

**MODELISATION OF HEAT TREATMENT OF
PORTUGUESE OAK WOOD (*Quercus pyrenaica* L.).
ANALYSIS OF THE BEHAVIOUR OF LOW
MOLECULAR WEIGHT PHENOLIC COMPOUNDS.**

**MODELIZAÇÃO DO TRATAMENTO TÉRMICO DE MADEIRA DE
CARVALHO PORTUGUÊS (*Quercus pyrenaica* L.). ANÁLISE DO
COMPORTAMENTO DOS COMPOSTOS FENÓLICOS DE BAIXO
PESO MOLECULAR.**

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(Manuscrito recebido em 10.10.00. Aceite para publicação em 28.11.00)

SUMMARY

The heat treatment is of primary significance for the barrel quality. In the last fifteen-years many papers have been focused on the effects of heat treatment on the phenolic composition of French and American oak woods, but the oak species grown in Portugal traditionally used in Portuguese cooperage have never been studied. In this study we characterised the toasting levels with temperature and time by modelling, in laboratory, the heat treatment applied to barrels of a Portuguese oak wood (*Quercus pyrenaica* L.) during coopering. The effect on some phenolic acids and aldehydes was assessed by HPLC. In all toasting levels and throughout the depth, it was found that the best curve to fit the data was given by a 5th degree polynomial equation. The analysis of phenolic composition indicates that the optimization of this technological operation, in order to maximize the quality of the wood barrels, implies the control of both temperature and time. The results also show that the time has a secondary role in comparison with temperature. The phenolic fraction trends to increase with toasting temperature over time. These effects essentially derive from the increment of ellagic acid and phenolic aldehydes contents, as a consequence of ellagitannins and lignins degradations respectively. Except for ferulic acid, it was observed a decrease of phenolic compounds contents from the surface layer (0 to 2 mm) to the depth layer (2 to 4 mm) of the stave. This could be due to the higher temperature in the surface layer, which certainly causes more intense degradation of the wood constituents, as well as the modification of wood physical and structural properties. Ellagic acid has a more pronounced

decrease than the lignin breakdown products throughout the depth, which could indicate that ellagitannins are more affected than lignins.

INTRODUCTION

According to the Dec.-Lei n° 323/94, of 29 December, that approves the statute of the Delimited region of “Lourinhã”, the raw distilled must be stored in oak barrels for a minimum of 24 months.

Wood is an essential element in the ageing of brandies. During the ageing process the organic extractable compounds, namely those of low molecular weight, are released from the wood to the distilled and contributes to the physico-chemical characteristics and sensorial properties of the brandy (Guymon and Crowell, 1968; Bricout, 1971; Puech *et al.*, 1985; Salagoity *et al.*, 1987; Artajona *et al.*, 1990; Lavergne *et al.*, 1990; Rabier and Moutounet, 1990; Viriot *et al.*, 1992; Viriot *et al.*, 1993; Moutounet *et al.*, 1995; Masson *et al.*, 1997).

The extraction of compounds from oak barrels into brandy depends both on the pool of potential extractable compounds originally present in the oak and on the ageing conditions.

The qualities of the oak used for cooperage can be affected by a large number of interdependent factors, that have been identified as being responsible for its pool of potential extractives: the botanical species and the geographical origin of the oak wood, that includes the forest environment and management, and the age of trees (Guymon and Crowell, 1970; Rous and Alderson, 1983; Scalbert *et al.*, 1986; Lavergne *et al.*, 1990; Keller, 1992; Miller *et al.*, 1992; Sefton *et al.*, 1993; Marco *et al.*, 1994; Scalbert and Lapierre, 1994; Mosedale and Ford, 1996; Mosedale and Savill, 1996; Canas *et al.*, 2000), the seasoning or drying of the staves (Pontallier *et al.*, 1982; Francis *et al.*, 1992; Sefton *et al.*, 1993; Chatonnet *et al.*, 1994; Mosedale and Ford, 1996; Vivas and Glories, 1996; Vivas *et al.*, 1997; Hale *et al.*, 1999), and the technological operations on barrel making process, namely the heat treatment (Guymon and Crowell, 1970; Rous and Alderson, 1983; Nishimura *et al.*, 1983; Chatonnet and Boidron, 1989; Artajona *et al.*, 1990; Lavergne *et al.*, 1990; Rabier and Moutounet, 1990; Sarni *et al.*, 1990a, b, c; Francis *et al.*, 1992; Chatonnet *et al.*, 1993; Baldwin, 1995; Mosedale and Ford, 1996; Martinez *et al.*, 1996; Towey and Waterhouse, 1996; Hale *et al.*, 1999; Goldschmidt, 1999; Matricardi and Waterhouse, 1999).

Among these factors the heat treatment is of primary significance for the barrel quality (Chatonnet and Boidron, 1989; Francis *et al.*, 1992; Mosedale, 1995; Singleton, 1995).

There are important differences in coopering methods between French crafting

using fire and American techniques using steam heat for bending staves. 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 bending the staves to the concave shape of a barrel without splitting (Sarni *et al.*, 1990c; Chatonnet *et al.*, 1994; Belchior, 1995). Then, the barrel is placed back over the fire to heat the inner surface to cause significant toasting in order to modify the structure, the physical properties (Biermann *et al.*, 1987; Bourgois and Guyonnet, 1988; Fengel and Wegener, 1989) and the chemical composition of wood, namely the low molecular weight compounds, and to transmit a distinct character to the brandies aged in it.

The designations of light, medium and strong toast are usual terms for the toasting level, but there are no industry standards for them. Between and within cooperages there can be variations in the execution of this operation that may have important repercussion on its result (Chatonnet e Boidron, 1989; Artajona *et al.*, 1990; Cantagrel *et al.*, 1992; Chatonnet *et al.*, 1993; Baldwin, 1995; Chatonnet, 1999).

In fact, the toasting level is controlled by the cooper who assesses it by visual and olfactive appreciation of the wood and by feeling the temperature of the barrel. These procedures do not provide accurate measures of the extent of toasting, but they are actually the only ones available in a cooperage. So, barrels of the same toasting level can vary considerably.

According to Fengel and Wegener (1989) it is not the temperature alone which causes changes in the wood constituents; there are additional factors that can influence thermal degradation processes, such as time of treatment, atmosphere, pressure and water content.

In the practice, there are several conditioning factors that determine the thermal parameters indicated above, such as the air circulation (the volume of air that can enter through the bottom of the barrel), the fire size, its maintenance level and frequency, and the type and frequency of moistening (Chatonnet and Boidron, 1989; Sarni *et al.*, 1990c; Cantagrel *et al.*, 1992; Matricardi and Waterhouse, 1999).

In the last fifteen-years many papers have been focused on the effects of heat treatment on the phenolic composition of French and American oak woods, but the oak species grown in Portugal traditionally used in Portuguese cooperage have never been studied.

The potentialities for cooperage of oak species grown in Portugal, traditionally used in the ageing of brandies, were only investigated on the project PAMAF 2052, that has analysed the chestnut and Portuguese oak woods in comparison with French and American oaks. The first results obtained revealed the qualities of Portuguese oak for cooperage (Carvalho, 1998), as well as its interest for

the ageing of brandies (Belchior *et al.*, 1998).

The purpose of the present work is to study the heat treatment parameters - temperature and time - and to attempt to understand the mechanisms involved, in order to achieve better control of it. Thus, we characterised the toasting levels by modelling, in laboratory, the heat treatment applied to barrels of a Portuguese oak wood (*Quercus pyrenaica* L.) during coopering. We also studied the behaviour of some phenolic compounds during this operation.

MATERIAL AND METHODS

Materials

Wood samples

The heartwood staves were seasoned in the open air, at a cooperage industry - JMA Gonçalves in the Northern of Portugal. Their anatomical identification was verified (Carvalho, 1998).

For this study a single stave of Portuguese oak - *Quercus pyrenaica* L. (Carvalho, 1998), was used to prepare eighteen wood pieces, with 60 mm long, 35 mm width, and 22 mm thickness.

Standards

Ellagic acid dihydrate (ellag), gallic acid monohydrate (gall), vanillic acid (van), syringic acid (syrg), ferulic acid (ferul), vanillin (vanil), were purchased from Fluka; syringaldehyde (syrd), coniferaldehyde (cofde), sinapaldehyde (sipde) and 4-hydroxybenzaldehyde, were purchased from Aldrich. All of them were used as standards without further purification. Solutions were prepared with ethanol 10% (v/v).

Methods

Experimental design

This study was based in a factorial experiment, with three factors: temperature or toasting level (light - QL, medium - QM and strong - QF), time (10, 25 and 45 minutes) and depth (0-2 mm and 2-4 mm), with two replications.

Wood toasting procedure

In laboratory toasting experiments, an electric plate (Combiplac) placed vertically was used as heat source. In each toasting level, six wood pieces were randomly placed in six windows made in a plate (400 mm long and 200

mm width) of refractory material (Skamolix-S-1100), three centimetres distant from the heat source. Two pieces were used for each length of time (10, 25 and 45 minutes).

Temperature was measured with K thermocouple probes (nickel/chromium and nickel /aluminium), which were placed at the heated surface, 1, 2, 4 and 6 mm depth. The temperature was recorded by a data acquisition system CR10X with a channel multiplication system AM 416 relay multiplexer (Campbell Scientific, Leicestershire, UK). This type of probe is especially suitable to this measurement because the sensor area is quite small and responds quickly to variation of temperature.

The measurements were performed with a frequency of 1 Hz (one measurement per second), and the means were recorded in periods of one minute.

After toasting, the wood pieces were cut into layers: one represents the wood at 0 to 2 mm (surface layer) and the other represents the wood at 2 to 4 mm (2 mm depth) from the surface.

The 2-mm-thick pieces of wood were then grounded in a hammer-mill (Wiley) and the corresponding wood powder was weighed.

Wood moisture

The wood powder moisture was determined in a moisture analyser (Mettler LJ 16), 12,5 min at 100 °C.

Wood extraction

Maceration of wood powder (1g) was carried out under rotary agitation for 180 min at 20 °C, with 20 ml of an ethanol-water solution at 55% v/v adjusted to pH 4,2 with hydrochloric acid, as described by Caldeira *et al.* (1996). The wood extracts were filtered through a glass microfibre filter (Whatman GF/C) on a Büchner funnel.

Analysis of low molecular weight phenolic compounds by High Performance Liquid Chromatography

Samples of wood extracts were added with an internal standard (4-hydroxybenzaldehyde, 20 mg/l), filtered through 0,45 µm membrane (Titan) and analysed by direct injection of 20 µl.

HPLC separations were performed using the chromatographic conditions already described in Canas *et al.* (1999).

Identification of chromatographic peaks

The identification of chromatographic peaks was made by comparison of their retention times and UV-Vis spectra with those of external standards (Canas *et al.*, 1999).

Statistical analysis

The variance analysis and part of the regression analysis were performed using Statgraphics v.5 (STSC inc., Rockville, USA).

RESULTS AND DISCUSSION

Characterisation of the thermal parameters

Preliminary essays were carried out to analyse the following aspects: regulation of the heat source and the corresponding wood surface temperature, stabilisation of the heat source temperature for each toasting level, temperature evolution profile with time, variation of the wood surface temperature as a function of wood pieces location in the refractory plate.

It was observed that the placement of wood pieces in the refractory plate had a considerable influence in the wood temperature during the heat treatment. This heterogeneity probably derives from the effect of the refractory walls on the radiant energy, the effect of air circulation on the convection heat transfer (Holman, 1989) and the heterogeneous heating of the electric plate used as heat source.

Thus, in the definitive essays we decided to randomise the wood pieces positions, using a table of random numbers (Ractliffe, 1967). The results obtained were the average of values from two wood pieces (two replications). In each toasting level the thermal parameters were controlled and its characteristics are presented in Table I.

TABLE I

Characteristic parameters of the different toasting levels
Parâmetros característicos dos diferentes níveis de queima

	Light toasting (QL)	Medium toasting (QM)	Strong toasting (QF)
Heat source temperature (°C)	± 250	± 300	± 350
Wood surface temperature (°C)=y	26 - 132	27 - 178	71 - 237
Adjusted model	Polynomial 5 th degree		
Equation coefficients	$y=ax^5+bx^4+cx^3+dx^2+ex+f$		
a	0.000006	0.000009	0.000006
b	-0.000746	-0.001178	-0.000822
c	0.037526	0.058474	0.042598
d	-0.923780	-1.402022	-1.096177
e	12.48896	18.21520	16.51391
f	29.84952	33.31069	78.42760
r ²	0.9802	0.9808	0.9959

All of the wood surface temperature corresponds to the endothermic phase of wood - drying level - in which occurs damages of its structure, conversion of the components and gaseous degradation products. The exothermic phase of wood - combustion or pyrolysis - begins at temperatures of more than 270 °C (Fengel and Wegener, 1989).

Figure 1 shows the surface temperature profiles for light, medium and strong toasted wood. A “best fit” line was drawn through the data points by a regression analysis. It was found that the best curve to fit the data, in all toasting levels, was given by a 5th degree polynomial equation (Table I).

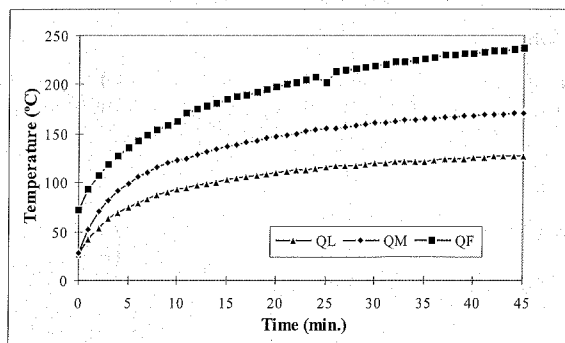


Fig. 1 - Evolution profile of inner surface temperature for light (QL), medium (QM) and strong (QF) toasted wood.

Evolução da temperatura da superfície interna da madeira na queima ligeira (QL), média (QM) e forte (QF).

The shape of the curves is similar: they start out with a strong slope (0 to 10 minutes), followed by a slight slope (between 10 and 25 minutes) and then start to flatten out towards the end of the heating process (25 to 45 minutes). The observed kinetics seems to imply a three-stage process, as reported by Hale *et al.* (1999): during a short initial length of time the heat transfer occurs very rapidly, because the temperature gradient is very large, in a second period the heat transfer still rapid but the increasing of wood temperature is more slow, and in the final period, the longest one, the wood temperature is higher but trends to be stable.

The results presented in Table II confirm that, for each toasting level, a high percentage of the total variance is explained by the regression, which has a calculated F higher than the Snedecor's F at 99,5% (3,35). The residual variance due to the adjustment error (lack-of-fit) is not significant in any case, which is shown by a calculated F lower than the Snedecor's F at 99,5% (1,98).

TABLE II

Variance analysis of the regression for different toasting levels
Análise de variância da regressão para os diferentes níveis de queima

Variation Source	SS	df	MS	F
<i>Light toasting (QL)</i>				
Regression	77513.73	5	15502.74	1308.66
Residual	1563.71	132	11.85	
pure error	1435.10	92	15.60	
lack-of-fit	128.61	40	3.22	0.21
Total	79077.44	137	577.21	
<i>Medium toasting (QM)</i>				
Regression	153564.82	5	30712.96	1344.87
Residual	3014.50	132	22.84	
pure error	2672.89	92	29.05	
lack-of-fit	341.61	40	8.54	0.29
Total	156579.32	137	1142.92	
<i>Strong toasting (QF)</i>				
Regression	222548.58	5	44509.72	6408.40
Residual	916.81	132	6.95	
pure error	699.76	92	7.61	
lack-of-fit	217.05	40	5.43	0.71
Total	223465.39	137	1631.13	

SS - sum of squares, df - degrees of freedom, MS - means squares

The evolution profile of the wood temperature in different layers throughout the depth (figure 2) follows the same curve, but it is evident the softening of the temperature along with the depth. This phenomenon seems to be governed by the heat conduction within the wood (there is an energy transfer from the high-temperature region to the low-temperature region), which is slower than the heat transfer between the heat source and the wood surface (Holman, 1989). It can, therefore, be concluded that heat conduction is the rate-controlling mechanism of the heat treatment effect.

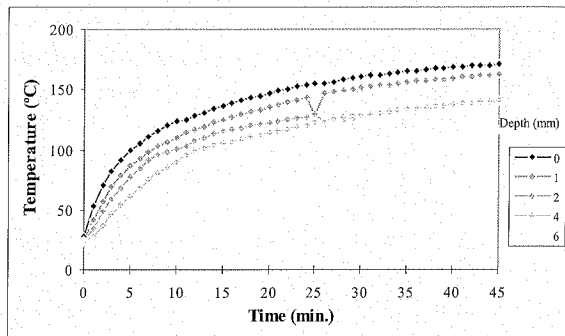


Fig. 2 - Temperature profile through the depth in medium toasted wood.
Perfil da temperatura ao longo da profundidade da madeira na queima média

The variation occurred in the temperature of 2mm depth (figure 2) was due to a little dislocation of the corresponding thermocouple.

Changes on the low molecular weight phenolic compounds

This selection of compounds (phenolic acids and aldehydes) was used to reflect the changes taking place in the wood extractable constituents during the heat treatment, which have a great influence on the sensorial properties of brandies. In fact, several studies (Reazin, 1981; Nishimura *et al.*, 1983; Puech *et al.*, 1984; Puech *et al.*, 1985; Rabier and Moutounet, 1990; Sarni *et al.*, 1990a,b; Monties, 1992) take us to accept unquestionably that one of the most characteristic aspects of ageing in oak barrels is the diffusion from the wood of phenolic compounds derived from lignin degradation.

Figure 3 shows the HPLC chromatograms of untoasted wood and medium toasted wood. Peak identification is shown in Table III.

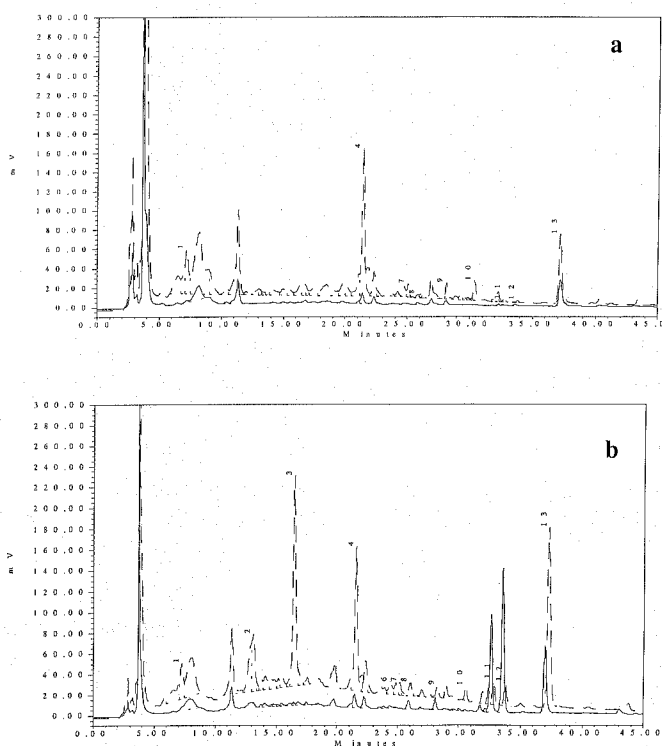


Fig. 3 - HPLC chromatograms of (a) untoasted wood and (b) medium toasted wood.

Detection: top tracing from 280 nm and bottom tracing from 320 nm.

Cromatogramas HPLC de (a) madeira não quimada e (b) madeira sujeita a queima média.

Detecção: 280 nm (tracejado) e 320 nm (cheio).

TABLE III

Retention times, spectral characteristics (maximum absorption wavelength) and identification of the chromatographic peaks

Tempos de retenção, características espectrais (comprimento de onda de absorção máxima) e identificação dos picos cromatográficos

Peak n°	Retention time (min) [§]	λ max (nm)		Identification
1	7,19 ± 0,15	271		Gallic acid (gall)
4	20,81 ± 0,37	221	285	4-hydroxybenzaldehyde
5	22,09 ± 0,67	262	295	Vanillic acid (van)
7	24,99 ± 1,05	276		Syringic acid (syrg)
8	25,08 ± 0,57	238	280 - 309	Vanillin (vanil)
9	27,73 ± 0,61	238	309	Syringaldehyde (syrd)
10	30,68 ± 1,04	236	296 - 323	Ferulic acid (ferul)
11	32,50 ± 0,58	243	306 - 342	Coniferaldehyde (cofde)
12	33,33 ± 0,85	246	347	Sinapaldehyde (sipde)
13	39,06 ± 1,49	252	365	Ellagic acid (ellag)

[§]x ± SD (mean ± standard deviation)

The results of the variance analysis of untoasted wood (Table IV) indicate that there is no significant effect of the depth on the phenolic acids and phenolic aldehydes contents. It means that the studied wood is homogeneous in this layer and, therefore, the chemical changes observed after the heat treatment are only due to this operation.

TABLE IV

Content of phenolic compounds in Portuguese untoasted oak wood extracts (concentrations in mg/L)

Teores de compostos fenólicos nos extractos de carvalho nacional não queimado (mg/L)

		gall	van	syrg	ferul	ellag	vanil	syrd	cofde	sipde	Total
<i>Depth</i>		<i>ns</i>	<i>ns</i>	<i>ns</i>	<i>ns</i>	<i>ns</i>	<i>ns</i>	<i>ns</i>	<i>ns</i>	<i>ns</i>	<i>ns</i>
0 - 2 mm	<i>x</i>	28,89	5,08	4,09	11,72	63,01	0,35	1,06	(0,11)	0,39	114,71
	<i>SD</i>	4,874	0,871	0,090	0,676	5,419	0,017	0,037	0,011	0,036	11,828
2 - 4 mm	<i>x</i>	25,63	4,41	4,18	11,33	62,46	0,27	1,07	0,16	0,33	109,85
	<i>SD</i>	2,579	0,454	0,273	0,363	1,014	0,020	0,054	0,055	0,048	1,315
0 - 4 mm	<i>x</i>	27,26	4,75	4,13	11,53	62,74	0,31	1,07	0,13	0,36	112,28
	<i>SD</i>	3,698	0,686	0,174	0,046	0,039	0,496	0,042	0,052	3,199	7,422

x = mean of 2 values, *SD* = standard deviation, *ns* = without significant effect, () indicates value < quantification limit of the chromatographic method.

Its important to point out the predominance of the phenolic acids, namely the ellagic acid (56%) and the gallic acid (24%), in comparison with the phenolic aldehydes (2%). This result is in agreement with the observations made by Vivas *et al.* (1996) and by Canas *et al.* (2000).

Temperature effect

The variance analysis (Table V) shows a very significant effect of the toasting temperature on the total content of phenolic compounds. As the temperature rises its amount increases, as a balance of the individual effects. This fact possibly derives from the availability increase of some soluble compounds proceeding from the wood constituents degradation, such as tannins and lignins, as well as the increase in wood permeability and the better access of solvents to wood extraction sites caused by the fragmentation of cell structures and reorganisation of lignocellulose network (Rabier and Moutounet, 1990; Sarni *et al.*, 1990a,b).

TABLE V

Effect of the temperature and the time of toasting on the content of phenolic compounds in Portuguese oak wood extracts (concentrations in mg/L)

Efeito da temperatura e do tempo de queima nos teores de compostos fenólicos de extractos de carvalho nacional (mg/L)

		gall	Van	syrg	ferul	ellag	vanil	syrd	cofde	sipde	Total
Temperature effect		**	**	**	**	**	**	**	**	**	**
<i>Light toasting (QL)</i>	x	25,73c	7,33b	5,21a	9,77b	94,75a	0,71a	1,02a	0,57a	1,34a	146,43a
	SD	6,815	1,558	0,448	1,918	10,019	0,306	1,046	0,765	1,335	11,472
<i>Medium toasting (QM)</i>	x	20,66b	4,88a	4,57a	9,18b	126,12b	1,35b	1,97a	7,17b	16,70a	192,61b
	SD	7,872	0,828	0,708	1,512	35,625	0,591	0,939	7,070	18,115	55,748
<i>Strong toasting (QF)</i>	x	7,91a	5,22a	7,68b	6,41a	160,25c	1,56b	5,49b	13,47c	43,13b	251,12c
	SD	6,339	1,681	4,012	2,862	46,244	0,720	3,588	8,463	30,522	78,157
Time effect		**	ns	ns	*	**	ns	**	ns	*	**
<i>10 min.</i>	x	23,17b	5,38	4,87	9,80b	99,90a	0,95	1,39a	3,53	8,23a	157,22a
	SD	3,698	1,264	0,708	1,857	25,865	0,356	0,818	5,467	13,933	40,545
<i>25 min.</i>	x	19,05b	6,18	5,80	8,08a	130,45b	1,28	2,89ab	8,08	23,76ab	205,56b
	SD	3,698	1,491	2,991	2,144	41,291	0,860	2,981	8,992	29,175	68,673
<i>45 min.</i>	x	12,07a	5,88	6,79	7,48a	150,78c	1,39	4,20b	9,61	29,17b	227,38b
	SD	3,698	2,368	3,350	3,151	45,214	0,642	3,611	8,968	30,552	78,623

x = mean of 12 values, SD = standard deviation. Means followed by the same letter in a column are not significantly different at 0,05* or 0,001 significance, ns = without significant difference

Different evolutions were observed according to the nature of the molecule. It is remarkable the increasing of ellagic acid along with the temperature, which probably results from the degradation of ellagitannins (Rabier and Moutounet, 1990; Sarni *et al.*, 1990a; Viriot *et al.*, 1993; Chatonnet, 1995; Matricardi and Waterhouse, 1999). The accumulation of ellagic acid in wood may also be a consequence of its high fusion point, that is higher than the observed temperatures, even in the strong toasting (Sarni *et al.*, 1990). Even in toasted wood, ellagic acid seems to be the most abundant compound (64%) within the analysed fraction.

The regular decreasing of gallic acid content with toasting intensity could be

explain by its thermal sensibility, as stated by many authors (Rabier and Moutounet, 1990; Chatonnet, 1995; Martinez *et al.*, 1996; Matricardi and Waterhouse, 1999).

The vanillic acid content decreases significantly from QL to QM, and increases slightly at QF. According to Puech *et al.* (1984), this last increment could be due to the oxidation both of vanillin and other guaiacylpropane units.

The syringic acid content presents a similar trend, with a slight decrease from QL to QM and a significant increase in QF, along with the increase of syringaldehyde, which is its main precursor (Puech *et al.*, 1984).

We observed a continuous decrease of ferulic acid content, which is very significant from QM to QF, as a consequence of its decarboxilation and thermal degradation under toasting effect (Chatonnet, 1995).

As the temperature increases (from QL to QF) the phenolic aldehydes concentrations rise, but their evolution patterns are different. It is evident the increasing importance of sinapaldehyde and coniferaldehyde contents at QF, becoming respectively the second (17%) and the third (5%) most important compounds of the phenolic fraction studied. The accumulation of syringaldehyde and, especially, of sinapaldehyde are closely related with their high thermal stability (Chatonnet *et al.*, 1989; Rabier and Moutounet, 1990; Sarni *et al.*, 1990a,b; Chatonnet, 1995; Canas *et al.*, 1999).

Particular attention must be paid to vanillin, the major flavour-active product of lignin breakdown (Francis *et al.*, 1992), whose content increases along with the temperature. This effect is accentuated by time, as observed by Rabier and Moutounet (1990).

The highest levels of extractable compounds were observed in strong toasted wood. These results contrast with those obtained by Sarni *et al.* (1990a,b), Chatonnet (1995) and Hale *et al.* (1999), probably because the differences in wood characteristics and the other conditions of heat treatment.

Time effect

The variance analysis (Table V) confirms the importance of the time as a conditioning element on the differentiation of wood phenolic composition by the heat treatment. Consequently, time must be considered as a toasting defining parameter, but since it does not affect all of the analysed compounds, we can conclude that it has a secondary role in comparison with temperature. Sarni *et al.* (1990c) pointed out similar conclusion.

It is noted a significant increase of ellagic acid content with the toasting time, that results in an accentuation of the temperature effect, as observed by Sarni

et al. (1990a,b). The increasing of syringaldehyde and sinapaldehyde amounts is also significant but less pronounced.

Concerning the phenolic aldehydes, it is interesting to verify that their contents increase gradually and similarly with the toasting time: there is a notorious difference between 10 and 45 minutes, while the length of 25 minutes can not be distinguished from the others.

In a general point of view the phenolic fraction trends to increase with time. Finally, increasing the duration of heat treatment resulted in an acceleration of these degradation phenomena, as observed in Limousin oak by Sarni *et al.* (1990a,b), and in different French and American oaks by Mosedale and Ford (1996).

There is no significant interaction between temperature and time, except for syringic acid, ellagic acid and syringaldehyde.

Depth effect

The variance analysis (Table VI) shows that the compounds present higher contents in the surface layer. This is mainly due to the higher temperature in this layer (Figure 2), which certainly causes more intense degradation of the wood constituents, as well as the modification of wood physical and structural properties.

TABLE VI

Content of phenolic compounds in Portuguese toasted oak wood extracts as a function of depth (concentrations in mg/L)

Teores de compostos fenólicos nos extractos de carvalho nacional queimado (mg/L) em função da profundidade

	gall	van	syr	ferul	ellag	vanil	syrde	cofde	sipde	Total
<i>Depth effect</i>	<i>ns</i>	<i>ns</i>	<i>ns</i>	<i>ns</i>	*	<i>ns</i>	<i>ns</i>	<i>ns</i>	<i>ns</i>	<i>ns</i>
0 - 2 mm	x 19,10	6,13	6,28	8,33	136,87 b	1,35	2,91	7,92	21,55	210,43
	SD 11,889	1,929	2,862	3,044	45,366	0,679	2,852	8,223	24,190	67,328
2 - 4 mm	x 17,10	5,49	5,36	8,57	117,22 a	1,06	2,74	6,22	19,23	183,01
	SD 8,470	1,549	2,459	2,095	39,019	0,629	3,044	8,287	29,311	70,739

x = mean of 18 values, SD = standard deviation. Means followed by the same letter in a column are not significantly different at 0,05 or 0,001** level of significance, ns = without significant difference.*

Ellagic acid has a more pronounced decrease than the lignin breakdown products throughout the depth, which could indicate that ellagitannins are more affected than lignins. So, changes in composition take place throughout the thickness of wood also depending upon the thermal stability of the precursors of the various extractable compounds.

These results are in agreement with those obtained by Moutonet *et al.* (1992), Chatonnet (1995) and Hale *et al.* (1999).

Differences in extractable compounds could not be simply explained by different heat treatments. Different woods may respond differently to identical treatments (Pontallier *et al.*, 1982; Chatonnet *et al.*, 1989; Mosedale, 1995; Mosedale and Ford, 1996). In fact, the physical properties and the structure of wood, such as the proportion of late to earlywood and the abundance of fibers, may influence heat conduction and reactions to heating. Higher levels of tannins in wood may also increase heat conductivity (Mosedale and Ford, 1996). Wood constituents may show other changes during heat treatment if they are in an isolated condition or if they are incorporated in the cell walls. The degradation of cellulose, polyoses and lignin, is considerably different as compared to each other or to wood (Fengel and Wegner, 1989). So, further experiments with different woods are required to better understand their behaviour in heat treatment, in order to rationalise it.

CONCLUSIONS

Despite the simplified conditions under this study was carried out we can point out some conclusions.

During heat treatment all of the wood surface temperature corresponds to the endothermic phase of wood - drying level - in which occurs damages of its structure, conversion of the components and gaseous degradation products.

In all toasting levels, it was found that the best curve to fit the data was given by a 5th degree polynomial equation. The shape of the curves is similar: they start out with a strong slope (0 to 10 minutes), followed by a slight slope (between 10 and 25 minutes) and then start to flatten out towards the end of the heating process (25 to 45 minutes). The evolution profile of the wood temperature in different layers throughout the depth follows the same curve, but it is evident the softening of the temperature along with the depth. This phenomenon seems to be governed by the heat conduction within the wood.

The analysis of phenolic composition indicates that, from a technological point of view, in the toasting level definition, it must be considered two parameters: temperature and time. Although in cooperage the evaluation of toasting level is usually based on the heating time, the results show that the time has a secondary role in comparison with temperature. It means that, in the practice the accurate control of the toasting temperature it is essential for the optimisation of this technological operation, in order to maximise the quality of the wood barrels.

The results show a very significant effect of the toasting temperature on the total content of phenolic compounds. As the temperature rises its amount

increases, as a balance of the individual effects: the significant increase of the phenolic aldehydes (vanillin, syringaldehyde, coniferaldehyde, and sinapaldehyde), syringic and ellagic acids, are largely higher than the decrease of gallic, vanillic and ferulic acids.

In a general point of view the phenolic fraction trends to increase with toasting time. This effect essentially derives from the increment of ellagic acid and phenolic aldehydes contents, since the evolution of gallic and ferulic acids contradict this tendency. Vanillic and syringic acids are not significantly affected by the time.

Concerning the phenolic aldehydes, it is interesting to verify that their contents increase gradually and similarly with the toasting time: there is a notorious difference between 10 and 45 minutes, while the length of 25 minutes can not be distinguished from the others.

Except for ferulic acid, it was observed a decrease of phenolic compounds contents from the surface layer (0 to 2 mm) to the depth layer (2 mm to 4 mm) of the stove. This could be due to the higher temperature in the surface layer, which certainly causes more intense degradation of the wood constituents, as well as the modification of wood physical and structural properties. Ellagic acid has a more pronounced decrease than the lignin breakdown products throughout the depth, which could indicate that ellagitannins are more affected than lignins. So, changes in composition take place throughout the thickness of wood also depending upon the thermal stability of the precursors of the various extractable compounds.

ACKNOWLEDGEMENTS

We thank to Eng. José Silvestre and Mr. Manuel Lopes for the technical support provided during the technological essay and to Eng. Ilda Caldeira and Eng. Estrela Carvalho for their help in the statistical analysis.

RESUMO

Modelização do tratamento térmico de madeira de carvalho português (*Quercus pyrenaica* L.). Análise do comportamento dos compostos fenólicos de baixo peso molecular.

O tratamento térmico constitui um factor determinante da qualidade da quartola. Nos últimos 15 anos muitos foram os trabalhos que abordaram os efeitos do tratamento térmico na composição fenólica de carvalhos franceses e americanos. Já as espécies cultivadas em Portugal e tradicionalmente utilizadas em taçaria nunca foram objecto deste tipo de estudo. No presente trabalho é efectuada a caracterização do nível de queima em madeira de carvalho português (*Quercus pyrenaica* L.) com base na temperatura e no tempo, através da simulação laboratorial

do tratamento térmico em tanoaria. A evolução da temperatura com o tempo, em qualquer dos níveis de queima e ao longo da profundidade da madeira, é explicada por um modelo matemático não linear (polinómio de 5º grau). A determinação dos teores de alguns ácidos e aldeídos fenólicos da madeira foi efectuada por HPLC. Pela análise da composição fenólica constata-se que a optimização do tratamento térmico, no sentido de maximizar a qualidade das quartolas produzidas, implica o controlo da temperatura e do tempo. A fracção fenólica tende a aumentar com a temperatura ao longo do tempo. Estes efeitos resultam essencialmente do aumento dos teores de ácido elágico e de aldeídos fenólicos, em consequência da degradação dos taninos elágicos e das lenhinas, respectivamente. À excepção do ácido ferúlico, observa-se um decréscimo dos teores dos compostos fenólicos da camada mais superficial (0 a 2 mm) para a camada subjacente (2 a 4 mm) da aduela. Este facto pode ser atribuído à temperatura mais elevada à superfície, a qual será certamente responsável por uma degradação mais intensa dos constituintes da madeira, bem como pela alteração da estrutura e propriedades da mesma. A diminuição mais acentuada do ácido elágico relativamente aos produtos de degradação da lenhina, ao longo da profundidade, poderá ser indicadora de uma maior afectação dos elagitaninos face às lenhinas.

RÉSUMÉ

Modélisation de la chauffe du bois de chêne portugais (*Quercus pyrenaica* L.). Analyse du comportement des composés phénoliques de faible poids molecular.

Les opérations de chauffe représentent un facteur fondamental de la qualité d'une barrique. Dans les dernières quinze années beaucoup de recherche ont été effectuée sur les effets de la chauffe sur la composition phénolique du bois des chênes français et américains. Cette recherche n'a pas été faite pour les espèces du Portugal qui sont utilisées par la tonnellerie. Dans ce travail il est réalisé la caractérisation des niveaux de brûlage de bois de chêne portugais (*Quercus pyrenaica* L.) par mesure de la température et du temps de chauffe au laboratoire. L'évolution de la température avec le temps, à différents dans niveaux de brûlage et de profondeur du bois est expliqué par un modèle mathématique non linéaire (polynôme de 5^{ème} degré). La détermination des teneurs de quelques acides et aldéhydes phénoliques dans le bois a été réalisée par HPLC. Par l'analyse de la composition phénolique on vérifie que l'optimisation du brûlage, dans le sens de maximiser la qualité des barriques, conduit au contrôle de la température et du temps de chauffage. La fraction phénolique à tendance à augmenter avec la température tout au long du temps. Ces effets résultent surtout de l'augmentation des teneurs de l'acide ellagique et des aldéhydes phénoliques, en conséquence de la dégradation des ellagitanins et des lignines. À l'exception de l'acide férulique on observe une diminution des composés phénoliques de la couche superficielle (0 - 2 mm) par rapport à la couche subjacente (2 - 4 mm) du merrain. On peut attribuer ce fait à une température plus élevée en surface, laquelle sera certainement responsable par une plus intense dégradation des composants du bois, ainsi que pour l'altération de la structure et propriétés du même. La plus forte diminution de l'acide ellagique comparativement aux produits de la dégradation de la lignine, tout au long de la profondeur, peut indiquer une plus grande dégradation des ellagitanins par rapport aux lignines.

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