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Modelling oxygen ingress through cork closures. Impact of test conditions

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ABSTRACT

Oxygen permeability data is relevant for selecting wine bottles closures. Market available stoppers, two natural and eight microagglomerated corks, were analysed for the oxygen ingress over time in stoppered bottles, under different temperatures (8, 23, and 40 °C), with and without contact between cork and wine simulant.

Weibull model described well the oxygen ingress. Differences were found between cork types in long-term oxygen pressure (*Po*) and ingress rates (τ). For microagglomerated corks, *Po* increased, and τ decreased with temperature, following the Arrhenius behaviour, with estimated activation energies of 15.3 and 35.2 kJ mol^{-1}, respectively. Microagglomerated corks exhibited slower initial oxygen ingress but higher long-term oxygen ingress than natural corks. Principal Component Analysis (PCA) showed that factors related to the bottleneck-cork interface contributed more to the variance of the system than cork type. Liquid contact reduces oxygen ingress around five times. The temperature impact in the oxygen ingress was lower for natural corks.

1. Introduction

1.1. Cork closures market and specifications

Wine cork stoppers represent 2/3 of the overall closure industry for wine bottles, with a total of *circa* 10 billion cork closures sold worldwide (internal data - Cork Supply, 2019).

Cork is the naturally renewed outer bark of cork oak (*Quercus suber*) extracted with no tree damages. Natural corks are manufactured from cork by using cylindrical drillers. The remaining material is used to produce technical cork closures after granulation and adding 60%–85% by weight of granules with a food-grade polyurethane binder.

Closures options are displayed to the market with specifications, such as dimensions, mechanical parameters related to sealing and opening performance, and the absence of transferable components to the wine. Additional value-propositions refer to the consistency of sensory neutrality, and less frequently to the oxygen barrier properties. Oxygen permeability measurements under standard conditions are available for technical corks but never for natural corks despite information in numerous studies. This may be justified by the natural material variability showing a non-normal distribution of results within a large range (Limmer, 2006; Faria et al., 2011) with permeability coefficients varying over three and four orders of magnitude as a result of the differences in the cellular morphology (Oliveira et al., 2013). Values of permeability coefficient ranging from 5×10^{-16} to 2×10^{-14} kg m^{-1} s^{-1} Pa^{-1} were reported for 48 mm cork samples (Lequin et al., 2012).

1.2. Oxygen ingress testing and reporting

In the food packaging field, the oxygen barrier typically refers to the rate of oxygen transfer (OTR) at steady state (ASTM F1307, 2020). Fig. 1a represents the typical curve corresponding to the increase in partial pressure of oxygen inside a corked empty bottle over time. OTR is not constant along the storage time, and therefore the period for the OTR specification is critical for comparing different closures (Lopes et al., 2006). Commercial technical datasheets accessible on the most representative wine closures' manufacturers websites present variable information for oxygen ingress data, hardly comparable for using different units and barely specifying the complete set of test conditions. Oxygen ingress is reported as a rate without specifying the reference time or as an averaged OTR based on one year, or as the total amount of oxygen transferred during a time interval corresponding in some cases to

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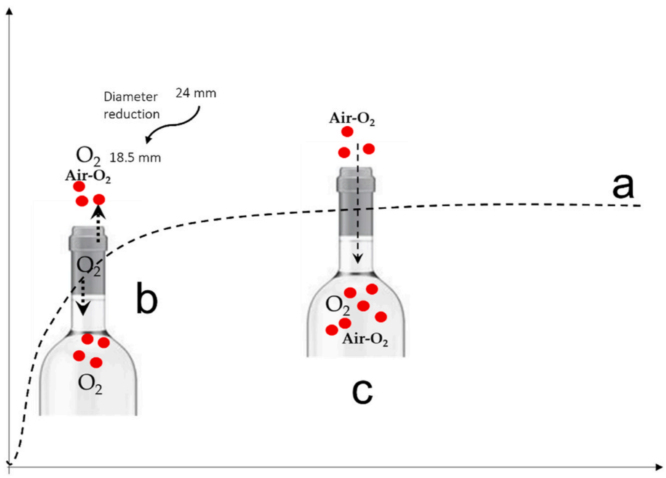

Fig. 1. Increase in partial pressure of oxygen inside a corked bottle over time. a) Typical curve b) Release of initial oxygen present in the cork c) Oxygen ingress through the cork.

intermediate storage times (e.g. 3 and 12 months) or to initial periods up to 6 months of storage. Furthermore, often there is no clear identification of used methodologies (Crouvisier-Urion et al., 2018).

The OTR measurements under standardised test conditions are hardly extrapolated to the actual oxygen ingress when applied to bottled wine. The wine itself may modify the oxygen barrier properties of the closure, either by the formation of films on the closure surface, or by swelling due to sorption of the liquid into the cellular matrix, and by affecting the cork mechanical properties, in particular fatigue of the closure along time (Fonseca et al., 2013; Lequin et al., 2013). Furthermore, the oxygen ingress pattern differs when the bottle has wine because of the occurring oxygen-consuming reactions that maintain the initial partial pressure difference between the external and internal faces of the stopper. The closure characteristics (diameter, length, relation between stopper diameter to bottleneck bore), wine contact, and the temperature, relative humidity, and time during testing (Crouvisier-Urion et al., 2018) should be considered for truthful performance comparison regarding oxygen ingress of different closures.

1.3. Mechanisms and kinetics of oxygen ingress modelling

The cork is compressed when the closure is inserted into the bottle reducing its diameter by about 25% to fit the bottleneck internal bore. The cellular air entrapped in the matrix contains *circa* 4 mg of oxygen for a 44 mm × 24 mm (Pereira, 2015) and gradually permeates out at each end of the cork (Fig. 1b). Thus, in the early stages of storage, the wine is essentially exposed to the oxygen released from the stopper (OIR) besides to the one already in the head-space (Lopes et al., 2005; Chevalier et al., 2019). Different oxygen release patterns may occur depending on the bottling technique, particularly if vacuum is applied (Teodoro and Mesquita, 2011).

The actual contribution of the transfer through the closure system becomes more relevant in the subsequent phase of the storage (Fig. 1c). The sealing effectiveness of the closure is a function of both the permeability of the material the closure is made of and the tightness/adherence of the closure to the bottleneck wall (Lagorce-Tachon et al., 2016; Poças et al., 2010). The contribution of the transfer through the interface between the closure and the glass may be significant compared to the actual transfer through the cork itself (Karbowiak et al., 2019; Lopes et al., 2007). The interfacial path is determined by the length of the closure and the ratio between the diameters of the closure and the bottleneck. Surface coatings of the closure also play a role in the transfer through this route (Poças et al., 2010).

The permeability of gases through the cork is related to the cellular structure morphology: the dimensions of the cells and the number and the orientation of the cell's wall plasmodesmata, the channels with approximately 100 nm of diameter that cross the cell wall. Transfer through channels in the cell's wall, and through the solid wall, have been appointed as contributing mechanisms (Faria et al., 2011).

The laws from Darcy, Knudsen, and Fick have been applied to describe mass transfer through heterogeneous materials, depending on the material structure (Cussler, 2009). The Knudsen and Fick mechanisms have been the most studied to describe the transfer through the natural corks. The description of oxygen transfer mechanisms through technical cork closures is much less investigated.

The transfer through the plasmodesmata channels under the molecular flow regime was described by the Knudsen mechanism (Brazinha et al., 2013). However, other researchers considered that this mechanism does not govern the oxygen transport through cork and that Fick's mechanism applies with the diffusion in cell walls as the limiting step (Lagorce-Tachon et al., 2014). This may explain why the permeability coefficient of the cork stopper measured with the cork compressed inserted in the bottleneck does not differ from that measured without being compressed (Lagorce-Tachon et al., 2016). Fick's law is the most used model to describe mass transfer in a dense, homogeneous and isotropic material. In heterogeneous matrixes such as cork closures, an effective diffusion coefficient (or an effective permeability coefficient) for the whole cork stopper is determined, not a diffusion coefficient at a molecular scale, because of local differences throughout the material. According to the literature it seems that there is no consensus on the mechanisms governing the oxygen transfer through this complex matrix, particularly dependent of several physical, mechanical and chemical variables.

1.4. Aim of the current work

To the authors' knowledge, the behaviour of oxygen ingress has not been analysed on the scope of a predictive model considering different test conditions. Most of the research around cork oxygen barrier performance has been conducted focusing on wine ageing, including its shelf-life (Karbowiak et al., 2010) and on the relationship between oxidative or reductive changes of wine and the closure oxygen permeability (Vidal and Moutounet, 2011; Vidal et al., 2017; Pons et al., 2019). This work addresses cork stoppers oxygen barrier aiming to understand the impact of measuring conditions and closure types. Rather than determining diffusion coefficients or highlighting the mechanisms of oxygen ingress, it aims at describing the oxygen ingress in the bottle through cork closures, using an empirical approach that reflects the type of cork closure, the impact of time, temperature, contact with the wine and dimensional parameters. The Weibull model was selected due to its versatility, application in various contexts, and simplicity as it is based on only three parameters. It generally describes well complex processes with high variability (Cunha et al., 2011). Although it is empirical, it is possible to identify the relationship between the model parameters and underlying physical phenomena.

2. Materials and methods

2.1. Cork stoppers samples

Two natural corks and eight technical corks (microagglomerated) were selected and collected from the market, ready to be used. The natural corks were selected from products commercially available in the middle range of visual grade quality for standard nominal lengths of 45 mm and 49 mm. Technical corks were chosen from the most representative market suppliers (A, B, and C) and correspond to various specifications shown in commercial literature regarding recommended storage time. Physical characteristics were measured using standard methods (ISO 9727, 2007) and are summarised in Table 1.

All cork stoppers were tested for oxygen barrier at room temperature.

Table 1
Closures characteristics. ('Nat' for natural cork and 'Tec' for technical cork).

Ref	Cork granules size, mm	N[a]	Length, mm	Diameter, mm	Density, kg m^{-3} Ave ± st.dev (min-max)
Nat_1	one piece	58	45	24.2	179 ± 21.6 (124–236)
Nat_2	one piece	20	49	24.1	173 ± 22.6 (140–283)
Tec_A1	0.5–2	29	44	24.0	269 ± 9.3 (246–287)
Tec_A2	0.5–1	55	44	24.1	281 ± 5.7 (268–293)
Tec_A3	0.5–1	30	49	24.1	295 ± 9.6 (274–323)
Tec_B1	<0.5	10	44	24.5	264 ± 7.7 (251–279)
Tec_B2	<0.5	28	44	24.2	291 ± 7.6 (272–305)
Tec_B3	<0.5	8	44	24.2	284 ± 9.8 (262–308)
Tec_B4	<0.5	10	47	24.5	317 ± 6.7 (301–330)
Tec_C	1–3	10	44	24.0	299 ± 3.7 (294–311)

[a] Number of replicates.

Two closures – Nat_1 and Tec_A2 – were tested at two additional temperatures and submitted to testing under wet and dry conditions.

2.2. Glass bottles

A set of 750 mL clear glass bottles with standardised bottleneck bores, 18.5 mm diameter (CEN EN 12726: 2018) were used. Bottles were coded to ensure traceability to the specific cork closure tested in each bottle. Oxygen sensor spots for contactless oxygen measurements were placed inside each bottle (Section 2.6).

2.3. Internal neck profiles

Bottle internal neck profiles were measured using a PerfiLab® instrument (Egitron, Portugal) to determine the internal neck volume occupied by the closure. Measures were taken from the rim to 50 mm depth at a 1 mm pace along the bottleneck. The volume occupied by the inserted closure was calculated as the integral of the diameter as a function of the neck depth. Fig. 2 presents an example of a bottleneck profile.

2.4. Corking operation

A semi-automatic corker MEP model P35 (Core-Equipment, UK) with corking jaws at 15.5 mm compression, corking time approximately 1.8 s, was used for all closures. The corking procedure was adapted accordingly to the dry and the wet test conditions. For trials under dry conditions (no contact with wine simulant), bottles were rinsed with a 70% (w/v) ethanol/water solution for 1 min, then N_2 was flushed for 2 min and immediately corked once partial pressure of oxygen was below 10 hPa. Rinsing with ethanol/water solution was necessary to avoid mould development during the oxygen ingress measuring period. Preliminary experiments indicated that this interfered with the oxygen measurements. Bottles were rinsed identically for the trials under wet conditions (contact with wine simulant). Then, 5 mL of 12% (w/v) ethanolic solution was introduced following a similar procedure for N_2 flushing and stoppering.

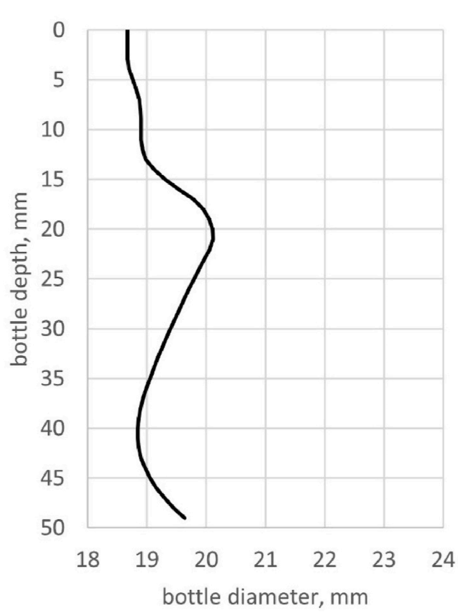

Fig. 2. Example of a bottle internal neck profile.

2.5. Storage conditions

Bottles were stored protected from light at the intended conditions in chambers with control of temperature, at 8 ± 2 °C, 23 ± 2 °C, and 40 ± 2 °C. For the trials under wet conditions, bottles were maintained upside down, thus keeping corks in contact with the ethanolic solution.

2.6. Monitoring oxygen ingress

The oxygen partial pressure inside the bottle over time was measured with the luminescence-based technique (Diéval et al., 2011). Optical fibre oximeter, Fibox 3 LCD trace v7 was used, with sensor spots SP-PSt6-NAU-D%-CAF (PreSens Precision Sensing GmbH, Germany) and the following measurement characteristics in the air: range = 0–41.4 hPa, LOD = 0.02 hPa, accuracy = 3% of measured oxygen concentration.

The oxygen partial pressure (hPa) inside the bottles was measured every 3–4 days during the earlier stage and then once a week until a linear increase with time was achieved. For each experimental set, the monitoring of oxygen partial pressure inside bottles occurred during a minimum of 63 days with at least 11 sampling points timely recorded. All readings were corrected with the initial oxygen partial pressure in each bottle.

2.7. Modelling and data analysis

Data handling, model parameters estimation, and statistical analysis were performed with IBM SPSS Statistics 26 for Windows® (SPSS Inc., Chicago, USA)) and Minitab 17 (Minitab Ltd., UK).

The Weibull model was used to describe the oxygen ingress in the bottle over time:

$$P(t) = P_0\left(1 - exp\left(-\frac{t}{\tau}\right)^{\beta}\right) \quad (1)$$

where *P(t)* is the oxygen partial pressure inside the bottle changing with time *t*, P_0 is the pressure at equilibrium, and the initial pressure is considered zero. The model has two empirical parameters: τ and β. τ is the system time constant associated with the process rate and has been found to depend on the temperature following the Arrhenius type behaviour. The parameter β and the corresponding shape of the curve at earlier times was found to relate to different mechanisms controlling the mass transfer. This empirical model has been used to describe various processes in food processing, quality, and safety, including mass transfer of additives from plastics into food (Poças et al., 2012).

The Weibull model was fit to the experimental points of each replicate of all trials. For each curve, the model parameters β (dimensionless), *Po* (hPa) and τ (days) were estimated by non-linear regression analysis using the Levenberg-Marquardt algorithm to minimise the sum of the squares of the differences between the predicted and experimental values. The precision of the parameters was evaluated by their 95% confidence intervals, and the regression quality assessed by residuals analysis (normality and randomness) and the coefficient of determination R^2.

A preliminary statistical analysis of the model parameters, using one-way ANOVA at 95% confidence, indicated that β was not significantly different from sample to sample while tested under the same conditions. Therefore, β values were set constant to the average for each test condition, thus reducing the number of model parameters and creating a more robust overall estimation. New fittings were performed to estimate the parameters τ and *Po* for all the closure types, temperature, contact conditions and replicates, with the following β values, set constant: to 1.2 for wet conditions at 23 °C, and for dry conditions to 1.0 for trials at 8 °C, and to 0.74 for trials at 23 °C and 40 °C.

ANOVA one-way (95% confidence) was applied to detect differences between the estimated parameters *Po* and τ for the different closures. Assumptions to use one-way ANOVA, normality, and homoscedasticity of data were tested using Kolmogorov-Smirnov/Shapiro-Wilk tests and Levene's tests, respectively. Post-hoc tests were performed to explore differences between multiple groups means. Results were confirmed with the non-parametric Kruskal Wallis test.

An exploratory data analysis was performed to search correlations between the model parameters describing the oxygen ingress obtained at different conditions of storage, and dimensional variables of the cork closures and the bottle, to assess the overall impact in oxygen ingress and the discrimination between various closures' types. In order to reduce the number of variables under analysis to a limited number of components, a Principal Component Analysis (PCA) with Varimax with Kaiser Normalization rotation method was performed. The Kaiser-Meyer-Olkin (KMO) values were 0.5 or higher. Criteria for the number of factors were eigenvalues higher than 1 and maximised explained variance.

3. Results and discussion

Fig. 3 presents the oxygen partial pressure curves obtained in different testing conditions showing patterns similar to previous reports (Lopes et al., 2005; Waters, 2008; Diéval et al., 2011), with an initial fast oxygen ingress and then a gradual deceleration of the rate of oxygen into the bottle. Under dry conditions and specifically for the temperature effect, it was observed that the first month accounted for 44% (8 °C) to 88% (40 °C) of the total oxygen ingress estimated over a period of 1 year. This was measured as 1.7 hPa, 4.4 hPa and 7.8 hPa for the natural cork and as 3.4 hPa, 5.4 hPa and 13.3 hPa for the technical cork, respectively at 8 °C, 23 °C and 40 °C. Then, the cumulative percentages reached

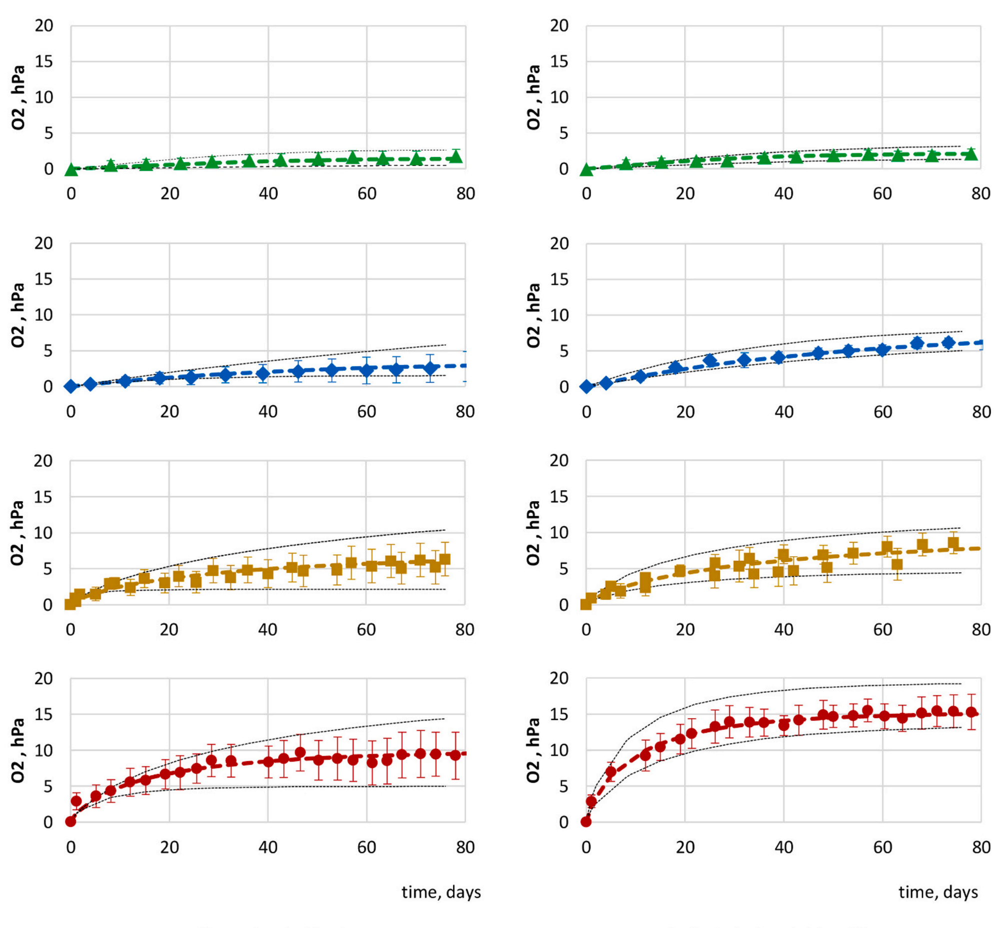

Fig. 3. Monitoring of oxygen ingress along time (dots for average, bars for standard deviation). Test with wine simulant contact at 23 °C (▲); Test in dry condition at 8 °C (◆), 23 °C (■), 40 °C (●). - - - - - model fit. ——— upper and lower curves represent the replicates with the higher deviation from the average curve.

69%–97% during the second month, respectively, at low and high temperatures. Therefore, results highlight that the largest fraction of oxygen ingress was completed within two months for all temperatures and closure's types.

Major oxygen ingress during the first two months was also observed in tests under 23 °C and wet conditions. Values reached around 60% of the total after the first month and around 90% after the second. This was measured in the first month as 0.9 hPa and 1.4 hPa, respectively, for the natural and the technical cork.

3.1. Weibull model parameters

The Weibull model described well the increase in oxygen partial pressure inside the bottle based on 243 fitted curves with $R^2 \geq 0.98$. The estimates for the parameters – β, *Po* and τ – are summarised in Table 2 for the closures tested under different conditions and Table 3 for all closures tested under dry conditions and at 23 °C. Fig. 4 presents a boxplot of the data with information on the statistical analysis.

3.1.1. Temperature and liquid contact effects

Results indicate that temperature and the contact with liquid affect the model parameter τ, the long-term oxygen partial pressure *Po,* and the parameter β (Table 2). The liquid contact reduces *Po* by 5 and 4 times, respectively, for natural and technical corks. This factor increases with temperature following an Arrhenius relationship. Statistical significance was only found for the technical closures with an estimated activation energy of 15.3 kJ mol^{-1}. For the natural corks, the impact of temperature on *Po* was not statistically significant due to the high dispersion between replicates, yet an increase in *Po* with the temperature was recorded (Fig. 4). *Po* represents the oxygen in the gaseous phase at long-term. The temperature dependence is connected to the partition of oxygen between the cork matrix and the gas outside the cork, with a higher level of oxygen retained on the matrix at lower temperatures.

Regarding τ, results indicate it depends mainly on the temperature, with statistical significance only for the technical corks. The time to reach a certain oxygen pressure is reduced with increased temperature, as could be expected. The decrease of τ with temperature also showed an Arrhenius type relationship with an estimated activation energy of 35.2 kJ mol^{-1} for the technical cork. Although no information was found in the literature related to the activation energy for diffusion of oxygen in cork, similar values were reported for the activation energy in drying kinetics of cork, with values of 25.3–48.1 kJ mol^{-1} (Abdulla et al., 2010) for temperatures ranging from 50 °C to 70 °C.

When testing the same cork stoppers under wet conditions, considerably lower oxygen transfer was observed. This fact is displayed on β and *Po* values (Table 2): the highest values of β were observed for testing under wet conditions then for the testing conditions at low temperatures. This result is consistent with the known influence of β in the kinetic curve shape showing a delay in the initial oxygen ingress. The changes in β with the liquid contact may indicate an effect on the mechanism of oxygen ingress through the moistened cork matrix, with lower transfer through and higher solubility of oxygen in the aqueous phase soaking the cork. These aspects were not investigated during this study. However, similar comments were noted in the literature, although not associated with a model describing the oxygen ingress (Karbowiak et al., 2010).

Results highlighted that although temperature influences the performance of the closures, the major effect on total oxygen ingress seems to be promoted by contact with the liquid. The liquid contact contribution has been acknowledged with a factor of 10 between gas permeation of wet cork compared to dry cork (Fonseca et al., 2013), which is fairly aligned with the current results. The impact seems to be higher for the technical closures than for the natural cork.

Table 2
Weibull parameters *Po* and τ (average ± standard error) for the closures tested under different temperature and liquid contact conditions.

Closure	Contact condition	Temperature, °C	N[a]	β	*Po*, hPa	τ, days
Nat-1	Dry	8	7	1.00	3.5 ± 1.4	45.5 ± 11.8
		23	28	0.74	7.0 ± 0.6	30.6 ± 4.3
		40	10	0.74	10.0 ± 1.2	16.8 ± 3.8
	Wet	23	9	1.20	1.6 ± 0.9	37.2 ± 4.3
Tec_A2	Dry	8	10	1.00	7.8 ± 0.3	51.6 ± 5.0
		23	25	0.74	9.5 ± 0.4	37.8 ± 3.2
		40	10	0.74	15.2 ± 0.6	11.0 ± 0.9
	Wet	23	10	1.20	2.1 ± 0.2	26.8 ± 3.2

[a] Number of replicates.

3.1.2. Effect of closures type

Table 3 presents the results for the Weibull model parameters (*Po* and τ) for the several closures tested at 23 °C under dry conditions. The parameter β was found constant among closures. The homogeneous subset groups obtained from one-way ANOVA are shown (Table 3). For *Po*, it was observed a tendency of Tec_B closures to be in groups 1, 2 and 3, whereas the Tec_A samples were in groups 4 and 5. The discrimination between the two cork types, based on *Po*, seems logical because this parameter should be related to stoppers' composition factors and respective contributions to interactions with oxygen (such as sorption).

As far as τ is concerned, the longer corks (Nat_A2, Tec_A3 and Tec_B4) were displayed within groups 1 or 2 (not to group 3). This grouping is consistent with τ being related to the rate of transfer, limited by the length of the path the oxygen needs to be transferred through.

These results for the model parameters that describe the dynamics of oxygen ingress did not clearly discriminate closures of different nature and characteristics, which led to theorising that additional variables could influence the oxygen ingress. This was explored with an analysis of principal components.

3.2. Principal components analysis (PCA)

The variables considered for the PCA were: the Weibull model parameters (*Po*, τ, β) and variables related to the pairing cork and bottle. For the closures, the factors were length (indirectly included in the volume, V) and material density (ρ). The diameter of the closures was disregarded because its tolerance is lower than the variance observed on the internal diameter of the bottles. For the bottleneck, the included variables were: internal volume occupied by the closure (V) and the extreme values of internal diameter (Dmin and Dmax). Finally, variables for the test conditions were temperature (T) and liquid contact condition (CONTACT).

The PCA was run with 243 data arrays. All the variables presented at least one correlation coefficient greater than 0.3, and therefore, all were considered in the analysis. The overall KMO value was 0.422, and Bartlett's test of sphericity was statistically significant ($p < .0005$), validating the data analysis. The first three components explained 68% of total variance with a minor contribution of the fourth component. The analysis was reviewed with the extraction method forcing to three main components.

Fig. 5 shows the loadings and score plots for the three components. Cork-bottleneck variables were associated with component 1. The density of the closures contributed only moderately. For component 2, wine contact condition, β and *Po* added the most. Component 3 was associated with τ and temperature. As expected, higher *Po* occurred for higher temperature (along with component 2), and higher τ values were observed for lower temperature and wine contact (along with

Table 3
Weibull parameters *Po* and τ (average ± standard error), for β constant at 0.74, for the closures tested at 23 °C and dry condition. Colors in ANOVA groups identify closures of the same type; thick borders highlight longer corks.

Closure	N(1)	*Po*, hPa	ANOVA group (α 0.05) 1	2	3	4	5	τ, days	ANOVA group (α 0.05) 1	2	3
Tec_B3	8	3.3 ± 0.6						30.7 ± 9.4			
Tec_B4	9	4.3 ± 0.2						31.4 ± 2.1			
Nat_2	18	5.2 ± 0.5						14.3 ± 1.2			
Tec_B1	10	5.4 ± 0.6						44.4 ± 6.6			
Tec_B2	26	6.5 ± 0.4						22.9 ± 3.0			
Tec_A1	29	6.5 ± 0.3						42.9 ± 4.2			
Tec_A3	30	7.0 ± 0.5						26.7 ± 2.5			
Nat_1	28	7.0 ± 0.6						30.6 ± 4.3			
Tec_C	9	8.6 ± 0.8						63.9 ± 11.1			
Tec_A2	25	9.5 ± 0.4						37.8 ± 3.2			

(1) Number of replicates

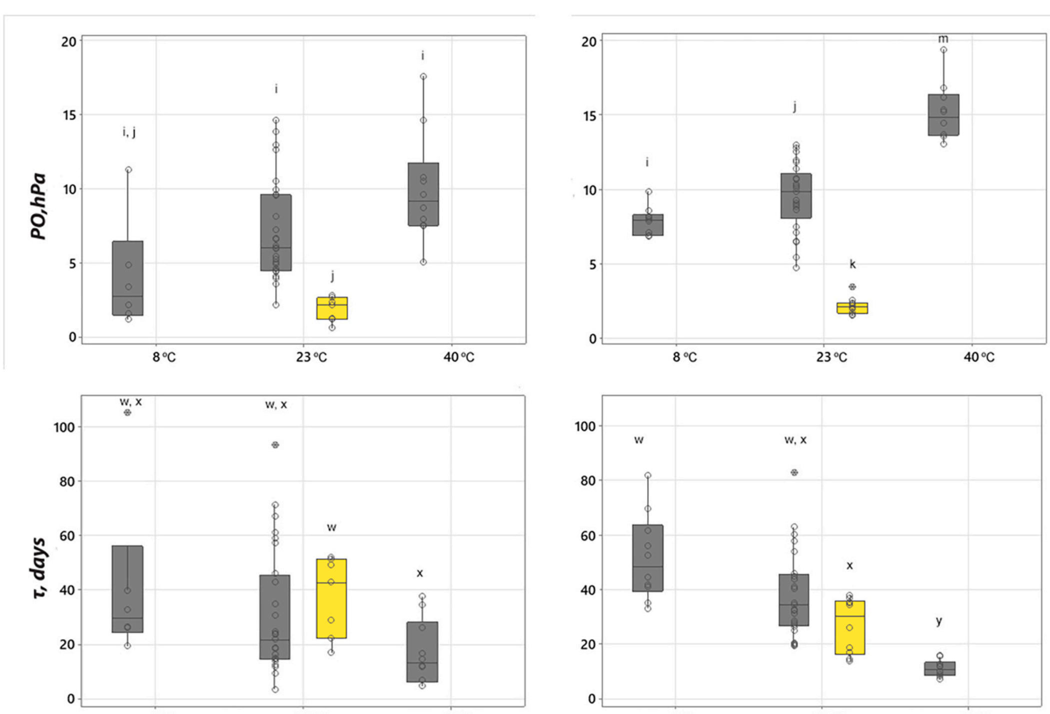

Fig. 4. Boxplot with individual data plot for *Po* and τ for each cork sample type (left: natural corks, righ: microagglomerated corks). Trials under 'dry' test conditions in grey. Trials under 'wet' conditions in yellow. Letters aside the interquartile range for ANOVA: groups at a 0.05.

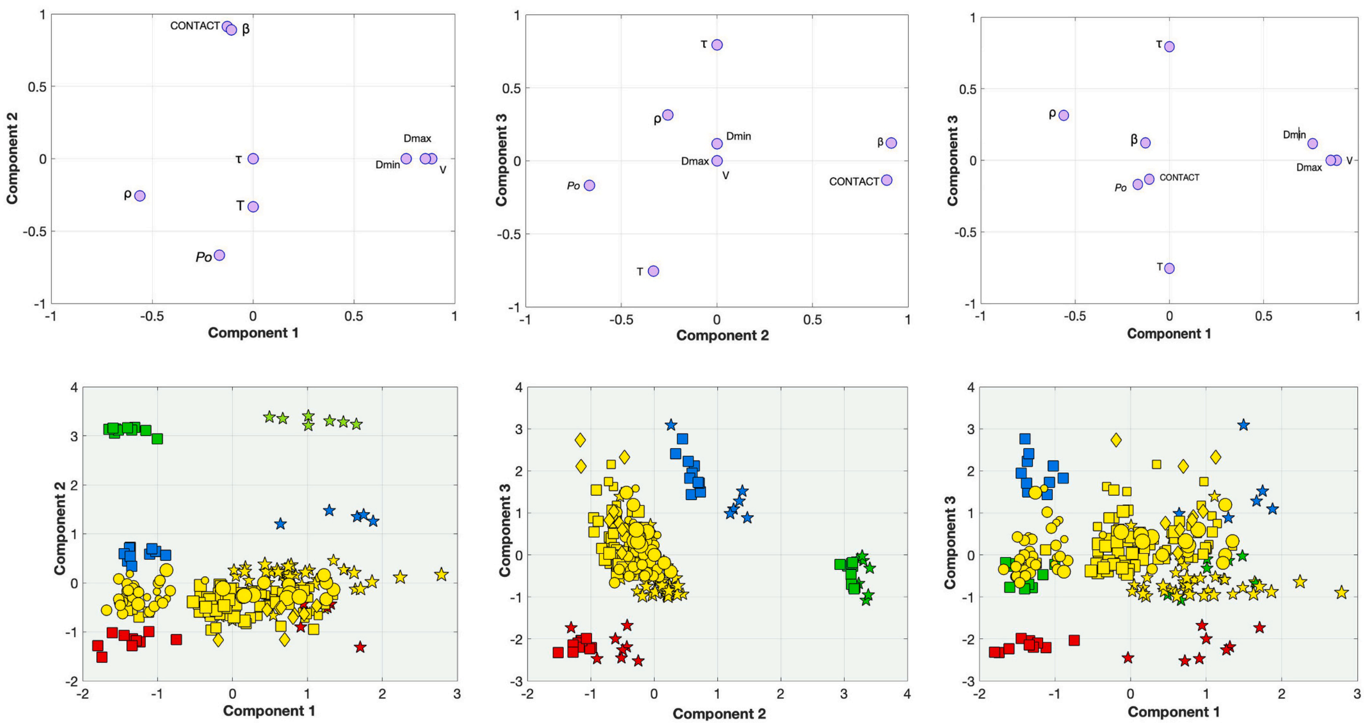

Fig. 5. PCA loadings and scoreplots with all variables. Natural (☆), Tec_A (□), Tec_B (○), Tec_C (◇). Symbol colour for temperatures: blue 8 °C, yellow 23 °C, red 40 °C and green for 23 °C under wet condition. Symbol sizes for different closures lengths.

component 3). The score plots underline that groups are formed joining several types of stoppers, with clear separation according to test conditions. Stoppers tested under wine simulant contact, and room temperature form a separate group. It is also verified that the data points at 8 °C, 23 °C and 40 °C, under dry conditions, group together the distinct cork stoppers, according to temperature. Among the green, blue and red areas, it is visible that technical corks tend to be isolated from the natural corks, mainly along with component 1.

Globally, it was found that the factors affecting more significantly the grouping of samples relate to testing conditions, with the major effect promoted by the wine contact and secondly by the temperature. The yellow cloud barely separates closure types by their behaviour, probably because the test conditions (temperature and contact) contributed enormously to the cork samples' variance and positioning in the plot.

Therefore, a new PCA was completed considering only tests under 23 °C and dry contact with 190 data arrays. The same variables regarding cork stoppers and bottlenecks were considered, but β was excluded as it was a constant within this dataset. Closures density did not meet the acceptance criterion, and PCA was performed with V, Dmin, Dmax, *Po* and τ (correlation matrix coefficients higher than 0.3). The KMO was 0.564, and Bartlett's test of sphericity was statistically significant ($p < .0005$).

Two components had eigenvalues greater than one and explained 69% of the total variance. The interpretation of the loading values was again consistent with variables related to cork-bottleneck dimensions along with component 1 and with Weibull parameters contributing to component 2 (Fig. 6). The plot organises the samples along with component 2 as natural corks (dark red, stars and triangles) on the lower section of the vertical axis and technical corks on the opposite side, thus separating closures by type and based on the Weibull model parameters. This adds to the information from Table 3: a tendency to higher τ and *Po* for technical closures. Furthermore, the longer natural corks (dark red triangles) are located in the plot at a lower position and less spread along with component 2, than the shorter natural corks (dark red stars), allowing to relate the longer length with lower τ and *Po* (lower long-term oxygen pressure). It is noted that the longer corks (represented by triangles) are more consistent along with component 2 compared to the shorter corks, regardless of the cork type. The smaller variation is consistent with the lower error ranges reported for the τ Weibull parameter for the longer closures (Table 3). The 45 mm length natural corks (red stars) share position among both the longer natural corks as well as the technical stoppers along with component 2, seldomly over positioning with the technical corks.

All cork stopper types seem to be widely distributed along with component 1 (x-axis), which contains the variables related to cork-bottleneck factors. For the longer corks, wider data dispersion along with component 1 is noted and can be explained by the tendency of higher internal bore variation along with bottleneck depth. Therefore, the bottleneck dimensions contributed more to the variance than the intrinsic corks' characteristics. This remark was also found in experiments with and without covering interface cork/glass, designed to elucidate the relative contribution of the bottleneck (Karbowiak et al., 2019).

4. Conclusions

It is essential to note the complexity of the permeation of gases through a closure system that includes several materials: in such multifactorial processes, the permeation is not only a function of the cork barrier properties but also of bottleneck relative dimensions and their consistency, and of time and storage conditions. The reported observations reveal the combined contribution of the material and the sealing tightness at the cork-glass interface.

The oxygen ingress curves highlighted that although temperature influences the performance of the closures, the major effect on total ingress seemed to be the liquid contact within the range of conditions tested. When the closure contacts the wine simulant, the long-term oxygen ingress (*Po*) is reduced by 5 and 4 times, respectively, for natural and microagglomerated corks. This result comes in line with the ability of the liquid to form a physical barrier to the transport of gases and contribute to intumescence of the material with consequent blocking of structures towards gas transport (Limmer, 2006). Consequently, the

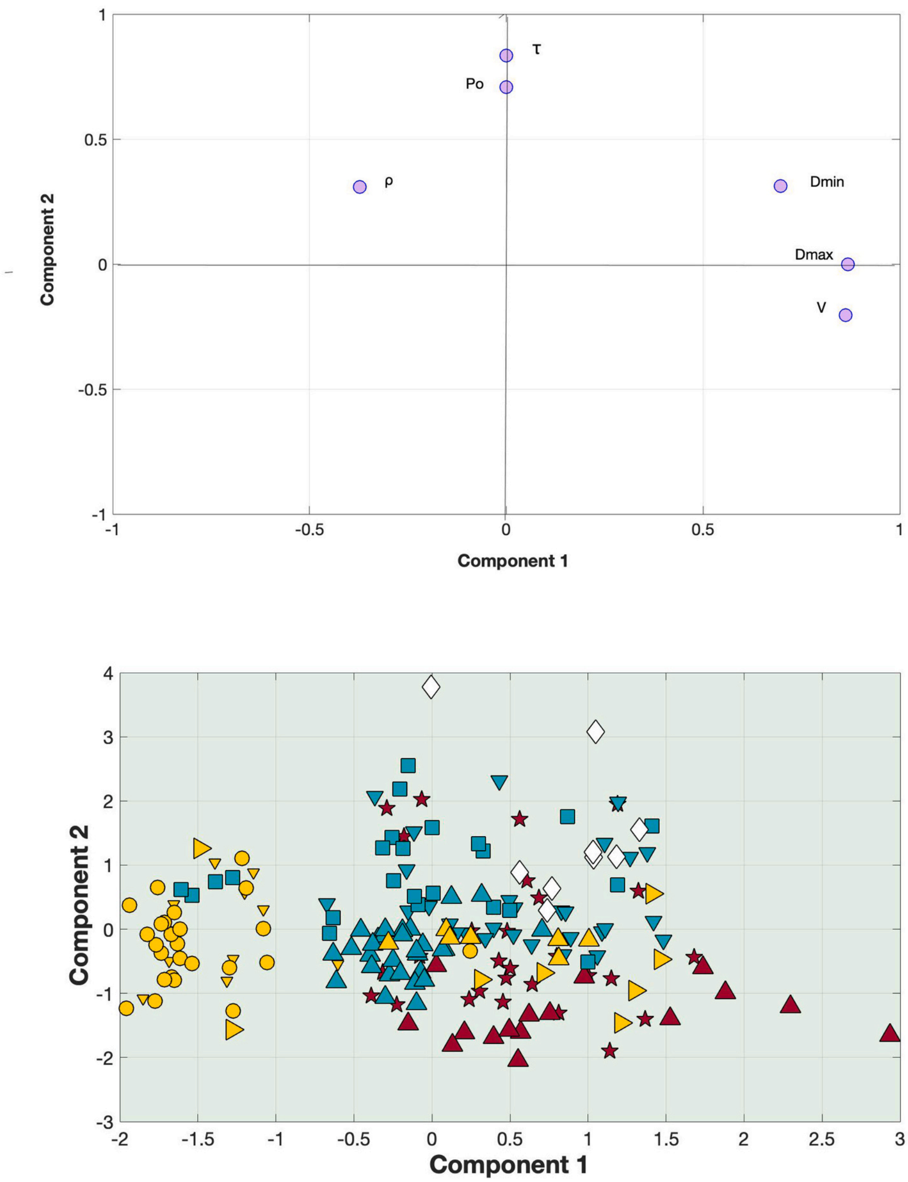

Fig. 6. PCA loadings and scoreplot for all closures tested under dry condition and 23 °C. NAT_1 (★), NAT_2 (▲), Tec_A1 (▼), Tec_A2 (■), Tec_A3 (▲), Tec_B1 (▼), Tec_B2 (●), Tec_B3 (▶), Tec_B4 (▲) Tec_C (◊). Thick line for natural cork closures; Blue area for longer corks; Yellow area for Tec_B corks.

technical information distributed in commercial literature should contain details about the test conditions to objectively interpret the effective barrier properties, especially when the comparison of data from different sources is required.

The Weibull model with parameters β, *Po* and τ described well the oxygen ingress under different conditions, and for all closures tested. The temperature dependence of *Po* (increase) and τ (decrease), followed an Arrhenius relationship. The natural cork closures were less affected to changes in oxygen barrier with the temperature (effect not statistically valid at $p < .05$) when compared to the microagglomerated cork closures.

Results show a tendency for higher τ and *Po* values for technical closures when compared to natural corks. This may be translated into slower initial oxygen ingress but higher long term oxygen ingress for the technical corks.

This work reveals the important contribution to oxygen ingress dynamics of aspects not related to the intrinsic corks' characteristics, specifically the variability in the bottleneck dimensions. Bottlenecks were found to be the major contributors to the system variability. Insufficient details may jeopardise the interpretation of differences between closures and justify different results, sometimes contradictory, from several sources referring to the same cork types. It seems relevant that the standardisation of measuring methods of oxygen ingress in bottles should include standard bottlenecks to eliminate this variable from impacting the outcomes.

CrediT author statement

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version, according to the following: Ana C Lopes Cardoso: Conceptualization, Methodology, Formal analysis, Investigation Resources, Writing - Original Draft, Chandisree Rajbux: Investigation, Cristina L.M. Silva: Methodology, Formal analysis, Resources, Writing - Review & Editing, Fátima Poças: Conceptualization, Methodology, Formal analysis, Resources, Writing - Review & Editing.

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.

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