Current Research in Food Science 9 (2024) 100900

Contents lists available at ScienceDirect

Current Research in Food Science

journal homepage: www.sciencedirect.com/journal/current-research-in-food-science

Applying kinetic models to the study of the influence of wood contact surface area/volume ratio on the ageing of B*randy de Jerez*

Rocío Trillo-Ollero [a,b], Luis M. Trillo-Gutiérrez [b], M. Valme García-Moreno [a,*], M. Carmen Rodríguez-Dodero [a], Dominico A. Guillén-Sánchez [a]

[a] *Departamento de Química Analítica, Facultad de Ciencias, Instituto Investigación Vitivinícola y Agroalimentaria (IVAGRO), Universidad de Cádiz, Campus Universitario de Puerto Real, 11510 Puerto Real, Cádiz, Spain*

[b] *Bodega González Byass S.L.U., Centro de Investigación, CIDIMA (Calidad, Investigación, Desarrollo, Innovación y Medio Ambiente), Bodega Las Copas Crta, Madrid-Cádiz Km. 641, 11407, Jerez de La Frontera, Cádiz, Spain*

ARTICLE INFO

Handling Editor: Dr. Maria Corradini

Keywords:
Brandy
Lagergren's model
Peleg's model
Intraparticle diffusion model
Parabolic model
Color
Phenolic compounds

ABSTRACT

The present study investigates the influence of the casks' wood surface/volume ratio on the extraction processes that take place during the first stages of the production of Sherry Brandy. For this purpose, the ageing of a spirit at 60% alcoholic strength has been examined in casks of two different volumes: 500 L and 250 L, made from three different types of wood: *Quercus alba* (American oak*), Quercus robur* (French limousin oak) and *Quercus petraea* (Spanish oak), either previously seasoned or non-seasoned with Sherry wine.

TPI, the sum of all the phenolic compounds analyzed (phenol extraction coefficient) and the variation in color compared to the initial distillate (CIEDE 2000) were evaluated in all the aged distillates. The casks with a higher surface/volume ratio produced brandies that generally presented higher values for all these parameters, with different increments depending on the type of oak wood. The seasoning of the casks reduced the contribution of phenolic compounds from the wood to the ageing spirit and resulted in brandies with a lighter color when aged in French and Spanish oak casks, but not when the American oak casks were used.

Four kinetic models have been applied to better understand the evolution of these parameters during the ageing stage: Lagergren, Peleg, Intraparticle and parabolic diffusion. Peleg's model was the best fit in all the cases, which suggests that 2 types of mechanisms are involved in ageing: a rapid and a slow one. Regarding the diffusion models, the results were better fitted to the parabolic model, which suggests that during the ageing of the spirit a number of parallel reactions take place that affect the values actually reached by the parameters considered in our study. It was also observed that higher wood surface/volume ratios resulted in higher values of phenolic compounds in the distillates, but did not represent a significant factor in relation to the color of the final distillates.

The sensory analysis of the samples aged for 16 months demonstrated that only the wine spirits aged in French oak wood presented significant differences depending on the size of the cask; however, all the brandies were registered significant differences associated to the seasoning of the casks.

1. Introduction

Sherry Brandy is defined as a spirit with an alcoholic strength of between 36% and 45% Alcohol by Volume (ABV), obtained exclusively from wine spirits and wine distillates aged in oak casks with a capacity of less than 1000 L (Consejería de Agricultura y Pesca, 2005). The cask must have been previously filled with wine from the Protected Designation of Origin (PDO) "Jerez-Xérès-Sherry" or from the PDO "Manzanilla-Sanlúcar de Barrameda" (Sherry Cask®) and the Criaderas and Solera ageing system that in the Sherry area must be employed (García Moreno and García Barroso, 2002).

The ageing process involves a number of physicochemical events related to the compounds contributed by the distillates and by the cask wood (García Moreno and García Barroso, 2002), (Sánchez-Guillén et al., 2019). Such events consist primarily in extraction phenomena, but also in a number of chemical processes, such as oxidation and

* Corresponding author. Departamento de Química Analítica, Facultad de Ciencias, Instituto Investigación Vitivinícola y Agroalimentaria (IVAGRO), Universidad de Cádiz, Campus Universitario de Puerto Real, 11510 Puerto Real, Cádiz, Spain.

E-mail address: valme.garcia@uca.es (M.V. García-Moreno).

https://doi.org/10.1016/j.crfs.2024.100900
Received 3 August 2024; Received in revised form 20 October 2024; Accepted 27 October 2024
Available online 29 October 2024

esterification, Maillard reactions or polymerization and poly-condensation reactions (Álvarez Batista, 1997). All of them may affect in one way or another the final organoleptic characteristics of the finally aged brandies. Therefore, the definite characteristics of aged brandies will depend on all of the factors involved in their production, namely, the raw material used, the distillation process itself and the ageing conditions (Canas, 2017), (Valcárcel-Muñoz et al., 2021), (Mosedale and Puech, 1998), i.e. the ageing length of time (Canas et al., 2008) and the properties of the wooden casks themselves, which are also related to specific factors such as the type of wood (Madrera et al., 2010), (Rodríguez Dodero et al., 2010), (Martínez-Gil et al., 2018), its toasting degree (Warren-Vega et al., 2021) and the cask volume, which will particularly govern the wood surface/volume ratio under which the spirits will be aged (González Gordon and Jerez-Xerez Sherish, 1970), (Cadahía Fernández et al., 2008), (Psarra et al., 2015).

Thus, during the ageing stage in the wooden casks, certain wood compounds are extracted by the solvent, which in this case is the wine spirits. This process is characterized by three phases: Firstly, there is solubilization that takes place as the liquid penetrates the wood, then a diffusion of the compounds from the internal parts of the wood towards the liquid-wood contact surface takes place, and finally these compounds get diffused into the liquid (Psarra et al., 2015), (Kadim and Mannheim, 1999). In view of this three-phase process, we can clearly understand why the ratio between the wood surface area and the volume of liquid contained in the cask can be one of most influential factors regarding the evolution of the characteristics of the wine spirits over their ageing (Psarra et al., 2015). Thus, not only has it been observed that higher wood surface/volume ratios, corresponding to smaller volume casks, result in greater yields of the wood soluble compounds, but it has also been noticed that the oxidation processes are enhanced by the greater contact of the beverage with the outer air as a consequence of the reduced thickness of the staves used to make smaller casks (Canas, 2017)., (Cadahía Fernández et al., 2008)

González Gordon, in his book *Jerez-Xerez-Sherish* (González Gordon and Jerez-Xerez Sherish, 1970), referred to the ageing process used in the Jerez region exclusively for the highest quality brandies, which comprises a combination of the method used in Cognac and the traditional Sherry method. This procedure consisted in initially ageing the brandies in the 250 L oak casks used in the region known as Cognac (Álvarez Batista, 1997), (González Gordon and Jerez-Xerez Sherish, 1970), and then continuing the ageing in the traditional 500 L sherry casks by following the same method used for Sherry wines, i.e., the Criaderas and Solera system. This method results in greater extractions of the wood compounds by the distillate during a first ageing stage, and in the homogenization and final organoleptic "rounding" of the brandies during a second stage. In Brandy de Jerez cellars, high color intensity as well as high total polyphenol indexes (TPI) have always been associated with superior quality of aged brandies.

The casks where Sherry Brandy is aged are traditionally made of American oak wood or, in exceptional cases, of French limousin oak wood (*Quercus robur*), although current regulations allow the usage of other types of oak wood for the ageing of this product. The wine industry is experiencing both a shortage and a growing need for new oak wood for cooperage (García-Moreno et al., 2020), (Caldeira et al., 2013), which emphasizes the need of new sources of quality wood and represents a business opportunity for other types of wood that have not been commonly used for winemaking until now. Thus, some studies have focused on the identification of new woods that could be suitable for the ageing of wines and distillates and have actually demonstrated that Spanish oak wood is suitable for oenological purposes (Martínez-Gil et al., 2018). In fact, these investigations have qualified Spanish oak as a viable alternative to American or French oak wood (Cadahía Fernández et al., 2008). However, these works have not investigated the behavior of the different woods as a function of surface/volume ratio, nor the influence of the previous treatment of the wood (seasoning) on the ageing of the distillates. For this reason, the present paper aims to determine the relevance that surface/volume ratio, oak wood type and the seasoning of the casks have with regard to the final product. For this purpose, the evolution that certain parameters such as color, TPI and phenol extraction coefficient exhibit over the ageing of a wine spirit have been examined. The wine spirit was aged in industrial casks of two different sizes (i.e. two wood surface/volume ratios), made of three different types of oak wood and either previously seasoned or non-seasoned with Sherry wine.

In the bibliography consulted we found some studies on the extraction kinetics of phenolic compounds in alcoholic beverages such as whisky (Baldwin and Andreasen, 1974), (Mosedale, 1995), wine (Canas et al., 2002), Armagnac (Puech and Goffinet, 1987), (Puech et al., 1985), brandies (Canas et al., 2002), (Caldeira et al., 2016), (Delgado-González et al., 2021), (Canas et al., 2013) and even model solutions (Psarra et al., 2015), (Kadim and Mannheim, 1999), (Spillman et al., 1998), but we have not found any studies focused on brandy de Jerez, and in particular on the effect of the size of the cask and the previous treatment it may have had as a prior treatment. These previous studies focus on the behavior of phenolic compounds (Kadim and Mannheim, 1999), (Baldwin and Andreasen, 1974), (Mosedale, 1995), (Canas et al., 2002) and volatile compounds (Spillman et al., 1998), and very few also focus on the behavior of color (Canas et al., 2002), (Delgado-González et al., 2021) during the ageing process.

In order to better understand the behavior of these woods during the ageing process of a wine distillate, a kinetic study of both parameters has been conducted based on four kinetic models relative to solid-liquid extraction processes that have previously been applied to foodstuffs (Psarra et al., 2015), (Delgado-González et al., 2021), (Jokić et al., 2010), (Lazar et al., 2016). These four models were selected based on the literature reviewed, as they are the most studies in the aging of various wines and spirits. As well as an organoleptic evaluation of the aged spirits, so that the potential use of these woods for the ageing of brandies could be evaluated in a comprehensive manner.

2. Materials and methods

2.1. Experimental desing and sampling

A wine spirit of the *Airén* grape variety with an alcohol strength of 60 % ABV obtained by column distillation with copper plates supplied by the distillery Bodega Las Copas, S.L., located in Tomelloso, Ciudad Real, which belongs to the González Byass S.L.U. group, was used for this study. Three types of oak wood were selected for the study: two of the most commonly used for Sherry brandy-ageing, namely American oak (*Quercus alba*) (AO) and French limousin oak (*Quercus robur*) (FO) as well as Spanish oak wood (*Quercus petraea*) (SO).

In order to investigate the ageing of the spirits in casks of different oak woods and surface/volume ratios, casks of two different capacities have been used: 500 L casks, known as "Botas" (B), with a surface/volume ratio of 74.9 cm^2/L, and 250 L casks, known as "Medias" (M), with a surface/volume ratio of 98.7 cm^2/L, all of them medium toast.

Four casks were used for the study on each type of oak wood and capacity, two of which were seasoned and two were unseasoned, i.e., for each type of wood there were 8 casks: 4 of 500 L and 4 of 250 L, and within these, by size, two were seasoned (S) and two were unseasoned (N). The seasoning treatment consisted in containing 18 % ABV oloroso wine for 5 months.

The oloroso wine and the oak casks were provided by Bodega González Byass Jerez S.L., a winery that is registered under the Protected Geographical Indication "Sherry Brandy". The materials used for these experiments are consistent with the provisions in the Technical Dossier of the official regulation for Sherry Brandy, which states that the wine spirit utilized must be exclusively derived from wine, and that the aging process of Sherry Brandy must extend for a minimum of six months in oak vessels with a capacity of less than 1000 L that have previously contained Sherry wine. The casks were sampled in duplicate on a monthly basis for a period of 16 months to cover two of the three categories of Sherry Brandy: Brandy Solera (minimum aging of 6 months) and Brandy Solera Reserve (minimum aging of 12 months). The study was extended for a few additional months to observe the evolution of both brandies. Table 1 includes all the experiments that have been conducted in this study. And Table SM1shows the analytical data of Oloroso wine and initial wine spirit used in this research.

2.2. Total polyphenol index (TPI) determination

TPI was determined by directly measuring the absorbance of the samples at 280 nm wavelength using a Cary 60 UV–VIS Agilent Technologies (Little Falls, DE, USA) spectrophotometer (Delgado-González et al., 2022) against unaged 60% ABV wine spirit. The data were expressed as mg gallic acid equivalent (GAE) per liter of distillate. The gallic acid used to generate the calibration line was purchased from Merck (Darmstadt, Germany). The standards used for the calibration line and the samples were analyzed in duplicate after performing the dilution of the samples as required.

2.3. Phenolic compounds

The phenolic compounds were determined by HPLC using an HP 1100 model, equipped with a multivariate UV–Vis detector and a C18 column, LiChrospher 100 RP-18, Merck (Darmstadt, Germany), at a temperature of 40 °C. The measurements were carried out at two wavelengths, 280 nm and 320 nm. The injection volume was 5 μL, the mobile phase flow rate 1.1 mL/min and the elution time 45 min. The mobile phase consisted of three eluents: ultrapure water (A, Milli-Q), methanol (B) and acetic acid (C), the last ones of HPLC quality as supplied by VWR Chemicals and the following gradient was applied: time 0 min, A: 97.5%, B: 0.5% and C: 2.0%; time 40 min: A: 44.0%, B: 54.0% and C: 2.0%; time 45 min, A: 97.5%, B: 0.5% and C: 2.0%. The samples were filtered prior to analysis through 0.22 μm pore membrane filters.

The compounds of interest were identified by comparison of their retention times against the standards. Nine phenolic compounds were found and quantified as follows: 3 phenolic acids (gallic acid, syringic acid and ellagic acid), 4 phenolic aldehydes (vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde), and 2 furanic aldehydes (furfural and 5-hydroxymethylfurfural). Data of calibration curves are shown in Table SM2and a HPLC chromatogram with the identifications of the quantified phenolic compounds is shown in Figure SM1.

The results were expressed as mg/L per family of phenolic or furanic compounds quantified as the sum of the concentrations of individual compounds, as shown below.

- Sum of phenolic acids: sum of the concentrations, in mg/L, of gallic, syringic and ellagic acids.
- Sum of phenolic aldehydes: sum of the concentrations, in mg/L, of phenolic aldehydes vanillin, syringaldehyde, coniferaldehyde and sinapaldehyde.
- Sum of furanic aldehydes: sum of the concentrations, in mg/L, of furanic aldehydes furfural and 5-hydroxymethylfurfural.
- Sum of all phenolic compounds (phenol extraction coefficient): sum of the concentrations of all the compounds quantified, except for the furanic aldehydes. This is a parameter used in local wineries as an indicator of phenolic compounds extracted from barrel wood.

Table 1
Experiments performed. Nomenclature, volume, nature of the casks, time of aging and time of seasoning of aged spirit.

Nomenclature	Volume of the casks (liters)	Wood	Seasoning	Time of seasoning (months)	Time of aging (months)
C (Control)	–	–	–	–	–
B-AON	500	American Oak	Non	–	16
B-AOS	500	American Oak	Oloroso	5	16
B-FON	500	French Oak	Non	–	16
B-FOS	500	French Oak	Oloroso	5	16
B-SON	500	Spanish Oak	Non	–	16
B-SOS	500	Spanish Oak	Oloroso	5	16
M-AON	250	American Oak	Non	–	16
M-AOS	250	American Oak	Oloroso	5	16
M-FON	250	French Oak	Non	–	16
M-FOS	250	French Oak	Oloroso	5	16
M-SON	250	Spanish Oak	Non	–	16
M-SOS	250	Spanish Oak	Oloroso	5	16

2.4. Color determination

Color measurements were carried out in duplicate using an Agilent Technologies (Little Falls, DE, USA) Cary 60 UV–VIS spectrophotometer, by measuring the transmittance of the samples in the 1 nm visible spectrum between 360 nm and 830 nm wavelengths compared to that of distilled water. All the samples were measured using 10 mm light path quartz cuvettes. The CIEL *a*b* color components were obtained based on the transmittance spectra data, as established by the ISO 11664-4 standard (ISO 11664-4, 2008). Tables SM3ato SM3c show the values of the a*, b* and L* color components of the CIEL *a*b* method.

In order to determine the color differences between the samples according to the CIEDE2000 parameter (ΔE_{00}), the aged samples were compared against the unaged wine spirits, which was used as control sample. The values of the ΔE_{00} parameter were obtained according to the ISO 11664-6 standard (ISO/CIE 11664-6, 2014), with the help of a Microsoft Excel spreadsheet (Microsoft Corporation, Redmond, WA, USA) elaborated according to the standards required by the Commission Internationale de l'Eclaraige (CIE) (Delgado-González et al., 2018). CIEDE2000 is a calculation system that evaluates the color difference between two simples, offering a better correlation with human color perception and yielding results that accurately represent how we perceive color differences.

2.5. Kinetic study

Four kinetic models have been applied to better understand and define the ageing stage and its correlation with the characteristics of the casks.

2.5.1. Lagergren's model

The first kinetic model to be applied was Lagergren's model, as defined in 1898 by Lagergren (Qiu et al., 2009), which in its linear form is represented by Equation (1):

$$\frac{dY(t)}{dt} = K_1(x - x_0) \tag{1}$$

By integrating the equation, the following exponential equation was obtained (Equation (2)):

$$Y(t) = Y_{eq}\left(1 - e^{-K_1 \bullet t}\right) \tag{2}$$

Where Y(t) is the amount of solute adsorbed at time t, K_1 is the pseudo first order rate constant and K_3 is the contact time in minutes. This model fits best when the analyte concentration is below its equilibrium concentration.

2.5.2. Peleg's model

Peleg's model is a pseudo-second order model (Bucić-Kojić et al., 2007). Peleg's model (Peleg, 1988) corresponds to Equation (3) as follows:

$$x(t) = \frac{t}{K_{p1} + K_{p2} \bullet t} \tag{3}$$

This model has two constants: constant K_{p1}, which is related to the initial velocity of the extraction process and constant K_{p2}, which is the theoretical constant of the analyte at equilibrium. When the values of these two constants are known, the initial extraction rate of the analyte (V_0) (Equation (4)) and its final concentration at equilibrium (X_{eq}) (Equation (5)) can be calculated.

$$V_0 = \frac{1}{K_{p1}} \tag{4}$$

$$X_{eq} = \frac{1}{K_{p2}} \tag{5}$$

2.5.3. Intraparticle diffusion model

This model claims that extraction is carried out solely by physical processes and no chemical reactions take place (Kitanović et al., 2008). Equation (6) below was the formula applied:

$$x(t) = K_1 + K_2 \bullet \sqrt{t} \tag{6}$$

Where: constant K_1 represents the physical process consisting in the rapid washing out of the compounds from the most superficial layers of the solid, K_2 is the velocity of the diffusive extraction process, and t is the extraction time in minutes.

2.5.4. Parabolic model

The parabolic model extends the intraparticle diffusion model by including a new constant, K_3, related to the chemical reactions that take place over the extraction process (Youl Kim et al., 2002) (Equation (7)).

$$x(t) = K_1 + K_2 \bullet \sqrt{t} + K_3 \bullet t \tag{7}$$

Constant K_3 allows us to know if there are chemical reactions that affect the velocity of the process (Youl Kim et al., 2002); thus, if this constant is close to zero, we can affirm that the chemical reactions that occur during the ageing of the spirits have a minimal effect on the extraction velocity.

2.6. Sensory analysis

After ageing the samples for 16 months, they were evaluated organoleptically, both in the nose (olfactory phase, via the ortonasal route) and in the mouth (olfactory-gustatory evaluation) on 9-point interval scales (1: absent). The descriptors used were the same as those already selected by the authors for a previous study (Guerrero-Chanivet et al., 2022). Thus, aromatic intensity, fruity, vanilla, toasted and spicy were the descriptors used for the olfactory evaluation, while sweetness, alcohol, smoothness, oak and balance were the gustatory variables to be scored.

25 mL of spirit diluted with pure water up to 25% ABV were poured into a standard wine glass (ISO 3591, 1977), capped until the time of evaluation to favor the concentration of aromas. The samples were presented to the judges in 3 different sessions, in each of which they evaluated 9 samples (4 aged distillates in duplicate and 1 replicate of the unaged distillate).

The panel of judges consisted of 9 members of staff from the Faculty of Sciences and the winery Bodegas González Byass between 33 and 64 years old, who perform sensory evaluations of aged distillates and other oenological products on a regular basis, so no specific training was required.

2.7. Statistical analysis

Nonlinear regressions of the TPI, phenol extraction coefficient and ΔE_{00} curves with respect to time were applied to all the kinetic studies using Microsoft Excel 2016 (Microsoft Corporation, Redmond, WA, USA) combined with the statistical package Statgraphic Centurion 19 (Statgraphics Technologies, Inc., The Plains, VA, USA).

The analyses of variance of the sensory evaluations were performed using Statistica 7.0 (StatSoft. Inc., USA). The spider charts were created by means of Microsoft Excel (2016) (Microsoft Corp., 141 Redmond, WA, USA). Taking into account the variance factor, three different analysis of variance studies were carried out:.

- ANOVA on the set of samples, considering judge and sample as the variance factors.
- ANOVA on the set of samples, considering the botanical species used to age the brandies as the variance factor.
- ANOVA on the samples aged in each oak wood type, considering seasoning and volume as the variance factors.

3. Results and discussion

3.1. TPI evolution review

Firstly, the evolution of the global content of phenolic compounds in the brandies over their ageing process was examined. Fig. 1 shows the evolution of the TPI, expressed as mg/L of GAE, versus the ageing time in each type of oak wood according to the size of the cask and whether or not the cask had been previously seasoned. A hyperbole-type behavior was observed in all the experiences that were carried out, regardless of the size of the cask, the type of wood, or the seasoning factor.

From the various graphs that were obtained, two, relatively differentiated stages could be observed: the first stage corresponded to a pronounced increase of the TPI, which is consistent with a stage of greater extraction of phenolic compounds from the wood by the distillate; the second stage presents a less pronounced increase of the TPI with respect to time, as the extraction of phenolic compounds is no longer so pronounced. However, after 10 months of ageing, a slight TPI increase continues to be observed, which indicates that the extraction processes of the phenolic compounds do not cease at any moment. This fact is in line with the study conducted by Valcárcel et al. (Valcárcel-Muñoz et al., 2021) on the ageing of brandies in used casks. These authors reported that the phenolic content in the samples of the brandies aged in heavily used casks continued to increase over time, even if less markedly.

According to wood types, SO and FO produced aged brandies with higher TPI levels, while AO aged brandies presented lower TPI values. These variations between the results registered for the different types of wood are coherent, since, as Lazar et al. (2016) affirmed, the differences between species are related to characteristics such as their phenolic load, the degree of homogeneity of their phenol distribution within the mass of the wood and their porosity, all of which govern diffusion velocity and rate during the ageing of the distillates. In our particular case, the three woods used were different, as American oak (*Quercus alba*) is a low-porosity wood characterized by a higher content of vanillin than *Quercus robur* or *Quercus petraea*, as well as a lower content of ellagitannins. On the other hand, the two latter types have similar quantities of these compounds. *Q. robur*, in turn, contains greater amounts of gallic, protocatechuic, caffeic, and sinapic acids, and a higher TPI than *Q. alba* (Zhang et al., 2015). In this study, it could be observed that the unseasoned FO casks and the seasoned SO ones yielded the most similar spirits with regard to overall phenolic content regardless of the cask volume.

With respect to the TPI values of the casks according to their volume, the 250 L (M) casks showed, in general, a higher value than the 500 L (B)

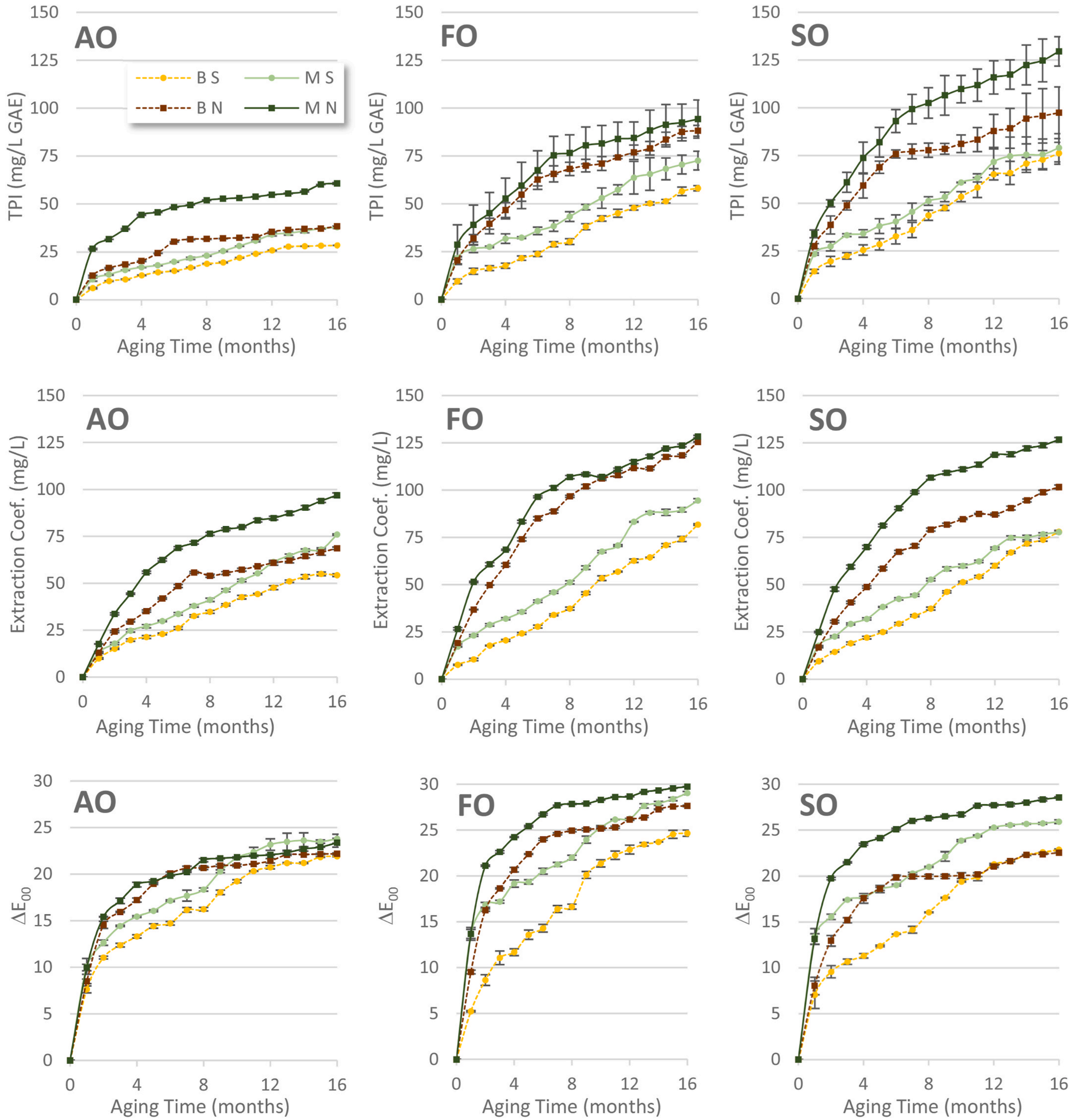

Fig. 1. Evolution of the TPI (in mg/L GAE), Extraction Coefficient (in mg/L) and ΔE_{00} in a wine distillate aged for 16 months. Legend in the first graphic (TPI in AO). Note: AO: American Oak; FO: French Oak; SO: Spanish Oak; B: *Bota* (cask with 500L of capacity); M: *Media* (cask with 250 L of capacity); S: Seasoned cask; N: No seasoned cask.

ones. These results are in agreement with those reported by other authors, which corroborates that the concentration of phenolic compounds in wood-aged distillates depends largely on the amount of wood surface in contact with the liquid, i.e. the wood surface/spirit volume ratio (Psarra et al., 2015) in combination with the type of wood used for the ageing. Some differences were also registered between the brandies aged in seasoned or unseasoned casks, so that the seasoned casks produced brandies with lower TPI levels than the unseasoned casks after ageing for the same length of time (Valcárcel-Muñoz et al., 2021). In conclusion, the unseasoned casks were the ones that gave rise to brandies with the highest TPI values. These results are in line with those reported by other authors (Valcárcel-Muñoz et al., 2021), (Guerrero-Chanivet et al., 2023), who observed that the seasoning of the casks favored a first extraction from the wood inner surface and only after this "washout" the spirit would get into direct contact with the actual wood surface. This would explain the limited amount of phenolic compounds extracted from seasoned woods by the spirit over the ageing stage.

3.1.1. Comparative study by wood type and seasoning conditions

To better understand the relevance of cask size on the ageing outcome of the distillates, a linear regression graphical comparison of the TPI values for both sizes of casks, by oak wood and by pretreatment of the casks, was carried out. Fig. 2 shows the graphs obtained and the equations of the regression lines together with the coefficient of determination (R^2) by representing the TPI values obtained for B (X axis) and M (Y axis), by type of wood and by pretreatment (seasoned and unseasoned). As can be seen, the regression lines obtained presented slopes greater than 1, with R^2 values close to 1. This allowed us to confirm that the extraction process of phenolic compounds is better favored in the 250 L casks (Y axis) than in the 500 L ones (X axis), i.e. in the casks with a higher surface/volume ratio.

From these graphs, we could also observe that AO was the wood that

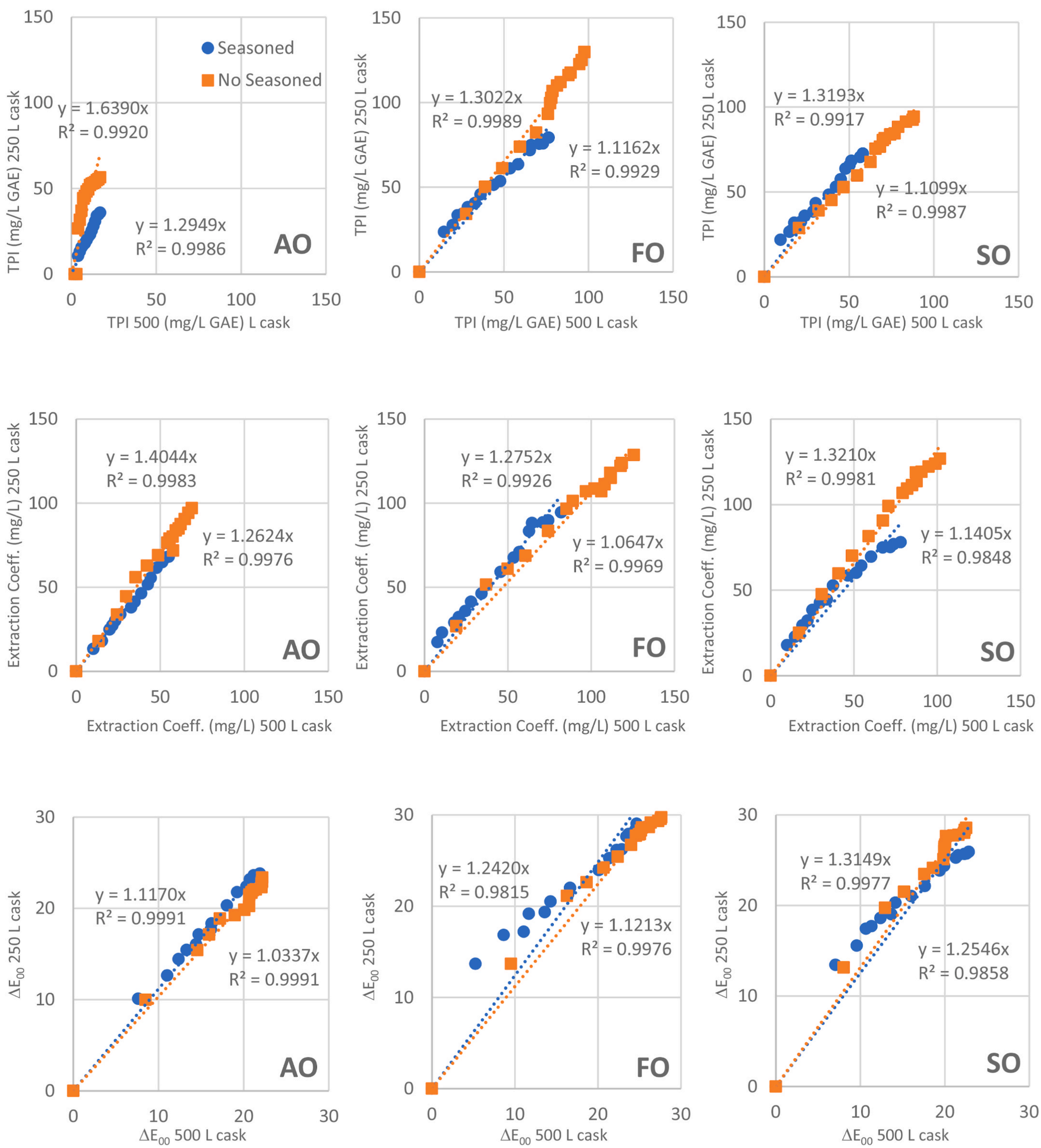

Fig. 2. Linear correlation of the TPI (in mg/L GAE), Extraction Coefficient (in mg/L) and ΔE_{00} between vessels from different oaks in a wine distillate aged for 16 months. Legend in the first graphic (TPI in AO). Note: AO: American Oak; FO: French Oak; SO: Spanish Oak;: Seasoned cask;: No seasoned cask.

presented the greatest differences depending on the size of the cask and its pretreatment. Thus, the unseasoned Medias casks of AO wood were the vessels that, proportionally, led to aged spirits with higher TPI values. The unseasoned casks presented a factor of 1.64 compared to 1.30 for the seasoned casks. French oak wood exhibited a similar behavior even if less pronounced, with a factor of 1.30 for the unseasoned casks and 1.12 for the seasoned ones. Spanish oak wood behaved differently, so that unseasoned casks produced brandies with very similar TPI (a factor of 1.11), while seasoned casks showed certain differences depending on size (a factor of 1.32) and greater TPI values in the Media casks.

3.1.2. Kinetic study of TPI progression

In order to know the dynamics of the phenolic compounds evolving in the distillates during the ageing process, a nonlinear regression adjustment of the curves obtained for the TPI versus the ageing time was carried out by applying four mathematical models: Lagergren's pseudo-first order model, Peleg's pseudo-second order model, the intra-particle diffusion model and the parabolic diffusion model. The first two models were used to obtain information on the kinetic order of the extraction process, while the last two models provided insight into the mechanisms of the extraction process.

All of these models have already been applied to exploring the extraction of phenolic compounds from different natural matrices (Rodriguez et al., 2023). As an example, Fig. 3 shows the TPI values measured throughout the ageing of the spirit in seasoned 500 L American oak casks (B), together with the theoretical fit obtained from each kinetic model. Table 2 shows the values of the R^2 coefficients obtained for the three types of wood studied and for the two pretreatment options.

When comparing the two kinetic order models, it can be seen that Peleg's model obtains higher values of the coefficient of determination (R^2) than Lagergren's (Table 2). That is, the evolution of the TPI during the ageing of the spirit in the wooden casks fits better to a model in which rapid and slow extraction mechanisms take place, rather than swift washouts. Wooden cask ageing is a complex process that involves a considerable number of physical and chemical phenomena, as well as a large number of compounds that are part of the wood composition, each of which has its own diffusion mechanism from the wood into the distillate, which depends on the nature of the compound itself and on its location within the structure of the cask's walls. This explains why Peleg's kinetic model fits better than Lagergren's, in particular, for extractions carried out in unseasoned casks, as both rapid (dissolution of the most superficial wood compounds) and slow processes (either extraction of the phenolic compounds from the deeper wood layers or chemical reactions between the wood and the distillate compounds) are involved in the extraction of the different compounds from the wood (Mosedale and Puech, 1998), (Delgado González, 2021),.

To better understand the kinetic results from this study, the values of TPI at equilibrium (TPI_{eq}) and the initial extraction velocities (V_0) were calculated for all the experiments (Table 3).

The TPI_{eq} values showed clear trends in relation to the previous treatment of the wooden casks used (seasoning), the volumes of the casks and the size of the casks. Thus, it was observed that, for the same type of wood, the TPI_{eq} values were higher for unseasoned barrels than for seasoned ones, being noticeably higher in Medias than in Botas. It was also observed that FO and SO seasoned Botas reached higher values than the rest of the casks in the study. It was also observed that the AO wood casks, whether seasoned or unseasoned, presented lower TPI_{eq} values. This difference in behavior could be explained by the nature of the woods used, FO and SO are much more porous and richer in phenolic

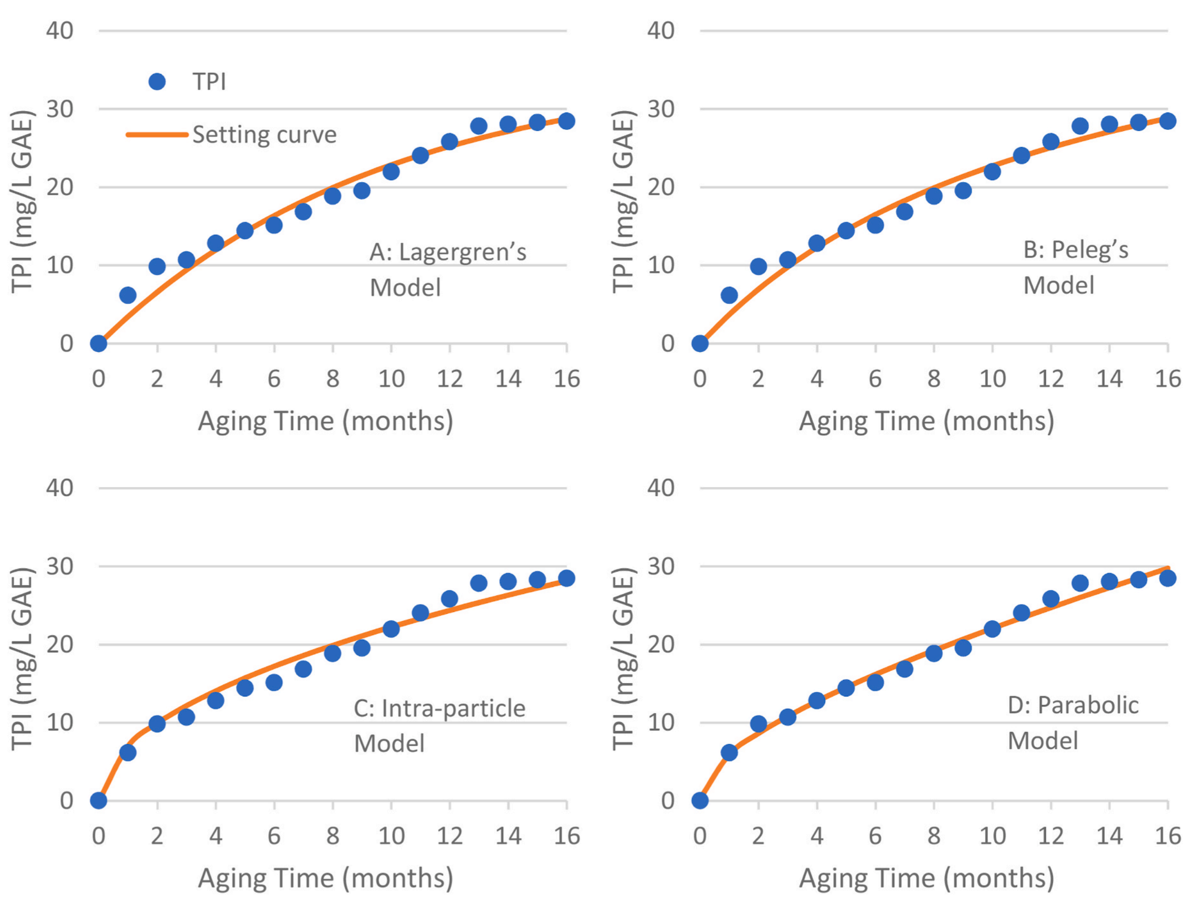

Fig. 3. Representation of the application of the four kinetic models studied for the evolution of the IPT (in mg/L GAE) parameter for a wine distillate aged in American Oak cask of 500 L capacity (Legend in Figure A).

Table 2
R^2 values obtained by adjusting the TPI, extraction coefficient and CIEDE2000 parameter (ΔE_{00}) values according to the four kinetic models studied for the aging experiments in casks.

	Samples	Kinetic order models		Extraction mechanism models	
		Lagergren's	Peleg's	Intraparticular	Parabolic
TPI					
Botas (500 L cask)	B-AON	0.9860	0.9889	0.9822	0.9751
	B-AOS	0.9883	0.9891	0.9902	0.9927
	B-FON	0.9940	0.9967	0.9932	0.9895
	B-FOS	0.9926	0.9926	0.9729	0.9933
	B-SON	0.9917	0.9953	0.9826	0.9758
	B-SOS	0.9920	0.9920	0.9745	0.9942
Medias (250 L cask)	M-AON	0.9812	0.9929	0.9572	0.9758
	M-AOS	0.9794	0.9803	0.9867	0.9903
	M-FON	0.9930	0.9957	0.9902	0.9860
	M-FOS	0.9742	0.9745	0.9799	0.9861
	M-SON	0.9957	0.9982	0.9910	0.9872
	M-SOS	0.9781	0.9789	0.9862	0.9880
Extraction Coefficient					
Botas (500 L cask)	B-AON	0.9957	0.9959	0.9865	0.9865
	B-AOS	0.9936	0.9937	0.9864	0.9960
	B-FON	0.9987	0.9981	0.9897	0.9895
	B-FOS	0.9970	0.9976	0.9587	0.9975
	B-SON	0.9982	0.9983	0.9922	0.9919
	B-SOS	0.9958	0.9964	0.9618	0.9969
Medias (250 L cask)	M-AON	0.9971	0.9983	0.9879	0.9181
	M-AOS	0.9925	0.9926	0.9810	0.9969
	M-FON	0.9957	0.9963	0.9835	0.9835
	M-FOS	0.9905	0.9905	0.9718	0.9930
	M-SON	0.9990	0.9987	0.9867	0.9867
	M-SOS	0.9922	0.9927	0.9914	0.9963
ΔE_{00}					
Botas (500 L cask)	B-AON	0.9948	0.9972	0.9204	0.9026
	B-AOS	0.9751	0.9848	0.9884	0.9916
	B-FON	0.9943	0.9978	0.9400	0.9284
	B-FOS	0.9916	0.9927	0.9939	0.9911
	B-SON	0.9916	0.9952	0.9340	0.9242
	B-SOS	0.9792	0.9819	0.9932	0.9900
Medias (250 L cask)	M-AON	0.9901	0.9977	0.9181	0.9287
	M-AOS	0.9666	0.9802	0.9797	0.9894
	M-FON	0.9925	0.9985	0.9008	0.9045
	M-FOS	0.9473	0.9701	0.9706	0.9926
	M-SON	0.9915	0.9990	0.9078	0.9199
	M-SOS	0.9475	0.9730	0.9592	0.9896

compounds than AO, so they end up producing spirits that are also richer in phenolic compounds (Diaz-Maroto and Tahir, 2019).

Regarding any possible differences in the initial velocity, it is observed that the extractions carried out in AO are those that present the lowest values, compared to FO and SO. AO presents the lowest values for this parameter, being lower in the Botas than in the Medias, and not presenting important differences according to the previous treatment (seasoning). FO and SO present differences according to the initial treatment, and according to the capacity of the barrel: in the Botas both woods presented higher initial speeds in those that were seasoned.

As noted above, the intraparticle diffusion model stated that extraction was solely carried out by physical processes and no chemical reactions were considered (Kitanović et al., 2008). The parabolic model extends this model so that includes the effect of the chemical reactions that actually occur during the extraction process (Youl Kim et al., 2002). Therefore, these models provide us with insights into the physical and chemical mechanisms that are involved in the evolution of the finally registered parameter values. If we compare the values of correlation coefficients of the different kinetic models for the extraction mechanisms (Table 2), it can be observed that the parabolic diffusion model fits better than the intraparticle model for extractions carried out in seasoned casks.

The values obtained for the kinetic constants K_1, K_2 and K_3 from the parabolic model (Table 3) indicate that the values of K_3 for the seasoned casks were higher than those corresponding to the unseasoned casks, since K_3 was zero in all of them. This value is correlated to the occurrence of certain chemical reactions that have an influence on the extraction process. Therefore, as the seasoning treatment facilitates the penetration of the distillate into the cask wood, this favors a greater contact between the liquid and the wood and increases the possibility of these reactions to take place.

If we compare the seasoned casks against each other, we can see that, for FO and SO, slightly higher K_3 values have been recorded in the Bota casks than in Media casks. This is so because, as the cask size is reduced, i.e. when the surface/volume ratio is increased, a greater contact between liquid and wood as they woods are more porous than the AO, and a greater contact between the liquid and the wood is favored and certain chemical reactions that take place during the ageing are enhanced, which results in higher K_3 values. American oak wood is the least porous of the three types tested because of the tylosis process that takes place in it. This makes it more difficult for the distillate to reach the internal areas of the wood and does not favor the contact between the compounds from the wood and the distillate during the ageing of the spirit.

On the other hand, the unseasoned casks were registered higher values of the K_3 constant (rapid washout) with respect to the seasoned casks. This is consistent with the results obtained for K_3, which confirms that, in the unseasoned casks, rapid diffusion is favored over chemical reactions. The K_2 constant presents higher values for the unseasoned casks, especially the FO and SO ones. In these two cases, the diffusion rate of the extracted compounds from the internal layers of the wood into the liquid took place more rapidly than in the AO casks.

3.2. Phenol extraction coefficient

The phenol extraction coefficient comprises the whole set of low molecular weight phenolic compounds from the degradation of the wood lignin and the hydrolysable tannins extracted during the ageing of the brandies. Fig. 1 shows the progression of this parameter over the 16 months of ageing studied and Fig. 2 shows the linear correlation between the phenol extraction coefficients obtained when using B (X axis) y M (Y axis) casks. As can be seen, in a similar way as what happened with the TPIs, for the same ageing times, the phenol extraction coefficients were greater when the casks were smaller and therefore the contact surface/volume ratio was higher (ratios greater than 1).

3.2.1. Phenol extraction coefficient comparison according to type of wood and seasoning

Different behaviors were observed depending on whether or not the wood had been previously seasoned. Regarding the seasoned casks, the ones made of FO presented a higher slope than the AO and SO ones. This suggests that there is a greater difference in the extraction coefficient between B and M casks, and that higher extraction velocities were to be expected from the smaller casks. The situation was rather different when comparing unseasoned casks, where the AO casks were the ones with the highest slope.

It can be observed that, generally in all the experiments, the seasoning of the casks decreased the extraction differences between B and M casks, since, as previously mentioned, this treatment reduces the extraction processes by removing the direct contact of the spirit with the outermost layers of the wood, before filling the cask with the spirits to be aged. This is confirmed by the fact that higher phenol extraction coefficients were reached in all of the casks that had not been previously seasoned.

Fig. 4 shows the concentration in mg/L of the sum of aldehydes and phenolic acids (phenol extraction coefficient) and the sum of furfural compounds in the distillates aged for 16 months in each of the three wood types studied, according to volume and seasoning treatment. In

Table 3
Parameters for Peleg's and Parabolic models fitting the curves for aged spirits for the TPI, extraction coefficient (EC) and CIEDE2000 parameter (ΔE_{00}) values over the aging time.

		Peleg's model parameters		Parabolic model parameters		
		Values at equilibrium	V_0	K_1 (fast washing)	K_2 (diffusion)	K_3 (reaction)
TPI		*TPIeq*				
Botas (500 L)	B-AON	9.80 ± 0.44	52.50 ± 4.02	2.90 ± 0.39	9.39 ± 0.15	0.00 ± 0.00
	B-AOS	4.03 ± 0.40	52.26 ± 10.27	0.38 ± 0.31	4.93 ± 0.32	0.61 ± 0.18
	B-FON	19.89 ± 1.76	119.95 ± 2.95	1.91 ± 1.40	22.22 ± 0.58	0.00 ± 0.00
	B-FOS	5.08 ± 0.44	210.34 ± 32.38	1.29 ± 0.24	3.66 ± 0.85	2.71 ± 0.15
	B-SON	28.10 ± 1.10	124.67 ± 17.65	7.55 ± 3.08	23.76 ± 3.40	0.00 ± 0.00
	B-SOS	6.91 ± 0.56	248.77 ± 4.31	2.32 ± 0.14	5.16 ± 0.88	3.43 ± 0.09
Medias (250 L)	M-AON	27.86 ± 2.64	69.95 ± 9.98	11.74 ± 0.11	13.08 ± 1.46	0.00 ± 0.00
	M-AOS	5.39 ± 0.41	65.09 ± 11.02	1.62 ± 0.55	5.87 ± 0.94	0.84 ± 0.10
	M-FON	27.13 ± 9.12	119.68 ± 4.03	5.75 ± 6.64	23.48 ± 1.07	0.00 ± 0.00
	M-FOS	9.54 ± 0.02	132.53 ± 23.66	4.28 ± 0.26	9.42 ± 0.29	1.95 ± 0.47
	M-SON	33.16 ± 3.57	168.95 ± 9.79	6.34 ± 0.58	32.14 ± 2.45	0.00 ± 0.00
	M-SOS	11.78 ± 1.15	136.03 ± 35.30	3.37 ± 1.16	12.95 ± 2.38	1.60 ± 1.06
Extraction Coefficient		EC_{eq}				
Botas (500 L)	B-AON	91.72 ± 0.32	15.93 ± 0.17	0.49 ± 0.26	17.76 ± 0.03	0.00 ± 0.00
	B-AOS	123.02 ± 2.57	6.41 ± 0.11	0.20 ± 0.20	7.51 ± 0.07	1.71 ± 0.03
	B-FON	180.96 ± 0.23	24.48 ± 0.17	0.00 ± 0.00	31.60 ± 0.22	0.12 ± 0.03
	B-FOS	–	5.06 ± 0.01	0.17 ± 0.03	0.18 ± 0.00	4.99 ± 0.01
	B-SON	147.57 ± 1.67	19.45 ± 0.01	0.00 ± 0.00	25.08 ± 0.01	0.22 ± 0.05
	B-SOS	1251 ± 392	5.29 ± 0.10	2.09 ± 0.18	0.39 ± 0.39	4.71 ± 0.09
Medias (250 L)	M-AON	125.12 ± 1.82	23.79 ± 0.42	1.75 ± 0.40	24.66 ± 0.21	0.00 ± 0.00
	M-AOS	196.32 ± 12.60	7.22 ± 0.22	1.64 ± 0.08	6.75 ± 0.53	2.85 ± 0.14
	M-FON	163.29 ± 0.11	34.36 ± 0.06	4.87 ± 0.07	32.51 ± 0.01	0.00 ± 0.00
	M-FOS	327.70 ± 0.75	8.48 ± 0.00	2.57 ± 0.21	6.20 ± 0.09	4.39 ± 0.01
	M-SON	3232.0 ± 0.0	10.39 ± 0.00	2.44 ± 0.16	33.32 ± 0.14	0.00 ± 0.00
	M-SOS	140.02 ± 1.98	7.88 ± 0.13	1.35 ± 0.09	12.39 ± 0.14	1.75 ± 0.05
ΔE_{00}		ΔE_{00eq}				
Botas (500 L)	B-AON	24.55 ± 0.03	15.58 ± 0.54	7.46 ± 0.17	3.86 ± 0.01	0.00 ± 0.00
	B-AOS	26.13 ± 0.40	7.29 ± 0.43	2.19 ± 0.25	5.24 ± 0.05	0.00 ± 0.00
	B-FON	33.33 ± 0.00	16.67 ± 0.00	7.89 ± 0.06	5.06 ± 0.00	0.00 ± 0.00
	B-FOS	38.53 ± 1.07	4.45 ± 0.33	0.00 ± 0.00	5.81 ± 0.40	0.17 ± 0.09
	B-SON	25.00 ± 0.00	12.70 ± 2.24	6.29 ± 0.64	4.20 ± 0.17	0.00 ± 0.00
	B-SOS	32.64 ± 1.86	4.63 ± 0.46	0.62 ± 0.45	5.44 ± 0.10	0.08 ± 0.06
Medias (250 L)	M-AON	25.69 ± 0.05	16.47 ± 0.10	7.66 ± 0.01	4.10 ± 0.01	0.00 ± 0.00
	M-AOS	27.31 ± 0.13	9.80 ± 0.29	3.37 ± 0.19	5.55 ± 0.01	0.00 ± 0.00
	M-FON	33.33 ± 0.00	25.00 ± 0.00	11.42 ± 0.15	4.76 ± 0.04	0.00 ± 0.00
	M-FOS	30.64 ± 0.29	14.39 ± 0.05	5.03 ± 0.00	6.27 ± 0.06	0.00 ± 0.00
	M-SON	100.00 ± 0.00	21.74 ± 0.00	10.57 ± 0.17	4.67 ± 0.02	0.00 ± 0.00
	M-SOS	27.59 ± 0.23	10.46 ± 1.21	5.39 ± 0.33	5.62 ± 0.06	0.00 ± 0.00

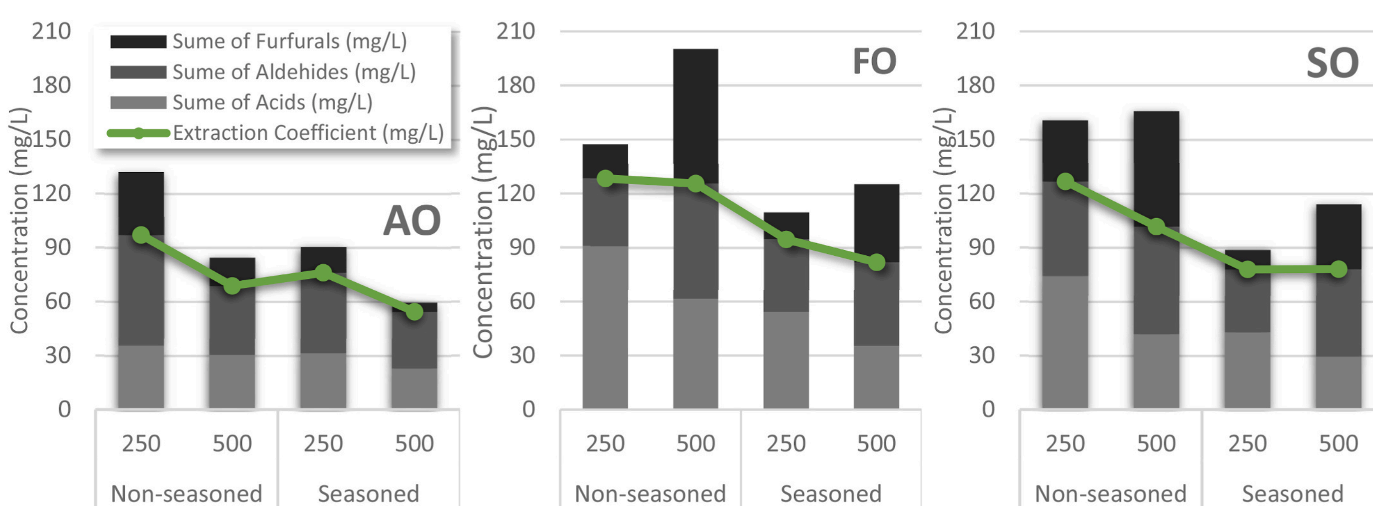

Fig. 4. Total content (in mg/L) of the concentration of furfurals, aldehydes and phenolic acids, and the extraction coefficient in the wine spirits aged for 16 months in seasoned and non-seasoned casks of 500 L and 250 L capacity, from American oak (AO), French oak (FO) and Spanish oak (SO).

general terms, the AO casks produced brandies with lower phenol extraction coefficients than the FO and SO ones, as reported in the literature (Zhang et al., 2015), (Canas et al., 2007). It can also be observed that the AO 500 L casks produced aged spirits with a lower concentration of phenolic and furfural compounds than the AO 250 L casks, regardless of their seasoning or not seasoning. However, this behavior was not so obvious in the case of French or Spanish oak wood casks, as FO produced brandies with similar phenol extraction coefficients in either casks size, with lower values corresponding to the seasoned ones. SO casks, in turn, exhibited an intermediate behavior, with seasoned large and small casks reaching similar values, while the unseasoned ones registered lower phenol extraction coefficients for the brandies that had been aged in the large volume casks. Likewise, the total content of furanic compounds also differed depending on the type of oak wood used, with AO casks producing aged spirits with a lower amount of furanic compounds when the size of the cask increases. The casks made of the other two oak species studied, i.e. FO and SO, produce brandies with greater total furfural concentration the larger the size of the cask (a greater burnt surface of the cask's inner wall), although lower concentrations were registered when the cask had been seasoned.

3.2.2. Kinetic study of phenol extraction coefficient

Of the four models studies, whose R^2 values are displayed in Table 3, Peleg's and the Parabolic models, for kinetic order and extraction mechanisms respectively, were the ones to best explain the behavior of this variable during the ageing of the distillates. It can be seen that the three types of wood had a similar behavior, and that casks size differences did not result in clear variations of the R^2 values. The seasoning, on the contrary, did prove to be a relevant factor, as the seasoned casks registered higher values in the Parabolic model, and the unseasoned ones exhibited the highest R^2 values in Peleg's model.

3.3. Color evolution of the ageing brandies

Color, and more specifically the parameter ΔE_{00}, was another parameter investigated in our study. Fig. 1 shows the evolution of ΔE_{00} with respect to ageing time in all the spirits tested and it can be observed that for all the woods, similarly to the TPI values, it exhibited a hyperbole-like behavior.

When observing the ΔE_{00} values in Fig. 1 as a function of the size of the casks, it can be seen that, regardless of the type of wood or the seasoning, the brandies aged in 250 L casks presented a greater coloration compared to those aged in 500 L casks. In any case, the differences were not as marked for other parameters, particularly when the brandies had already exceeded one year of ageing.

With respect to color changes between seasoned and unseasoned casks, it could be seen that this pretreatment had a clear influence on the color of the aged brandies, particularly during the early stages of the ageing process. Thus, it could be observed that, in general, the brandies aged for less than a year, presented higher ΔE_{00} values when aged in unseasoned casks rather that in the seasoned ones. However, this behavior moderated after longer aging periods, as fully aged brandies presented rather similar ΔE_{00} values. In those cases, the brandies aged in AO casks presented particularly similar values after aging for over a year, either in seasoned or unseasoned casks. Similarly, brandies aged for over a year in M-FO or B-SO casks also registered comparable ΔE_{00} values, regardless of the seasoning of the casks.

It can be observed that, of the three types of wood, FO was the one to produce brandies with the greatest color increment regardless of the rest of cask parameters, while the AO casks produced the brandies with the lowest ΔE_{00} values. It was, therefore, confirmed again, that the values of ΔE_{00} depended mainly on the wood species. FO and SO produced brandies of similar color evolution over the first months of ageing, with increments of around 15 units during the first month. Given that FO and SO woods are richer than AO in the tannins and phenolic compounds that derive from the wood lignin, the extraction of these compounds led to oxidation reactions that resulted in greater color increases than in the AO casks. García-Moreno et al. (2020) reported that *Quercus petraea* gave rise to aged distillates with a higher phenolic composition and color intensity in comparison to those obtained when *Quercus alba* was used. Delgado González et al. (Delgado-González et al., 2021) observed significant color differences between wine spirits aged in SO when compared against those aged in FO or AO casks. Cadahía et al. (2007) registered higher contents of extractable components in SO with respect to FO or AO, with AO being the wood with the lowest concentration of phenolic compounds and therefore the one to produce brandies with the least color intensity. This different behavior was attributed to the greater porosity of Spanish and French oaks with respect to the American species.

3.3.1. Color comparison according to type of wood and seasoning

The simple linear regression study of the ΔE_{00} data of the aged spirits for both cask sizes, wood types and pretreatment (Fig. 2) shows similar results to those already commented, i.e. the brandies aged in 250 L casks evolved faster than those contained in the 500 L ones, as there was a direct correlation between the brandies ΔE_{00} value and the contact surface/volume ratio of the casks.

By type of wood, no noticeable differences were observed in the slope values between non-seasoned and seasoned casks. Of the three types of wood, it was the AO the one to present slopes values closest to 1, indicating that both types of barrels exhibit similar behavior throughout the aging process.

3.3.2. Kinetic study of color evolution (ΔE_{00}) during the ageing process

The R^2 data of the nonlinear regression fit by applying the four kinetic models for the parameter ΔE_{00}, are shown in Table 2. As was the case for TPI and consistently with the referred bibliography, the color difference in aged distillates fits better to a second order model (Peleg's), where the enhancement of the color of the brandies is closely related to the extraction of phenolic compounds. Such extraction, as already mentioned, is driven by two mechanisms: rapid wood washout and slow diffusion of the extracted compounds into the distillate. The R^2 values of the seasoned casks were lower than those of the unseasoned ones in either of the two models examined (Delgado González, 2021), (Puech, 1981), while no clear differences were observed when the R^2 values corresponding to B or M casks were compared.

Table 3 presents the values obtained through Peleg's kinetic model by adjusting the evolution of the color curve along the ageing process. We can observe that in all the cases the initial color extraction rate was higher for M than for B casks, regardless of the type of oak, or whether or not they had been previously seasoned. This difference between M and B casks could be clearly observed in the brandies aged in SO and FO casks, where the initial velocity of B was about half that of M. This is probably due to the nature of these two types of wood as they have a higher porosity than AO wood (Ruppitsch et al., 2021), (Robert et al., 2017). Such higher porosity favors the extraction of the compounds associated to color contribution during the first stages of the ageing of the brandies. When comparing the initial extraction rate of the unseasoned against the seasoned casks, we could observe that, as expected, in all cases the color values of the brandies aged in unseasoned casks were higher than those corresponding to seasoned-cask aged brandies.

The color values obtained at equilibrium were lower for the brandies aged in American oak than for those aged in French or Spanish oak, either in B or M casks. French oak in particular, whether seasoned or unseasoned, produced the brandies with the strongest coloration of all the wood types. This data is in agreement with the values that had been collected from the phenol extraction coefficient study, where it could be seen that this wood (FO) gave rise to aged brandies with the highest concentration of individual phenolic compounds (Fig. 4). When the ΔE_{00} values at equilibrium corresponding to the two FO cask sizes were compared against each other, no major differences were noted, which would lead us to conclude that either size cask would produce brandies with similar color as long as the equilibrium between the distillate and the wood has been reached. This was actually a different behavior to that registered for TPI, where we could see that the TPI values at equilibrium were different for M and B casks.

In the case of the kinetic diffusion models, the comparison between the R^2 values obtained (Table 2), reveals that in 4 of the 6 experiments carried out in unseasoned casks, the parabolic model fits better than the intraparticle model. Table 3 shows the values of the parabolic model constants obtained for the color parameter. It can be seen that the K_1 constant that corresponds to the rapid extraction processes, is higher for the 250 L casks. This behavior is similar to that observed in TPI studies and consistent with the literature consulted, which is explained by the more rapid extraction of the wood compounds that confer color to the distillate that takes place in smaller casks (Álvarez Batista, 1997), (González Gordon, 1970). On the other hand, the K_2 constant, which corresponds to the velocity of the diffusion, presented similar values for either cask size, which indicates that the process represented by this constant occurs in a similar way regardless of the size of the cask. Finally, it could be observed that the K_3 constant, related to the chemical reactions that occur over the ageing of the brandies, was zero for most cases, which means that such chemical reactions do not play a role with regard to the color acquisition of the brandies.

3.4. Sensory analysis

On the top row of Table 4 we can see the average scores granted by the panel (together with the standard deviations) for each descriptor and sample evaluated and, at the bottom row, the average score of the samples aged using the same oak wood type. These data are also accompanied by the p-values obtained from the analyses of variance realized.

The results from the two-factor judge x sample ANOVA confirmed the homogeneity of the panel for the evaluation of the different descriptors, since no p-value was lower than 0.05, neither for the judge factor nor for the interaction of the judge factor with the sample (ISO 11132, 2012).

When the effect of the botanical origin of the oak on the sensory profile of the brandy was examined, it was found that 6 out of the 10 descriptors presented significant differences. As expected, the ageing of the brandies in any of the oaks increased the intensity of some of their olfactory notes such as vanilla or toast, and also their oak olfactory-gustatory notes, even if not to the same extent. Thus, the highest intensities were perceived in the brandies aged in Spanish oak and particularly spicy notes as well as alcoholic sensation, while the lowest descriptor scores, except for vanilla, were granted to the brandies that had been in contact with American oak. Finally, the brandies that had been made using French oak wood were scored with intermediate intensities for these highly discriminating descriptors. Having confirmed these differences, the brandies were studied separately, taking into account the type of wood used for aging.

When examining the effect that the factors volume and seasoning have on the descriptors of each brandy depending on the type of wood used, it can be observed that the brandies aged in American oak were the most influenced by these two variables. Thus, for brandies aged in American oak, of the 10 descriptors analyzed, the volume of the cask significantly affected ($p < 0.05$) the scores given to aromatic intensity, spiciness and smoothness. Furthermore, even if with somewhat lesser significance ($p < 0.1$), volume and seasoning also had an influence on the vanilla, toast and oak descriptors. With respect to the role specifically played by volume on the evolution of the descriptors considered, all the brandies aged in Medias (M) were granted higher scores for all the descriptors, with the exception of smoothness, as was to be expected.

Table 4
Analysis of variance applied to the sensory profile of wine spirits aged for 16 months in seasoned (S) and non-seasoned (N) casks of 500 L and 250 L capacity, from American oak (AO), French oak (FO) and Spanish oak (SO). A different letter indicates a significant value difference of the factor for $p < 0.05$ (*). The scores are expressed as the mean ± standard deviation of the tasting panel.

Sample (Cod.)	p_{ANOVA}	Aromatic Intensity	Fruity	Vanilla	Toasted	Spiced	Sweetness	Alcohol	Smoothness	Oak	Balance
	p_{judge}	0.923	0.251	0.199	0.481	0.227	0.618	0.201	0.809	0.644	0.711
	$p_{judgeXsample}$	0.889	0.112	0.370	0.785	0.552	0.923	0.698	0.331	0.428	0.455
Control		7.8 ± 0.5	7.5 ± 0.6 ^{b}	1.8 ± 1.0^{a}	1.8 ± 1.0 ^{a}	6.5 ± 0.6 ^{a,b}	5.7 ± 0.6	4.5 ± 0.6 ^{a}	6.3 ± 1.0	1.5 ± 1.0 ^{a}	7.0 ± 1.4
AO		7.4 ± 0.5	5.9 ± 1.2^{a}	6.6 ± 0.8^{c}	6.4 ± 1.1^{b}	6.1 ± 0.8^{a}	5.4 ± 1.1	4.7 ± 0.9^{a}	6.1 ± 1.0	6.7 ± 1.1^{b}	6.5 ± 1.0
FO		7.6 ± 0.7	6.9 ± 0.8^{b}	5.9 ± 1.1^{b}	6.6 ± 1.3^{b}	7.2 ± 1.2^{b,c}	5.9 ± 1.1	6.4 ± 0.6^{b}	5.9 ± 1.0	7.2 ± 1.0^{b,c}	6.3 ± 1.1
SO		7.5 ± 0.6	6.9 ± 0.9^{b}	6.9 ± 0.7^{c}	7.7 ± 0.5^{c}	7.7 ± 0.6^{c}	6.1 ± 0.9	6.6 ± 1.0^{b}	6.4 ± 1.1	7.6 ± 1.0^{c}	6.6 ± 1.0
	$p_{oak/control}$	0.821	0.007*	0.000*	0.000*	0.000*	0.230	0.000*	0.728	0.000*	0.634
B-AON		7.3 ± 0.5	6.6 ± 1.5	6.3 ± 1.0	6.7 ± 0.6	5.0 ± 0.0	5.8 ± 1.0	5.3 ± 0.5	6.0 ± 0.8	7.0 ± 0.8	7.0 ± 0.8
B-AOS		7.0 ± 0.0	5.5 ± 1.0	6.3 ± 0.5	5.3 ± 1.0	5.8 ± 0.5	4.8 ± 1.3	4.3 ± 1.0	7.0 ± 0.8	5.5 ± 0.6	6.5 ± 1.3
M-AON		8.0 ± 0.0	6.3 ± 1.0	7.0 ± 0.8	7.0 ± 0.8	6.5 ± 0.6	5.3 ± 0.6	5.3 ± 0.5	5.0 ± 1.0	7.0 ± 1.2	5.8 ± 0.5
M-AOS		7.5 ± 0.6	5.5 ± 1.3	7.0 ± 0.8	6.8 ± 1.0	6.8 ± 0.5	5.8 ± 1.0	4.0 ± 0.8	6.0 ± 0.8	7.3 ± 1.0	6.8 ± 1.3
	$p_{seasoning}$	0.073	0.148	1.000	0.090	0.069	0.544	0.009*	0.045*	0.191	0.633
	p_{volume}	0.007*	0.722	0.082	0.066	0.000*	0.585	0.712	0.046*	0.070	0.347
	$p_{seas.Xvol.}$	0.525	0.742	1.000	0.220	0.335	0.199	0.735	1.000	0.066	0.167
B-FON		7.3 ± 1.0	6.3 ± 1.2	5.8 ± 1.0	6.5 ± 1.3	7.3 ± 1.0	7.7 ± 0.6	6.8 ± 0.5	6.5 ± 1.0	7.5 ± 0.6	7.7 ± 0.6
B-FOS		7.5 ± 0.6	7.0 ± 0.0	5.3 ± 1.0	6.3 ± 1.3	6.5 ± 1.0	5.7 ± 0.6	6.0 ± 0.8	6.0 ± 1.0	5.8 ± 1.0	6.3 ± 1.3
M-FON		8.0 ± 0.8	7.3 ± 1.0	7.0 ± 0.8	8.0 ± 0.0	8.3 ± 1.0	5.5 ± 0.6	6.0 ± 0.0	6.3 ± 1.0	8.0 ± 0.0	6.0 ± 0.8
M-FOS		7.5 ± 0.6	7.0 ± 0.8	5.5 ± 1.0	5.7 ± 1.1	6.8 ± 1.3	5.3 ± 1.0	7.0 ± 0.0	5.0 ± 0.8	7.5 ± 0.6	5.5 ± 0.6
	$p_{seasoning}$	0.745	0.635	0.110	0.050*	0.053	0.015*	0.689	0.102	0.003*	0.059
	p_{volume}	0.344	0.306	0.049*	0.463	0.257	0.007*	0.611	0.228	0.004*	0.022*
	$p_{seas.Xvol.}$	0.337	0.352	0.147	0.114	0.489	0.046*	0.003*	0.460	0.070	0.336
B-SON		7.5 ± 0.6	6.5 ± 1.3	6.8 ± 1.3	7.8 ± 0.5	7.5 ± 1.0	6.3 ± 1.0	6.8 ± 1.3	6.3 ± 1.0	7.8 ± 0.5	6.5 ± 0.6
B-SOS		7.3 ± 0.5	7.7 ± 0.6	6.5 ± 0.6	8.0 ± 0.0	7.5 ± 0.6	6.0 ± 0.8	5.8 ± 0.5	6.5 ± 1.3	7.0 ± 0.8	6.5 ± 1.3
M-SON		7.8 ± 0.5	6.8 ± 1.0	7.0 ± 0.0	7.8 ± 0.5	7.8 ± 0.5	6.3 ± 1.0	7.3 ± 1.0	7.0 ± 0.8	8.3 ± 1.0	7.0 ± 1.2
M-SOS		7.5 ± 1.0	6.8 ± 0.5	7.3 ± 0.5	7.5 ± 0.6	8.0 ± 0.0	6.0 ± 1.2	6.5 ± 0.6	5.0 ± 0.0	7.5 ± 1.3	6.3 ± 1.2
	$p_{seasoning}$	0.414	0.245	1.000	1.000	0.605	0.619	0.069*	0.144	0.135	0.592
	p_{volume}	0.474	0.497	0.199	0.308	0.256	1.000	0.180	0.512	0.306	0.771
	$p_{seas.Xvol.}$	1.000	0.245	0.510	0.335	0.698	1.000	0.781	0.101	1.000	0.513

The inverse correlation that was detected between the volume and the oak descriptor must be carefully described as it seems to be also associated to the seasoning of the casks. With respect to the gustatory descriptors in particular, the brandies aged in American oak casks were the most affected by the seasoning treatment ($p < 0.05$), so that they were perceived as less alcoholic and smoother than the brandies aged in unseasoned casks of the same type of wood. On the nose, these seasoned-wood aged brandies were perceived as less aromatic, with lighter spicy notes and a more pronounced toasty character.

The brandies aged in French oak casks also presented some differences depending on the volume of the barrel and the barrel seasoning. Thus, on the nose, the unseasoned casks contributed more significantly with spicy and toasted notes, while the vanilla notes were more noticeable in the brandies aged in Media casks. On the palate, the casks that had been seasoned reduced the sweetness and oak notes in their brandies, while the higher surface/volume ratio of the Media casks enhanced the oak and diminished the sweetness notes. As a result, the brandies aged in 500L casks (B) were found to be more balanced than those aged in 250L casks (M) and this better balance was even more pronounced in unseasoned casks than in the seasoned ones.

The brandies aged in Spanish oak seemed to be the least affected by the operational variables investigated, since only a significant difference with a $p < 0.1$ was perceived in the alcoholic mouthfeel, which was even greater in those that were in contact with unseasoned casks. Perhaps the previously mentioned significant contribution of Spanish oak could be the reason why the effects of barrel size and barrel seasoning were less evident.

4. Conclusions

Brandies aged in 250 L barrels (M) showed higher TPI content compared to those aged in 500 L casks (B). Unlike color, TPI continued to increase for all wood types throughout the experiment, indicating continuous modification of the brandy's phenolic content.

Regarding seasoning effects, brandies aged in unseasoned Botas and Medias showed higher TPI and phenol extraction coefficient values than those in seasoned casks. In contrast, the evolution of the color increment parameter (ΔE_{00}) varied depending on the wood type used and its prior treatment. Significant color changes were observed in brandies aged in FO and SO during initial months, with their color stabilizing compared to other brandies after 12 months.

Seasoning of any oak wood types reduced their phenolic compound content, resulting in more homogeneous extraction compared to unseasoned woods, thereby reducing brandy astringency.

Based on the results from the four kinetic models used for this study, the evolution of parameters related to distillates aging is directly related to the seasoning treatment of the casks, rather than to the size of the barrels. The aging of distillates in untreated (unseasoned) casks is best described by a pseudo-second order kinetic model (Peleg's model). This model assumes that there are two types of mechanisms involved in aging, a rapid extraction (outermost layers of the inner surface of the wooden casks) and another slower one (innermost layers). On the other hand, the aging of distillates in seasoned casks is best described by a diffusion model, specifically the parabolic diffusion model, in which physical phenomena of diffusion and chemical reactions between the extractant (spirit) and the extractant (wood) are taken into account.

Comparing these parameters during the initial aging stages reveals that initial extraction rates were consistently higher in Medias than in Botas, regardless of seasoning. After reaching equilibrium, no specific trends were observed in any of the experiments, likely due to the complex nature of processes influenced by wood type.

Sensory analysis of 16-month aged brandy samples revealed heterogeneous results for the three types of oak wood evaluated. Brandies aged in AO were strongly influenced by cask size, with higher ratings observed for those in Media casks compared to Botas. Variations were also observed in brandies aged in FO wood casks based on cask sizes.

Overall, the results obtained in this study suggest that the extraction process is primarily influenced by the wood type, seasoning, and the cask volume, which in turn determines the wood contact surface/spirit volume ratio.

Credit author statement

Rocío Trillo Ollero: Conceptualization, Formal analysis, Investigation, Methodology, Roles/Writing - original draft, Writing - review & editing.

Luis M. Tillo Gutiérrez: Conceptualization, Formal analysis, Investigation, Methodology, Supervision, Writing - review & editing.

M. Valme García-Moreno: Conceptualization, Funding acquisition, Methodology, Project administration Supervision, Writing - review & editing.

M. Carmen Rodríguez Dodero: Formal analysis, Investigation, Methodology, Supervision, Writing - review & editing.

Dominico A. Guillén-Sánchez: Conceptualization, Funding acquisition, Methodology, Project administration Supervision, Writing - review & editing.

Funding

The authors would like to thank Bodegas Gonzalez Byass S.L. for the analysis of phenolic compounds, the provision of samples and the materials used in this research within the framework of the "Agreement between the University of Cadiz and the company Bodegas Gonzalez Byass S.L. for collaboration in the promotion of the training of research staff for the realization of doctoral theses in companies" (Agreement 35-22, of April 8, 2022). We would also like to thank the Institute of Agri-Food Research (IVAGRO) of the University of Cadiz for the analysis of the samples.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crfs.2024.100900.

Data availability

The authors do not have permission to share data.

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