spirits, with respect to other alcohols, must be attributed to the fact that this alcohol is predominant in tails, due to its high boiling point, and which furthermore presents low solubility in water, which promotes a low recovery in spirit. This alcohol could contribute to the aroma of AD with floral or rose notes (Salo, 1970; Rodriguez Madrera et al., 2006; Versini et al., 2009). The levels of 2-phenylethanol detected in AD were in range 2.97-4.75.

Monoterpenes level can derive from the free forms often after acid catalysed rearrangements during the distillation, as well as from bound forms present in the mash (Skouroumounis & Sefton, 2000; Versini et al., 2009). Cis and trans furanic linalool oxides dominate (linalool, α-terpineol, 4-terpineol). These compounds contribute to the floral aroma of products (Versini et al., 2009).

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Table 2 Average contents (mg/L) of the volatile components of apple distillates

	AD1	AD2	AD3	AD4	AD5
Ethyl acetate	56.57	54.20	44.31	57.49	57.27
Isoamyl acetate	25.60	25.80	24.96	27.32	27.35
Acetaldehyde	12.76	12.96	12.22	28.68	28.51
Ethyl octanoate	15.92	12.69	12.92	19.18	17.18
Ethyl decanoate	11.74	10.91	11.18	11.20	11.19
2-phenylethyl acetate	2.37	1.87	1,97.	2.84	2.76
Ethyl hexanoate	2.47	1.57	n.i.	2.82	2.74
Ethyl lactate	3.07	1.41	n.i.	4.10	3.95
2-phenyl ethanol	2.97	3.52	3.45	4.75	4.73
Linalool	0.63	0.87	1.33	0.11	0.02
α-terpineol	3.1	3.78	3.17	5.23	5.17
4-terpineol	3.01	3.02	3.45	5.40	5.50
Limonene	11.14	12.16	13.27	7.23	16.16

AD1: distillate by column process with rectification index 1; AD2: distillate by column process with rectification index 1.75; AD3: distillate by column process with rectification index 2.60; AD4: distillate by classic process of distillation in *Alambic*; AD5: distillate by double distillation in *Alambic*

Sensory analyses

Sensory analyses of apple distillates (AD) were conducted according to German *DLG* model (Koch, 1986). Total points of sensory analyses of AD ranged from 80.60 to 98.50 (Table 3). Different sensory characteristics of AD can be addressed to distillation protocol, since other factors in the production of distillates were same for all AD. AD produced by column process had significantly higher grades of sensory properties. The best evaluated sample was AD3 (produced by column process with rectification index 2.60) which had 98.5 total points, followed by AD1 (96.5), AD2 (96.3), AD5 (81.0) and AD4 (80.6).

The samples produced in column with different index of rectification had pleasant recognizable apple fruity aroma, without sharp odour tones (caused mainly by malic acid).

Table 3 Results of sensory analyses of apple distillates (*German DLG model*)

Sample	Assessment characteristics				**TOTAL** (max 100 points)
	Colour (max 15 points)	**Clearness** (max 15 points)	**Odour** (max 25 points)	**Taste** (max 45 points)	
AD1	14.80	14.80	24.50	42.40	96.50
AD2	14.80	14.80	23.50	43.20	96.30
AD3	15.00	15.00	24.50	44.00	98.50
AD4	14.70	14.40	15.50	36.00	80.60
AD5	14.70	14.70	15.50	36.00	81.00

AD1: distillate by column process with rectification index 1; AD2: distillate by column process with rectification index 1.75; AD3: distillate by column process with rectification index 2.60; AD4: distillate by classic process of distillation in *Alambic*; AD5: distillate by double distillation in *Alambic*

CONCLUSIONS

Apple distillates produced by column process had significantly higher ethanol content, but lower adehydes and higher alcohols. Distillates produced by *alambic* process had higher alcohols concentration than the minimum value accepted by the EU Regulation of 2000 mg/L of a.a. All samples had very low concentration of methanol and furfural. Distillates produced by *alembic* process had higher

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concentration of esters and monoterpenes compared to those produced by column process.

Apple distillates produced by column process had significantly higher grades of sensory properties. The best evaluated sample was produced by column process with rectification index 2.60 which had 98.5 total points (max 100).

Increasing the index of rectification could be promising approach in processing of the apples distillates for industrial productions of apple brandy.

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