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1 **Unravelling CO<sub>2</sub> transfer through cork stoppers for Champagne and sparkling wines**

2

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17 **Abstract**

18

19 The diffusion of CO<sub>2</sub> through macro- and micro-agglomerated cork stoppers for sparkling  
20 wine was studied by a manometric technique. The effective diffusion coefficients for each  
21 part of the stopper (cork body, cork disc and adhesives) were determined for the first time.  
22 The results show that a small particle size along with a high adhesive content and level of  
23 compression favor the gas barrier properties of the cork stopper. Although the cork discs  
24 placed at one end of the stopper present no resistance to gas transfer, the adhesive film  
25 between them constitutes a high barrier to gas transfer. The mechanism that controls the gas  
26 transfer is the solution-diffusion process through the polymeric chains of the adhesive.  
27 Although the aging of the cork stopper and the gas transfer at the glass/stopper interface were  
28 not considered, results clearly showed that the cork stoppers studied were capable of  
29 maintaining a CO<sub>2</sub> concentration in the bottle that is sufficient for conserving a good  
30 effervescence of sparkling wines over several years.

31

32

33 **Keyword:** Agglomerated cork stopper, CO<sub>2</sub>, diffusion, gas transfer

## 1. Introduction

Cork has been used for centuries as corking material for wine conservation, from the amphora to the glass bottle. Agglomerated cork stoppers, made of cork particles with adhesives, were developed at the beginning of the twentieth century[1], first for sparkling wines and then extended to still wines. Cork particles, calibrated as a function of their mean diameter, form the “body” of the sparkling wine stopper. Since the 1970s, the agglomeration of cork particles has been made with polyurethane (PU) adhesives[2] to replace casein glue, which was initially used. In addition, two cork discs are usually glued with an aqueous dispersion of PU on one end of this agglomerated body, thus forming the “miroir”, which is in contact with the wine (Fig. 1).

Such agglomerated cork stoppers are used for the conservation of sparkling wines, such as Champagne, Crémant, Cava, Prosecco, Sekt, but also ciders and beers. Stoppers are highly compressed in the bottleneck. In the case of Champagne wine, this leads to a reduction in diameter of 45 % (from 31 mm to 17.5 mm diameter)[3], which corresponds to a reduction of 70 % in volume. After alcoholic fermentation has produced a still “base wine”, these sparkling beverages are obtained either from a second fermentation step (using mainly *Saccharomyces cerevisiae*) or from carbonation, both leading to the presence of CO<sub>2</sub> dissolved in the liquid phase. Dissolved CO<sub>2</sub> concentrations range from 5 g.L<sup>-1</sup> for ciders and beers[4] up to 12 g.L<sup>-1</sup> for carbonated and sparkling wines[5]. When these beverages are bottled, the thermodynamic equilibrium between the gas-phase and dissolved CO<sub>2</sub> causes a partial pressure of gas-phase CO<sub>2</sub> in the headspace ranging from about 0.3 to 0.6 MPa (considering a Henry’s constant value of  $4.4 \times 10^{-4} \text{ mol.m}^{-3}.\text{Pa}^{-1}$  at 12 °C)[6]. Consequently, the high partial pressure gradient of gas-phase CO<sub>2</sub> between the inside and outside of the bottle leads to a CO<sub>2</sub> transfer through the stopper, which causes a progressive loss of dissolved CO<sub>2</sub> from the liquid phase. Nevertheless, below a partial pressure close to 0.13 MPa

60 in the headspace (at 12 °C)[6], corresponding to a critical concentration of dissolved CO<sub>2</sub>  
61 close to 2.5 g.L<sup>-1</sup>, a sparkling wine becomes thermodynamically unable to promote  
62 effervescence. The precise knowledge of the permeability of a cork stopper with regard to  
63 gas-phase CO<sub>2</sub> becomes therefore crucial to understand how a bottle of sparkling wine  
64 progressively loses its dissolved CO<sub>2</sub> content, and therefore its bubbling potential.

65 The first study dealing with gas transfer through the cork stopper was conducted in the  
66 mid-1990s[7]. Since then, numerous studies have investigated the gas transfer through wine  
67 stoppers, in particular to the O<sub>2</sub> transfer, because of its impact on wine oxidation[8]. Several  
68 techniques have been developed to study gas transfer through stoppers, such as coulometric  
69 detection, manometric devices, chemiluminescence, SO<sub>2</sub> titration, and colorimetric method.  
70 Synthetic stoppers exhibit the highest oxygen transfer rate (from 10<sup>-6</sup> to 10<sup>-4</sup> mmol O<sub>2</sub>.m<sup>-2</sup>.s<sup>-1</sup>),  
71 followed by natural cork (10<sup>-7</sup> to 10<sup>-3</sup> mmol O<sub>2</sub>.m<sup>-2</sup>.s<sup>-1</sup>), screwcaps (10<sup>-8</sup> to 10<sup>-4</sup> mmol O<sub>2</sub>.m<sup>-2</sup>.s<sup>-1</sup>)  
72 and technical stoppers (10<sup>-7</sup> to 10<sup>-5</sup> mmol O<sub>2</sub>.m<sup>-2</sup>.s<sup>-1</sup>), at room temperature for an oxygen  
73 partial pressure gradient of 0.21 MPa[9]. However, only a few studies have addressed the  
74 issue of CO<sub>2</sub> transfer[10-13], and only two deal with sparkling wine stoppers[5, 6]. Based on  
75 the CO<sub>2</sub> concentration decrease in sparkling wine bottles and using modeling (based on  
76 Henry's and Fick's laws), the effective CO<sub>2</sub> diffusion coefficient has recently been estimated  
77 to be between 5 x 10<sup>-11</sup> and 3 x 10<sup>-10</sup> m<sup>2</sup>.s<sup>-1</sup>[5, 6]. However, to date, there has been no direct  
78 and accurate experimental measurement of the effective diffusion coefficient of CO<sub>2</sub> through  
79 composite materials such as agglomerated stoppers, in which each part constitutes an  
80 individual resistance to gas transfer.

81 Sparkling wine stoppers, made of a body of agglomerated cork particles with two cork  
82 discs fixed on one end with two films of adhesive can be considered as an equivalent system  
83 composed of five resistances to mass transfer connected in series (Fig. 2). This macroscopic  
84 view could obviously be more detailed depending on the scale that is considered. Cork itself

85 is an alveolar material composed of empty closed cells of about 30  $\mu\text{m}$  characteristic  
86 dimension with a cell wall around 1  $\mu\text{m}$  thickness. It also contains macroscopic pores called  
87 lenticels with a diameter in the millimeter scale. In the case of agglomerated cork stopper,  
88 cork particles are surrounded by polyurethane. There is also an intergranular porosity between  
89 these particles, which may be either opened or closed. Therefore, it is essential to identify the  
90 limiting step for gas transfer and the associated diffusion mechanism. Three mass transfer  
91 mechanisms can occur in such a material[9]: (i) the molecules move in macropores according  
92 to Darcy's law, when the mean free path of the diffusing molecule is lower than the pore  
93 diameter; (ii) the molecules diffuse in mesopores following a Knudsen's regime, when the  
94 mean free path of the diffusing molecule is larger than the pore diameter; and (iii) the  
95 molecules move by jumping from one sorption site to another one in a phenomenon called  
96 surface diffusion or solution-diffusion process in the case of polymeric networks [14].

97 The objective of this study was to measure the effective diffusion coefficient of gas-phase  
98  $\text{CO}_2$  through an agglomerated cork stopper and then to identify the limiting step to gas  
99 transfer depending on the composite material structure. To that purpose, it was necessary to  
100 experimentally determine the gas transfer through each part of the sparkling wine stopper.  
101 Furthermore, the different parameters that can control the gas transfer, such as the cork  
102 particle size, the adhesive content, the presence of cork discs, and the effect of the  
103 compression were investigated. The results of  $\text{CO}_2$  transfer through sparkling wine stoppers  
104 are critically analyzed in order to better understand the gas barrier properties of stoppers and  
105 to estimate their impact on the shelf life of sparkling wines.

106

## 2. Materials and methods

### 2.1. Material: Cork stoppers

Agglomerated cork stoppers were supplied by the Relvas (Mozelos, Portugal) and Prats & Bonany (Reims, France) companies. Two types of stoppers were studied: stoppers composed of a macro-agglomerated body with two cork discs at one end (referred to as MA2D) and stoppers composed only of a micro-agglomerated cork body (referred to as MI). Two cork particle size distributions, determined according to the NP ISO 2031:2015 standard, were used to formulate macro-agglomerated (2.5-8 mm diameter) and micro-agglomerated (0.5-2.8 mm diameter) stoppers. An aromatic glue, composed of toluene diisocyanate (TDI) isomers (2,6-TDI and 2,4-TDI), was used at mass ratios ( $w_{\text{glue}}/w_{\text{cork}}$ ) of 8 % and 15 % for macro-agglomerated and at 20 % and 25 % for micro-agglomerated stoppers. Agglomerated cork bodies were obtained after polymerization at 120 °C for 45-65 min using an industrial scale processing, based on individual molding. Two cork discs (6 mm thick) were glued at one end of the agglomerated cork body with an aqueous dispersion of PU. They are referred to as “aromatic adhesive for cork body” and “cork disc adhesive”, respectively, in the present paper. The resulting stoppers were then sanded down and chamfered to obtain the final cork stopper for sparkling wine. The diameter was reduced to 30 mm to meet the requirements of the bottling machine (TDD Grillat, BM 800).

### 2.2. Gas transfer measurement

The gas transfer through the samples was measured using a homemade manometric device. The equipment and the procedure used to determine the effective diffusion coefficient were previously detailed in Chanut *et al.* (2020)[15]. It is based on the pressure measurement in two compartments separated by the sample. For the present work, the initial pressure was fixed at 0.6 MPa of pure CO<sub>2</sub> in the first compartment, corresponding to the pressure of CO<sub>2</sub>

133 inside a Champagne wine bottle at the end of the fermentation step. The second compartment  
134 of the device was maintained under dynamic primary vacuum (0.1 hPa). The pressure drop in  
135 the first compartment, due to CO<sub>2</sub> transfer through the sample, was recorded over time. The  
136 temperature was kept constant at 25 °C. The accuracy of the pressure sensor was 0.01 MPa.  
137 As the calculation of the effective diffusion coefficient requires the knowledge of the  
138 solubility of CO<sub>2</sub> in the materials, the sorption isotherms of CO<sub>2</sub> on the agglomerated cork  
139 and on the adhesives were previously determined from 0 to 5 MPa, at 25 °C, using a magnetic  
140 suspension balance (Rubotherm GmbH). Rectangular samples (~ 150 mm<sup>3</sup>) were first  
141 outgassed at 25 °C under primary vacuum until mass equilibrium. The gas pressure in the  
142 balance was then increased step-by-step (once mass equilibrium was reached for each  
143 pressure step). A specific module allowed measuring the gas phase density in order to take  
144 into account the buoyancy effect. For each sample, the sorption and desorption isotherms of  
145 CO<sub>2</sub> were determined, as displayed in Fig. 3, and allows to determine the partition coefficient  
146  $\psi$ , defined as the ratio between the concentration of CO<sub>2</sub> sorbed on the material (mol.m<sup>-3</sup>) and  
147 the concentration of CO<sub>2</sub> in the gas phase in contact with the film (mol.m<sup>-3</sup>) at equilibrium.

148         The different geometries used to determine the effective diffusion coefficient of CO<sub>2</sub>  
149 according to the sample are summarized in Table 1. To reduce the experimental time, gas  
150 transfer was not measured on full-length stoppers, but on reduced-thickness samples. To  
151 determine the gas transfer on a full-length stopper, an extrapolation model was applied,  
152 following the procedure detailed in Lagorce-Tachon *et al.* (2016) and Chanut *et al* (2020)[15,  
153 16], as shown in Fig. 4 for a macro-agglomerated cork body containing 8 % aromatic  
154 adhesive. CO<sub>2</sub> transfer measurements were carried out on agglomerated corks, both  
155 compressed and non-compressed, on the different adhesive films composing the stopper  
156 (~700 μm thickness films obtained by polymerization at 20 °C) and on the cork discs. The  
157 compressed samples were obtained using a corking machine (TDD Grillat, BM 800) equipped



158 with a special homemade device, which allowed insertion of the cork slice in a sample holder  
159 of 17.0 ( $\pm 0.5$ ) mm diameter (corresponding to a Champagne bottleneck).

### 160 2.3. Helium pycnometry

161 The porosity of the samples has been measured by helium pycnometry with a  
162 homemade manometric device. Prior to the measurement, the sample was outgassed under  
163 primary vacuum at room temperature. A cork body sample of known apparent volume  $V_{app}$   
164 (measured with a caliper) was introduced in the helium pycnometer and the real volume of the  
165 sample  $V_s$  was determined from pressure measurements. The porous fraction  $V_p$  is defined as  
166 the ratio of the volume accessible to helium over the apparent volume, according to the  
167 following equation:

$$168 \quad V_p (\% V/V) = \left( \frac{V_{app} - V_s}{V_{app}} \right) \times 100 \quad (1)$$

169 Helium pycnometry was performed at 25 °C on 10 macro- and micro-agglomerated cork  
170 bodies (with an apparent diameter of  $3.00 \pm 0.01$  cm and a length of  $4.80 \pm 0.02$  cm, which  
171 corresponds to an apparent volume of  $34.4 \pm 0.3$  cm<sup>3</sup>).

### 172 2.4. Scanning electron microscopy (SEM)

173  
174 Agglomerated cork stoppers for sparkling wine were observed by SEM using a Jeol JSM  
175 7600F instrument. Prior to imaging, samples were cut with a razor blade and coated with 15-  
176 20 nm carbon. A vacuum of  $9 \times 10^{-6}$  Pa was applied with an accelerating voltage of 15 kV.

177

### 3. Results and discussion

#### 3.1. Effect of particle size and adhesive concentration of the cork body

Fig. 5 displays the extrapolated distribution for CO<sub>2</sub> effective diffusion coefficients (D) obtained for non-compressed macro- and micro-agglomerated cork bodies with two different amounts of aromatic adhesive. The mean values of effective diffusion coefficients are also indicated in Table 2. It is noteworthy that the distribution of effective diffusion coefficient values is very large. This is due to the heterogeneity of the porosity of such agglomerated materials, which are composed of cork particles having various sizes and geometries. Both the increase in adhesive concentration and the reduction in the cork particle size lead to a decrease in the mean value of D. A decrease by a factor of 3 (from  $3 \times 10^{-5}$  to  $9 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$ ) is observed for the macro-agglomerated cork body with an increase in the adhesive content from 8 % to 15 %, and by a factor of 4 (from  $8 \times 10^{-8}$  to  $2 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$ ) when the adhesive content increases from 20 % to 25 % for the micro-agglomerated cork body (Table 2). Regarding the cork particle size, the reduction from macro (2.5-8 mm) to micro (0.5-2.8 mm) leads to a decrease in the CO<sub>2</sub> effective diffusion coefficient by a factor of 375 (from  $3 \times 10^{-5}$  to  $8 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$ ). This clearly highlights that within the investigated range, particle size is a predominant factor in the reduction of effective diffusion coefficient compared with the increase in adhesive concentration. Nevertheless, the effect of these two factors cannot be fully separated, the micro-agglomerated cork formulation requiring a higher adhesive concentration to obtain an agglomerated body suitable for stopper application.

The decrease in the CO<sub>2</sub> effective diffusion coefficient in agglomerated cork with increasing adhesive concentration may be due to the barrier property of the adhesive used for agglomeration. The aromatic PU glue used in sparkling wine stoppers has an average CO<sub>2</sub> effective diffusion coefficient value of  $8 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$  (Table 2). This value is in agreement

204 with those found in the literature. Depending on the nature of the monomer used and its  
205 content, there is a variation in D values from  $7 \times 10^{-11}$  to  $1 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ [17].

206 Our results show that the higher the adhesive content, the better the CO<sub>2</sub> barrier  
207 property. This effect is probably due to the presence of a continuous adhesive film  
208 surrounding the cork particles, which is favored when the particles are small. In addition, the  
209 intergranular porosity decreases in the micro-agglomerated cork body with smaller particle  
210 size. Moreover, in the latter case, the cork particles are smaller and more spherical in shape  
211 than those used for the macro-agglomerated cork. This modification in size and shape induces  
212 a reduced intergranular porosity[18, 19]. For a deeper understanding of the difference  
213 between the macro- and micro-agglomerated cork bodies, it is thus necessary to measure the  
214 intergranular porosity. For this purpose, tests were carried out using helium pycnometry on  
215 macro-agglomerated (8 % aromatic adhesive) and micro-agglomerated (20 % aromatic  
216 adhesive) cork bodies. These measurements give an open porosity of 1.8 % (v/v) for macro-  
217 agglomerated cork. However, the open porosity was not measurable with this technique in the  
218 case of micro-agglomerated cork. This means that micro-agglomerated cork is either  
219 nonporous or the porosity is not accessible to helium. This confirms the decrease in porosity  
220 observed by SEM when smaller cork particles are used. In macro-agglomerated cork, an  
221 important intergranular porosity is visible (Fig. 6a). By contrast, for micro-agglomerated cork,  
222 this porosity appears to be absent and the adhesive is obstructing the residual porosity  
223 between the cork particles (Fig. 6b), thus contributing to increase the barrier property of  
224 agglomerated cork.

225

226 3.2. Effect of compression

227

228 The CO<sub>2</sub> barrier properties of agglomerated cork bodies presented above were determined  
229 for non-compressed samples (Table 1). In fact, considering the oenological application, the  
230 stoppers are compressed in the bottleneck (17 mm diameter). This leads to a total volume  
231 reduction of 70 %, and can thus strongly impact the gas transfer. The effect of such a  
232 compression level on the CO<sub>2</sub> effective diffusion coefficient is reported in Fig. 7 for the  
233 macro- and micro-agglomerated corks.

234 There is a significant reduction in the effective diffusion coefficient for both macro-  
235 and micro-agglomerated corks when the agglomerated cork body is compressed. The effective  
236 diffusion coefficient value decreases by a factor of around 6000 for macro-agglomerated cork  
237 (from  $3 \times 10^{-5}$  to  $5 \times 10^{-9}$  m<sup>2</sup>.s<sup>-1</sup>) and by a factor of around 1000 for micro-agglomerated cork  
238 (from  $8 \times 10^{-8}$  to  $8 \times 10^{-11}$  m<sup>2</sup>.s<sup>-1</sup>) (Table 2). The level of compression, as applied in the  
239 bottleneck, therefore greatly reduces the transfer of gas through the agglomerated cork body.  
240 This improvement in barrier properties can be explained, in a large part, by the very high  
241 reduction in volume. By reducing the intergranular porosity and increasing the tortuosity, the  
242 compression slows down the diffusion processes of Darcy and Knudsen. This is particularly  
243 true for macro-agglomerated cork for which the intergranular porosity is larger than for  
244 micro-agglomerated cork. The decrease in the effective diffusion coefficient due to  
245 compression was 6 times larger than for micro-agglomerated cork. In addition, there is also a  
246 significant reduction in the width of the distribution, which means that the compression also  
247 makes the samples more homogeneous from the diffusion point of view.

248

### 249 3.3. Role of the cork discs

250

251 Previous investigations have clearly shown that the formulation parameters, as well as  
252 the compression, can strongly change the barrier properties of the agglomerated cork body. It

253 is also important to study the role that the two cork discs attached at one end of the cork body  
254 may play in the gas transfer through the sparkling wine stopper. The cork disc is punched in  
255 the plane perpendicular to the radial direction, and thus it is sprinkled with lenticels, which are  
256 channels oriented in a direction parallel to the gas flow. Permeation tests were carried out on  
257 single cork discs, but the gas flow is too fast for being measured with our manometric device.  
258 In this case and the CO<sub>2</sub> effective diffusion coefficient is taken equal to the value in air (Table  
259 2). Thus, the cork disc alone is not an efficient barrier to the gas diffusion, at least when it is  
260 considered non-compressed.

261         Nevertheless, in the cork stopper, these cork discs are glued together with an aqueous  
262 dispersion of PUs. The effective diffusion coefficient of CO<sub>2</sub> was measured through a film of  
263 ~700 μm thickness of this adhesive. A mean value of  $4 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$  was found (Table 2). In  
264 order to get closer to the industrial cork manufacturing process, the effective diffusion  
265 coefficient of CO<sub>2</sub> was also measured through the two cork discs glued together with a single  
266 film of adhesive in between (a sample of ~9 mm thickness was taken from the two discs at the  
267 end of a MA2D industrial stopper). In this case, the mean value is  $6 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$  (Table 2).  
268 This is very surprising. Such a difference can be explained by the following reasons. i) As we  
269 consider no resistance to gas transfer in cork discs, this effective diffusion coefficient is  
270 calculated by taking a thickness of adhesive film of 10 μm, roughly estimated from SEM  
271 observation (Fig. 8). ii) During the industrial process, the adhesive layer is deposited in excess  
272 and can migrate into the lenticels, causing a local increase in the thickness of the adhesive  
273 film. iii) Polymerization under industrial conditions differs considerably from that applied  
274 under laboratory conditions to obtain a self-supporting film at 25°C. iv) Reactions occurring  
275 at the interface between cork and adhesive may locally create an additional barrier to gas  
276 transfer. These effects may also explain the large distribution of effective D values measured  
277 on this system (ranging from  $9 \times 10^{-14}$  to  $3 \times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ ).

278 Therefore, it appears that the adhesive film used to glue the two cork discs can act as a  
279 significant barrier to the CO<sub>2</sub> transfer, provided that the film is sufficiently thick and  
280 homogeneous.

281

### 282 3.4. Critical discussion of CO<sub>2</sub> transfer in a sparkling wine cork stopper

283

284 This work allows the determination of the effective diffusion coefficient values for the  
285 different parts composing a sparkling wine stopper as well as the formulation and processing  
286 parameters that can influence the gas transfer. For a deeper understanding, it is essential to  
287 couple these data together in order to elucidate the mechanisms involved in the gas diffusion  
288 when considering the material as a whole (Fig. 9).

289

#### 290 **Gas transfer through the agglomerated cork body**

291 For the gas transfer through the cork body, the CO<sub>2</sub> effective diffusion coefficient for a  
292 non-compressed macro-agglomerated cork is about  $3 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$ . This very high value  
293 shows that the gas diffusion is very fast, probably because of an important intergranular  
294 porosity. As the CO<sub>2</sub> diffusion coefficient in air is  $1.39 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$  (at 24 °C and 0.1  
295 MPa)[20], it can be assumed that the porosity is totally open along the entire macro-  
296 agglomerated cork body. In such a case, the diffusion is mainly governed by Darcy's and  
297 Knudsen's mechanisms in the intergranular porosity, considering the very high value of D.  
298 This is reinforced by the fact that similar effective diffusion coefficients were obtained for O<sub>2</sub>  
299 on non-compressed macro-agglomerated cork body (data not shown). However, the solution-  
300 diffusion mechanism may also still be involved to cross the cork cell walls as well as the  
301 adhesive network at some points. For the micro-agglomerated cork, solution-diffusion process  
302 is probably the main mechanism involved and acting as the limiting step to gas transfer (even

303 if Darcy's and Knudsen's mechanisms occur), since the porosity is reduced, leading to a  
304 lower CO<sub>2</sub> effective diffusion coefficient of around 10<sup>-8</sup> m<sup>2</sup>.s<sup>-1</sup> in non-compressed samples. In  
305 this case, there is also a difference between O<sub>2</sub> and CO<sub>2</sub> effective diffusion coefficients,  
306 indicating that the solution-diffusion process plays a more important role than in the macro-  
307 agglomerated cork body (data not shown). In conclusion, the three mechanisms coexist  
308 simultaneously and in parallel within the stoppers. On the one hand, the higher the  
309 interconnected porosity, the greater the permeability will be governed by Darcy's and  
310 Knudsen's mechanisms. On the other hand, the smaller the porosity, or the higher the  
311 adhesive concentration, the more the permeability will be governed by the solution-diffusion  
312 process, and therefore the gas transfer will be slowed down.

313

#### 314 **Gas transfer through the cork discs and the adhesive film between them**

315 For the cork discs, Darcy's mechanism is obviously involved in the lenticels oriented  
316 in the transfer direction. As above-mentioned, it is experimentally impossible to determine  
317 such a high effective diffusion coefficient value with the manometric method. However,  
318 considering the lenticels as macropores, it can reasonably be assumed that the effective  
319 diffusion coefficient would be at least of the same order of magnitude as its molecular value  
320 in air (~ 10<sup>-5</sup> m<sup>2</sup>.s<sup>-1</sup>).

321 The adhesive film between the two cork discs acts as an efficient barrier to gas  
322 transfer. The gas transfer through this film is controlled by a solution-diffusion mechanism.  
323 As we know the values of the CO<sub>2</sub> effective diffusion coefficient in the adhesive film between  
324 the cork discs ( $D = 6 \times 10^{-13}$  m<sup>2</sup>.s<sup>-1</sup>), the surface area of the film S taken as the section of the  
325 bottleneck (m<sup>2</sup>) and the temperature T (K), the gas flow J (mol.s<sup>-1</sup>) can be calculated as a  
326 function of the film thickness L (m) with the following equation:

327 
$$J = D \times S \times \frac{\Delta p \times \psi}{R \times T \times L} \quad (2)$$

328 where  $\psi$  is determined from the CO<sub>2</sub> sorption isotherm and corresponds to the partition  
329 coefficient, defined as the ratio between the concentration of CO<sub>2</sub> sorbed on the material  
330 (mol.m<sup>-3</sup>) and the concentration of CO<sub>2</sub> in the gas phase in contact with the film (mol.m<sup>-3</sup>) at  
331 equilibrium. A value of 0.3 was experimentally determined from the sorption isotherms for  
332 the adhesive (Fig. 3).

333 The dependence of the gas flow on thickness is shown in Fig. 10. From this plot, a critical  
334 thickness ( $L_{crit}$ ) was determined by applying the tangent method on the hyperbolic curve and a  
335 constant thickness ( $L_{cst}$ ) was defined as the thickness value above which the variation in gas  
336 flow becomes less than 5 % for each additional micrometer. Above a  $L_{cst}$  of around 20  $\mu$ m,  
337 the gain in barrier property remains very low. By contrast, the gas flow drastically increases  
338 for a thickness lower than the  $L_{crit}$  value (around 5  $\mu$ m). In the latter case, each micrometer  
339 decrease leads to a 20 to 50 % increase in the gas flow. In addition, SEM observations were  
340 performed on a cross-section of the two glued cork discs (Fig. 8). The film separating the two  
341 cork discs could be distinguished. In the upper disc, a lenticel is partially obstructed by the  
342 adhesive. As the adhesive has been deposited in excess, the excess glue has been evacuated at  
343 the periphery of the cork disc or through the open lenticular channels, as previously  
344 mentioned. Moreover, the adhesive film does not display a homogeneous thickness. It is on  
345 average quite thin, around 10  $\mu$ m thickness (Fig. 8b). It also appears up to three times thicker  
346 at some places (Fig. 8c). Furthermore, the average thickness of the film between the two discs  
347 lies between  $L_{crit}$  and  $L_{cst}$  values, as previously defined (Fig. 10), which means that this film  
348 globally represents an efficient barrier to gas transfer.

349

350 **Global effective diffusion coefficient through the full cork stopper**



351 The different parts of the sparkling wine stopper are disposed in series as displayed in  
352 Fig. 2. Nowadays, two different cork stoppers are mainly used in the market for sparkling  
353 wine. (i) stoppers composed of a macro-agglomerated body with two cork discs at one end  
354 (MA2D) and (ii) stoppers composed only of a micro-agglomerated cork body (MI).  
355 Considering their respective assembly, a global resistance to mass transfer  $R$  ( $s.m^{-1}$ ) and a  
356 global effective diffusion coefficient  $D$  ( $m^2.s^{-1}$ ), can be calculated for these two types of  
357 stoppers.

358 A rather complex case is that of the MA2D stopper, composed of a macro-  
359 agglomerated cork body of 36 mm, with two cork discs of 6 mm each and two adhesive films  
360 of 10  $\mu m$  each, as shown in Fig. 1. The global resistance to gas transfer is therefore the sum of  
361 local resistances corresponding to each part of this stopper (Fig. 2). Unlike the MI stopper,  
362 which is considered a homogeneous system with a single effective diffusion coefficient, the  
363 MA2D stopper is heterogeneous with, for each part, a corresponding effective diffusion  
364 coefficient and a solubility for  $CO_2$ . Its global effective diffusion coefficient can therefore be  
365 determined according to the following equation:

$$366 \quad \frac{L_{stopper}}{D_{stopper}\psi_{stopper}} = \sum_i \frac{L_i}{D_i\psi_i} \quad (3)$$

367 The values calculated for the global effective diffusion coefficient of each stopper are  
368 shown in Table 3, with, for each part composing the stopper, the respective values of  
369 thickness, partition coefficient, effective diffusion coefficient and resistance.

370 In this calculation, the following assumptions have been made. i) The effective  
371 diffusion coefficient values used for these calculations are taken from Table 2. It is assumed  
372 that that the corresponding effective diffusion coefficient in the cork body is not significantly  
373 different for the considered thickness in the cork stopper (as shown in Fig. 4). ii) The  $D$  value  
374 on one adhesive layer between two cork discs was measured on a non-compressed system. It

375 may be different when compressed. In addition, for the cork disc alone, it was not possible to  
376 measure the effective diffusion coefficient on a compressed disc because it breaks during  
377 compression. iii) The compression brought by the muselet on the outer part of the stopper is  
378 not taken into account. iv) For the cork disc, a partition coefficient of 1 is used as the transfer  
379 follows Darcy's mechanism. A value of 0.9 is used for the stopper and 0.3 for the adhesive  
380 (Fig. 3). v) The gas transfer that may occur at the cork/bottleneck interface is not considered  
381 in this work.

382 From equation 3, the limiting step to the gas transfer is therefore associated with the  
383 part having the strongest resistance to gas transfer (Fig. 2). In this case, this is the adhesive  
384 films used to glue the two cork discs (Table 2). Assuming that these films have no defect and  
385 have sufficient thickness over the entire disc surface, this is the essential part that is  
386 responsible for the barrier properties of MA2D stoppers. The global effective diffusion  
387 coefficient of MI stopper was also calculated considering a micro-agglomerated cork body of  
388 48 mm. When considered as non-compressed materials, the global resistance to gas transfer is  
389 higher for MA2D than for MI stoppers (Table 3).

390 However, when used in compressed conditions for sparkling wine conservation, the  
391 global effective diffusion coefficient and resistance to mass transfer change. Let us consider a  
392 stopper partially inserted in a bottleneck with a penetration depth of 24 mm inside the  
393 bottleneck and 16 mm remaining non-compressed outside. The global effective diffusion  
394 coefficient  $D$  and resistance  $R$  calculated in these conditions for the MA2D and MI stoppers  
395 are reported in Table 3. Regarding the value obtained, when the stoppers are considered as  
396 compressed in the bottleneck, MI stoppers have a resistance to mass transfer 3 times higher  
397 than a MA2D stopper.

398 Liger-Belair *et al.* were the first to estimate a  $\text{CO}_2$  effective diffusion coefficient  
399 through MA2D cork stoppers for sparkling wine, based on the dissolved  $\text{CO}_2$  concentration

400 decrease in different Champagne wine vintages (from 2 months to 35 years of storage)[5, 6].  
401 However, they did not focus in detail on the transfer mechanisms acting in such a composite  
402 material. In the present work, the detailed study of the agglomerated cork stoppers allows us  
403 to clearly identify the limiting step to gas transfer and thus the parameters responsible for  
404 providing good barrier properties. The global effective diffusion coefficient value determined  
405 in our study is in the same order of magnitude ( $4 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ ) as those reported by Liger-  
406 Belair *et al.* (from  $5 \times 10^{-11}$  to  $3 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ ) and measured *in situ* on different aged  
407 Champagne wine samples[5, 6]. The global effective diffusion coefficient calculated from the  
408 individual effective diffusion coefficients measured on each part is therefore in good  
409 agreement with the global effective diffusion coefficient values obtained from their *in situ*  
410 experiments.

411

412 **Toward the shelf life prediction of corked bottles of sparkling wine based on CO<sub>2</sub>**  
413 **effective diffusion through the stopper**

414 Bubble formation is indeed the hallmark of sparkling wines. The intensity of effervescence  
415 and the bubbles' size, two characteristics of paramount importance for sparkling wines lovers,  
416 both depend on the level of dissolved CO<sub>2</sub> found in a sparkling wine[21]. Nevertheless, below  
417 a critical level of dissolved CO<sub>2</sub> close to  $2.5 \text{ g} \cdot \text{L}^{-1}$  (at  $12 \text{ }^\circ\text{C}$ ), namely  $C_L^*$ , a sparkling wine  
418 becomes thermodynamically unable to promote any bubble formation under standard tasting  
419 conditions (i.e., in a glass, with micrometric particles or glass anfractuosités acting as bubble  
420 nucleation sites), as described by Liger-Belair[22]. The precise knowledge of the permeability  
421 of a cork stopper with regard to gas-phase CO<sub>2</sub> becomes therefore crucial to be able to  
422 understand how a sparkling wine will age as time proceeds, especially concerning its  
423 progressive decrease in dissolved CO<sub>2</sub>. In bottles of sparkling wines sealed with cork stoppers,  
424 because the partial pressure of gas-phase CO<sub>2</sub> in the bottleneck reaches up to 6 bar (at  $12 \text{ }^\circ\text{C}$ ),

425 CO<sub>2</sub> slowly diffuses from the bottle to the ambient air, either through the cork bulk or through  
 426 the cork/bottleneck interface. By combining both Henry's and Fick's laws, an exponential  
 427 decay-type model was found for the theoretical time-dependent level of dissolved CO<sub>2</sub> found  
 428 in champagne during aging (in the MKS system of units)[5]:

$$429 \begin{cases} C_L(t) \approx C_0 \exp\left(-\frac{t}{\tau}\right) \\ \text{with } \tau = \frac{L(V_G + k_H R T V_L)}{D S} \end{cases} \quad (4)$$

430 with  $C_0$  the initial level of dissolved CO<sub>2</sub> after corking the bottle,  $t$  the aging period of time,  
 431  $\tau$  the timescale of the exponential decay-type model,  $L$  the total length of the cork,  $V_L$  the  
 432 volume of the liquid phase in the sealed bottle,  $k_H$  the temperature-dependent Henry's law  
 433 constant of CO<sub>2</sub> (conveniently expressed in mol.m<sup>-3</sup>.Pa<sup>-1</sup>)[22],  $V_G$  the volume of gas phase  
 434 (the headspace) in the sealed bottle,  $R$  the ideal gas constant (8.31 J.K<sup>-1</sup>.mol<sup>-1</sup>),  $T$  the  
 435 temperature,  $D$  the global diffusion coefficient of gas-phase CO<sub>2</sub> through the cork stopper,  
 436 and  $S$  the cross section of the cork stopper (equivalent indeed to the cross section of the  
 437 bottleneck). The global  $D$  values (given in Table 3) are used in this calculation.

438 Following the exponential decay-type law given by equation 4, it becomes therefore possible  
 439 to predict the shelf life of corked bottles of sparkling wines (i.e., the time beyond which the  
 440 concentration of dissolved CO<sub>2</sub> fall below the critical concentration of 2.5 g.L<sup>-1</sup> required for  
 441 bubbling)[6]. Replacing  $C_L(t)$  in equation 4 by the critical concentration of dissolved CO<sub>2</sub>  
 442 below which bubble formation would become impossible, and developing, leads to the critical  
 443 aging period of time, denoted  $t_B^*$ , beyond which bubbling would become impossible through  
 444 lack of dissolved CO<sub>2</sub>:

$$445 t_B^* \approx \tau \ln\left(\frac{C_0}{C_L^*}\right) \quad (5)$$

446 By replacing in the latter equation each parameter by its numerical value, it becomes therefore  
447 possible to approach the maximum period of aging (and therefore a shelf life prediction)  
448 beyond which a bottle of sparkling wine could become flat. For a standard 75 cL bottle of  
449 sparkling wine initially holding a level of dissolved CO<sub>2</sub> close to 12 g.L<sup>-1</sup>[21], the theoretical  
450 mean shelf life prediction is in the order of 10 years if the bottle is sealed with a MA2D cork  
451 stopper. The distribution is rather large, from 2 to 65 years, if we consider the minimum and  
452 maximum values for all the parts composing the stopper, and underlines the crucial barrier  
453 role of the adhesive film between the discs. If the same bottle of sparkling wine is sealed with  
454 a MI cork stopper, its theoretical mean shelf life prediction is increased to about 30 years. In  
455 this case, the distribution is reduced, ranging from 20 to 50 years. A shelf life prediction of 30  
456 years before the sparkling wine would become flat is nevertheless quite hard to verify in situ,  
457 because MI cork stoppers have only been used for about two decades only. In contrast, MA2D  
458 cork stoppers have been used to seal bottles of champagne and sparkling wines for several  
459 decades. Time series data recordings of dissolved CO<sub>2</sub> were already done in situ with cuvees  
460 sealed with MA2D cork stoppers and aged from several years up to several decades[5, 6, 23].  
461 The dissolved CO<sub>2</sub> content found in these bottles having aged for a much longer period of  
462 time than the theoretical shelf life prediction of 10 years was found to be still much higher  
463 than the critical level of 2.5 g.L<sup>-1</sup> required for bubble formation. Moreover, it is worth noting  
464 that the global diffusion coefficients determined under compressed conditions in the present  
465 work do not take into account the gas transfer that may occur at the cork/bottleneck  
466 interface[16, 24]. Taking this into account would even more increase the respective global  
467 diffusion coefficients, therefore leading to theoretical shelf life predictions even shorter. We  
468 are therefore strongly tempted to conclude that the real storage conditions experienced by the  
469 corks are in favor of a much better impermeability with regard to gas-phase CO<sub>2</sub>. This is the

470 reason why Champagne and sparkling wine bottles can age for several decades before they  
471 lose their bubbling capacity.

472 A crucial point also finally unveiled by this work is that, the dry compressed  
473 conditions, under which global CO<sub>2</sub> diffusion coefficients have been determined in the present  
474 work, are still far from the real conditions found in a bottleneck. In a bottleneck, the cork ages  
475 in contact with the wine (if bottles are stored horizontally) or in contact with a vapor phase  
476 saturated with water and ethanol (if the bottles are stored vertically). Changes in the structure  
477 of the cork during aging could therefore alter the way in which CO<sub>2</sub> molecules move from the  
478 headspace of the bottle to the ambient air, either through the cork stopper, or through the  
479 interface between the bottleneck and the cork stopper. Moreover, it is possible that prolonged  
480 aging could progressively moisturize the cork stopper, thus filling the pores, and reducing in  
481 turn the global diffusion coefficient of CO<sub>2</sub> through the cork stopper. Further experiments are  
482 needed to fully understand how the global diffusion coefficient of CO<sub>2</sub> through cork stopper  
483 could change as time proceeds during aging.

484

#### 485 **4. Conclusion**

486

487 This study clearly identified the parameters that can influence the gas barrier properties  
488 through sparkling wine cork stoppers. The parameter having the strongest impact on the  
489 barrier properties is the compression of the agglomerated cork body, which drastically reduces  
490 the effective diffusion coefficient, when applying a 70 % reduction in volume, corresponding  
491 to the compression in the bottleneck. Other parameters with a significant impact on the CO<sub>2</sub>  
492 effective diffusion are the cork particle size along with the adhesive concentration in the  
493 agglomerated cork body. The smaller the cork particles and, correlatively, the higher the  
494 adhesive concentration, the higher the CO<sub>2</sub> barrier property. Both of these associated

495 parameters result in a decrease of the intergranular porosity. Nevertheless, this effect tends to  
496 be mitigated when the samples are highly compressed.

497 The limiting step to gas transfer is the diffusion through the adhesive present both in the  
498 network of the agglomerated cork body and in the film between the two cork discs. The  
499 diffusion mechanism involved is thus the solution-diffusion process through the adhesive  
500 polymeric network. Given these results, it is therefore essential that the adhesive network,  
501 particularly that between the two cork discs, is as homogeneous as possible and sufficiently  
502 thick to act as an efficient barrier to gases.

503 Finally, it should be pointed out that the values reported in this study agree rather well  
504 with those obtained in real conditions of aging of Champagne wine, even if only the cork  
505 stopper is considered. Indeed, the role of the interface between the stopper and the bottleneck,  
506 and the surface treatment applied on the stopper were not taken into account. Moreover, the  
507 evolution of the mechanical and barrier properties during real bottle aging could also play an  
508 important role, in particular when considering the stopper in contact with an hydroethanolic  
509 solution. However, this study clearly shows the effectiveness of the cork stopper for the  
510 conservation of the sparkling wine and its ability to maintain a sufficient dissolved  
511 concentration and partial pressure of CO<sub>2</sub> in the headspace over many years.

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517 ACKNOWLEDGMENT

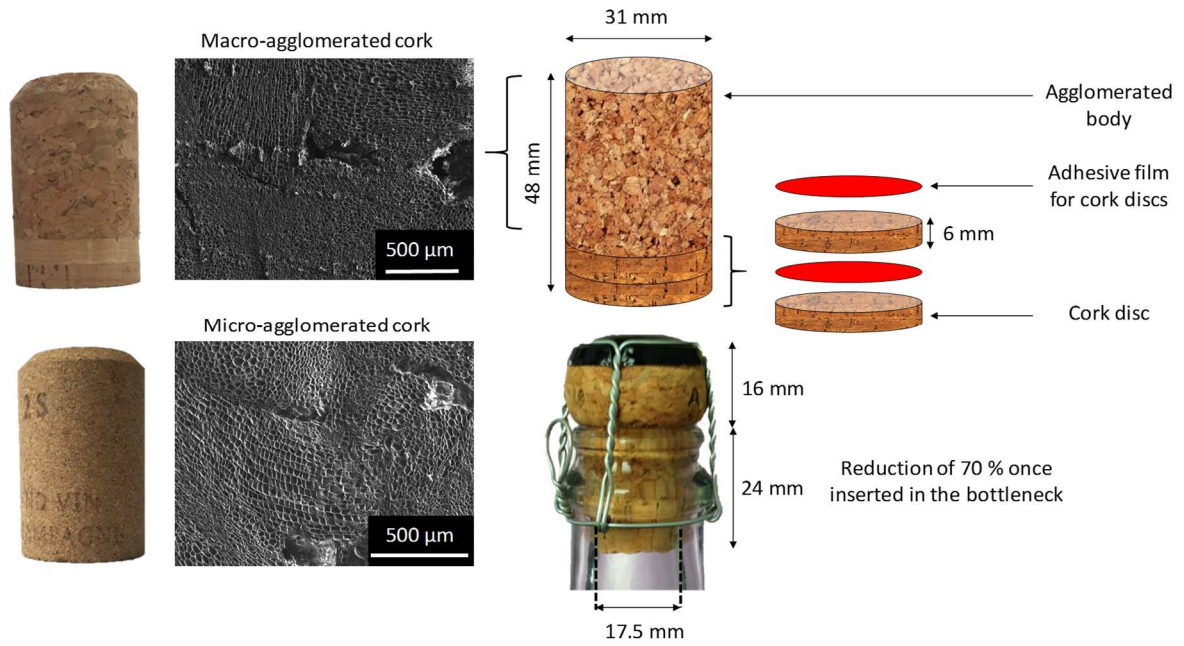
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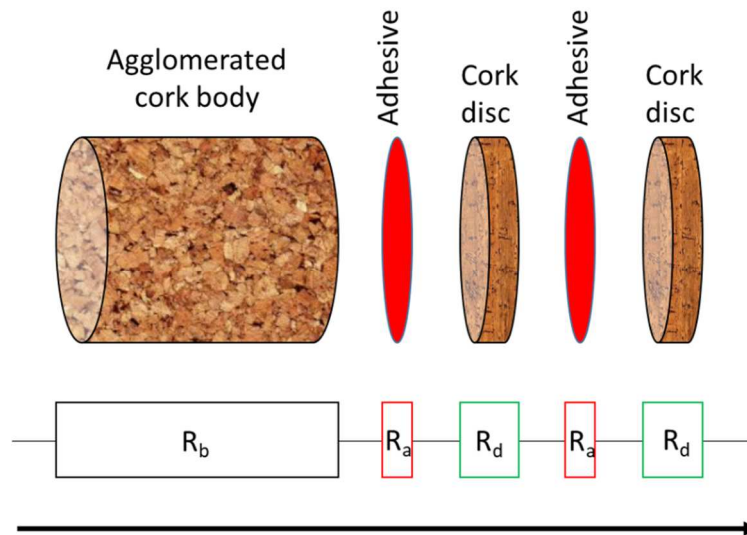


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1

2 Fig. 1. Detailed structure of agglomerated cork stoppers used for sparkling wines,  
 3 consisting of macro or micro cork particles, and usually two additional cork discs. The  
 4 reduction in volume when the cork stopper is inserted into a bottleneck is also indicated.



1

2

$$R_{stopper} = \sum_i R_i$$

3

4

$$\frac{L_{stopper}}{D_{stopper}\psi_{stopper}} = \sum_i \frac{L_i}{D_i\psi_i}$$

5

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8

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Fig. 2: The global resistance to mass transfer  $R_{stopper}$  is the sum of local resistances  $R_i$  of each part of the sparkling wine stopper. The resistance to mass transfer ( $R$ ) corresponds to the ratio of the thickness ( $L$ ) to the effective diffusion coefficient ( $D$ ) and the partition coefficient ( $\psi$ ) of each part of the stopper the gas has to go through.

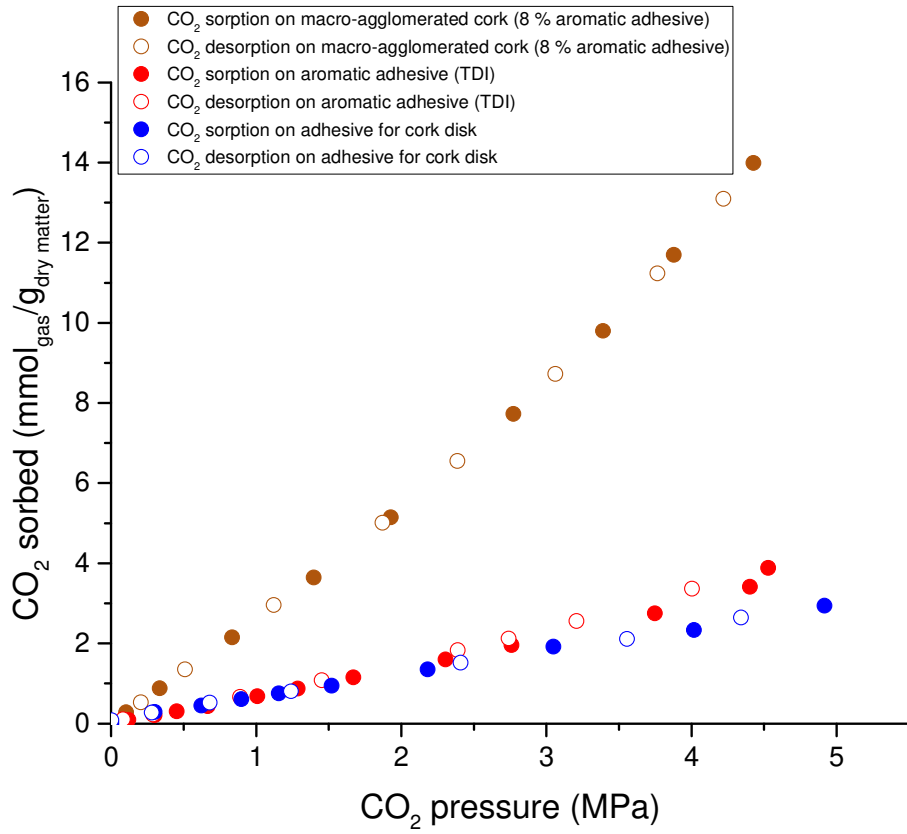
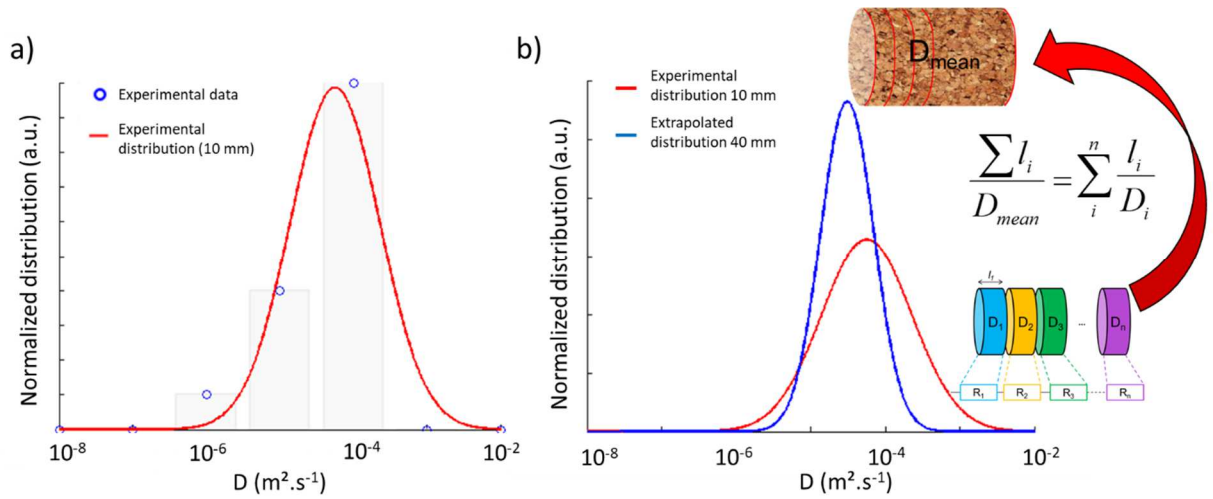
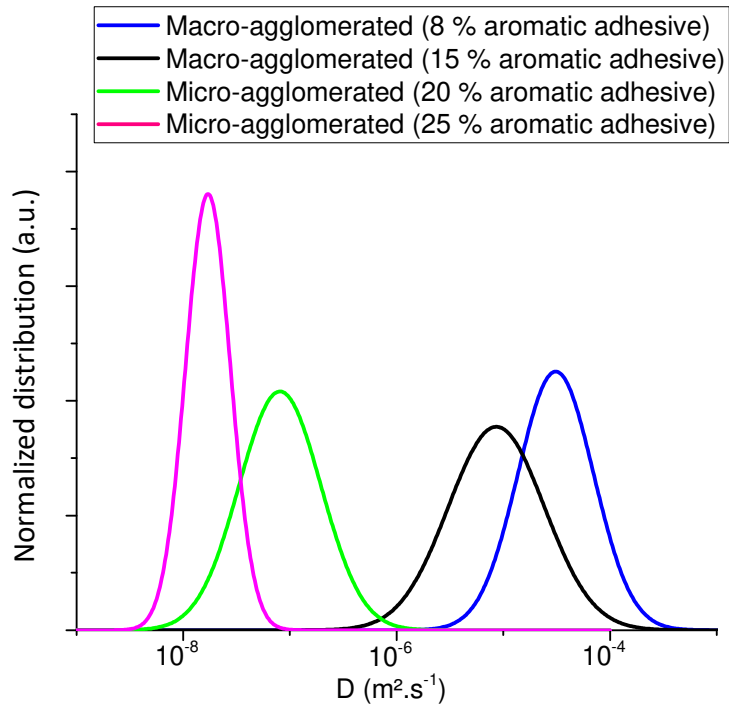


Fig. 3: Sorption-desorption isotherms of CO<sub>2</sub> on macro-agglomerated cork, aromatic adhesive and adhesive for cork disk, at 25 °C. The quantity of CO<sub>2</sub> sorbed is given in mmol of CO<sub>2</sub> per gram of dry matter.



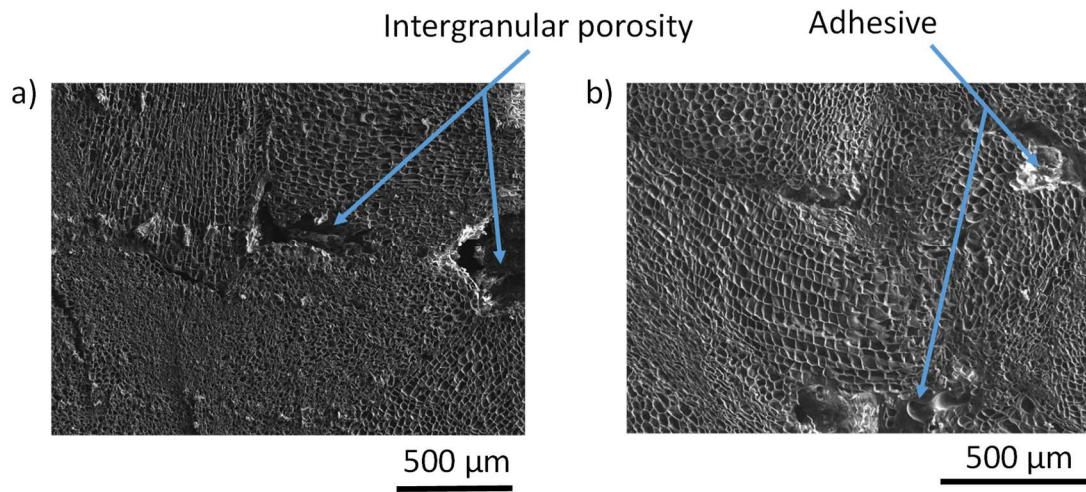
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2 Fig. 4: a) Experimental data and normalized distribution obtained for the CO<sub>2</sub> effective  
 3 diffusion coefficient values measured on 10 mm slices of macro-agglomerated cork body with  
 4 8 % of aromatic adhesive. b) Extrapolated distribution of the CO<sub>2</sub> diffusion coefficient (-) for  
 5 a full-length stopper (40 mm) obtained from the experimental distribution (-) on 10 mm slices.



1

2 Fig. 5: Extrapolated distribution of CO<sub>2</sub> effective diffusion coefficients (D) through non-  
 3 compressed full-length (40 mm) macro-agglomerated cork body (with 8 % and 15 % m/m of  
 4 aromatic adhesive) and micro-agglomerated cork body (with 20 % and 25 % of aromatic  
 5 adhesive).

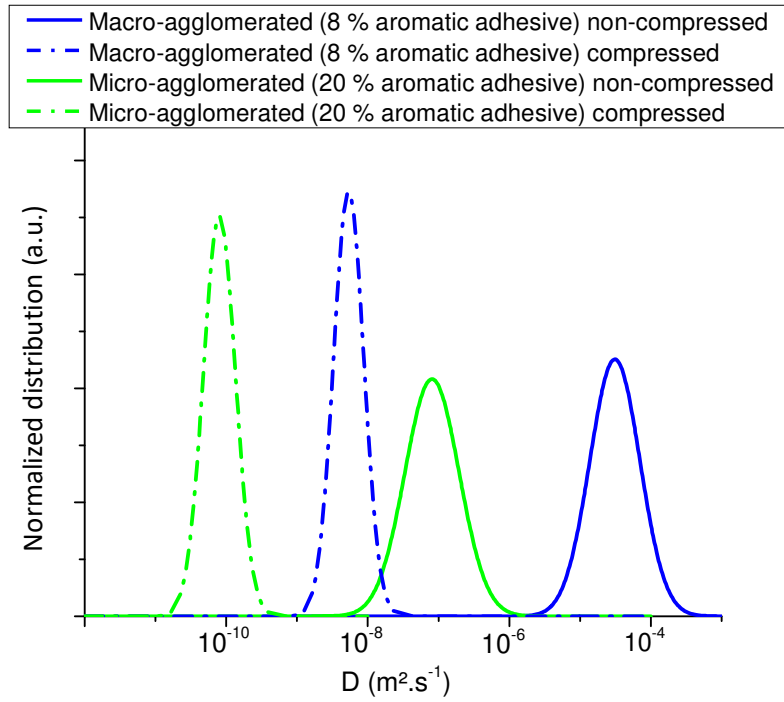


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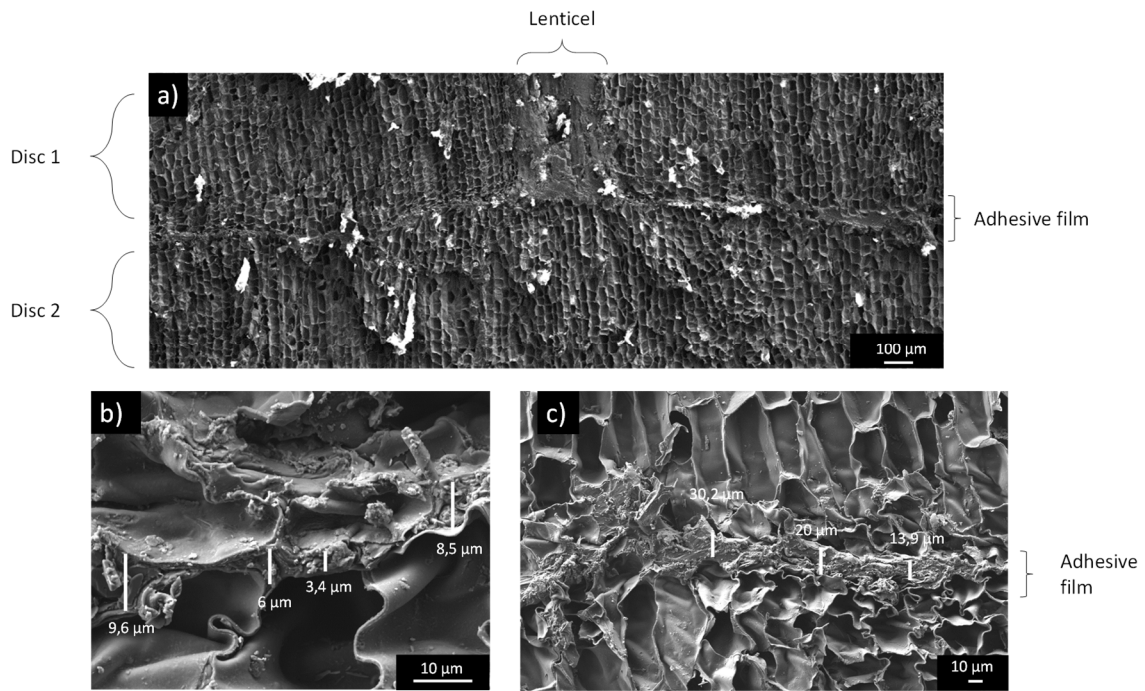
Fig. 6: SEM images of a) macro-agglomerated cork with intergranular porosity and b) micro-agglomerated cork with adhesive.



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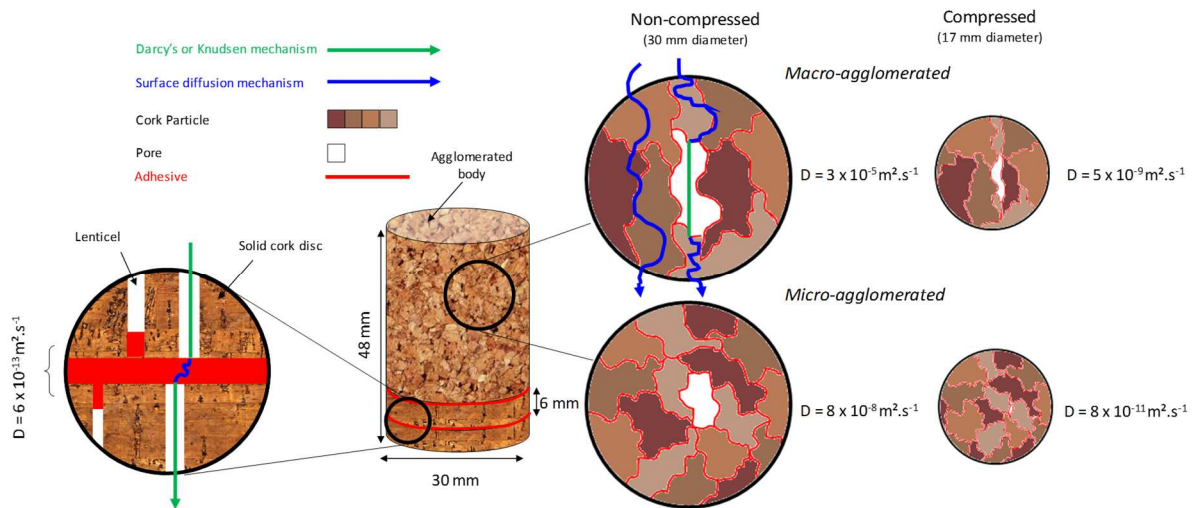
2 Fig. 7: Extrapolated distribution of CO<sub>2</sub> effective diffusion coefficient (D) through full-  
 3 length (40 mm) macro-agglomerated cork body (with 8 % of aromatic adhesive) non-  
 4 compressed (-) and compressed (- · -) and micro-agglomerated cork body (with 20 % of  
 5 aromatic adhesive) non-compressed (-) and compressed (- · -). Sample diameters are  
 6 reduced from 30 to 17 mm with the compression.





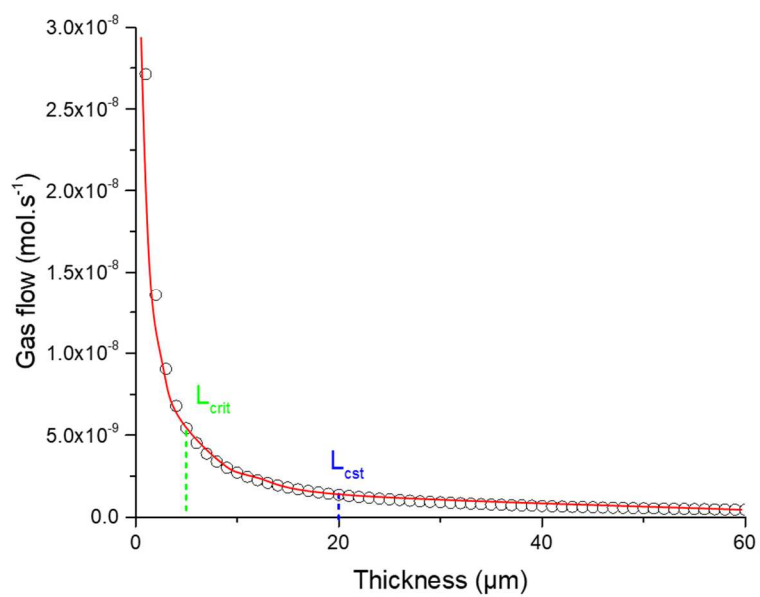
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2 Fig. 8: SEM observations of: a) the adhesive film (aqueous dispersion of PUs)  
 3 separating the two cork discs at the end of a sparkling wine stopper; b) and c) magnified  
 4 selected film sections with indication of the thickness.



1

2 Fig. 9: Comprehensive overview of CO<sub>2</sub> effective diffusion coefficient values  
 3 determined for the different parts comprising a cork stopper for sparkling wine and  
 4 depiction of the mechanisms involved in the gas transfer. The diffusing mechanisms are  
 5 only represented for the non-compressed macro-agglomerated cork, but occur in a  
 6 similar manner in the micro-agglomerated cork and the compressed samples.



1

2 Fig. 10: Effect of the film thickness on the CO<sub>2</sub> flow through the adhesive film used  
3 between the two cork discs. The gas flow was calculated from the Equation 2 for a film  
4 thickness from 1 to 60 μm (each point corresponds to 1 μm).

1 Table 1: Sample geometry and conditions used to determine the effective diffusion  
 2 coefficient of CO<sub>2</sub> in the different parts composing the sparkling wine stopper.

Sample part	Geometry	Extrapolated length	Number of replicates
Agglomerated cork body Non-compressed	Slice of 10 mm thickness Diameter: 30 mm	40 mm	15
Agglomerated cork body Compressed	Slice of 6 mm thickness Diameter: 17 mm	40 mm	10
Adhesive for agglomerated body Non-compressed	Film of ~700 μm thickness	-	10
Adhesive for cork discs Non-compressed	Film of ~700 μm thickness	-	10
Two cork discs with the adhesive layer in between Non-compressed	Slice of 9 mm thickness Diameter: 30 mm	-	15




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1 Table 2: Mean values of CO<sub>2</sub> effective diffusion coefficient, D (m<sup>2</sup>.s<sup>-1</sup>), at 25 °C,  
 2 obtained from the extrapolated distribution to 40 mm length for the agglomerated cork  
 3 samples or from the experimental distribution for the adhesive film samples. Data in  
 4 brackets are minimum and maximum values including standard deviation from the  
 5 corresponding distribution. (n.d.: not determined)

Sample	Mean D (m <sup>2</sup> .s <sup>-1</sup> ) ( <i>D<sub>min</sub></i> - <i>D<sub>max</sub></i> )
Macro-agglomerated 8 % aromatic non-compressed cork body	3 x 10 <sup>-5</sup> (1 x 10 <sup>-5</sup> – 7 x 10 <sup>-5</sup> )
Macro-agglomerated 15 % aromatic non-compressed cork body	9 x 10 <sup>-6</sup> (3 x 10 <sup>-6</sup> – 2 x 10 <sup>-5</sup> )
Micro-agglomerated 20 % aromatic non-compressed cork body	8 x 10 <sup>-8</sup> (3 x 10 <sup>-8</sup> – 2 x 10 <sup>-7</sup> )
Micro-agglomerated 25 % aromatic non-compressed cork body	2 x 10 <sup>-8</sup> (1 x 10 <sup>-8</sup> – 3 x 10 <sup>-8</sup> )
Macro-agglomerated 8 % aromatic compressed cork body	5 x 10 <sup>-9</sup> (3 x 10 <sup>-9</sup> – 9 x 10 <sup>-9</sup> )
Micro-agglomerated 20 % aromatic compressed cork body	8 x 10 <sup>-11</sup> (5 x 10 <sup>-11</sup> – 1 x 10 <sup>-10</sup> )
Aromatic adhesive for cork body (film of ~700 μm thickness)	8 x 10 <sup>-11</sup> (2 x 10 <sup>-11</sup> – 3 x 10 <sup>-10</sup> )
Adhesive for cork disc (film of ~700 μm thickness)	4 x 10 <sup>-11</sup> (2 x 10 <sup>-11</sup> – 9 x 10 <sup>-11</sup> )
Cork disc	n.d. ≈ D CO <sub>2</sub> in air (≈ 10 <sup>-5</sup> )
One adhesive layer in between two cork discs, non-compressed (film of 10 μm estimated thickness, based on SEM pictures)	6 x 10 <sup>-13</sup> (9 x 10 <sup>-14</sup> – 3 x 10 <sup>-12</sup> )

1 Table 3: Values of the global effective diffusion coefficient  $D$  ( $\text{m}^2 \cdot \text{s}^{-1}$ ) calculated from  
 2 the mean effective diffusion coefficient of the different individual parts, their  
 3 partitioning coefficient for  $\text{CO}_2$  and their respective thickness  $L$  (m), considering  
 4 various assembly geometries. The global  $D$  value (given in bold for each case) was  
 5 calculated assuming the global resistance to mass transfer as the sum of the resistances  
 6 of all stopper parts.

Stopper	Stopper part	Thickness $L$ ( $\times 10^{-3}$ m)	Partitioning coefficient $\psi$	Effective diffusion coefficient $D$ ( $\text{m}^2 \cdot \text{s}^{-1}$ )	Resistance $R$ ( $\text{s} \cdot \text{m}^{-1}$ )
	Non-compressed macro-agglomerated cork body	36	0.9	$3 \times 10^{-5}$	$1 \times 10^3$
	Adhesive layer (x2) *	0.01	0.3	$6 \times 10^{-13}$	$6 \times 10^7$
	Cork disc (x2) **	6	1	$1 \times 10^{-5}$	$6 \times 10^2$
	<b>MA2D non-compressed</b>	<b>48</b>	<b>0.9</b>	<b><math>4 \times 10^{-10}</math></b>	<b><math>1 \times 10^8</math></b>
	Non-compressed micro-agglomerated cork body	48	0.9	$8 \times 10^{-8}$	$7 \times 10^5$
	<b>MI non-compressed</b>	<b>48</b>	<b>0.9</b>	<b><math>8 \times 10^{-8}</math></b>	<b><math>7 \times 10^5</math></b>
	Non-compressed macro-agglomerated cork body	16	0.9	$3 \times 10^{-5}$	$6 \times 10^2$
	Compressed macro-agglomerated cork body	12	0.9	$5 \times 10^{-9}$	$2 \times 10^6$
	Adhesive layer (x2) *	0.01	0.3	$6 \times 10^{-13}$	$6 \times 10^7$
	Cork disc (x2) **	6	0.3	$1 \times 10^{-5}$	$6 \times 10^2$
<b>MA2D inserted in bottleneck**</b>	<b>40</b>	<b>0.9</b>	<b><math>4 \times 10^{-10}</math></b>	<b><math>1 \times 10^8</math></b>	
	Non-compressed micro-agglomerated cork body	16	0.9	$8 \times 10^{-8}$	$2 \times 10^5$

	Compressed micro-agglomerated cork body	24	0.9	$8 \times 10^{-11}$	$3 \times 10^8$
<b>MI inserted in bottleneck***</b>	<b>40</b>	<b>0.9</b>	<b><math>1 \times 10^{-10}</math></b>	<b><math>3 \times 10^8</math></b>	

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\*Value measured on one adhesive layer between two cork discs, non-compressed

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\*\* Value taken as  $D_{CO_2}$  in air

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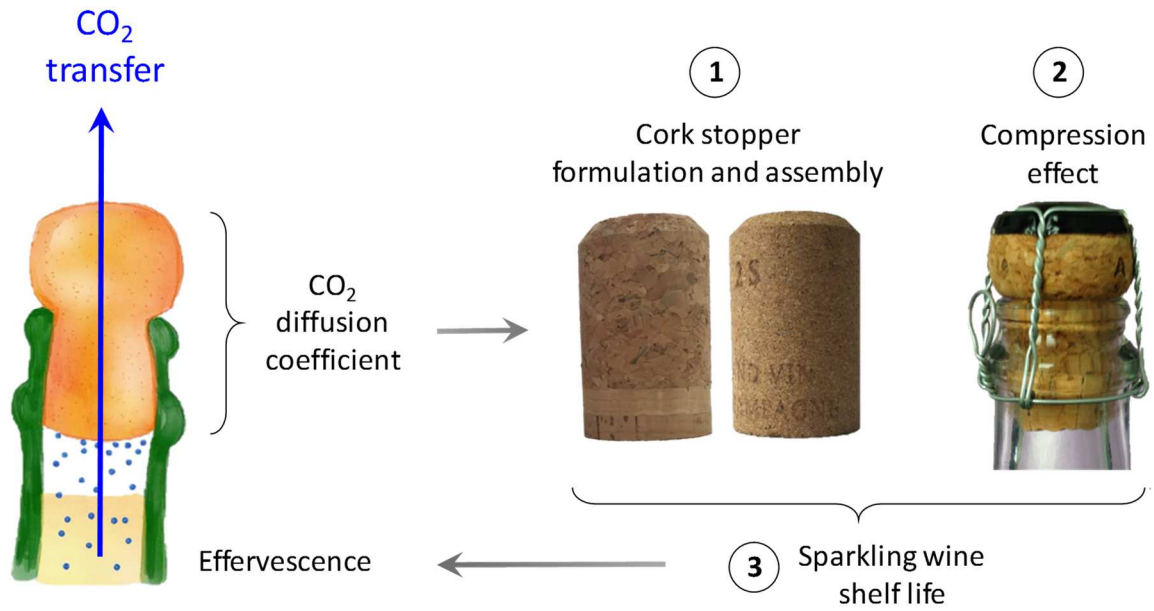
\*\* The gas transfer that may occur at the cork/bottleneck interface was not considered in this work (The bottleneck is only used for illustration purpose of the corresponding case study)

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1 Graphical abstract

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