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Micro-oxygenation level as a key to explain the variation in the colour and chemical composition of wine spirits aged with chestnut wood staves

Sara Canas [a,b,*], Ofélia Anjos [c,d,e], Ilda Caldeira [a,b], Tiago A. Fernandes [f,g], Nádia Santos [h], Sílvia Lourenço [a], Joana Granja-Soares [i], Laurent Fargeton [j], Benjamin Boissier [j], Sofia Catarino [k,l]

[a] *Instituto Nacional de Investigação Agrária e Veterinária, Pólo de Dois Portos, Quinta de Almoinha, 2565-191, Dois Portos, Portugal*
[b] *MED–Mediterranean Institute for Agriculture, Environment and Development, Institute for Advanced Studies and Research, Universidade de Évora, Pólo da Mitra, Ap. 94, 7006-554, Évora, Portugal*
[c] *Instituto Politécnico de Castelo Branco, Quinta da Senhora de Mércules, 6001-909, Castelo Branco, Portugal*
[d] *CEF–Centro de Estudos Florestais, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017, Lisboa, Portugal*
[e] *CBP-BI–Centro de Biotecnologia de Plantas da Beira Interior, Quinta da Senhora de Mércules, 6001-909, Castelo Branco, Portugal*
[f] *CQE–Centro de Química Estrutural, Associação do Instituto Superior Técnico para a Investigação e Desenvolvimento (IST-ID), Universidade de Lisboa, 1049-001, Lisboa, Portugal*
[g] *DCeT–Departamento de Ciências e Tecnologia, Universidade Aberta, Rua da Escola Politécnica,141-147, 1269-001, Lisboa, Portugal*
[h] *Adega Cooperativa da Lourinhã, Av. de Moçambique, 2530-111, Lourinhã, Portugal*
[i] *DCEB–Departamento de Ciências e Engenharia de Biossistemas, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017, Lisboa, Portugal*
[j] *Vivelys, Domaine du Chapître, 34750, Villeneuve-les-Maguelone, France*
[k] *LEAF-Linking Landscape, Environment, Agriculture and Food Research Center, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017, Lisboa, Portugal*
[l] *CEFEMA–Center of Physics and Engineering of Advanced Materials, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1, 1049-001, Lisboa, Portugal*

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ABSTRACT

A deep knowledge of oxygenation level effect on wine spirits' ageing is imperative to understand ageing chemistry and to select the most suitable technological option towards quality and sustainability. Following two articles on the same trial, this work focused on colour, total phenolic index (TPI) and basic chemical characteristics of a wine spirit aged in 50 L demijohns with chestnut wood staves together with three micro-oxygenation (MOX) levels. Chromatic characteristics and TPI were monitored over time (8–365 days) while sensory colour, alcoholic strength, acidity, pH and dry extract were assessed at the end of ageing. Results showed that stronger oxygenation promoted significantly faster colour evolution (lower lightness, higher chroma, red, yellow and brown hues) and higher TPI than mild and intermediate oxygenation until 60 days, probably by favouring the leaching of outer wood layers and extraction/degradation of tannins. No significant differences were found between these ageing modalities at 365 days. Outcomes suggest that the stronger MOX is the most suitable modality in terms of quality and sustainability. Significant differences between wine spirits resulting from MOX and control modality (slower colour evolution, lower TPI and dry extract) confirms the oxygen pivotal role in wine spirit's ageing, particularly in the colour evolution.

1. Introduction

Ageing is a key stage of the wine spirit (WS) production process since it encompasses several physicochemical phenomena involving the distillate and the wood that promote positive changes in its chemical composition and sensory properties (Puech, Leaute, Mosedale, & Mourgues, 1998). Furthermore, the quality of an aged WS cannot be described as a single and simple attribute, but rather as the combination of many characteristics. Specifically, the colour enhancement resulting from the release of phenolic compounds occurring during wood contact (Delgado-González, García-Moreno, Sánchez-Guillén, García-Barroso, & Guillén-Sánchez, 2021) is of utmost importance. Indeed, colour is the first sensory attribute perceived by the consumer and allows predicting other sensory sensations of the beverage or food, thus having a remarkable influence on the choice and purchase decision (Pathare, Opara, & Al-Said, 2013). Colour can be examined by instrumental

* Corresponding author. Instituto Nacional de Investigação Agrária e Veterinária, Pólo de Dois Portos, Quinta de Almoinha, 2565-191, Dois Portos, Portugal.
E-mail address: sara.canas@iniav.pt (S. Canas).

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methods of analysis (objective), based on several chromatic characteristics that define it as a point in a colour space; the most used in the food industry are those of Commission Internationale de l'Éclairage (CIE): CIELab and CIELCh (Pathare et al., 2013). It can also be assessed by visual measurements during sensory analysis (Lawless & Heymann, 1999, pp. 406–429). Since the latter one is subjective, but more representative of what the consumer sees, it is convenient to characterise the beverage's colour using both approaches.

In addition, the basic chemical characteristics of a spirit beverage, such as alcoholic strength, acidity, pH and total dry extract, are also influenced by the ageing process (Anjos, Caldeira, Pedro, & Canas, 2020; García-Moreno et al., 2020; Sánchez-Guillén et al., 2019). Thus, besides specific determinations of phenolic and volatile composition, the colour and these basic features together with sensory analysis are needed to fully characterise the aged WS and to understand the effect of the ageing technology on its *lato sensus* quality.

Previous research showed that wood species and oxygen govern the phenomena occurring during ageing and, consequently, the characteristics acquired by the aged WS (Canas, Caldeira, Anjos, & Belchior, 2019; Granja-Soares et al., 2020). Among the kinds of wood used for this purpose, the chestnut wood (*Castanea sativa* Mill.) stood out by the high quality and the faster ageing imparted to the aged beverages due to specific chemical and anatomical features (Canas et al., 2019; García-Moreno et al., 2020).

In the traditional ageing technology, the oxygen supply is ensured by the wooden barrel (Del Alamo-Sanza, Cárcel, & Nevares, 2017). Alternatives have recently been pursued to address this technology drawbacks (time-consuming and costly, resulting in low production efficiency and low profitability for the producer, implying a high demand for wood, and causing great loss of WS by evaporation) and therefore to achieve a more sustainable WS ageing. In this scenario, the last approach made by our team was based on MOX applied to the WS, stored in stainless steel tanks with wood staves inside, to replicate the oxygen transfer occurring in the barrel (Anjos et al., 2020; Canas et al., 2019; Granja-Soares et al., 2020). Notwithstanding the promising results attained, a single flow rate of oxygen (2 mL/L/month) was assayed. Thus, in the pursuit of an optimised technology, intending maximization of WS quality and ageing sustainability, investigation is currently made under the Project Oxyrebrand (https://projects.iniav.pt/oxyrebrand/index.php/pt/), by applying three levels of MOX or nitrogen (control) to the same WS kept in 50 L glass demijohns with chestnut wood staves inside. For this purpose, a better understanding of the ageing chemistry is essential, resorting to a broad approach on the influence of the MOX level on several physicochemical characteristics and sensory properties of the aged WS. Within this project, two articles have already been published with a detailed analysis of phenolic compounds, furanic aldehydes, iron and copper (Canas et al., 2020), and of volatile compounds and the related sensory profile (Caldeira et al., 2021) of the WSs aged through these ageing modalities. To accomplish the outlined strategy, this work aims to examine the evolution of chromatic characteristics and total phenolic index (TPI) over the ageing time (365 days), as well as to characterise the WSs based on these parameters, and on the colour perceived by the tasters and other chemical parameters (alcoholic strength, total acidity, fixed acidity, volatile acidity, pH and total dry extract) correlated with the WS quality, at the end of ageing process.

2. Materials and methods

2.1. Experimental design and aged WSs sampling

The trial was carried out in pilot scale, in 50 L glass demijohns, including four ageing modalities: three MOX modalities (O15, O30, and O60) and one modality with nitrogen application (N; control), with two replicates (Fig. 1). Each demijohn was closed with a specific silicon bung as described by Canas et al. (2020).

Staves from Portuguese chestnut (*C. sativa* Mill.) were used in all modalities. The staves (50 cm length × 5 cm width × 1.8 cm thickness) were manufactured by J.M. Gonçalves cooperage (Palaçoulo, Portugal). The staves were heated in an industrial oven under controlled temperature to attain the same toasting level: medium plus level resulting from 90 min at an average temperature of 240 °C; 1.8 cm of toasting thickness. The quantity of staves inserted into the demijohns reproduced the surface area to volume ratio of a 250 L barrel (85 cm^2/L), which corresponds to the barrel size more often used in WSs ageing.

A wine distillate (alcoholic strength, 78.3% v/v; pH, 5.33; total acidity, 0.12 g acetic acid/L absolute ethanol; volatile acidity, 0.09 g acetic acid/L absolute ethanol) produced by Adega Cooperativa da Lourinhã (Lourinhã, Portugal) was used to fill the demijohns, which were placed in its cellar in the same environmental conditions.

MOX was applied to the WS during the ageing period, supplying pure oxygen (X50S Food, Gasin, Portugal) through a multiple diffuser micro-oxygenator (VISIO 6, Vivelys, France) with ceramic diffusers, at different flow rates according to the ageing modality. Flow rates were selected based on the results of our previous study (Canas et al., 2019), and in view of an adequate oxygen supply (avoiding excessive oxidation), possibility of shortening the ageing period and reducing the ageing's costs to achieve a sustainable ageing technology. The micro-oxygenator, of volumetric type, was adapted by Vivelys to provide the intended low flow rates. In addition, during the trial, pure nitrogen (X50S Food, Gasin, Portugal) was continuously applied through a specific device (Gasin, Portugal) to the WS in one of the ageing

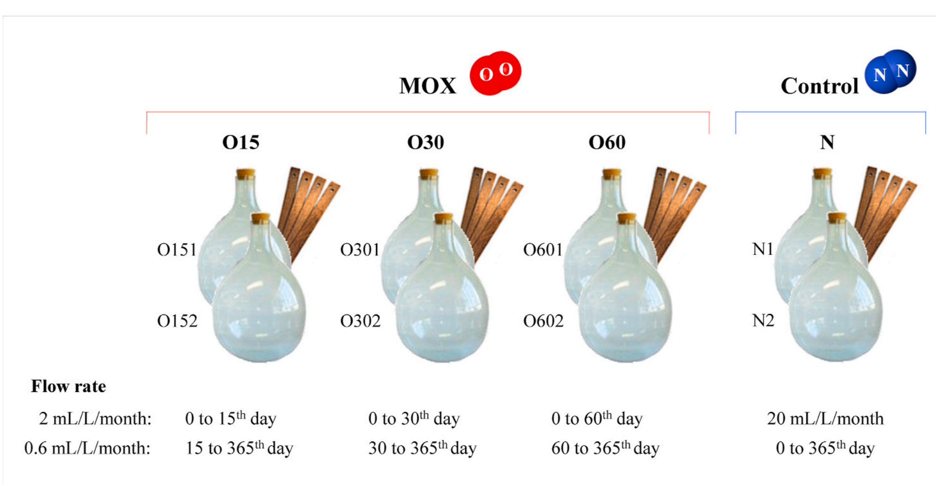


Fig. 1. Ageing trial scheme.

modalities in order to decrease the dissolved oxygen as much as possible, acting as a control. This modality was chosen as the best option for studying the role of oxygen in the WS's ageing in a technological trial, that is, to compare the effects of nearly no oxygen against three levels of oxygen applied through MOX on the characteristics acquired by this beverage. The knowledge gained will be critical to understand the ageing chemistry and therefore to better explore the associated technology.

The ageing period was set at 365 days. The eight aged WSs were sampled at 8, 21, 60, 180, 270, and 365 days of ageing, as reported by Canas et al. (2020); a total of 48 samples were taken.

The amount of WS collected in each sampling time was limited to avoid a significant decrease of the WS volume in the demijohn and the change of surface/volume ratio. For this reason, the chromatic characteristics and the TPI were analysed over the ageing time, but the other chemical analyses and the assessment of colour by the tasters/sensory analysis were only performed at 365 days because a substantial amount of WS was required.

2.2. Chemicals

All solvents used were analytical grade purchased from Merck (Darmstadt, Germany). Ultrapure water (conductivity<0.055 µS/cm) was produced using Arium Comfort I equipment (Sartorius, Göttingen, Germany).

2.3. Chromatic characteristics

The WSs chromatic characteristics were determined (in duplicate) by the CIELab/CIELCh method (Pathare et al., 2013) with a Varian Cary 100 Bio spectrophotometer (Santa Clara, California, USA) and a 10-mm glass cell. Transmittance measurement was made every 10 nm from 380 to 770 nm, using a D65 illuminant and a 10° standard observer. The chromatic characteristics assessed were: lightness (L*), chroma (C) - $C = \sqrt{(a^*)^2 + (b^*)^2}$, chromaticity coordinates (a* and b*), and absorbance at 470 nm, as described by Canas et al. (2019).

2.4. Basic chemical characteristics

Several analyses were carried out (in duplicate) to characterise the WSs from the different ageing modalities: TPI; alcoholic strength; total acidity; fixed acidity; volatile acidity; pH; total dry extract.

TPI was analysed as described by Cetó et al. (2012); the WSs were diluted with ethanol/water 78:22 v/v, and the absorbance was measured at 280 nm using a Varian Cary 100 Bio spectrophotometer (Santa Clara, California, USA) and a 10-mm quartz cell. TPI was calculated by multiplying the measured absorbance by the dilution factor.

Alcoholic strength was analysed by distillation and electronic densimetry (OIV, 2019); the results were expressed as a volumetric percentage of ethanol in the WS.

Total acidity (by colorimetric titration), fixed acidity (by colorimetric titration of the water solution of dry extract), and volatile acidity (by calculation: total acidity minus fixed acidity) were analysed according to Belchior et al. (2001); the results were expressed as grams of acetic acid per litre of absolute ethanol.

pH was analysed by potentiometry (potentiometer micro pH2002, Crison, Barcelona, Spain) (OIV, 2019).

Total dry extract was assessed by gravimetry (OIV, 2019); the results were expressed as grams per litre.

2.5. Colour perceived by the tasters

The colour of WSs sampled at 365 days of ageing was assessed by quantitative descriptive analysis using a panel of tasters previously selected and trained (Caldeira et al., 2021). The tasting panel comprised eight judges (four females and four males, aged between 27 and 56 years). Before and during this study, several training sessions were carried out, and several samples of wine distillates and aged WSs were evaluated.

The sensory sessions took place in a tasting room, under natural light and temperature at about 20 °C, around 10 a.m. The eight WSs samples (30 mL) were served in standard wine-tasting glasses (ISO standard 3591, 2010), which were coded with three random digits, and examined in balanced order to eliminate first-order carryover effects (Macfie, Bratchell, Greenhoff, & Vallis, 1989). The tasters were asked to score the intensity of five colour attributes (yellow-green, yellow-straw, golden, amber, and greenish), based on a structured scale from 0 (without perception) to 5 (stronger perception) (Granja-Soares et al., 2020).

2.6. Statistical analysis

One-way analysis of variance (ANOVA) was carried out to assess the effect of ageing technology, as a fixed factor, on the chromatic characteristics and TPI of the WSs for each sampling time. Additional one-way ANOVA was made to examine the effect of the ageing time, as a fixed factor, on the chromatic characteristics and TPI. At 365 days of ageing, the same approach was used to analyse the influence of ageing technology on the other chemical parameters and colour perceived by the tasters. Fisher's least significant difference (LSD) test was applied for averages' comparison when a significant difference ($p < 0.05$) was found.

Besides, Principal Component Analysis was carried out for the overall assessment of the data at 365 days of ageing.

All calculations were performed using Statistica version 7.0 software (Statsoft Inc., Tulsa, USA).

3. Results and discussion

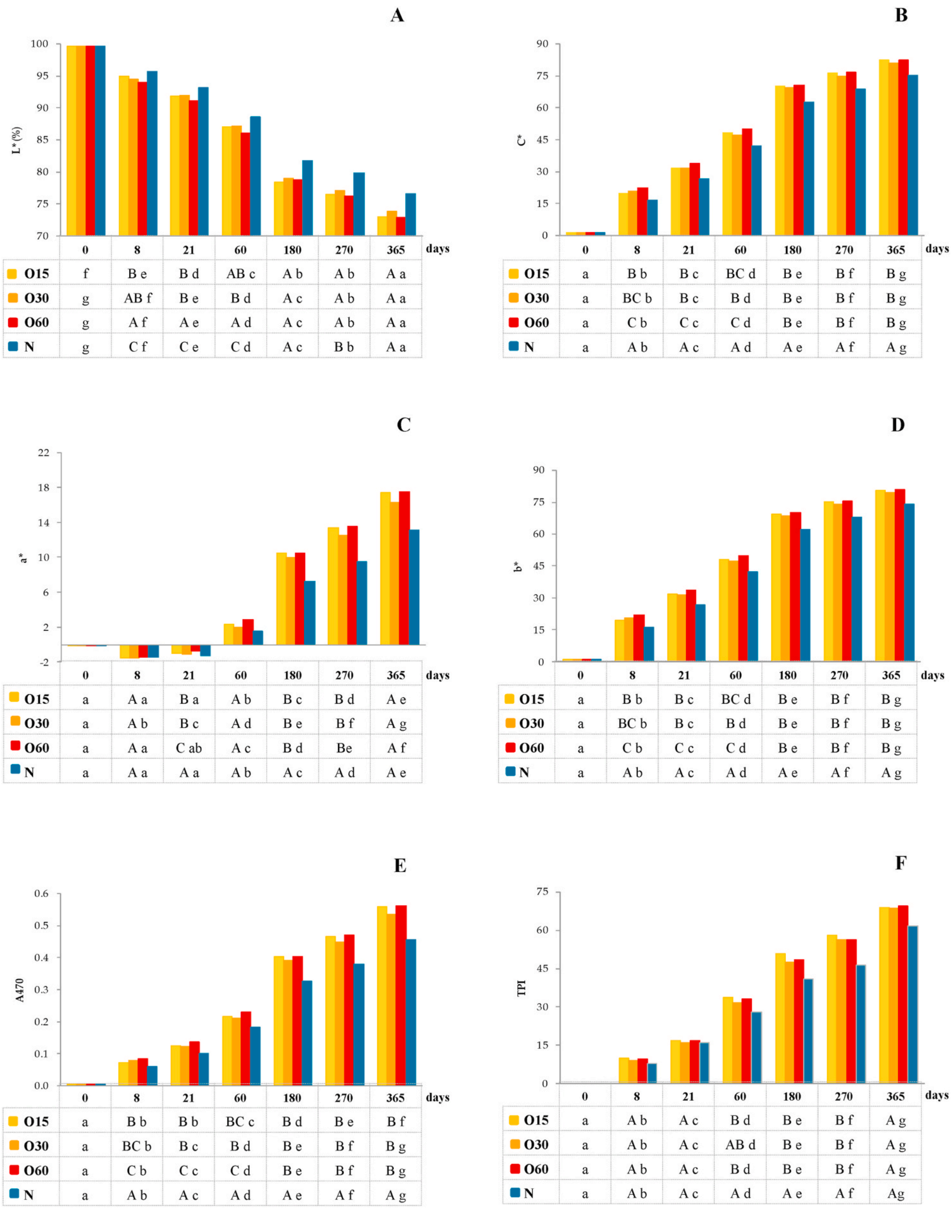
3.1. Evolution of chromatic characteristics and total phenolic index over time

The ANOVA results for chromatic characteristics of the WSs aged for 365 days by different modalities (O15, O30, O60, and N) are shown in Fig. 2. In general terms, they reveal a continuous evolution of lightness (L*), chroma (C), green-red hue (a*), yellow hue (b*) and brown hue (A470) of the WSs as the ageing time progressed.

Lightness intends to reflect the luminosity, which describes the gray scale component in each colour (Pathare et al., 2013), from fully transparent/bright (100%) to fully opaque/dark (0%). This chromatic characteristic was significantly higher in the wine distillate (99.68%) - Fig. 2A. Then, a regular decrease was observed in all aged WSs regardless of the ageing modality, ranging from 72.93% to 76.54% at 365 days. However, such a decrease was more marked in O60 and O30 WSs (showing significant differences between all sampling times) than in O15 (showing similar average values at 180 and 270 days of ageing).

During the first 60 days of ageing, the highest level of MOX (O60) promoted a significantly faster decrease of lightness (darker colour) than the intermediate and lower levels (O30 and O15, respectively), which had similar effect. Conversely, the control WS (N) showed the highest lightness over time, which emphasizes the importance of oxygen and therefore the oxidation of WSs substrates on lightness evolution during ageing.

Chroma depicts the quantitative colourfulness feature of the beverage judged in proportion to its brightness; the higher the chroma value, the greater the colour intensity perceived by the human eye (Pathare et al., 2013). A significantly lower value was found in the wine distillate (1.34), and the ageing process induced its gradual increase in all WSs, which ranged between 75.33 and 82.70 at 365 days (Fig. 2B). At any sampling time, chroma was significantly lower in the control WS. Regarding the MOX modalities, significant differences were only observed until 60 days of ageing and mainly resulted from the greater



A

	0	8	21	60	180	270	365
O15	f	B e	B d	AB c	A b	A b	A a
O30	g	AB f	B e	B d	A c	A b	A a
O60	g	A f	A e	A d	A c	A b	A a
N	g	C f	C e	C d	A c	B b	A a

B

	0	8	21	60	180	270	365
O15	a	B b	B c	BC d	B e	B f	B g
O30	a	BC b	B c	B d	B e	B f	B g
O60	a	C b	C c	C d	B e	B f	B g
N	a	A b	A c	A d	A e	A f	A g

C

	0	8	21	60	180	270	365
O15	a	A a	B a	A b	B c	B d	A e
O30	a	A b	B c	A d	B e	B f	A g
O60	a	A a	C ab	A c	B d	Be	A f
N	a	A a	A a	A b	A c	A d	A e

D

	0	8	21	60	180	270	365
O15	a	B b	B c	BC d	B e	B f	B g
O30	a	BC b	B c	B d	B e	B f	B g
O60	a	C b	C c	C d	B e	B f	B g
N	a	A b	A c	A d	A e	A f	A g

E

	0	8	21	60	180	270	365
O15	a	B b	B b	BC c	B d	B e	B f
O30	a	BC b	B c	B d	B e	B f	B g
O60	a	C b	C c	C d	B e	B f	B g
N	a	A b	A c	A d	A e	A f	A g

F

	0	8	21	60	180	270	365
O15	a	A b	A c	B d	B e	B f	A g
O30	a	A b	A c	AB d	B e	B f	A g
O60	a	A b	A c	B d	B e	B f	A g
N	a	A b	A c	A d	A e	A f	Ag

Fig. 2. Evolution of the chromatic characteristics and total phenolic index of the WSs over 365 days of ageing according to the ageing modalities (O15, O30, O60, N); lightness (A); chroma (B); chromaticity coordinate a* (C); chromaticity coordinate b* (D); absorbance at 470 nm (E); total phenolic index (F). Significance of means comparison (Fisher's test; $p < 0.05$) is shown in tables below graphics. For each analytical determination: different uppercase letters (A, B, C) in the same column denote significant differences between ageing modalities in each sampling time; different lowercase letters (a, b, c, d, e, f, g) in the same row denote significant differences between sampling times for each ageing modality.

chroma of WS underwent stronger oxygenation (O60). After 60 days, O60 had slightly higher chroma than O15, followed by O30.

Coordinate a* takes positive values for the red hue and negative values for the green one. The wine distillate had a slight green hue (−0.15) and became greener up to 21 days of ageing (−1.53<a*<−1.42) - Fig. 2C. This behaviour was already found in our first study on MOX using chestnut wood staves and 2 mL/L/month as oxygen flow, in which the WSs exhibited a green hue in the first 15 days of ageing (Canas et al., 2019). Thus, the following hypothesis arises: the green hue observed in the early ageing period may have resulted from the direct extraction of wood compounds that contribute to green hue, under less oxygenation and before their degradation, which had the main contribution to the WSs colour. Coumarins (scopoletin and umbelliferone, which have UV–vis absorption up to 420 nm), despite having slightly different spectra can cause green colour in earlier samples by not absorbing between 500 and 565 nm. The ring rupture during their degradation will contribute less to the green hue as they will absorb only at 350 nm, adding also the blue and purple hues (Perkowska et al., 2021; Schulz & Dörmann, 2019; Smith, Dunford, & Roberts, 2010). Inorganic species present in the WS (Canas et al., 2020), such as iron hydroxocomplexes, iron dimers, hydrated iron(II) oxide ($FeO{\cdot}nH_2O$), as well as iron(II) hydroxide ($Fe(OH)_2$), may also contribute as green pigments on early samples. The hydrolysis of iron(III) is also well-known, and the evidence of different polynuclear species has been established (Flynn, 1984; Milburn & Vosburgh, 1955). The aqueous equilibria for simple iron(III) dimers have been established and studied by several authors. Fig. 3 summarizes the equilibria equations and also shows the corresponding colours (Powell & Heath, 1994; Yang, Ratner, & Schatz, 2013; Zhu et al., 2013).

$$Fe(H_2O)_6^{\ 3+} \rightleftharpoons Fe(H_2O)_5OH^{2+} + H^+$$

pale → yellow

$$Fe(H_2O)_5OH^{2+} \rightleftharpoons Fe(H_2O)_4(OH)_2^{\ 2+} + H^+$$

yellow

$$Fe(H_2O)_5OH^{2+} \rightleftharpoons (H_2O)_4Fe(OH)_2Fe(OH_2)_4^{\ 4+} + 2H_2O$$

greenish-yellow

$$(H_2O)_4Fe(OH)_2Fe(OH_2)_4^{\ 4+} + 2H_2O \rightleftharpoons (H_2O)_5FeOFe(OH_2)_5^{\ 4+}$$

Deep orange-brown

Fig. 3. Equations of chemical equilibrium for Fe(III) dimers.

Iron(II) hydroxide species in the presence of oxygen can be oxidized into iron(III) oxide, which has reddish colour (Morgan & Lahav, 2007).

a* values became positive (red hue) at 60 days of ageing and then increased significantly in all WSs, ranging from 13.17 to 17.52 at 365 days, reflecting the predominance of extraction/formation of contributors to red pigments under the higher oxygen accumulation. In particular, the slight and progressive increase of total iron concentration in all WSs until 270 days of ageing, reported in our previous work (Canas et al., 2020), is consistent with these observations.

Change in red hue intensity was more pronounced in the WSs from MOX modalities than in the control one. As for L* and C, the results suggest that 60 days corresponded to a marked change in the colour evolution.

Concerning each sampling time, the main significant difference was found between the MOX modalities and the control one (lower red hue intensity). Among MOX modalities, O60 tended to confer higher red hue intensity followed by O15 and finally O30.

Coordinate b* takes positive values for the yellow hue and negative values for the blue one. The wine distillate had a slight yellow hue (1.34) that increased during the trial in all aged WSs, ranging from 74.17 to 80.82 at 365 days (Fig. 2D). These outcomes are similar to those of chroma, as reported in previous works regardless of the ageing technology (Canas, Belchior, Caldeira, Spranger, & Sousa, 2000; Canas et al., 2016), which points to a stronger influence of coordinate b* than coordinate a* on the chroma. WS from O60 presented significantly higher intensity of yellow hue (higher b*) than the WS from O15 and O30 until 60 days; afterward, only a slight difference among ageing modalities was observed. The control WS showed the weaker intensity over time.

The absorbance at 470 nm aids perception of the complementary colour, brown hue (Martins & van Boekel, 2003). This hue had a minor contribution to the colour of the wine distillate (0.005) and of the aged WSs, although it has increased considerably over time, ranging from 0.46 to 0.56 at 365 days of ageing (Fig. 2E). The WSs from O30, O60 and N showed a gradual increase (with significant differences between all sampling times) whereas the WS from O15 presented similar average values at 8 and 21 days of ageing. The WSs from O60 and N stood out from the others by the highest and lowest intensity of brown hue, respectively. Regarding the differences between WSs, the MOX effect on this chromatic characteristic was more pronounced in the first 60 days of ageing, and thereafter the lowest and the highest oxygenation levels induced the same brown hue in the WS: O15<O30<O60 at 8 days, then O15≈O30<O60 at 21 days, O30<O15<O60 at 60 days, and thereafter O30<O15≈O60 remained until 365 days. The brown pigments released from the wood (Alañón, Rubio, Díaz-Maroto, & Pérez-Coello, 2010), as well as those formed by non-enzymatic reactions of phenolic compounds occurring in the WS during ageing, are probably the main responsible for browning, as in other foods and beverages (Gökmen & Şenyuva, 2006; Pathare et al., 2013). Indeed, ring aromaticity rupture occurs when some organic extracts undergo oxidation or hydrolysis reactions, resulting in new metabolite species contributing less to the greenish-yellow hue and more to the brown one. For this reason, the more intense oxygenation in O60 modality may have induced more oxidation reactions, especially in the first 60 days, that gave rise to greater concentration of coloured compounds responsible for the development of brown hue in that WS.

These results are in agreement with previous ones attained in the traditional ageing technology (Canas et al., 2000) and in the alternative ageing technology without MOX (Canas et al., 2016; Schwarz et al., 2020) or with a single MOX flow (Canas et al., 2019).

In addition, higher a* and b* values were observed in the present work, regardless of the MOX modality, than in the previous one, using a single MOX flow (2 mL/L/month) (Canas et al., 2019) at 180 days of ageing. Similar behaviour was found for L*, C and A470. This difference can be ascribed to the experiment scale, as well as to the wine distillate, wood and toasting variability.

TPI (Fig. 2F) was also influenced by the ageing technology. TPI was non quantifiable in the wine distillate because it was devoid of phenolic compounds and of furanic aldehydes except furfural (Caldeira et al., 2021; Canas et al., 2020). During ageing, the WS was progressively enriched in compounds extracted from the wood, namely those of low molecular weight (as reported in the cited articles), which explains the significant increase in TPI between all sampling times in all WSs, ranging between 61.65 and 69.40 at 365 days. Even in the control modality, transfer of the aforementioned compounds was also referred in the cited works, having been ascribed to their slowly release from the wood triggered by some oxygen contained in the wood itself (estimated at 8.67 mg per 100 g of staves by Del Álamo, Nevares, Gallego, Fernández de Simón, & Cadahía (2010)).

Regarding each sampling time, significant differences between WSs according to the ageing modality were only found from 60 to 270 days. The main difference was observed between WSs from the MOX modalities and the control one, which presented the highest and the lowest levels of TPI, respectively. Despite the absence of significant differences among MOX modalities, TPI was consistently lower in O30, while some variation between O60 and O15 occurred over time. Indeed, slightly higher levels of TPI were found in O15 at 8, 60, 180 and 270 days, and in O60 at 21 and 365 days of ageing. Interestingly, these results reflect the kinetics of individual phenolic compounds monitored in the same WSs (Canas et al., 2020). Kinetics of gallic acid, syringic acid and vanillin (whose higher concentrations over time were closely related to mild oxidative conditions, O15), and those of ellagic acid, syringaldehyde, coniferaldehyde and sinapaldehyde (whose higher concentrations were closely related to stronger oxidative conditions, O60, especially during the last ageing phase) can explain the TPI levels found in O15 and O60 over time; besides, the lowest contents of phenolic compounds were quantified in the control WS (Canas et al., 2020).

In summary, it is noteworthy the faster evolution of chromatic characteristics in the WS aged with higher oxygen supply. The WS produced with lower (O15) and intermediate oxygenation (O30) showed similar evolution, while the control exhibited a weaker one. Thus, evidence exists on the crucial role of oxygen on the formation and development of colour during the WS' ageing, confirming our previous findings (Canas et al., 2019), as well as the influence of MOX level on this phenomenon. These results are also coherent with those previously reported (Canas et al., 2020), which showed more intense extraction of phenolic compounds and furanic aldehydes, reactions involving their precursors in the liquid medium (additive phenomena), and the subsequent oxidation reactions and interactions with other compounds (subtractive phenomena) promoted by the highest level of oxygen supplied.

Considering the ageing time, it is interesting to note that the main colour differences were found until 60 days. The colour of aged spirit beverages is closely related to the pool of phenolic compounds released from the wood (Canas et al., 2020; García-Moreno et al., 2020; Rodríguez-Solana, Salgado, Domínguez, & Cortés-Diéguez, 2014). So, this pattern reflects the extraction phases described by Delgado-González et al. (2021): the colour evolution of the spirit beverages is ruled by Peleg's pseudo-second-order kinetics model, that is, there is an initial phase, characterised by fast leaching of compounds from the outer layers of the wood, and a second phase that comprises the slow diffusive extraction occurring inside the wood pores, and reactions of oxidation, condensation and polymerization. Thus, the main colour differences observed in the first two months of ageing were a consequence of the first phase, in which the extraction was faster but differentiated according to the ageing technology (level of oxygenation). Thereafter, the colour acquired by the WS resulted from the second phase. Since the more differentiated behaviour of the low molecular weight compounds studied in the same WSs was observed in this second ageing stage (Canas et al., 2020), the outcomes also point to the contribution of other compounds, likely of higher molecular weight, to the colour formation in the beginning of ageing. Tannins (an extended family existing in the wood, easily extracted, highly reactive, and prone to oxidation) and their derivatives (Chira et al., 2020; García-Estévez, Escribano-Bailón, & Alcalde-Eon, 2019; Vignault et al., 2018; Viriot, Scalbert, Lapierre, & Moutounet, 1993), should play an essential role in this phase. This argument is also plausible to explain the differences found in the WS's chromatic characteristics according to the oxygenation level. Indeed, literature shows that: i) ellagitannins attain their maximum contents in the beverage in the beginning of ageing (García-Estévez et al., 2019; Vignault et al., 2018); ii) the higher the dissolved oxygen level, the higher the contents and degradation rate of ellagitannins by oxidation and other reactions (García-Estévez et al., 2017, 2019); iii) our previous results on low molecular weight compounds of the same WSs (Canas et al., 2020) suggested that these reactions were more intense in O60 modality; iv) oxidation of wood ellagitannins can give rise to yellow pigments (Fujieda, Tanaka, Suwa, Koshimizu, & Kouno, 2008); v) condensation reactions between tannins mediated by acetaldehyde and by phenolic aldehydes are also likely to occur (Canas et al., 2019).

3.2. *Colour perceived by the tasters at the end of ageing*

After 365 days of ageing, the tasters characterised the colour of the aged WSs predominantly as amber (Fig. 4). Greenish attribute (i.e. greenish reflection that sometimes exists at the edge of the beverage inside the tasting glass) is closely related to amber, being a distinctive feature of older WSs (Canas et al., 2000). The O15 and O60 WSs were scored with the highest intensities of amber and greenish (that made them be perceived older than the O30 and control ones). The control WS was scored with the lowest intensity of greenish, and the highest intensity of golden and yellow-straw attributes.

Amber is the main colour of older WSs, resulting from the combination of higher positive values of a* (red hue) and b* (yellow hue), while golden and yellow-straw prevail in WSs with less ageing time (Canas et al., 2000). Since the ageing time was the same, differentiation made by the tasters based on the colour attributes resulted from the evolution imparted by the ageing technology. It is important to highlight the coherence between the sensory attributes and chromatic characteristics for the different WSs.

3.3. *Basic chemical characteristics of WSs at the end of ageing*

The one-way ANOVA results for the basic chemical composition of WSs at 365 days of ageing are shown in Table 1. Among the studied parameters, only the total dry extract was significantly influence by the ageing technology, separating the control WS from the others (lower and higher contents, respectively). Although without significant differences, the control WS also exhibited the lowest total acidity, fixed acidity and volatile acidity, and the highest pH. Regarding the WSs produced through MOX modalities, the higher the oxygenation level, the higher

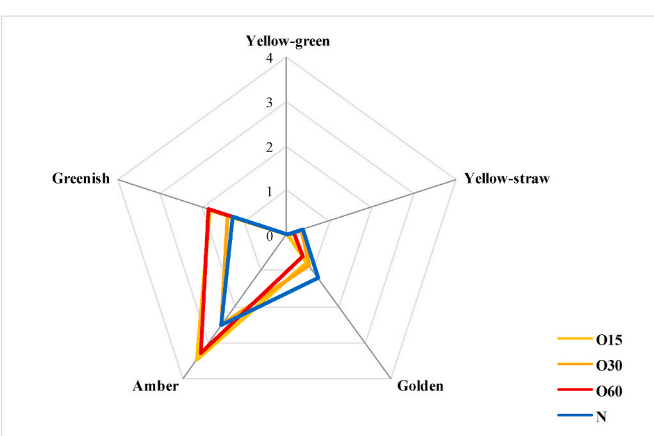


Fig. 4. Colour profile based on the average panel score's attributes for the aged WSs. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Average values of the basic chemical characteristics of WSs at 365 days of ageing according to the ageing modality.

	p	MOX + staves			N + staves
		O15	O30	O60	
Alcoholic strength (% v/v)	*0.2126*	77.80 ± 0.01	76.83 ± 0.46	77.32 ± 0.41	77.28 ± 0.39
Total acidity (g $_{acetic\ acid}$/L AE)	*0.0533*	0.64 ± 0.05	0.65 ± 0.00	0.67 ± 0.01	0.57 ± 0.01
Fixed acidity (g $_{acetic\ acid}$/L AE)	*0.1632*	0.29 ± 0.02	0.28 ± 0.01	0.28 ± 0.01	0.25 ± 0.01
Volatile acidity (g $_{acetic\ acid}$/L AE)	*0.0791*	0.36 ± 0.03	0.37 ± 0.01	0.39 ± 0.01	0.32 ± 0.02
pH	*0.0917*	4.13 ± 0.03	4.16 ± 0.03	4.13 ± 0.05	4.25 ± 0.04
Total dry extract (g/L)	*0.0176*	2.44 ± 0.10 b	2.38 ± 0.00 b	2.38 ± 0.05 b	2.13 ± 0.01 a

Results expressed as mean ± standard deviation; Means within the same row followed by different letters are significantly different ($p < 0.05$) according to Fisher's Test; MOX – micro-oxygenation; O15, O30, O60 – MOX levels; N – Nitrogen (control). AE – absolute ethanol.

the total acidity and volatile acidity. Volatile acidity was the main part of the total acidity, as in previous studies (Anjos et al., 2020; García--Moreno et al., 2020), and acetic acid is the main responsible for that (Bertrand, 2003). Actually, this acid already exists in the wine distillate, is also released from the wood, and derives from the oxidation of acetaldehyde during ageing (Nishimura, Ohnishi, Masahiro, Kunimasa, & Ryuichi, 1983). The last two phenomena explain the higher level of acetic acid (Caldeira et al., 2021), volatile acidity (and, therefore, total acidity) found in the WS from O60. The fixed acidity and the total dry extract were slightly higher in the WS produced with lower oxygenation (O15); similar behaviour was noticed for the alcoholic strength. The high alcoholic strength after 365 days of ageing (always >76% v/v *versus* 78.3% v/v in the wine distillate) confirms the slight WS evaporation in this technology reported by Anjos et al. (2020), as well as in other technologies and spirits (Del-Toro et al., 2019; Withers, Piggott, Conner, & Paterson, 1995), which is a remarkable economic advantage.

WS from MOX modalities showed similar chemical characteristics at the end of ageing time, which means that the oxygenation level did not significantly affect the WS matrix except the total dry extract.

Previous works on traditional ageing of WSs under different conditions (kind of wood and toasting level) showed that higher total acidity, volatile acidity and total dry extract were associated with the most suitable conditions, which promoted a faster ageing and high quality as consequence of a better balance between extraction and oxidation of wood compounds (Caldeira, Mateus, & Belchior, 2006).

Considering 365 days of ageing, the O15 and O60 WS had similar physicochemical characteristics, as shown above and in previous results of this project (Canas et al., 2020), but O60 imparted better sensory properties (Caldeira et al., 2021). Therefore, it seems that O60 is the most promising MOX modality.

3.4. *Global assessment of the WSs at the end of ageing*

The outcomes of the Principal Component Analysis (Fig. 5), considering all the characteristics assessed, emphasized the similarities and dissimilarities between WSs at the end of ageing.

Indeed, the first component, accounting for 63.8% of the total variance, made a clear separation between the control WS and the WSs from MOX modalities. The control WS was placed on the positive side of this component, while the WSs of MOX modalities were placed on the opposite side. PC1 had strong positive vector loading for lightness, pH, and the colour attribute golden, and strong negative vector loading for TPI, dry extract, fixed acidity, absorbance at 470 nm, chroma, coordinates a* and b*, and total acidity. These results are in accordance with those of ANOVA, which showed the lower evolution of the WS aged

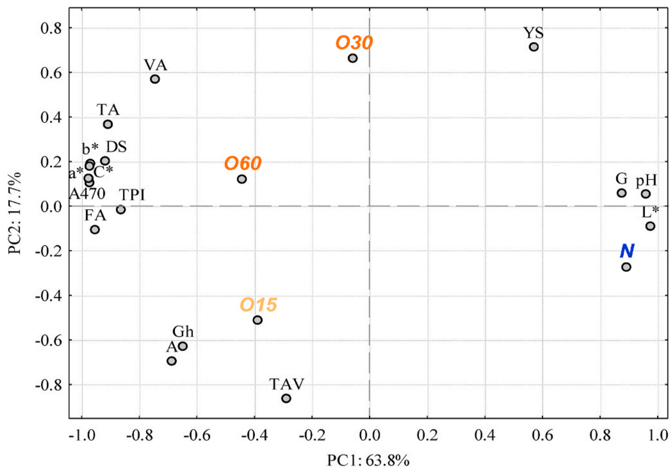


Fig. 5. Projection of WSs aged for 365 days, chemical features, chromatic characteristics and colour attributes perceived by the tasters in the space defined by the two first principal components. WS identification according to the ageing modalities (O15, O30, O60, N); L* - lightness; C - chroma; a*, b* - chromaticity coordinates; A470 – absorbance at 470 nm; TPI – total phenolic index; YG – yellow-green; YS – yellow-straw; G – golden; A – amber; Gh – greenish; TA – total acidity; AF – fixed acidity; AV – volatile acidity; DE – dry extract. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

under nitrogen application.

The second component, making the separation of the WSs from different MOX modalities, only accounted for 17.7% of the total variance, reinforcing the ANOVA outcomes on the negligible difference between them at the end of ageing.

4. Conclusions

WS aged under stronger oxidative conditions (60 days at 2 mL/L/month followed by 0.6 mL/L/month until 365 days) stood out from those aged under mild oxidative conditions (15 days at 2 mL/L/month followed by 0.6 mL/L/month until 365 days) by a faster evolution, which was associated with lower lightness and higher chroma, red, yellow and brown hues, and higher TPI. The most significant differences between these WSs were observed until 60 days, being minimal at the end of ageing. Besides, alcoholic strength, acidity and the colour perceived by the tasters were also similar at the end of ageing. Significant differences between MOX modalities and the control one in all characteristics assessed over time were found, confirming the pivotal role of oxygen on the extraction and subsequent reactions of wood compounds and their great impact on the colour formation and development.

The high alcoholic strength of WSs after 365 days of ageing confirms the slight evaporation in this alternative technology in comparison with the loss reported for barrel ageing in the literature, which is a remarkable economic advantage.

The similarity at 365 days between WSs aged in mild and stronger oxidative conditions, and the results of low molecular weight compounds and other sensory attributes obtained in the same trial, reported in our previous articles, suggest that the MOX modality with higher oxygen application is the most suitable technological option towards WS's quality and ageing sustainability.

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CRediT authorship contribution statement

Sara Canas: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Ofélia Anjos:** Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Ilda Caldeira:** Formal analysis, Investigation, Writing – review & editing. **Tiago A. Fernandes:** Investigation, Writing – review & editing. **Nádia Santos:** Investigation, Writing – review & editing. **Sílvia Lourenço:** Formal analysis, Writing – review & editing. **Joana Granja-Soares:** Formal analysis, Writing – review & editing. **Laurent Fargeton:** Investigation, Writing – review & editing. **Benjamin Boissier:** Investigation, Writing – review & editing. **Sofia Catarino:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare they have no conflicts of interest.

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