

EFFECT OF HEAT TREATMENT ON THE THERMAL AND CHEMICAL MODIFICATIONS OF OAK AND CHESTNUT WOOD USED IN BRANDY AGEING

EFEITO DO TRATAMENTO TÉRMICO NAS MODIFICAÇÕES TÉRMICAS E QUÍMICAS DAS MADEIRAS DE CARVALHO E DE CASTANHEIRO UTILIZADAS NO ENVELHECIMENTO DE AGUARDENTES

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SUMMARY

The effects of temperature and frequency of moistening during the first phase of the heat treatment (bending phase) on the simultaneous response of different kinds of wood (Portuguese chestnut, Rumanian and American oak wood) used in brandy ageing were studied. The evolution of the wood temperature was measured by K thermocouple probes. The wood extractable compounds (phenolic acids, phenolic aldehydes, coumarins and furanic derivatives) were analysed by HPLC. The results showed that the thermal distribution along the thickness of the stave is influenced by the temperature and frequency of moistening, and also by the botanical species. It was verified that the bending phase is of great importance for the barrel quality not only for its impact on the physical and mechanical properties of the wood but also for its effect on the wood chemical composition.

RESUMO

No presente trabalho são estudados os efeitos da temperatura de vergatura e da frequência do humedecimento durante a primeira fase do tratamento térmico (fase de vergatura) na resposta simultânea, do ponto de vista térmico e químico, de diferentes madeiras (castanheiro português, carvalho americano e carvalho romeno) usadas no envelhecimento de aguardentes víquicas. Para a determinação da temperatura da madeira recorreu-se a termopares do tipo K. Os compostos extraíveis da madeira (ácidos fenólicos, aldeídos fenólicos, cumarinas e aldeídos furânicos) foram analisados por HPLC. Os resultados evidenciam que a distribuição da temperatura ao longo da espessura da aduela e a composição química da madeira são influenciadas pela temperatura de vergatura e pela frequência do humedecimento, bem como pela espécie botânica da madeira. É demonstrado que a fase de vergatura é de extrema importância para a qualidade da vasilha não apenas pelo seu impacto nas propriedades físicas e mecânicas da madeira, mas por constituir também uma etapa determinante da composição química da mesma.

Keywords: oak; chestnut; cooperage; heat treatment; thermal and chemical modifications

Palavras chave: carvalho; castanheiro; tratamento térmico; modificações térmicas e químicas

INTRODUCTION

The wooden barrel quality, the chemical characteristics of brandies, namely low molecular weight extractable compounds that are released from wood to the distilled during the ageing process, and the sensory properties of aged brandies are largely determined by heat treatment protocol (Puech *et al.*, 1985; Artajona *et al.*, 1991; Lavergne *et al.*, 1991; Rabier and Moutounet, 1991; Canas *et al.*, 1999; Belchior *et al.*, 2001; Caldeira *et al.*, 2002).

In European cooperage, the raised barrel is heated over a fire of wood chips with various techniques of spraying or swabbing with water to enable the bending of the staves to the concave shape of a barrel. Then, the barrel is placed again over the fire to heat the inner surface to cause significant toasting in order to modify the structure, the physical properties and the chemical composition of wood, and to confer a distinct character to the brandies aged in it. In the last twenty years several papers have focused on the

study of variables that are relevant for the heat treatment and their effects on the phenolic composition of French oak wood (Chatonnet and Boindron, 1989; Chatonnet, *et al.*, 1989; Sarni *et al.*, 1990; Sarni *et al.*, 1991; Chatonnet, 1995) and American oak wood (Hale *et al.*, 1999; Matricardi and Waterhouse, 1999). More recently the study has been extended to include Portuguese oak wood – *Quercus pyrenaica* Willd. (Canas *et al.*, 2000a). However, the simultaneous response of different kinds of wood, namely oak from different geographical origins and chestnut, to the same temperature and moisture conditions of the heat treatment has never been analysed.

The results of our previous studies have demonstrated that chestnut wood is suited for cooperage (Carvalho, 1998) and has interesting properties for the ageing of brandies (Canas *et al.*, 1999; Belchior *et al.*, 2001; Caldeira *et al.*, 2002). On the other hand, oak wood originated from Eastern Europe (Rumania,

Russia and Hungary) is increasingly used in the European cooperage due to its ease of supply and low price. Nevertheless, to our knowledge, its chemical composition has been investigated only occasionally (Prida and Puech, 2006). Concerning the heat treatment, some work has been done in order to improve and rationalize the heat treatment only with French oak wood (Chatonnet *et al.*, 1993; Chatonnet, 1999), reducing the variability associated with the empiric nature of the process (Towey and Waterhouse, 1996). Furthermore, there are only few studies published on the effects of moistening and heating of the wood, during the bending phase, on the oak wood characteristics (Chatonnet and Boindron, 1989; Sarni *et al.*, 1991; Boeglin *et al.*, 1993; Matricardi and Waterhouse, 1999). Thus, the purpose of this work is to study the effects of temperature and moistening on the temperature profile and on the content of low molecular weight compounds of the different kinds of wood, in order to achieve a better control of the process and, consequently, to improve the quality of aged brandies. Then the phase of bending the staves is

the three kinds of wood and three levels of moistening frequency: H0, H3 and H7 protocols under the same bending temperature - VA (150–155 °C). Two barrels (replications) were used to test each moistening protocol. Experiment 2 was carried out to analyse the effect of the bending temperature, using the three kinds of wood and two levels of bending temperature: VA and VB protocols under the same moistening frequency - H3 (three applications of water). Two barrels (replications) were used to test each temperature protocol.

Wood samples

The heartwood staves of three different kinds of wood were: Portuguese chestnut – *Castanea sativa* Mill. from the North of Portugal (CT), Rumanian oak – *Quercus robur* L. from Lugoj (RO), and American oak – *Quercus alba* L. from Pennsylvania (AO). The staves were seasoned in the open air for three years, at a cooperage industry - JM Gonçalves - in Northern of Portugal. Each barrel integrated two staves of each kind of wood, placed opposite each other, as shown in Figure 1.

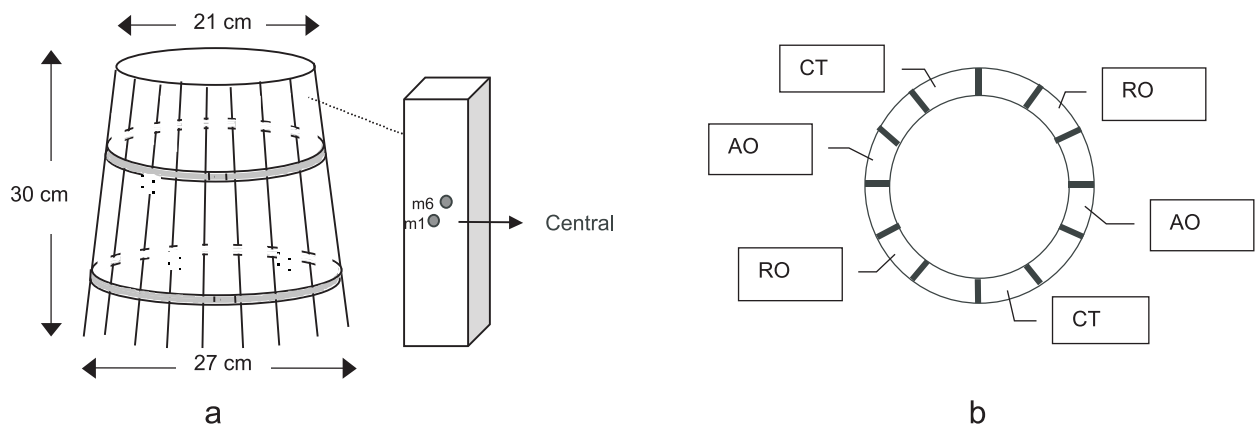


Fig. 1 - Wooden barrel scheme, according to (a) longitudinal and (b) cross sections, and positioning of the thermocouple probes along the stave thickness.

Esquema da vasilha de madeira, segundo os planos (a) longitudinal e (b) transversal, e posicionamento dos termopares na espessura da aduela.

characterized by monitoring, in a pilot-scale, the temperature and the frequency of moistening applied to barrels, integrating simultaneously staves of Portuguese chestnut, American and Rumanian oak woods.

MATERIALS AND METHODS

Experimental design

This study was based on two factorial experiments, involving two factors. Experiment 1 was performed to analyse the effect of the moistening frequency, using

Wood heating procedure

Concerning the fire, its temperature varied between 850 °C and 1000 °C, and the wood offcuts used were from chestnut, Rumanian oak and American oak. The wooden barrel was placed on a stand, 3 cm above the floor level and heated over a fire of wood offcuts. A stainless steel cable was placed around the bottom of the barrel to gradually arch the staves and tighten them to obtain the shape of the barrel. Considering the results of preliminary experiments and the results of our previous study in the laboratory (Canas *et al.*, 2000a), it was decided that the bending phase should last 25 minutes.

In experiment 1, the protocols tested for the moistening process were: no moistening (H0); application of water after 5 minutes, 12 and 19 minutes (H3); application of water after 5 minutes, 7, 10, 13, 16, 19 and 22 minutes (H7). In each application, the water (15 mL) was applied with a sprayer in all directions, to wet the entire internal surface of the barrel, done in conditions comparable to those used industrially. In experiment 2, the temperature protocol used was: progressive increase of the wood temperature up to 150–155 °C (VA) or up to 120–125 °C (VB). A portion of each stave was not heat treated and kept as control group (V0). The temperature was measured with centrally-placed K thermocouple probes (nickel/chromium and nickel/aluminum), which were put inside the six staves at 0.1 cm depth (*m1*) and 0.6 cm depth (*m6*) (Figure 1).

The temperature was recorded by a data acquisition system CR10X with a channel multiplication system AM 416 relay multiplexer (Campbell Scientific, Leicestershire, UK). The measurements were performed with a frequency of 1 Hz (one measurement per second), and the means were recorded in periods of 1 minute.

Wood extraction

After the heat treatment the wood chips of the central part (4 cm long, 4.6 cm width and 0.2 cm thickness from inside) of each stave were obtained by planing and then they were gathered and grounded in a hammer-mill (Wiley, USA). Hydroalcoholic wood extracts were obtained with 50 g of milled wood macerated under rotary agitation for 180 min at 20 °C, with 1000 mL of an ethanol-water solution at 55% v/v adjusted to pH 4.2 with hydrochloric acid (Caldeira *et al.*, 2004). The hydroalcoholic wood extracts were filtered through a glass microfibre filter (Whatman GF/C, UK) in a Büchner funnel.

HPLC analysis

Samples of wood extracts were added with an internal standard (4-hydroxybenzaldehyde, 20 mg/L), filtered through 0.45 µm membrane (Titan) and analyzed by direct injection of 20 µl. Chromatography was performed as described by Canas *et al.* (2003).

Chemicals

Ellagic acid dihydrate, gallic acid monohydrate, vanillic acid, syringic acid, ferulic acid, vanillin, 5-hydroxymethylfurfural, 5-methyl-furfural, furfural, scopoletin, and umbelliferone were from Fluka (Buchs, Switzerland); syringaldehyde, coniferaldehyde, sinapaldehyde and 4-hydroxybenzaldehyde were from Aldrich (Steinheim, Germany). All of them were used as standards without further purification. The solutions were prepared with ethanol/water (55:45 v/v) and were prepared fresh

prior to use.

All solvents used were HPLC gradient grade purchased from Merck (Darmstadt, Germany).

Statistical analysis

The treatment of the data consisted in regression analysis and two-way analysis of variance that were performed using Statistica vs '98 edition (Statsoft Inc., Tulsa, USA).

RESULTS AND DISCUSSION

Effect of moistening on the thermal distribution along the thickness of the stave

In Figure 2, for each kind of wood and each frequency of moistening, the curves show the evolution of

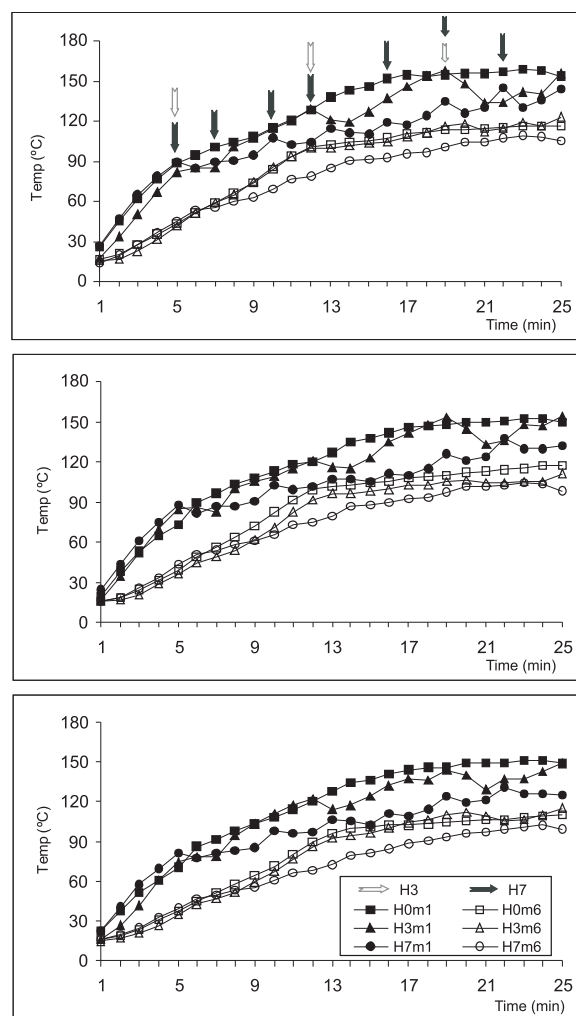


Fig. 2 - Effect of moistening on the evolution of wood temperature along the thickness of the stave. The arrows point the time for moistening.

Efeito do humedecimento na evolução da temperatura da madeira ao longo da espessura da aduela. As setas indicam os momentos de humedecimento.

average temperatures at *m1* and *m6* (means of the temperatures measured in two barrels).

The analysis of the curves shows that the time dependence on the temperature observed in different positions of the stave is similar to that observed in our previous study (Canas *et al.*, 2000a). The temperatures belong to the endothermic phase of wood. Furthermore, the assessment of the moistening frequency effect on the evolution of the temperature in each kind of wood was firstly based on a regression analysis for modelling the curves. As regards to all the studied curves, logarithmic regression [$y = a + bLn(x)$] is the best model for establishing a relationship between the wood temperature and the time, based on the following statistical criteria: the correlation coefficient is higher than 0.95 (high percentage of variance is explained by the regression) and the residual variance due to the adjustment error (lack-of-fit) is not significant. Calculations were carried out by the least-squares method (analysis of variance with statistical F-test, including evaluation of the model lack-of-fit). The results obtained for slope, intercept, standard deviations of the slope and intercept, and correlation coefficient are presented in Table I.

of *Q. alba*. In oak woods there is only significant decrease of the temperature at *m1* between H0 and H7, and between H3 and H7. So, temperature decrease at *m1* caused by H3 is higher in chestnut wood than in oak wood. This fact could be explained by the difference in permeability of the different kinds of wood, higher in chestnut, whose porous structure (width of growth rings, proportion of early wood vessels and fibres) poses lower resistance to water diffusion through the wood (Feuillat and Keller, 1997; Carvalho, 1998). It is also shown that, for all kinds of wood, the decrease of temperatures observed at position *m6* is only significant from H3 to H7, indicating that seven applications of water is the most effective protocol to lower the wood temperature in the deeper portion of the 0.6 cm layer. On the other hand, the frequency of moistening produces less effect on the temperature at *m6* than at positions closer to the inner surface. Concerning all moistening protocols, and for chestnut and American oak woods, the temperature observed at position *m1* is significantly higher than the temperature observed at position *m6*. The temperature difference between *m1* and *m6* with the H0 moistening protocol is higher in chestnut than in the other kinds of wood tested. This

TABLE I

Parameters of the wood temperature curves relative to different moistening protocols
Parâmetros das curvas de temperatura das madeiras relativas aos diferentes protocolos de humedecimento

	Curve	a ^a	SDa ^b	b ^c	SDb ^d	r ^e
CT	H0m1	15.479	1.909	45.789	0.131	0.985
	H3m1	7.288	2.618	45.155	0.176	0.973
	H7m1	24.901	2.113	34.436	0.142	0.970
	H0m6	-7.735	2.661	33.776	0.179	0.964
	H3m6	-11.839	2.645	41.371	0.178	0.967
	H7m6	-4.472	1.974	35.524	0.133	0.973
RO	H0m1	7.7883	3.014	46.318	0.203	0.966
	H3m1	8.0232	2.130	44.290	0.143	0.981
	H7m1	23.738	2.052	32.799	0.138	0.969
	H0m6	-10.456	2.653	40.294	0.178	0.965
	H3m6	-12.102	2.859	38.092	0.192	0.956
	H7m6	-4.1521	2.089	33.022	0.141	0.968
AO	H0m1	5.738	1.875	46.579	0.126	0.987
	H3m1	2.160	2.147	45.098	0.144	0.981
	H7m1	20.417	1.790	32.841	0.120	0.976
	H0m6	-10.165	2.855	37.880	0.192	0.955
	H3m6	-15.641	3.056	39.765	0.206	0.954
	H7m6	-5.262	2.268	32.000	0.153	0.960

^aintercept; ^bstandard deviation of the intercept; ^cslope; ^dstandard deviation of the slope; ^ecorrelation coefficient; m1 - temperature measured at 0.1 cm depth; m6 - temperature measured at 0.6 cm depth; H0 - no moistening; H3 - three applications of water; H7 - seven applications of water.

Secondly, a student's t-test at the significance level $\alpha=0.05$ was used to perform the comparison of the intercepts and the slopes of the different curves (Bouvier, 1994) - Table II. The results shown in Figure 2 and those obtained in all comparisons (Table II) pointed to the continuous and significant decrease of the temperature at *m1* in chestnut wood caused by the increase of the moistening frequency. Matricardi and Waterhouse (1999) reported a similar behavior

could derive from the lower thermal conductivity of the former, probably associated with its higher porosity. However, the temperature difference between *m1* and *m6* with the H3 moistening protocol is lower in chestnut wood than in oak woods. The different behavior of chestnut in the case of H3 could also be justified by the difference in porosity. The material with higher porosity presents higher water absorption and the absorbed water can improve the

TABLE II

Comparison of the wood temperature curves using the student's t-test (moistening effect)
 Comparação das curvas de temperatura das madeiras através do teste t de student (efeito do humedecimento)

Wood	Comparisons		t _{exp} for slope	t _{exp} for intercept
CT	At m1	H0-H3	2.888 (*)	2.528 (*)
		H0-H7	58.730 (*)	3.309 (*)
		H3-H7	47.367 (*)	5.236 (*)
	At m6	H0-H3	30.096 (*)	1.094
		H0-H7	7.844 (*)	0.985
		H3-H7	26.338 (*)	2.232 (*)
	Between m1 and m6	H0	54.155 (*)	7.089 (*)
		H3	15.116 (*)	5.140 (*)
		H7	5.594 (*)	10.159 (*)
RO	At m1	H0-H3	8.169 (*)	0.064
		H0-H7	55.117 (*)	4.374 (*)
		H3-H7	57.767 (*)	5.314 (*)
	At m6	H0-H3	8.392 (*)	0.422
		H0-H7	32.013 (*)	1.867
		H3-H7	21.284 (*)	2.245 (*)
	Between m1 and m6	H0	22.300 (*)	4.543 (*)
		H3	25.844 (*)	5.645 (*)
		H7	1.132	9.525 (*)
AO	At m1	H0-H3	7.723 (*)	1.255
		H0-H7	78.789 (*)	5.663 (*)
		H3-H7	65.187 (*)	6.532 (*)
	At m6	H0-H3	6.700 (*)	1.309
		H0-H7	23.973 (*)	1.345
		H3-H7	30.335 (*)	2.728 (*)
	Between m1 and m6	H0	37.857 (*)	4.655 (*)
		H3	21.228 (*)	4.766 (*)
		H7	4.328 (*)	8.889 (*)

m1 - temperature measured at 0.1 cm depth; m6 - temperature measured at 0.6 cm depth; H0 - no moistening; H3 - three applications of water; H7 - seven applications of water.

(*) indicates a significant difference between t_{experimental} and t_{tabulated}; t_{tab} (98; 0.05)=1.9873

conduction properties of the system. With the H7 protocol, the temperature differences between m1 and m6 in the different kinds of wood are small.

Effect of moistening on the content of low molecular weight compounds of the wood

The analysis of variance reveals that moistening only

affects significantly the content of syringic acid and coniferaldehyde (Table III). Two different responses to the moistening are identified: syringic acid increases with H3 and decreases with H7 indicating that its synthesis is favoured only by a certain quantity of water, while coniferaldehyde presents the opposite behaviour, which demonstrates that three applications

TABLE III

Average concentration of low molecular weight compounds in wood extracts under moistening effect (mg/L, except for coumarins, which are in µg/L)
 Concentração média dos compostos de massa molecular baixa dos extractos de madeira sob efeito do humedecimento (mg/L, excepto cumarinas, em µg/L)

	HMF ^a	furf ^b	5mfurf ^c	ellag ^d	gall ^e	van ^f	syrg ^g	ferul ^h	vanil ⁱ	syrd ^j	cofde ^k	sipde ^l	umb ^m	scop ⁿ	Total
<i>Moistening effect</i>															
	ns	ns	ns	ns	ns	ns	*	ns	ns	ns	*	ns	ns	ns	ns
H0	14.46	40.47	2.76	133.31	51.08	3.92	5.95 a	6.29	2.47	8.53	23.97 b	84.35	0.49	349.30	377.91
H3	14.53	42.29	2.90	119.84	27.24	3.27	9.00 b	4.95	2.24	9.47	16.87 a	68.41	0.58	302.24	321.29
H7	16.77	40.91	2.68	118.29	41.53	3.36	6.91 ab	5.70	2.16	8.38	19.67 ab	68.97	0.77	387.88	335.72
RSD (%)	26-53	27-38	20-53	75-90	149-154	46-69	26-47	41-53	17-40	17-32	33-47	26-43	17-126	128-134	45-48
<i>Botanical species effect</i>															
	ns	**	ns	**	**	**	ns	**	**	ns	**	**	ns	**	**
RO	14.65	38.72 a	2.76	82.40 b	5.87 a	2.65 a	7.18	6.13 b	2.28 b	9.11	24.59 b	81.18 b	0.52	137.71 a	277.67 a
AO	14.20	33.74 a	2.74	37.36 a	4.84 a	1.81 a	6.10	7.91 c	1.80 a	8.79	20.81 b	86.83 b	0.78	881.37 b	227.79 a
CT	16.91	51.22 b	2.84	251.68 c	109.14 b	6.09 b	8.57	2.91 a	2.79 c	8.49	15.10 a	53.72 a	0.54	20.34 a	529.46 b
<i>Interaction Moistening x Botanical species</i>															
	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

H0 - no moistening; H3 - three applications of water; H7 - seven applications of water.

^a5-Hydroxymethylfurfural; ^bFurfural; ^c5-Methylfurfural; ^dEllagic acid; ^eGalic acid; ^fVanillic acid; ^gSyringic acid; ^hFerulic acid; ⁱVanillin;

^jSyringaldehyde; ^kConiferaldehyde; ^lSinapaldehyde; ^mUmbelliferone; ⁿScopoletin.

Means followed by the same letter in a column are not significantly different at the 0.05* or 0.01** level of significance; RSD - relative standard deviation (minimum value - maximum value); ns - without significant difference.

of water are not sufficient to control the rise of the wood temperature in order to avoid the degradation of this compound formed from lignin. Therefore, the results show the important role of the water during the bending phase, not only for the alteration of fibres plasticity and the control of the wood temperature, but also as a reagent on the transformation of wood polymers (Lapierre *et al.*, 1986; Matricardi and Waterhouse, 1999) and their derivatives, although with a differentiated action. The absence of effect on the majority of the analysed compounds could be explained by the great variability associated with the bending operation, expressed by the relative standard deviation. Even so, in the essayed conditions, the H3 protocol presents some advantages, due to its positive

interaction between moistening and wood botanical species.

Effect of bending temperature on the thermal distribution along the thickness of the stave

In Figure 3, for each kind of wood and each bending temperature, the curves display the evolution of average temperatures at *m1* and *m6* (means of the temperatures measured in two barrels).

The assessment of the bending temperature effect on the evolution of the temperature in each kind of wood was also based on a regression analysis. For all of the studied curves, logarithmic regression [$y = a + b \ln(x)$] is the best model for establishing a relationship

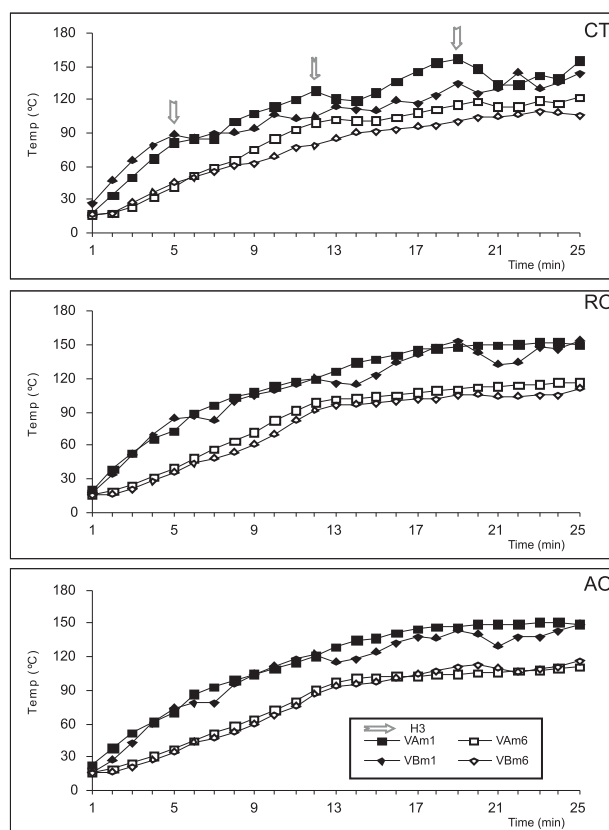


Fig. 3 - Effect of bending temperature on the evolution of wood temperature along the thickness of the stave. The arrows point the time for moistening.

Efeito da temperatura de vergatura na evolução da temperatura da madeira ao longo da espessura da aduela. As setas indicam os momentos de humedecimento.

influence on the content of some important compounds for the brandy overall quality and differentiation, namely furfural, 5-methylfurfural (Canas *et al.*, 2003; Caldeira, 2004) and ellagic acid (Goldberg *et al.*, 1999; Duriez *et al.*, 2001; Canas *et al.*, 2003). The H7 protocol seems to originate more uniform temperature on the wood layer with a thickness of 0.6 cm starting from the inside out, but within a range that should not be sufficient to promote the required chemical alterations. Despite the very significant effect of the botanical species on the content of some compounds, there is no significant

between the wood temperature and the time, based on the statistical criteria referred above.

The results obtained for slope, intercept, standard deviations of the slope and intercept, and correlation coefficient are presented in Table IV.

The results obtained by the student's t-test at the significance level $\alpha=0.05$ were presented in Table V. The results shown in Figure 3 and those of Student's t-test (Table V) demonstrate that the increase of the bending temperature causes a significant increase of the temperature at *m1* in oak wood (American and Rumanian). Chestnut wood responds differently to

TABLE IV

Parameters of the wood temperature curves relative to different bending temperature protocols
Parâmetros das curvas de temperatura das madeiras relativas aos diferentes protocolos de temperatura de vergatura

	Curve	a ^a	SDa ^b	b ^c	SDb ^d	r ^e
CT	VAm1	-4.472	11.446	34.524	0.770	0.973
	VBm1	24.901	2.113	34.436	0.142	0.970
	VAm6	-11.839	2.645	41.371	0.178	0.967
	VBm6	-4.472	1.974	34.524	0.133	0.973
RO	VAm1	8.023	2.130	44.29	0.143	0.981
	VBm1	23.738	2.052	32.799	0.138	0.969
	VAm6	-12.102	2.859	38.092	0.192	0.956
	VBm6	-4.152	2.089	33.022	0.141	0.968
AO	VAm1	-2.160	2.503	45.098	0.168	0.981
	VBm1	20.417	1.790	32.841	0.120	0.976
	VAm6	-15.641	3.056	39.765	0.206	0.954
	VBm6	-5.262	2.268	32.000	0.153	0.960

^aintercept; ^bstandard deviation of the intercept; ^cslope; ^dstandard deviation of the slope; ^ecorrelation coefficient; m1 - temperature measured at 0.1 cm depth; m6 - temperature measured at 0.6 cm depth; VA - progressive increase of the wood temperature up to 150–155 °C; VB - progressive increase of the wood temperature up to 120–125 °C.

TABLE V

Comparison of the wood temperature curves using the student's t-test (bending temperature effect)
Comparação das curvas de temperatura das madeiras através do teste t de student (efeito da temperatura de vergatura)

Wood	Comparisons	t _{exp} for slope	t _{exp} for intercept	
CT	At m1	0.112	2.524 (*)	
	At m6	30.842 (*)	2.232 (*)	
	Between m1 and m6	VA	8.665(*)	0.627
		VB	0.452	10.159 (*)
RO	At m1	57.767 (*)	5.314 (*)	
	At m6	21.284 (*)	2.245 (*)	
	Between m1 and m6	VA	25.844 (*)	5.645 (*)
		VB	1.132	9.525 (*)
AO	At m1	59.225 (*)	7.338 (*)	
	At m6	30.335 (*)	2.728 (*)	
	Between m1 and m6	VA	20.072 (*)	3.413 (*)
		VB	4.328 (*)	8.889 (*)

m1 - temperature measured at 0.1 cm depth; m6 - temperature measured at 0.6 cm depth; VA - progressive increase of the wood temperature up to 150–155 °C; VB - progressive increase of the wood temperature up to 120–125 °C.

(*) – indicates a significant difference between t_{experimental} and t_{tabulated}; t_{tab} (98; 0.05)=1.9873

bending temperature, being its temperature at m1 less dependent on the fire intensity. As reported previously, the response to the fire intensity depends on the anatomical and structural characteristics of the wood (Feuillat and Keller, 1997), as well as on the amount of biopolymers and extractable compounds (Fengel and Wegener, 1989) present.

Regarding the temperatures observed at position m6, there is a significant increase between VB and VA in all kinds of wood, being the highest difference observed in chestnut wood. As for all temperature protocols, the temperature observed at position m1 is significantly higher than the temperature observed at position m6 in American oak. In Rumanian oak the temperature difference between m1 and m6 is only significant with VA protocol. In chestnut wood the differences are not significant. Besides, the difference in temperature between m1 and m6 with the VA protocol is higher in Rumanian oak and lower in chestnut wood (Figure 3 and Table V). The VB

protocol permits higher uniformity of the temperature along the thickness of the stave, especially in chestnut and Rumanian oak.

Effect of bending temperature on the content of low molecular weight compounds of the wood

The bending temperature has a great influence on the content of low molecular weight extractable compounds analysed (Table VI). The total content increases significantly with the lowest bending temperature (VB - temperature up to 120–125 °C) and decreases with the rising of the bending temperature (VA - temperature up to 150–155 °C), as a result of the individual effects.

Individually, similar behavior was observed on HMF, sinapaldehyde, and especially coniferaldehyde, which had a very significant decrease at VA. These results indicate that large amounts of these compounds were formed at 120–125 °C and were volatilized at temperatures over than 150–155 °C. The increase of

TABLE VI

Average concentration of low molecular weight compounds in wood extracts under bending temperature effect (mg/L, except for coumarins, which are in µg/L)

Concentração média dos compostos de massa molecular baixa dos extractos de Madeira sob efeito da temperatura de vergatura (mg/L, excepto cumarinas, em µg/L)

	HMF ^a	furf ^b	5mfurf ^c	ellag ^d	gall ^e	van ^f	syrg ^g	ferul ^h	vanil ⁱ	syrd ^e	cofde ^k	sidp ^l	umb ^m	scop ⁿ	Total
<i>Bending temperature effect</i>															
	**	**	**	**	*	*	**	**	*	**	**	**	**	ns	**
V0	nd	nd	nd	41.34 a	74.08 b	8.45 b	36.06 b	18.45 b	4.34 b	1.30 a	0.35 a	0.70 a	0.10 a	388.26	185.45 a
VB	17.14 b	32.42 b	2.56 b	102.56 b	43.69 a	3.43 a	6.09 a	7.95 a	2.05 a	7.85 b	24.96 c	82.76 b	0.43 b	310.02	333.77 b
VA	14.53 b	42.29 c	2.90 b	119.84 b	27.24 a	3.27 a	9.00 a	4.95 a	2.24 a	9.47 c	16.87 b	68.41 b	0.55 c	291.27	321.27 b
RSD (%)	0-53	0-34	0-53	30-90	141-153	46-133	26-171	41-57	17-154	21-41	23-47	21-43	26-113	114-136	42-104
<i>Botanical species effect</i>															
	ns	ns	ns	**	**	**	**	ns	**	ns	*	ns	ns	**	**
RO	9.63	24.02	1.79	69.20 b	8.18 a	3.30 a	5.79 a	8.78	1.64 a	6.48	16.53 b	53.91	0.37	195.78 a	209.46 a
AO	9.95	23.37	2.11	30.68 a	3.90 a	1.91 a	4.31 a	10.32	1.51 a	6.17	15.00 ab	56.83	0.36	770.06 b	166.83 a
CT	12.91	27.82	2.52	163.85 c	132.93 b	9.94 b	41.04 b	12.25	5.47 b	5.96	10.64 a	41.14	0.35	23.73 a	466.50 b
<i>Interaction Bending temperature x Botanical species</i>															
	ns	ns	ns	**	*	ns	**	**	**	ns	ns	ns	ns	ns	ns

V0 – control group; VA - progressive increase of the wood temperature up to 150–155 °C; VB - progressive increase of the wood temperature up to 120-125 °C.

^a5-Hydroxymethylfurfural; ^bFurfural; ^c5-Methylfurfural; ^dEllagic acid; ^eGallic acid; ^fVanillic acid; ^gSyringic acid; ^hFerulic acid; ⁱVanillin; ^jSyringaldehyde; ^kConiferaldehyde; ^lSinapaldehyde; ^mUmbelliferone; ⁿScopoletin.

Means followed by the same letter in a column are not significantly different at the 0.05* or 0.01** level of significance; RSD – relative standard deviation (minimum value –maximum value); ns – without significant difference; nd – not detected.

HMF under lower temperature effect contradicts the conclusions of Sarni *et al.* (1991) and suggests that this compound proceeds from the hexoses of some polysaccharides of the wood, other than cellulose. The decrease of coniferaldehyde at VA leads us to question the thermal resistance of this aldehyde to temperature higher than 150 °C reported by Sarni *et al.* (1991), and to assume its dependence on other bending conditions. It is interesting to point out the synchronism between the evolution of vanillin and coniferaldehyde (its main precursor), i.e., they present opposite behaviours along with the raise of bending temperature. The concentrations of gallic acid, ferulic acid and vanillic acid decrease with bending temperature intensity, reflecting their low thermal resistance. As for the first two compounds, there is a significant interaction between the temperature and the wood botanical species. The bending temperature favoured the formation of ellagic acid, syringaldehyde, umbelliferone, furfural and 5-methylfurfural, mainly between V0 and VB. The absence of significant difference of ellagic acid content between VA and VB could indicate low effect of this range of temperatures on the hydrolyzable tannins degradation, since this compound presents high fusion point (> 450 °C). Under bending effect, the ellagic acid became the most abundant compound of the wood and gallic acid became less important, which could derive from higher degradation of elagitannins (Rabier and Moutounet, 1991; Chatonnet, 1995) than from gallotannins (Canas *et al.*, 2004) and the thermal sensitivity of gallic acid (Rabier and Moutounet, 1991). The syringaldehyde is produced by lignin degradation and/or by oxidation

of sinapaldehyde, presenting high thermal stability (Sarni *et al.*, 1991). The umbelliferone seems to have higher thermal resistance than scopoletin. The continuous increase of furfural is a consequence of a higher degradation of hemicelluloses than the degradation of this furanic derivative at temperature lower than 165 °C (Sarni *et al.*, 1991; Chatonnet *et al.*, 1989; Boeglin *et al.*, 1993). Syringic acid has a significant decrease at VB and a slight increase at VA, along with the alteration of syringaldehyde, which is its main precursor (Puech *et al.*, 1984). The evolution of this phenolic acid depends significantly on the wood botanical species. The wood botanical species have also a very significant influence on the total content of phenolic acids and vanillin, which present the highest values in chestnut and the lowest in American oak, as already observed in non-toasted woods (Canas *et al.*, 2000b). The ellagic acid concentration allows differentiating all of the studied woods, which explains the very significant interaction between the bending temperature and the botanical species. The lower concentration of coniferaldehyde in chestnut than in oak woods is also a prevailing characteristic of the non-toasted woods (Canas *et al.*, 2000b). American oak wood presents the highest level of scopoletin and the chestnut wood presents the lowest one, as observed in non-toasted woods (Canas *et al.*, 2000b). So, the extreme abundance of scopoletin in American oak, largely noticed in the literature as a phenolic marker of this wood, is not significantly affected by the first phase of the heat treatment of the wood. The differences in the amounts of lignin derivatives between the different kinds of wood could derive from the anatomical and structural

characteristics of each wood (Feuillat and Keller, 1997) and/or from the wood chemical specificities (Fengel and Wegener, 1989; Canas *et al.*, 2000b; Prida and Puech, 2006), namely the contents of soluble tannins, gallic acid and ellagic acid that can determine their response to bending temperature, as well as the permeability and the delignification process of the wood (Puech and Sarni, 1990).

CONCLUSIONS

This study provides, for the first time, specific information about the simultaneous thermal and chemical modifications of some Portuguese chestnut, American and Rumanian oak wood caused by the bending conditions during the barrel cooperage. In the essayed conditions, moistening frequency, bending temperature and kind of wood were shown to affect the time evolution profiles of the temperature at different positions of the staves. Concerning the thermal effect, from the tested protocols, three applications of water are the most appropriate for the chestnut wood studied, while seven applications of water are the most suitable for the oak woods analysed. From the chemical point of view three applications of water are preferable in the essayed conditions. Regarding the temperature, it is preferable to use lower temperatures (120-125 °C) during the bending phase in order to obtain higher uniformity of the temperature along the thickness of the stave and the most positive chemical effect. Both moistening and heating play important roles in the physical and chemical modifications of the wood during the bending phase of the heat treatment. As for the latter, alteration induced in the hemicelluloses and lignin derivatives are relevant. So, the bending phase is of great importance for the barrel quality not only for its impact on the physical and mechanical properties of the wood but also as a determinant step on the wood chemical composition during the heat treatment.

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