KINETICS OF IMPREGNATION/EVAPORATION AND RELEASE OF PHENOLIC COMPOUNDS FROM WOOD TO BRANDY IN EXPERIMENTAL MODEL

CINÉTICAS DE IMPREGNAÇÃO/EVAPORAÇÃO E TRANSFERÊNCIA DE COMPOSTOS FENÓLICOS DA MADEIRA PARA A AGUARDENTE EM MODELO EXPERIMENTAL

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(Manuscrito recebido em 09.04.02. Aceite para publicação em 10.05.02.)

SUMMARY
An essay was carried out under model conditions, simulating the natural ageing of brandies in 250 dm³ wooden barrels, to study the kinetics of impregnation/evaporation of brandy and the release of phenolic compounds from wood into the brandy. The influence of wood botanical species (Limousin oak and Portuguese chestnut), toasting level (light and strong) and ageing time (0, 42 and 250 days) was investigated. In parallel, a reduced essay with red wine was made to compare the kinetics of impregnation/evaporation of wine and brandy.

The great loss of wine or brandy and the highest extraction of phenolic compounds occur in the first month of the ageing process. Brandy and wine show different kinetics of impregnation/evaporation that seem to be governed by the impregnation rate, in the beginning mostly dependent on water content (15 days) and then mainly determined by their non-volatile composition. The total loss of brandy per year is more pronounced than wine (5–15% versus 5-9%) and the corresponding impregnated layer is about two-fold thicker.

In spite of the significant effect of wood botanical species, toasting level and ageing time on total phenolic compounds and color intensity of wood and brandy, as verified in previous works, it is also evident the strong influence of wood intraspecific variability (differences between trees and in heartwood age) and toasting procedure variability.

Key words: brandy, woods, ageing, impregnation, physical and chemical characteristics
INTRODUCTION

The knowledge of the phenomena that occur in the wood during the ageing of beverages has been a reason for many research studies.

Some works (Ribéreau-Gayon et al., 1976; Feuillat et al., 1994) have been made to evaluate the loss of liquid during the ageing process, resulting both from impregnation and volatilization, in wine and in model solutions.

Other important related phenomenon is the release of extractable compounds, especially phenolic compounds, from the wood into the liquid, which has considerable repercussions on its physical-chemical characteristics and sensorial properties (Guymon and Crowell, 1968; Viriot et al., 1993).

Several papers have been focused on the extraction kinetics of phenolic compounds in wines (Rous and Alderson, 1983; Kadim and Mannheim, 1999), in whiskies (Baldwin and Andreasen, 1974; Mosedale, 1995) and in model solutions (Moutoune et al., 1989; Puech et al., 1996; Kadim and Mannheim, 1999), but few studies were made with brandies (Puech et al., 1985).

The extraction of compounds from oak barrels into brandy depends on the pool of potential extractable compounds originally present in the oak, on the composition of the liquid and on the ageing conditions. Thus, this mechanism is conditioned by a large number of interdependent factors, namely the botanical species and the geographical origin of the wood (Guymon and Crowell, 1970; Miller et al., 1992; Marco et al., 1994; Mosedale and Ford, 1996; Mosedale and Savill, 1996; Canas et al., 2000c), the heartwood age (Peng et al., 1991; Klumpers et al., 1994; Viriot et al., 1994), the heat treatment (Nishimura et al., 1983; Artajona et al., 1990; Rabier and Moutoune, 1990; Sarni et al., 1990; Hale et al., 1999; Canas et al. 2000b), the relative proportion of water and ethanol (Guymon and Crowell, 1970; Baldwin and Andreasen, 1974; Singleton, 1995), the container size (Guymon e Crowell, 1970; Kadim and Mannheim, 1999) and the warehouse conditions (Cantagrel et al., 1992; Mosedale, 1995; Singleton, 1995).

The objective of this work was to monitoring the loss of brandy during 250 days, under model conditions, simulating the natural ageing of brandies. It was also performed the physical and chemical analysis of woods and corresponding brandies after 42 days and in the final of the period. In parallel, a reduced essay with red wine was made to compare the kinetics of impregnation/evaporation of wine and brandy.
MATERIAL AND METHODS

Experimental design

This study was based in a factorial experiment, with three factors - wood botanical species, toasting level, with two replications, and ageing time.

The essay was carried out from 18th October 2000 to 26th June 2001.

Materials

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 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 constitute the control group and the others were used to construct the experimental units, with a glass piece (Figure 1), which had been developed respecting the ratio

![Image](image.png)

**Fig. 1** – Experimental unit scheme (longitudinal plan).
*Esquema da unidade experimental (plano longitudinal)*.

surface area/volume of a 250 dm³ wooden barrel (86 cm²/dm³). The linkage between glass and wood was made with silicone - food quality.

Brandy

32 experimental units were filled with the same Lourinhã brandy (485 cm³) 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.
**Wine**

Three experimental units (CAST QF, CFL QF and CFL QL) were filled with the same red wine, produced at Estação Vitivinícola Nacional, and were placed near the brandy’s experimental units.

**Methods**

*Measurement of the liquid volume*

The measurements of the brandy and wine volumes into the experimental units were performed in mm and converted into cm³. The frequency of measurements was: daily during the first ten weeks, twice a week for 16 weeks and then weekly for 20 weeks (250 days). Whenever necessary the experimental unit was refilled with brandy or wine to the original volume.

The kinetic curves were drawn from the mean values of liquid loss of three to five experimental units.

Cellar temperature and relative humidity were also monitoring during the essay.

*Wood and brandy sampling*

T (0 days) - eight wood pieces (control group) were cut into layers of two mm from the inner surface to outer surface and the two-mm-thick pieces of wood were then grounded in a hammer-mill (Wiley). The corresponding wood powder was immediately analyzed. The brandy (control) was also analyzed.

T1 (42 days) and T2 (250 days) – two experimental units of each wood x toasting level were randomly selected. The unit was emptied and the brandy was homogenized and sampled. Then the unit was destroyed and the wet layer of the wood piece was measured and cut. The wood chips were grounded, homogenized, weighed and the sample was kept.

*Wood extraction*

Maceration of wood powder (1g) was carried out under rotary agitation for 180 min at 20 °C, with 20 cm³ of an ethanol/water solution (55:45 v/v and pH 4.2 adjusted 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.

*Analytical methods*

Color intensity (A440) – measurement of absorbance at 440 nm (Belchior e 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 in a Shimatsu UV-265 spectrophotometer using a quartz cell of 0,1 cm path length, and were referred to 1 cm path length.


Statistical analysis

The two-way analysis of variance and the correlations analysis were performed using Statgraphic v.5 (STSC inc., Rockville, USA).

RESULTS AND DISCUSSION

Kinetics of Impregnation/evaporation

The kinetics of impregnation/evaporation of brandies shown in Figure 2 (b) represent a three-stage process: during the initial phase (15 days) there is a slow increasing of the brandies loss, followed by a sharp increasing (30 days)

![Kinetics of impregnation/evaporation](image)

**Fig. 2** - Kinetics of impregnation/evaporation according to wood x toasting level in: (b) brandies and (wi) wines.

CAST QF; CAST QL; CFL QF; CFL QL.

Cinéticas de impregnação/evaporação de acordo com madeira x nível de queima em: (b) aguardentes e (wi) vinhos.
and, finally, during the third stage the increment trends to diminishing. The brandies ageing in CFL QL has a slightly different behavior, with a more pronounced second phase.

In wines (Figure 2 wi) the kinetics curves seem to imply only a two-stage process, starting with a strong slope and then trends to diminishing.

The main difference between brandies and wines is their behavior in the initial stage that could be explained by their water content (88% in wine versus 23% in brandy). The faster penetration through the wood of water than ethanol (Guymon e Crowell, 1970; Singleton, 1995) causes a more rapid loss of wine than brandy.

Since the water/ethanol content of wine and brandy is practically constant during the essay, the total loss of wine is much less than that of brandy – 5 to 9% versus 5 to 15%, the wet layer found in woods that had contacted with wine (3–4.5 mm) is thinner than in woods that had contacted with brandy (8–9 mm), then the process seem to be governed by the impregnation rate, which is mostly dependent on the water content in the beginning (15 days) and then is mainly limited by the non-volatile composition (Mosedale, 1995) and probably facilitated by the alcohol content of wine or brandy.

Although Feuillat et al. (1994) had reported the influence of warehouse temperature and humidity on the total loss of liquid, the kinetics of impregnation/evaporation obtained do not reveal this fact. This discrepancy can be justified by: the lower thermal amplitude of our cellar (Figure 3); the type of the liquid

![Figure 3](image-url)

**Fig. 3 –** Warehouse temperature and relative humidity during the essay.

*Temperatura e humidade relativa da cave durante o ensaio.*

used to fill the experimental units; the thickness of the wood pieces (9 mm versus 27 mm); the intraspecific variability of wood.

The results obtained (Figure 2 b) in brandies show the strong influence of intraspecific variability of wood that overlaps the effect of the other factors,
such as botanical species (Feuillat et al., 1994) and toasting level. So, it is not
evident the influence of the toasting intensity on the wood porosity and
accessibility of brandy to wood extraction sites, as reported by Sarni et al.
(1990). Also the differences of permeability between oak and chestnut woods,
derived from their specific anatomical features – types of ray parenchyma and
abundance of tyloses (Feuillat and Keller, 1997; Vivas et al., 2000), are not
clear.

**Extraction of phenolic compounds**

The results of variance analysis (Table I) show a very significant effect of the
wood botanical species on the content of phenolic compounds of wood and
brandy, as well as on the dry extract of brandies. Chestnut wood is the richest

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<td>A440</td>
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<td>1,02a</td>
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<td>CFL</td>
<td>x</td>
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<td>1,17b</td>
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<td>T2</td>
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<td>20,09c</td>
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| Botanical specie and toasting level: x = mean of 12 values; Ageing time: x = mean of 8 values. Means followed by
| the same letter in a column are not significantly different at 0,05* level of significance; SD = standard deviation;
| ns = without significant difference. |

**A440** - color intensity; Ipt - total polyphenol index.

in those compounds, as already verified (Canas et al., 2000c). The corresponding
brandies are also richer in phenolic compounds and dry extract than those
aged in oak wood.
The color intensity of the brandy is very significantly affected by the wood botanical species, while the color intensity of the wood is only significantly affect by this factor. The weak correlation between color intensity of wood and brandy is probably explained by the different behavior of CFL QF wood (Figure 4), which causes some distortion of the mean value of wood color intensity.

**Fig. 4** – Evolution of total phenolic content and color intensity of: (wo) woods and (b) brandies.

\[ CAST\ QF: - CAST\ QL: - CFL\ QF: - CFL\ QL. \]

Evolução dos polifenóis totais e da intensidade da cor de: (wo) madeiras e (b) aguardentes.

Higher color intensity of brandies aged in chestnut than in oak wood is coherent with that observed in three-year-aged brandies in 250 dm³ wooden barrels (Canas et al., 2000a). It can mean that this trend becomes evident immediately from the first month of ageing, revealing the great importance of extraction and oxidation processes in this early period.

Toasting level has a very significant influence on the total content of phenolic compounds in wood and on the color intensity of wood and brandy (Table I). The woods with light toasting show the highest content of phenolic compounds, but the lowest color intensity, while the corresponding brandies present lower content of phenolic compounds and lower color intensity than the brandies aged in wood with strong toasting. Brandies cannot be distinguishing by their dry extract as a function of wood toasting level, but light toasting induces higher dry extract.
The results of total phenolic content in woods do not follow the general
trend that QF>QL (Canas et al., 2000b).

According to the toasting level, differentiation of brandies by their color intensity
is in agreement with that observed in a previous work (Canas et al., 2000a).

It is reliable that the content of phenolic compounds in wood is affected by
the behavior of CFL QF wood. On the other hand, the results obtained could
be partially explained by the variability of wood toasting procedure (Chatonnet
and Boidron, 1989; Artajona et al., 1990; Chatonnet et al., 1993; Chatonnet,
1999; Canas et al., 2000b) and by the intraspecific variability of wood
anatomical characteristics (Polge and Keller, 1973; Deret-Varcin, 1983;
Mosedale et al., 1996b) and chemical composition (Peng et al., 1994; Viriot
et al., 1994; Masson et al., 1995; Mosedale et al., 1996a,b; Feuillat et al.,
1997), owing to differences between trees and in heartwood age.

Except the total phenolic content of wood, the studied parameters of woods
and brandies depend largely on the ageing time (Table I). It is observed that
increasing ageing time increases these parameters in brandy and decreases
wood color intensity.

The ageing time effect is also conditioned by the behavior of CFL QF wood,
which causes the increase of wood total phenolic content and color intensity
at T1, while the tendency is to diminishing with time. Similarly, the evolution
of CFL QF brandy affects the mean value of brandies color intensity.

It is interesting to point out the synchronism of the decreasing trend of total
phenolic content in woods and its increasing in brandies with the ageing time
(Figure 4), as a consequence of the release of phenolic compounds from
the wood to the brandy. This fact is also supported by the significant correlation
between them.

The more pronounced extraction of phenolic compounds occurring in the first
month (T1) of the ageing process could derive both from the higher availability
of those compounds in wood surface and the higher gradient between wood
and brandy, which facilitate their transfer into the brandy (Kadim and
Mannheim, 1999). On the other hand, the higher impregnation(evaporation
rate verified during this period could also contribute to that phenomenon.

During the second stage (T2) the total phenolic content of brandy is probably
determined by the resistance to mass transfer on the wood side.

In a methodological point of view the experimental model satisfying the
proposed objectives. However, a rigorous control of the wood must be paid
in order to eliminate the highest number of variability factors. It means that
wood staves that will be used in future essays must be obtained from the same
tree and from the same position in the trunk.
CONCLUSIONS

The great loss of wine or brandy and the uppermost extraction of phenolic compounds occur in the first month of the ageing process.

Brandy and wine show different kinetics of impregnation/evaporation that appear to be governed by the impregnation rate, which is initially dependent on their water content (15 days) and then mainly determined on their non-volatile composition.

There is a higher loss of brandy per year (5–15%) than wine (5-9%), and the corresponding wet layer in woods that had contacted with brandy (8–9 mm) is thicker than in those that had contacted with wine (3–4,5 mm).

Although the significant effect of wood botanical species, toasting level and ageing time on the content of phenolic compounds and color intensity of wood and brandy, it is evident the strong influence of wood intraspecific variability and toasting procedure variability.

The results are in agreement with those obtained in enological practice.

ACKNOWLEDGEMENTS

We thank to Mr. Manuel Lopes for the technical support provided during the essay and to Ms. Amélia Soares and M. Deolinda Mota for their help in some analytical determinations.

RESUMO

Cinéticas de impregnação/evaporação e transferência de compostos fenólicos da madeira para a aguardente em modelo experimental

Com o objectivo de estudar as cinéticas de impregnação/evaporação da aguardente e a transferência de compostos fenólicos da madeira foi realizado um ensaio em condições modelo, simulando o envelhecimento natural de aguardente em vasilhas de madeira de 250 dm³. Foi analisada a influência da espécie botânica da madeira (carvalho Limousin e castanho português), do nível de queima (ligeiro ou forte) e do tempo de envelhecimento (0, 42 e 250 dias). Através de um ensaio paralelo, em pequena escala, utilizando vinho tinto, procurou-se comparar as cinéticas do vinho e da aguardente.

A grande perda de aguardente e de vinho e a maior extração de compostos fenólicos da madeira pela aguardente ocorrem logo no primeiro mês de envelhecimento. A aguardente e o vinho apresentam cinéticas de impregnação/evaporação diferentes, que parecem ser determinadas pela taxa de impregnação, inicialmente dependente sobretudo do seu teor de água (15 dias) e depois principalmente condicionada pela sua composição não-volátil. A perda total anual de aguardente é mais acentuada que a de vinho (5–15% versus 5-9%) e a correspondente camada de madeira impregnada é cerca de duas vezes mais espessa.
Apesar do efeito significativo da espécie botânica, do nível de queima e do tempo de envelhecimento no teor de compostos fenólicos e na intensidade da cor de madeiras e aguardentes, como verificado em trabalhos anteriores, torna-se bastante evidente a influência da variabilidade intraespecífica da madeira (associada às diferenças entre árvores e à idade da madeira) e da variabilidade da queima.

RÉSUMÉ

Cinétiques d’imprégnation/évaporation et transfert des composés phénoliques du bois pour l’eau-de-vie en modèle expérimental

Ce travail consiste en l’étude des cinétiques d’imprégnation/évaporation de l’eau-de-vie et le transfert de composés phénoliques du bois, en conditions modèles, avec un dispositif expérimental, simulant le vieillissement naturel de l’eau-de-vie en fût de bois de 250 dm³. L’influence de trois facteurs est analysée: l’espèce botanique (chêne Limousin et châtaignier portugais), le niveau de brûlage (léger et fort) et le temps de vieillissement (0, 42 et 250 jours). Un essai parallèle, moins complet, a été conduit sur du vin rouge pour comparer les cinétiques de ce vin et celles de l’eau-de-vie.

La plus grande perte en eau-de-vie et en vin et la plus grande extraction des composés phénoliques du bois par l’eau-de-vie ont lieu très rapidement pendant le premier mois de vieillissement. L’eau-de-vie et le vin présentent des cinétiques d’imprégnation/évaporation différentes qui semblent être déterminées par le taux d’imprégnation. L’imprégnation initiale dépend surtout de la teneur en eau (15 jours) et après de la fraction non volatile. La perte totale annuelle de l’eau-de-vie est plus importante que celle du vin (5-15% contre 5-9%), ce qui correspond à une couche de bois imprégnée environ deux fois plus importante.

Bien que l’effet de l’espèce botanique, du niveau de brûlage et du temps de vieillissement sur les composés phénoliques totaux et sur l’intensité de la couleur soit significatif, comme déjà vérifié dans des travaux précédents, les résultats sont également fortement influencés par la variabilité intra spécifique du bois (inter arbres et âge du bois de cœur) et par la variabilité du brûlage.

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