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EFFECT OF BRANDIES' AGITATION ON THE KINETICS OF EXTRACTION/OXIDATION AND DIFFUSION OF WOOD EXTRACTABLE COMPOUNDS IN EXPERIMENTAL MODEL

REPERCUSSÃO DA AGITAÇÃO DA AGUARDENTE NAS CINÉTICAS DE EXTRACÇÃO/OXIDAÇÃO E DE DIFUSÃO DE COMPOSTOS EXTRAÍVES DA MADEIRA EM MODELO EXPERIMENTAL

I. Patrício[1,2], S. Canas[1], A. P. Belchior[1]

[1] INIAP. Estação Vitivinícola Nacional. 2565-191 DOIS PORTOS. Portugal.
E-mail:inia.evn.quim@oninet.pt
[2] Student of Universidade Lusófona de Humanidades e Tecnologias. 1749-024 LISBOA. Portugal.

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SUMMARY

This study provides, for the first time, specific information about the effect of brandy's agitation on the kinetic of extraction/oxidation and diffusion of wood low molecular weight compounds during the first two months of ageing, in barrels of Limousin oak wood and chestnut wood submitted to light toasting (QL) and strong toasting (QF).

A concentration gradient of compounds was observed in brandy dependent of their chemical nature, the botanical species (higher in the brandies that contact with the chestnut wood) and the wood toasting level (higher in the strong toasting). These aspects justify therefore the brandy's agitation in the first months of ageing, mainly in barrels of chestnut wood and strong toasting.

Independently of the wood and the toasting level, the monthly agitation showed to be the more efficient than the static system and the agitation after each sampling, leading to brandies with higher dry extract weight, higher total polyphenol index and higher content of low molecular weight compounds, favouring the balance between extraction and diffusion phenomena.

Key words: wood, toasting, brandy, agitation, chemical composition
Palavras-Chave: madeiras, queima, envelhecimento, agitação, composição química

INTRODUCTION

The brandy ageing in wood is an essential stage so that brandy reaches its sensorial fullness. In this process they are involved extraction and transformation phenomena of wood compounds, as well as the evaporation of brandy. From the wood a great diversity of organic compounds is extracted, mostly low molecular weight phenolic compounds (Guymon *et al.*, 1970; Puech *et al.*, 1987). These compounds have a strong influence on the chemical characteristics and sensory properties of the brandy, improving its quality (Canas, 2003).

The most used botanical species in cooperage has been the oak wood (Taransaud, 1976; Belchior, 1995; Mosedale, 1995; Singleton, 1995; Simon *et al.*, 1996; Vivas, 1996; Canas, 2003; Caldeira, 2004), however, the chestnut wood has come to prove itself for the characteristics conferred to the aged brandies (Canas *et al.*, 1999; Caldeira *et al.*, 2002; Belchior *et al.*, 2001; Canas *et al.*, 2002; Belchior *et al.*, 2003; Canas, 2003; Caldeira, 2004).

Several studies had demonstrated that the chemical composition of the brandy depends on the pool of potential extractives of the wood that in turn is determined by the botanical species (Fengel and Wegner, 1989; Mosedale, 1995, Canas *et al.*, 2000b,c), the geographical origin (Miller *et al.*, 1992; Canas *et al.*, 2000c; Doussot *et al.*, 2002) and by the age of the tree (Peng *et al.*, 1991; Singleton, 1995; Simon *et al.*, 1996), being also conditioned by the technological operations on barrel making process, namely the seasoning (Puech, 1987; Caldeira, 2004) and the heat treatment (Canas *et al.*, 2000a; Canas *et al.*, 2002; Caldeira *et al.*, 2002).

On the other hand, some interdependent factors inherent to the ageing process influence the extraction of wood compounds such as the relative proportion of water and ethanol, the characteristics of the barrel (volume and use), the warehouse conditions and the technological operations (Canas *et al.*, 2002).

Concerning the technological operations performed during the ageing process there is few scientific support, being only known the studies recently developed in the EVN (Canas *et al.*, 2002; Belchior *et al.*, 2003), based on laboratorial assays in static conditions. Such works have focused on the study of the botanical species and the wood toasting level effects on the kinetics of brandy's evaporation/impregnation and extraction/oxidation of wood low molecular weight compounds to the brandy. The observed differences had lead to study the effect of the agitation during the ageing period.

So, with the present work it is proposed to study the effect of brandy's agitation on the kinetics of extraction/oxidation and diffusion of wood low molecular weight compounds (phenolic acids, phenolic aldehydes, coumarins and furanic aldehydes), during the two first months of ageing in different botanical species and wood toasting levels, under model conditions, simulating the natural ageing of brandies.

MATERIAL AND METHODS

Materials

Experimental design

This study was based in a factorial experiment, with three factors - wood botanical species (two levels), toasting degree (two levels) and agitation (three levels), with two replications.

The essay was carried out from 1st July to 1st September 2004.

Wood

Two heartwood staves of Limousin oak wood (*Quercus robur* L.) - CFL and two heartwood staves of Portuguese chestnut wood (*Castanea sativa* Mill.) - CAST were supplied by a cooperage industry - JMA Gonçalves, where they were seasoned during three years in the open air and toasted. One stave of each wood was submitted to light toasting (QL) and the other was submitted to strong toasting (QF). After that they were cut into pieces with 110 mm long, 110 mm width and 27 mm thickness. Two pieces of each wood x toasting level were used to make the experimental units, with a glass part (Figure 1), which had been developed respecting the ratio surface area/volume

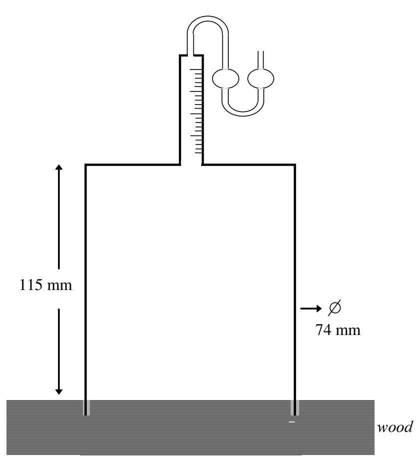


Fig. 1 - Experimental unit scheme (longitudinal plan).

Esquema da unidade experimental (plano longitudinal).

of a 250 L wooden barrel (86 cm^2/L). The linkage between glass and wood was made with silicone - food quality.

Brandy

24 experimental units were filled with the same *Lourinhã* distillate with an alcohol content of 75 % v/v (485 mL) and placed at the cellar of Estação Vitivinícola Nacional, in similar environmental conditions, to simulate the enological practice.

The experimental units of wood x toasting level were identified as CAST QF, CAST QL, CFL QF and CFL QL.

Agitation

Three modalities of agitation were used. One is static (A) and two are dynamic (B1 and B2). In the last two the manual agitation was performed after each sampling (B1) and monthly (B2). Shaking the experimental unit during 3 minutes did the manual agitation.

Methods

Monitoring of the liquid volume

The monitoring of the brandy volume in each experimental unit was carried out daily during the overall essay. The measurement of the brandy volume was performed in mm and converted into mL. Whenever necessary the experimental unit was refilled with distillate to the original volume.

Cellar temperature and relative humidity were also monitoring during the essay (Figure 2).

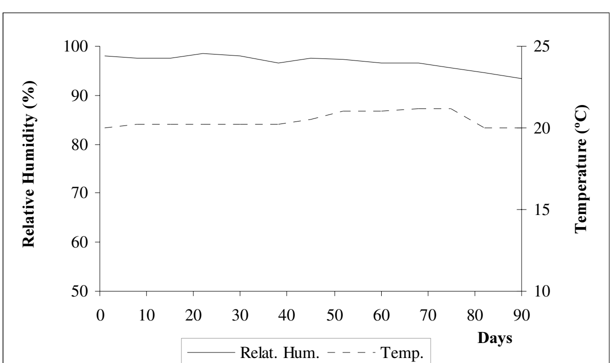


Fig. 2 - Warehouse temperature and relative humidity during the essay.

Temperatura e humidade relativa da cave durante o ensaio.

Brandy sampling

The brandy (control) was analyzed in the beginning of the essay. The aged brandy's sampling was performed after 1 day, 8, 16, 30, 45 and 60 days.

In the initial phase (1 day) it was observed a colour gradient between the bottom (darker) and the top (brighter) of the brandies inside the experimental units, as expected (Belchior, 1974; Canas *et al.*, 2004). This led to collect the samples of brandy in each experimental unit in two depths: 4 mL from the layer near the wood, with approximately 1,5 cm - 2 cm height, and 4 mL from the layer distanced about 7 cm from the wood.

Analytical methods

Color intensity (A440) – measurement of absorbance at 440 nm (Belchior and Carvalho, 1983).

Total polyphenol index (Ipt) – product of the measured absorbance at 280 nm by the dilution factor (Ribéreau-Gayon, 1970).

All measurements were carried out on a *Shimatsu UV-265* spectrophotometer using a quartz cell of 0,1 cm path length, and were referred to 1 cm path length.

Dry extract weight – usual method of OIV (1994). This analysis was only performed in the last sampling time (60 days).

Analysis of low molecular weight extractable compounds by High Performance Liquid Chromatography – Samples of brandies were added with an internal standard (20 mg/L of 4-hydroxybenzaldehyde – 4-hydroxybenz), filtered through 0,45 mm membrane (Titan) and analyzed by direct injection of 20 mL. Chromatography was performed as described by Canas et al. (2003), with a HPLC Lachrom Merck Hitachi system equipped with a quaternary pump L-7100, a column oven L-7350, a UV-Vis detector L-7400, and an autosampler L-7250, coupled to a HSM D-7000 software (Merck) for management, acquisition and treatment of data. A Merck Lichrospher RP18 (5 mm) column (250 mm x 4 mm i.d.) was used as the stationary phase.

The low molecular weight extractable compounds analyzed were: gallic acid (gall), 5-(hydroxymethyl)furfural (HMF), furfural (furf), vanillic acid (van), 5-methylfurfural (5mfurf), syringic acid (syrg), vanillin (vanil), syringaldehyde (syrde), ferulic acid (ferul), coniferaldehyde (cofde), sinapaldehyde (snpde), ellagic acid (ellag), umbelliferone (umb) and scopoletin (scop).

Statistical analysis

The two-way analysis of variance was performed using *Statistica vs '98 edition* (Statsoft Inc., E.U.A.).

RESULTS AND DISCUSSION

Effect of the agitation in the total polyphenol index, the colour intensity and the dry extract weight of brandy

The variance analysis results (Table I) show that does not exist a significant effect of the agitation on the content of phenolic compounds and the colour intensity of the brandy. However, the phenolic compounds content is higher for the brandies submitted to the static and monthly agitation modalities.

The dry extract weight of brandy does not depend significantly of the agitation frequency (Table I). Despite this, the content of this parameter is higher in brandies submitted to the monthly agitation. It confirms that the most frequent agitation (made after each sampling) does not present benefits for the ageing. This effect is something surprising, once it was expected that a more frequent agitation, favouring the diffusion of wood extractable compounds in the brandy, contributed to increase more the extraction than the monthly agitation and, mainly, than in the inexistence of agitation (static modality). Then, the observed behaviour might be result from the fact that the most frequent agitation promotes a diffusion that is not enough to compensate the extraction and, as balance, originates a global decrease on the total polyphenol index and dry extract weight comparatively to the others assayed modalities. Therefore, a frequent agitation of brandy (agitation after each sampling) could not be so beneficial for the acceleration of compounds extraction and diffusion and, consequently, to shorten the ageing period.

		A440	Ipt	Dry extract
		ns	ns	ns
A	*x*	0,21	14,56	0,68
B1	*x*	0,12	11,17	0,45
B2	*x*	0,19	15,86	0,62

Table I

Effect of the agitation modality on the colour intensity, total polyphenol index and dry extract weight (g/L) of brandy

Efeito da modalidade de agitação na intensidade da cor, índice de polifenóis totais e extracto seco (g/L) da aguardente

Effect of the agitation in the contents of low molecular weight compounds of brandy

Figure 3 presents the chromatograms (HPLC) of brandies aged in experimental units submitted to the different modalities of agitation during 60 days of ageing. The chromatograms show the separation and quantification of the low molecular weight extractable compounds that existed in the analysed brandies. Comparing them, the difference between the three different modalities of agitation is observed and is verified that the brandies not submitted to agitation and with monthly agitation are the most rich in the analysed compounds.

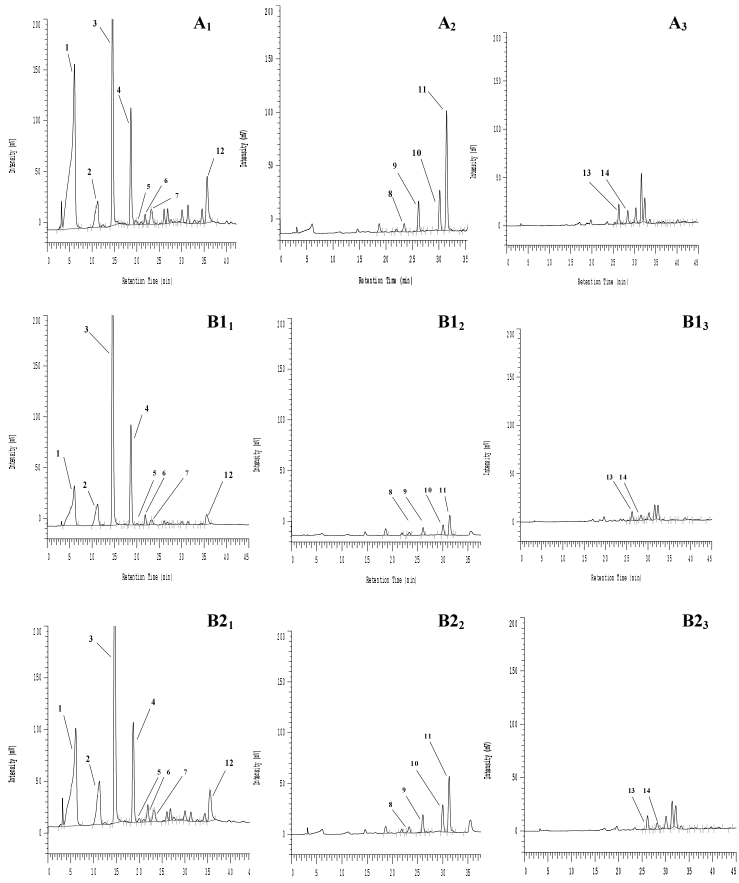


Fig. 3 - Chromatograms (HPLC) of the brandies aged with (**A**) static modality, (**B1**) agitation after each sampling and (**B2**) monthly agitation, detected at (**1**) 280 nm, (**2**) 320 nm and (**3**) 325/454 nm. 1 - gall; 2 - HMF; 3 - furf; 4 - 4-hidroxybenz; 5 - van; 6 - 5mfurf; 7 - syrg; 8 - vanil; 9 - syrde; 10 - cofde; 11 - snpde; 12 - ellag; 13 - umb; 14 - scop.

*Cromatogramas (HPLC) das aguardentes envelhecidas sujeitas a modalidade (**A**) estática, (**B1**) com agitação após cada amostragem e (**B2**) com agitação mensal, com detecção a (**1**) 280 nm, (**2**) 320 nm e (**3**) 325/454 nm. 1 – ac. gal; 2 – HMF; 3 – furf; 4 – 4-hidroxibenz; 5 – ac. van; 6 – 5mfurf; 7 – ac. sg; 8 – vanil; 9 – sgald; 10 – cfald; 11 – snald; 12 – ac. elg; 13 – umb; 14 – escop.*

The variance analysis (Table II) shows the existence of different effects of the agitation on the low molecular weight compounds content analyzed in brandy.

Table II

Effect of the agitation modality on the content of low molecular weight compounds of brandy (mg/L)

Efeito da modalidade de agitação nos teores dos compostos de massa molecular baixa da aguardente (mg/L)

		gall	van	syrg	ellag	HMF	furf	5mfurf	vanil	syrde	cofde	sipde	umb	scop
Effect		*	**	*ns*	*ns*	**	**	**	*ns*	*ns*	**	**	**	*ns*
A	*x*	87,96 ***b***	2,33 ***a***	3,16	32,64	8,18 ***a***	45,36 ***a***	2,77 ***a***	2,98	6,30	8,08 ***b***	25,43 ***b***	0,004 ***b***	0,05
B1	*x*	39,53 ***a***	2,54 ***a***	2,17	24,83	8,69 ***ab***	58,09 ***b***	3,57 ***b***	2,41	4,55	4,98 ***a***	10,29 ***a***	0,002 ***a***	0,05
B2	*x*	49,52 ***ab***	3,05 ***b***	2,56	26,13	12,45 ***b***	59,00 ***b***	5,18 ***c***	2,98	5,33	6,98 ***b***	16,75 ***a***	0,003 ***ab***	0,05

Concerning the phenolic acids, it is observed only a significant effect for the gallic acid and a very significant effect for the vanillic acid. In global terms the behaviour of phenolic acids relatively to the agitation reflect the lesser diffusion of these compounds in brandy, which is associated with their chemical nature, as observed by Canas *et al.* (2004) and that ahead it will be approached more in detail.

To the phenolic aldehydes, it is verified that for benzoic aldehydes (vanillin and syringaldehyde) does not exist a significant effect of the agitation and for cinnamic aldehydes (coniferaldehyde and sinapaldehyde) the effect is very significant. This difference could be associated to the chemical structure of these compounds (number of carbon atoms), which will influence their diffusion in the brandy. Canas *et al.* (2004) had verified that phenolic aldehydes presented a reduced diffusion in brandy.

The variance analysis shows that the only difference on coumarins is between the static modality and the others, which could be justified based on its low diffusion.

For furanic aldehydes a very significant effect of the agitation is denoted. These compounds are better spread out in the brandy (Canas *et al.*, 2004). So, promoting the agitation, which will favour their diffusion and compensate the extraction from the wood, enriching gradually brandy. This aspect will have positive implications in the aromatic point of view faced to the positive correlation found between furanic aldehydes and the descriptors “dry fruits” and “caramel” in aged brandies (Caldeira, 2004).

In global terms, for the analysis of Table II it is verified that the biggest low molecular weight compounds content are found in brandies not submitted to agitation and with monthly agitation. The same is evidenced for the dry extract weight, the total polyphenol index and the colour intensity.

To complement the analysis of agitation effect on the chemical composition of the brandy, a more detailed analysis of variance was performed, in order to examine the effect of the three modalities in each one of the botanical species used.

The variance analysis (Tables III and IV) demonstrates that a significant effect of the agitation involves a higher number of compounds in brandy that contacted with the chestnut wood than the brandy that contacted with the oak wood. This result, coherent with those reported by Canas (2003) and Canas *et al.* (2004), justifies therefore the necessity of a more frequent agitation in chestnut wood barrels than in oak wood barrels during the first months of ageing.

Table III

Effect of agitation modality on the content of low molecular weight compounds of brandy (mg/L) aged in chestnut wood

Efeito da modalidade de agitação nos teores dos compostos de massa molecular baixa da aguardente (mg/L) envelhecida em madeira de castanheiro

	gall	van	Syrg	ellag	HMF	furf	5mfurf	vanil	syrde	cofde	sipde	umb	scop
	*	**	*Ns*	*ns*	**	**	**	*ns*	**	**	**	*	**
x	168,67 ***b***	3,20 ***a***	5,65	48,26	13,96 ***a***	64,26 ***a***	4,60 ***a***	4,30	10,34 ***b***	10,81 ***b***	42,31 ***b***	0,007 ***b***	0,013 ***b***
x	65,29 ***a***	3,67 ***a***	3,76	36,17	15,26 ***a***	90,83 ***b***	6,21 ***b***	3,20	5,51 ***a***	5,03 ***a***	12,89 ***a***	0,003 ***a***	0,006 ***a***
x	93,66 ***ab***	4,73 ***b***	4,70	38,41	23,21 ***b***	93,05 ***b***	9,40 ***c***	4,28	8,31 ***ab***	8,58 ***ab***	24,64 ***a***	0,005 ***ab***	0,008 ***a***

A – static; B1 - after each sampling; B2 – monthly; x – mean of 48 values; means followed by the same letter in a column are not significantly different at the 0,05 or 0,01** level of significance; ns = without significant difference.*

Table IV

Effect of agitation modality on the content of low molecular weight compounds of brandy (mg/L) aged in Limousin oak wood

Efeito da modalidade de agitação nos teores dos compostos de massa molecular baixa da aguardente (mg/L) envelhecida em madeira de carvalho Limousin

		gall	van	syrg	ellag	HMF	furf	5mfurf	vanil	syrde	cofde	sipde	umb	scop
		ns	*ns*	*ns*	**	*ns*	*ns*	*ns*	*ns*	*ns*	*ns*	*ns*	*ns*	*ns*
A	*x*	7,26	1,47	0,67	17,03 ***b***	2,40	26,47	0,94	1,70	2,25	5,36	8,55	0,001	0,090
B1	*x*	13,76	1,42	0,57	13,48 ***a***	2,12	25,36	0,94	1,62	3,58	4,94	7,69	0,001	0,084
B2	*x*	5,38	1,37	0,41	13,84 ***a***	1,70	24,96	0,96	1,69	2,35	5,38	8,86	0,001	0,090

A – static; B1 - after each sampling; B2 – monthly; x – mean of 48 values; means followed by the same letter in a column are not significantly different at the 0,05 or 0,01** level of significance; ns = without significant difference.*

However, even to brandies ageing in chestnut wood, it will be preferable to effect the monthly agitation to the agitation after each sampling once the former induces the highest enrichment of brandy in low molecular weight compounds. Consequently, it will be able to become a more fast ageing, with the achievement of a quality brandy.

To brandies ageing in barrels of Limousin oak wood this question it seems to assume lesser importance, which means that, the extraction and diffusion of wood extractive compounds to brandy is not so dependent of the agitation made in the beginning of the ageing, but it implies a longer process of ageing so that an enrichment in these compounds is equivalent reached to the brandies aged in chestnut wood (with the same toasting level).

Once more it was possible to confirm that the brandies aged in chestnut wood present a faster ageing, corresponding to a higher dry extract weight, a higher total polyphenol content, and a greater content of low molecular weight compounds. They are also the brandies that present the highest colour intensity.

The toasting level showed also to be determinant of the brandies physico-chemical characteristics, being the strong toasting responsible for a faster evolution. The ageing time also influences the brandies characteristics, confirming that the biggest wood compounds extraction occurs during the first month of ageing (Canas *et al.*, 2002; Canas *et al.*, 2004).

Effect of the agitation in the diffusion of low molecular weight compounds of brandy

By the analysis of Figure 4 is possible to deduce that in the first 60 days of ageing the monthly agitation (B2) showed, in the conditions of the assay, to be the most efficient once it allowed reducing significantly the concentration gradient. Moreover, it facilitates the diffusion of all studied compounds. It means therefore that it is the modality that allows the acceleration of the ageing process, such as referred above.

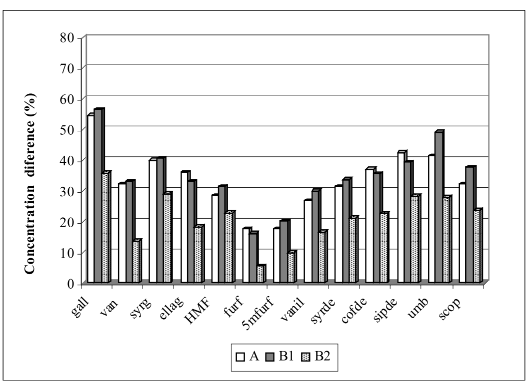
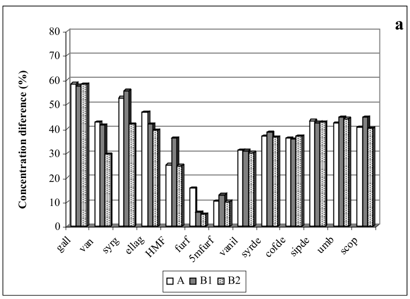


Fig. 4 – Difference of mean content of extractable compounds in the two depths of brandy in function of the agitation modality during the first 60 days of ageing.

Diferença de concentração média dos compostos extraíveis nas duas profundidades da aguardente em função da modalidade de agitação, nos primeiros 60 dias de envelhecimento.

Figure 5 shows the concentration differences of compounds analyzed in each one of the assayed modalities, from 45th day, time where the concentration difference reflected effectively the three practised modalities. It is verified that from 45th for 60th day the major decrease of the concentration gradient of the analyzed compounds corresponds to the brandy subjects on monthly agitation (B2). In contrast, the agitation after each sampling (B1) originates in some compounds a higher difference of concentration than in the static modality.



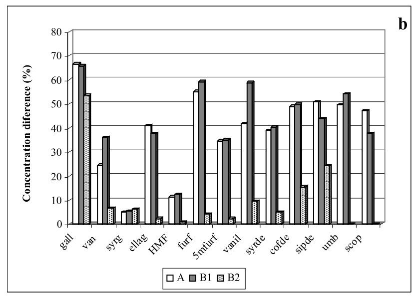


Fig. 5 – Difference of mean content of extractable compounds in the two depths of brandy in function of the agitation modality, after (**a**) 45 and (**b**) 60 days of aging.

*Diferença de concentração dos compostos extraíveis nas duas profundidades da aguardente em função da modalidade de agitação, após (**a**) 45 e (**b**) 60 dias de envelhecimento.*

The results explain that the decrease of concentration gradient of low molecular weight compounds promoted by the monthly agitation will be responsible for the beneficial effect of this modality on the extraction and that is expressed by a higher enrichment in wood extractable compounds and a faster evolution of the brandy, as already have been referred. Thus, independently of the botanical species and the wood toasting level, it will be to promote the agitation of the barrels only in the end of the first month of ageing, remaining this frequency during the first year, to accelerate the ageing process, with all the advantages that from there happen.

It was also possible to conclude that the colour gradient that was observed in the brandies since the beginning of the ageing seems to be related with the concentration gradient on some analyzed compounds, presenting higher content in the small adjacent volume of brandy to the wood. These gradients are dependent on the compounds chemical nature, the wood botanical species (higher in the brandies aged in chestnut wood), the wood toasting level (higher in strong toasting) and the type of agitation (higher in the static and agitation after each sampling modalities).

CONCLUSIONS

Considering the assay conditions, it is possible to conclude that the wood botanical species, the wood toasting level and the ageing time are determinant factors on the brandy's physical and chemical characteristics.

This study provides, for the first time, specific information about the effect of brandy's agitation. The results obtained allow understanding that the agitation is an operation that affects the evolution of the physical and chemical characteristics of the brandy, once it influences the extraction, the diffusion of wood extractable compounds and, therefore, the duration of the ageing process.

In contrast of what it would be to expect, this study demonstrated that a more frequent agitation could not be so beneficial for the speediness of the extraction and diffusion of compounds phenomena, and consequently to shorten the ageing period. This modality seems to promote a diffusion that is not enough to compensate the increase provoked in the extraction and, as result, originates less rich brandies in analyzed compounds and lesser evolution of the chromatic characteristics.

In global terms, the major contents of low molecular weight compounds, dry extract weight, total polyphenol index are found in brandies not submitted to agitation and with monthly agitation, in similarity to the colour intensity.

A significant effect of the agitation for the extraction is found to the majority of the compounds analyzed in brandy that was aged in chestnut wood, not being this effect so pronounced for the one aged on Limousin oak wood, justifying the necessity of a more frequent agitation of the chestnut wood barrels than to the oak wood barrels during the first months of ageing. However, it will be preferable to effect a monthly agitation for being the modality that induces the biggest enrichment of brandy on analyzed compounds, becoming more speed the ageing.

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RESUMO

Repercussão da agitação da aguardente nas cinéticas de extracção/oxidação e de difusão de compostos extraíveis da madeira em modelo experimental

No presente trabalho é estudado, pela primeira vez, o efeito da agitação da aguardente nas cinéticas de extracção/oxidação e de difusão de compostos de massa molecular baixa da madeira, ao longo dos primeiros dois meses de envelhecimento, em vasilhas de carvalho

Limousin e de castanheiro, sujeitas a queima ligeira ou forte. É observado que o gradiente de concentração dos compostos de massa molecular baixa na aguardente depende da natureza química dos mesmos, da espécie botânica (superior nas aguardentes que contactaram com a madeira de castanheiro) e do nível de queima da madeira (tendencialmente mais elevado na queima forte). Estes aspectos justificam pois a agitação da aguardente logo nos primeiros meses de envelhecimento, sobretudo em vasilhas de madeira de castanheiro e de queima forte. Independentemente da madeira e da queima, a agitação mensal revelou-se a mais eficaz, relativamente ao sistema estático e à agitação após cada amostragem, conduzindo à obtenção de aguardentes com maior extracto seco, maior índice de polifenóis totais e maiores teores de compostos de massa molecular baixa, por favorecer o equilíbrio entre os fenómenos de extracção e de difusão.

RÉSUMÉ

Effet de l'agitation des eaux-de-vie sur la cinétique d'extraction/oxydation et la diffusion des composés extractibles du bois dans le modèle expérimental

Dans ce travail l'effet de l'agitation de l'eau-de-vie dans la cinétique d'extraction/oxydation et de diffusion des composés de faible poids moléculaire du bois a été étudié pour la première fois, pendant les deux premiers mois de vieillissement, dans des fûts de bois de Chêne du Limousin et de Châtaignier ceux ont été soumis à le brûlage léger (QL) et brûlage fort (QF). On a observé un gradient de concentration des composés dans l'eau-de-vie dépendent sur la nature chimique, de l'espèce botanique (supérieure dans les eaux-de-vie qui entrent en contact avec du bois de châtaignier) et du niveau en bois de brûlage (plus élevé dans le brûlage fort). Ces aspects justifient donc l'agitation de l'eau-de-vie pendant les premiers mois du vieillissement, principalement dans les fûts de bois de châtaignier et le brûlage fort. Indépendamment du bois et du niveau de brûlage, de l'agitation mensuelle c'est montré le plus efficace, relativement au système statique et à l'agitation après chaque prélèvement, menant aux eaux-de-vie avec le poids d'extrait sec plus haut, l'index de polyphenols totaux plus élevés et les plus hautes concentrations des composés à faible poids moléculaire, favorisant l'équilibre entre les phénomènes d'extraction et de diffusion.

REFERENCES

Belchior A.P., 1974. Unpublished work.

Belchior A.P., 1995. Programa: Tecnologias de utilização de madeira no envelhecimento de aguardentes e vinhos. Instituto Nacional de Investigação Agrária. Estação Vitivinícola Nacional.

Belchior A.P., Almeida T.G.T., Mateus A.M., Canas S., 2003. Ensaio laboratorial sobre a cinética de extracção de compostos de baixa massa molecular da madeira pela aguardente. *Ciência. Tec. Vitiv.*, **18**, 29-41.

Belchior A.P., Caldeira I., Costa S., Lopes C., Tralhão I., Ferrão A.F.M., Mateus A.M., Carvalho E., 2001. Evolução das características físico-químicas e organolépticas de aguardentes Lourinhã ao longo de cinco anos de envelhecimento em madeiras de carvalho. *Ciência. Tec. Vitiv.*, **16**, 81-94.

Belchior A.P., Carvalho E., 1983. A cor em aguardentes vínicas envelhecidas: método espectrofotométrico de determinação e relação com os teores em fenólicas totais. *Ciência. Tec. Vitiv.*, **2**, 29-37.

Caldeira I., 2004. *O aroma de aguardentes vínicas envelhecidas em madeira. Importância da tecnologia de tanoaria.* 238 p. Tese de Doutoramento, Instituto Superior de Agronomia, Universidade Técnica de Lisboa.

Caldeira I., Belchior A. P., Clímaco M.C., Bruno de Sousa R., 2002. Aroma profile of Portuguese brandies aged in chestnut and oak woods. *Analytica Chimica Acta*, **458**, 55-62.

Canas S., 2003. *Estudo dos compostos extraíveis de madeiras (Carvalho e Castanheiro) e dos processos de extracção na perspectiva do envelhecimento em Enologia.* 303 p. Tese de Doutoramento, Instituto Superior de Agronomia, Universidade Técnica de Lisboa.

Canas S., Belchior A.P., Caldeira I., Spranger M.I., Sousa R.B., 2000a. Evolution de la couleur des eaux-de-vie de Lourinhã au cours des trois premières années de vieillissement. *Ciência. Tec. Vitiv.*, **15**, 1-14.

Canas S., Belchior A.P., Mateus A.M., Spranger M.I., Bruno-de-Sousa R., 2002. Kinetics of impregnation/evaporation and release of phenolic compounds from wood to brandy in experimental model. *Ciência. Tec. Vitiv.*, **17**, 1-14.

Canas S., Belchior A.P., Spranger M.I., Bruno de Sousa R., 2003. High-performance liquid chromatography method for analysis of phenolic acids, phenolic aldehydes and furanic derivatives in brandies. Development and validation. *J. Sep. Sci.*, **26**, 496 -502.

Canas S., Belchior A.P., Spranger M.I., Bruno-de-Sousa R., 2004. Extracção e difusão dos compostos de massa molecular baixa da madeira ao longo do primeiro ano de envelhecimento de uma aguardente *Lourinhã*. *In*: *Actas do 6º Simpósio de Vitivinicultura do Alentejo*, Vol. 2, 121-128.

Canas S., Grazina N., Belchior A.P., Spranger M.I., Bruno-de-Sousa R., 2000b. Modelisation of heat treatment of Portuguese oak wood (Q*uercus* pyrenaica L.). Analysis of the behaviour of low molecular weight phenolic compounds. *Cênciia. Tec. Vitiv.*, **15**, 75-94.

Canas S., Leandro M.C., Spranger M.I., Belchior A.P., 1999. Low molecular weight organic compounds of chestnut wood (*Castanea sativa* L.) and corresponding aged brandies. *J. Agric. Food Chem.*, **47**, 5023-5030.

Canas S., Leandro M.C., Spranger M.I., Belchior A.P., 2000c. Influence of botanical species and geographical origin on the content of low molecular weight phenolic compounds of woods used in Portuguese cooperage. *Holzforschung*, **54**, 255-261.

Doussot F., Jéso B., Quideau S., Pardon P., 2002. Extractives content in cooperage oak wood during natural seasoning and toasting, influence of tree species, geographic location, and single-tree effects. *J. Agric. Food Chem.*, **50**, 5955-5961.

Fengel D., Wegner G., 1989. *Wood chemistry, ultrastructure, reactions*. 612 p. Walter de Gruyter, Berlin.

Guymon J.F., Crowell E.A., 1970. Brandy aging. Some comparisons of American and French oak cooperage. *Wines & Vines*, 23-25.

Miller D.P., Howell G.S., Michaelis C.S., Dickmann D.I., 1992. The content of phenolic acid and aldehyde flavour components of white oak as affected by site and species. *Am. J. Enol. Vit.*, **43**, 333-338.

Mosedale J.R., 1995. Effects of oak wood on the maturation of alcoholic beverages with particular reference to whisky. *Forestry*, **68**, 203-230.

OIV, 1994. Recueil des méthodes internationales d'analyse des boissons spiritueuses, des alcools et de la fraction arômatique des boissons, 311 p., OIV, Paris.

Peng S., Scalbert A., Monties B., 1991. Insoluble ellagitannins in *Castanea sativa* and *Quercus petrae* woods. *Phytochemistry*, **30**, 775-778.

Puech J.-L., 1987. Extraction of phenolic compounds from oak wood in model solutions and evolution of aromatic aldehydes in wines aged in oak barrels. *Am. J. Enol. Vit.*, **38**, 236-238.

Ribéreau-Gayon P., 1970. Le dosage des composés phénoliques totaux dans les vins rouges. *Chim. Anal.*, **52**, 627-631.

Simon F.B., Conde E., Cadahia E., Garcia-Vallejo M.C., 1996. Low-molecular-weight phenolic compounds in wood of Spanish, French and American oak. *J. Sci. Tech. Tonnellerie*, **2**, 13-23.

Singleton V.L., 1995. Maturation of wines and spirits: comparisons, facts, and hypotheses. *Am. J. Enol. Vit.*, **46**, 98-115.

Taransaud J., 1976. Le livre de la tonnellerie. La roue à livres diffusion, Paris.

Vivas N., Glories Y., Bourgeois G., Vitry C., 1996. The heartwood ellagitannins of different oak (*Quercus* sp.) and chestnut species (*Castanea sativa* Mill). Quantity analysis of red wines aging in barrels. *J. Sci. Tech. Tonnellerie*, **2**, 51-75.

Puech J.-L., Goffinet B., 1987. Adjustment of nonlinear models for lignin and its degradation products during the aging of Armagnac. *J. Food Sci.*, **52,** 1280-1282, 1301.