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The parameters that affect the supercritical extraction OF 2,4,6-trichloroanisol from cork

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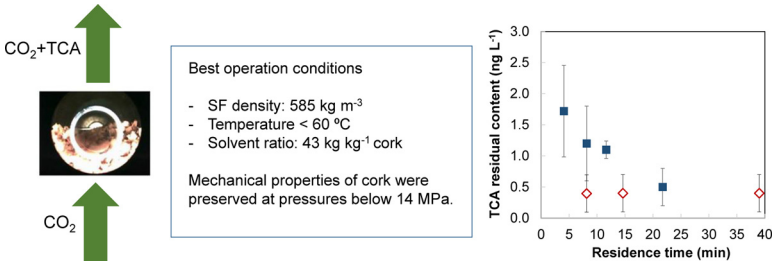
GRAPHICAL ABSTRACT



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ABSTRACT

The contamination of wine by 2,4,6-trichloroanisol (TCA) derived from the cork stopper is a huge problem for the wine industry. This work shows the results of TCA extraction using supercritical CO_2. Cork granules (6% moisture) were placed forming a fixed bed within a high-pressure vessel. The CO_2 was made to continuously flow over this. The TCA removal was compared at different operating conditions (pressure, temperature, flow rate or extraction time). TCA removal was not possible in dried cork. Density had a positive impact in TCA removal due to the solvent capacity increase. An increase in the supercritical fluid temperature over 60 °C impaired the TCA extraction. High residence times benefited the extraction. At high CO_2 density of 585 kg m^{-3}, TCA elimination below the detection level was achieved in 8 min residence time. This required relatively low solvent to cork mass ratios (43 kg CO_2 kg^{-1}).

1. Introduction

The cork is a natural polymeric material based on suberin obtained from the outer of the cork oaks (*Quecus suber L.*). Its average composition is suberin (45%), lignin (27%), polysaccharides (12%), tannins (5%) and ceroids (5%). Molecules of interest such as fatty acids, terpenes and long chain aliphatic compounds can also be found [1,2] Some of the triterpenes such as frideline, betulin, betulinic acid were extracted by organic solvents but it was recently proposed the use of supercritical CO_2 ($scCO_2$) [3]. Additionally, metabolites produced by various microorganisms can be found in cork.

The cork industry is of major importance in countries such as Portugal and Spain, the largest producers in the world, although Corsica, Sardinia and Turkey also produce it [4]. Cork is used mainly as a stopper for wine bottles and sparkling wines (cava and champagne), and as an insulator, in packaging or for construction.

Currently, the industry demands more than 12 billion stoppers per year [5]. But the contamination of wine with aromas derived from the cork stopper of the bottle is a huge problem for the wine industry, with its global impact already valued at more than $ 100 billion in 1995 [6].

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Although there may be other compounds responsible for the degradation of the organoleptic qualities of wine, 2,4,6-trichloroanisol (TCA) is the main one. Fuller estimated that between 2 and 5% of wine bottles are contaminated by TCA [6] whereas Soleas et al. analyzed more than 2000 wine bottles and detected TCA in 6.1% of them [7].

The most important reason why this compound ruins the enjoyment of a glass of wine is the very low detection threshold which is situated below 5 ng L^{-1}. This fact makes any procedure aimed at eliminating such contamination very demanding and analytical methods having a very low detection limit.

The TCA molecule is generated in the cork by the action of a series of microorganisms, mainly filamentous fungi by methylation of chlorophenol into an anisole [8]. To prevent contamination, stopper manufacturers monitor the level of TCA in them as well as in the water where they boil the material for further analysis [9].

Currently, cork stoppers are available in three distinct categories. The top-quality cork is the solid cylindrical cork directly extracted from the bark of the cork oak. There are also lower quality corks made of agglomerated granules or of two solid cork disks at the ends of agglomerated granules.

The use of $scCO_2$ in the extraction of TCA was presented by Chouchi et al. in 1997 [10]. At present, there are several industrial processes that use supercritical technology to eliminate TCA and other harmful contaminants from cork granules. These processes are patented in many countries [11–13]. In particular, OENEO has cork treatment plants in Spain and France commissioned by Natex [14,15]. However, the information published on this operation is practically non-existent. In solid cork, an exploratory work was recently presented in a conference [16]. This work analyzes the parameters that mostly affect the TCA removal from cork granules using supercritical CO_2.

2. Materials and methods

Cork of 2–3 mm standard granulometry was used with a moisture in equilibrium with the environment of 6 ± 1% depending on the time of year and density of 55 kg m^{-3}. It contained a TCA load of 8.5 ± 0.5 ng L^{-1} (ppt). The CO_2 (99.99%) was supplied by Carburos Metálicos, Spain.

2.1. Moisturization of cork

To obtain cork with different moistures, the cork was introduced in a thermostatic closed bath at 60 °C, placing it on a perforated tray above the water level. This was maintained until the desired moisture was reached. It was then collected and allowed to cool prior to extraction in an enclosed can to maintain the reached moisture.

2.2. Determination of moisture in the cork

The moisture content of cork before and after the treatment was measured by weight loss. 5 g of cork were placed in a beaker and placed in an oven previously heated to 105 °C, maintaining them until reaching a constant weight. Measurements were performed on a minimum of six samples.

2.3. Cork compaction study

The behavior of the CO_2-cork mixture under supercritical conditions was visualized in a high-pressure cell of variable volume. The cell consisted of a stainless steel cylindrical chamber which contained a movable piston that allowed the internal volume of the cell to be varied. The content of the cell was illuminated and viewed through a sapphire window using a borescope and a digital camera connected to a computer. The cell could be heated to 100 °C with a silicone heating tape. The temperature inside the cell was controlled and measured by a type J thermocouple housed inside. The sample could be compressed (up to 30 MPa) and decompressed by moving the piston using a manual pressure generator that used water as a hydrostatic fluid. The pressure was measured directly on the part of the cell containing the sample by means of a pressure transducer.

9.2510 g of CO_2 were added together with 0.4568 g of cork. Observations of the mixture were carried out at pressures between 14.0 and 20.0 MPa and temperatures between 40 and 60 °C.

On the other hand, to determine the degree of compaction that took place in the bed during the supercritical extractions, different operating and depressurizing conditions were evaluated. The experiments were carried out in the installation described next, with increasing amounts of cork granules, occupying between 70 and 100% of the extractor volume. The supercritical extraction cycle was carried out as explained in the following section; while the depressurization was carried out with different rates of CO_2 output. After the total depressurization, the extractor was opened to check the state of compaction and deformation of the cork granules by visual inspection.

2.4. Supercritical extraction procedure

For the supercritical extraction of TCA in cork granules, a 100-mL stainless steel cylindrical extractor was used, with a length to diameter ratio of 5. The temperature inside was controlled by a heating tape located on the outside of the extractor. The CO_2 flow rate was fixed with a membrane pump (Milroyal D, Dosapro Milton Roy, France), while the pressure was controlled by a back-pressure regulator (BPR, 26-1761-24-161, TESCOM Europe, Germany) valve. The amount of CO_2 passing through the bed was measured by a flow meter (M-10 SLPM-D, Alicat Scientific, USA) at the end of the line, this procedure was described in previous works [17]. The 45.0 MPa assays were developed in the pilot plant of AINIA (Valencia) using a 5 L extractor.

Approximately 4 g of cork granules with an accuracy of ± 0.005 g were introduced into the extractor forming a bed that occupied around 70% of the volume of the extractor. Higher amounts were introduced in assays aimed to evaluate the impact of the extractor filling degree.

The extractor was closed and preheated to the desired temperature. After that, the CO_2 was pumped in, and, once the desired pressure was reached, the BPR was opened to provide a continuous flow of the CO_2 through the cork. The residence time was calculated as the void volume of the extractor divided by the volumetric flow rate of the solvent. At the end of the extraction, the extractor was slowly depressurized and the exhausted cork unloaded for analysis.

2.5. Determination of TCA in cork

The 2,4,6-trichloranisol of the cork was analyzed by a procedure based on the standard UNE 56930: 2005 in the Centro Tecnológico da Cortiça, Portugal. The maceration was carried out by immersing the sample in a 12% hydroalcoholic solution in a 2-l vessel. The liquid was analyzed using the Solid Phase Micro-Extraction (SPME) technique and Gas Chromatography analysis with detection of mass–mass spectrometry (GC–MS/MS) with automatic injection. Because of this measure, the residual TCA concentration in the cork granules is reported in ng L^{-1}. The detection limit was 0.4 ng L^{-1} (ppt). The data presented are the mean of at least 3 trials. The experimental error was deduced from the repetition of certain trials six times. The large deviation of the data is due to the difficulty on measuring such low TCA quantities on quite small cork samples.

2.6. Determination of the mechanical properties of cork

The hardness of the cork after the supercritical extraction was determined with a texturometer as was previously used in other natural polymers and pharmaceutical gels and semisolids [18]. An image of the same is shown in Fig. 1, where the probe used for compression and the arrangement of the cork granule in the cell are visualized. The test

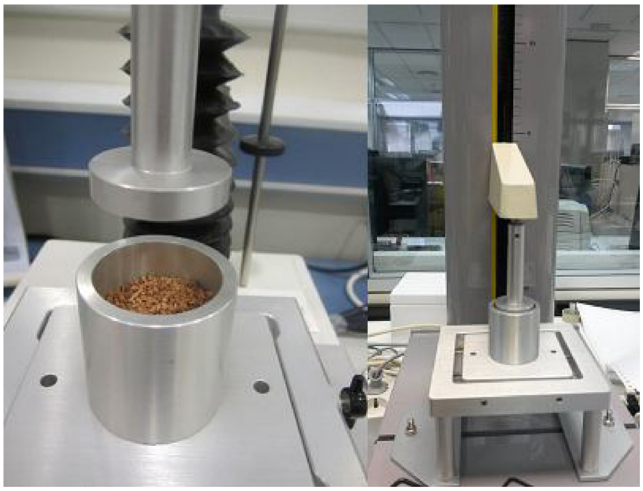

Fig. 1. Image of the texturometer used to perform the mechanical tests on the cork granule.

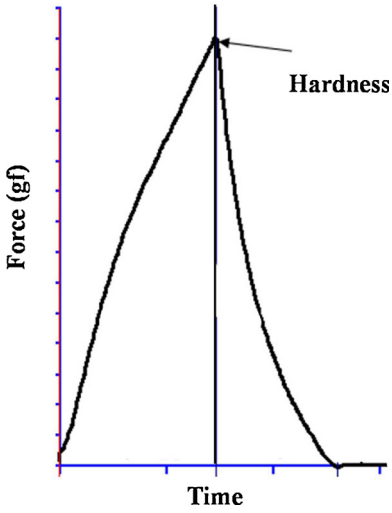

Fig. 2. Example of the evolution of the compression force over time.

consisted of a compression of the cork samples (3.5 g) with a flat section probe (35 mm) at a defined speed (0.5 mm s^{-1}) with a fixed compression distance (20 mm). Once the compression distance was reached, the plunger ascended to the starting position. The equipment recorded the compression force curve. Hardness is related to the force required to achieve a certain deformation, in this case a certain height, so it was measured as the height of the peak in the compression curve as shown in Fig. 2, in units of gram-force (gf). For example, the hardness of the cork granules without any treatment was 19100 gf.

3. Results and discussion

The extraction of the TCA was carried out by keeping the bed of cork granules in contact with a continuous flow of supercritical solvent. During the operation, several transportation mechanisms took place. In the first place, the cork particles absorbed CO_2. Fig. 3 shows two images of the interior of a view cell with the CO_2-cork mixture. Although the piston position in the images is different and therefore the proximity of the cork particles to the observation window varied, the swelling of the cork in the presence of CO_2 was clear. The TCA was then dissolved (as defined by equilibrium). Subsequently, the TCA molecules were transported to the surface of the particles (internal transport) and, finally, they passed from the surface to the bulk of the stream of CO_2 that crossed the bed.

The images of the view cell also showed that the cork did not float on the CO_2 phase although the density of the cork was much smaller than that of the CO_2. This could mean that the CO_2 penetrated the pores of the cork granules soaking them.

Many parameters may be relevant to the operation. First, the condition of the solid in terms of the moisture content of the particles and the bed that formed in the extractor. Then, the process variables, mainly pressure, temperature and flow rate. This section presents and discusses the influence of all these parameters on the TCA elimination from the cork. Finally, the mechanical quality of treated cork was studied.

3.1. The impact of the cork moisture

The starting moisture of the solid matrix significantly affects the internal transfer. The absence of water makes it difficult for the solvent to penetrate due to shrinkage of the structure; thus, reducing the extraction yield [19,20]. However, an excess water could create a barrier to the TCA and the solvent transportation, from and to, the bulk of the supercritical fluid. For these reasons, the water content of the solid needed to be optimized [21].

Table 1 shows the result of the extraction when using corks of different degrees of moisture. Dried cork had an average moisture content of less than 4%; the cork in equilibrium with the environment humidity had a water content of about 6% while the moistened cork had a water content of 12%. With this latter product, it was reproduced the moisture that the cork granules had after a washing by steam entrainment.

Under equal conditions of CO_2 density and residence time, the extraction from wet cork was much more effective than with dried cork ($< 4\%$). In this latter material, it was necessary to operate with high residence times (47 min) to remove the TCA below the detection limit. Contrarily, TCA removal below the detection level was achieved with cork wet (12%) when residence time was 8 min. The phenomenon of improved extraction performance when the cork was wet is probably due to the swelling of the solid matrix by the water which allows a better penetration of CO_2 and a better TCA diffusion outward.

The following tests were carried out on the cork with the moisture (6%) in equilibrium with the environment humidity.

3.2. Compaction tests

One of the first concerns regarding the use of supercritical CO_2 in cork treatment was that the operating pressure could cause compaction of the cork granules. Therefore, trials were conducted to verify this fact and to determine under what conditions it might occur. Thus, two parameters that a priori could be relevant in the occurrence of this phenomenon were investigated: the bed occupancy (estimated as percentage of the volume occupied) and the rate of depressurization. The results are shown in Table 2. When the filling degree of the extractor was higher than 73% and the depressurization was faster than 0.5 MPa min^{-1}, the cork granules were compacted forming a “stopper” difficult to remove from the extractor. The rest of the assays were conducted fixing the extractor occupancy and the depressurization rate to these values.

3.3. Effect of operating conditions

Density directly affects the dissolving capacity of the supercritical solvent and it is strongly influenced by the operating conditions. An increase in pressure increases the density while the opposite effect occurs with a temperature increase.

On the other hand, an increase of temperature favors the vaporization of the solute (as expressed in the Antoine equation). In this sense, temperature has conflicting effects on the solubilization of solutes by supercritical solvents. Consequently, it is necessary to study

Fig. 3. Photographs of the cork inside the view cell at different pressure and temperature conditions. The image on the left corresponds to a CO_2-cork mixture at 40 °C and 14.0 MPa, the image on the right corresponds to a CO_2-cork mixture at 60 °C and 20.0 MPa.

each system to determine which of the effects has the greatest impact. This depends on the operating pressure.

In addition, the modification of these two operating parameters may significantly vary the mass transfer properties of CO_2 and the solute. Therefore, it is difficult to predict the influence of the operating variables in the extraction of a specific solute from a natural matrix.

3.3.1. Density

One of the most significant characteristics of supercritical fluids is the wide range of densities that can be reached by slightly varying pressure and temperature, being one of the keys to the great selectivity of supercritical fluids as extraction medium. Table 3 shows the influence of the solvent density on the TCA removal from cork granules. Temperature of these assays was 40 °C. An increase in the density of the fluid benefited the extraction in a marked way. To achieve the target TCA residual content of less than 0.5 ng L^{-1}, it was necessary to raise the density of the fluid to 580 kg m^{-3}. This was due to the direct improvement in CO_2 dissolving power.

However, the beneficial effect of increasing dissolution capacity upon increasing pressure was not fulfilled throughout the range of pressures explored. As can be seen in Table 3, there was a point from which the use of excessive high pressure worsened the extraction efficiency. This may be due to the noticeable increase in the viscosity of the CO_2 (shown in Table 3) hampering the access and penetration into the tortuous pores of the cork granules. Similarly, the TCA transportation from the granules to the bulk fluid would be retarded at very high pressures. Besides at 45 MPa, it was observed that the cork got crushed as described in section 3.6. This probably worsened the transportation within the granules.

3.3.2. Temperature

The residual concentration of TCA in the cork granules after extraction at 12.0 MPa and different temperatures is shown in Fig. 4. The CO_2 density is shown on top of the symbols. An increase in the temperature of the fluid impaired the extraction of the solute because of the decrease in the density of the CO_2. Extraction was performed in the temperature range where the impact of the decrease in density was more intense than that of increasing TCA volatility. The vapor pressure of the TCA is 3.04 Pa at room temperature; while its boiling temperature is 241 °C at atmospheric pressure, which means that the TCA is a low volatile compound.

Table 4 shows the solubility of TCA in supercritical CO_2 obtained by Maricato et al. [21] in which isothermal (40 °C) and isobaric (14.0 MPa)

Table 2
Degree of compaction of the cork granules in the extractor depending on the extractor occupancy and the depressurization speed. Operating conditions: 15.0 MPa, 60 °C; bulk density of the cork in the bed: 55 kg m^{-3}; estimated bed porosity: 0.50.

Filling degree of the extractor (%)	Depressurization velocity (MPa min^{-1})	Observed compaction
100	1.5	Yes
100	1.0	Yes
84	0.5	Some
73	0.5	No
52	0.5	No
48	0.5	No

Table 3
The impact of operating pressure on the properties of the supercritical solvent on the removal efficiency of the TCA. Temperature was 40 °C. CO_2 flow rate, 4 g min^{-1}; extraction time, 60 min.

Density (kg m^{-3})	Presure (MPa)	Viscosity (Pa s 10^{-5})	Residual TCA (ng L^{-1})
37	2	2	5
580	9.5	4	< 0.4
736	14	7	< 0.4
975	45	11	1

Table 1
Effect of cork moisture and residence time in the extraction of TCA from cork. CO_2 density = 326 kg m^{-3}.

	CO_2 flow rate (g min^{-1})	Solvent ratio (kg CO_2 h^{-1} kg $cork^{-1}$)	Residence time (min)	Operation time (min)	Residual TCA (ng L^{-1})
Dried cork (< 4%)	8	120	4	30	3
	4	60	8	60	2
	1.5	23	22	160	1
	0.7	23	47	340	< 0.4
Cork in equilibrium with the environment humidity (6%)	8	120	4	30	2
	4	60	8	60	1
	3	42	12	80	< 0.4
Wet cork (12%)	8	120	4	30	1
	4	60	8	60	< 0.4

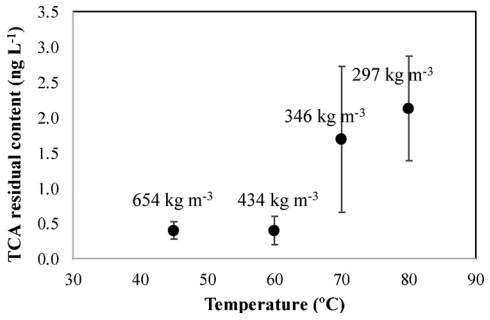

Fig. 4. Influence of temperature on the residual concentration of TCA in cork after carrying out extractions at 12.0 MPa. CO_2 flow rate, 4 g min^{-1}; extraction time, 60 min.

Table 4
Solubility of TCA in CO_2 at different conditions [20].

P (MPa)	T (°C)	TCA solubility (kg TCA kg^{-1} CO_2)
10.0	40	$1.5{\cdot}10^{-5}$
12.0	40	$1.6{\cdot}10^{-5}$
14.0	40	$2.2{\cdot}10^{-5}$
16.0	40	$4.4{\cdot}10^{-5}$
14.0	40	$2.2{\cdot}10^{-5}$
14.0	50	$1.5{\cdot}10^{-5}$
14.0	60	$0.4{\cdot}10^{-5}$

conditions were explored. The solubility increased directly as the pressure increased. In the opposite sense, the increase of temperature decreased the solubility of the TCA in CO_2. These bibliographical results are consistent with our observations and advise to work at low temperatures to remove the TCA where the density of the CO_2 is highest.

3.4. The influence of CO_2 flow rate

An increase in the CO_2 flow rate enhances linear velocities, Re numbers and so external mass transfer coefficients. Moreover, when the solvent flow rate is incremented, the global driving force is increased, so a positive effect on extraction rate is achieved, thereby, reducing the necessary extraction time. However, operating at high flow rates reduces the residence time in the extractor and increases pumping and capital costs. Perrut demonstrated that the price of a supercritical installation delivered on a turnkey basis varies near to a straight line with a slope of 0.24 versus the log of the design flow rate [22]. Therefore, this parameter has to be optimized.

In operation with continuous passage of the CO_2 over the bed of the cork granules with no solvent recirculation, the residence time of the CO_2 in the extractor was the time available to remove the TCA. Fig. 5 shows the influence of the augmentation of residence time at the expenses of reducing the solvent flow rate on the TCA removal efficiency, at two dissimilar densities. At high density, the target residual TCA content was achieved in 8 min residence time. On the contrary, at low CO_2 density of 326 kg m^{-3}, to achieve a satisfactory extraction efficiency, 22 min residence time was required. This involved relatively low solvent ratios (23 kg CO_2 h^{-1} kg^{-1} cork).

3.5. Effect of the solvent mass ratio (CO_2 consumption)

The ratio between the amount of CO_2 used in the extraction, and the amount of raw material, is a fundamental parameter on an industrial scale because it determines the economic viability of the process in terms of raw materials consumption and compression costs.

Fig. 6 shows the effect of the mass ratio on the extraction of TCA from the cork granules with CO_2 at two different densities (326 kg m^{-3} and 585 kg m^{-3}). At high density, the total elimination of TCA was

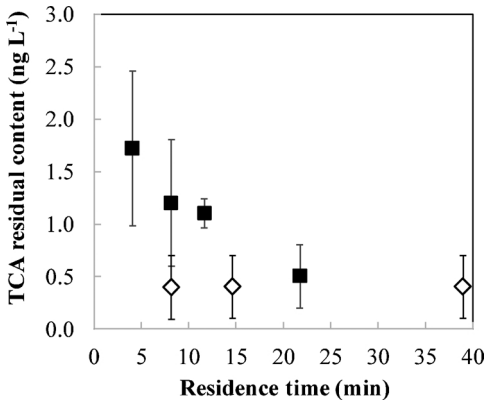

Fig. 5. Residual concentration of TCA in the cork granules after carrying out extractions at different residence times, ■ ρ = 326 kg m^{-3} (70 °C, 11.5 MPa), →ρ = 585 kg m^{-3} (50 °C, 12 MPa). CO_2 flow rate was 1.5, 3, 4 and 8 g min^{-1}. The CO_2-cork mass ratio was 60.

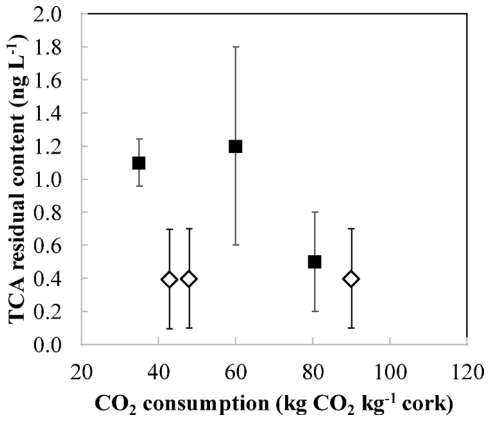

Fig. 6. Effect of CO_2-cork mass ratio on the residual content of TCA in the cork granules at different densities: ■ ρ = 326 kg m^{-3} (70 °C, 11.5 MPa), → ρ = 585 kg m^{-3} (50 °C, 12 MPa). CO_2 flow rate was 4 g min^{-1}. Extraction time was increased from 35 to 90 min.

achieved at low solvent mass ratios, 43 kg CO_2 per kg of cork; on the contrary, at low density (326 kg m^{-3}) a high CO_2 consumption, > 80 kg CO_2 kg^{-1} cork, was required to reduce the TCA below the detection limit.

From the solubility data of TCA in supercritical CO_2 it is possible to know how much solvent would be required at minimum to extract all the TCA that was retained in the particles of the cork. At 12.0 MPa and 60 °C, solubility was 1.5 10^{-4} kg TCA kg^{-1} CO_2 [20]. If there was an initial concentration of 8.5 ng TCA g^{-1} cork and that 4 g of cork were placed into the extractor, $6{\cdot}10^{-6}$ kg CO_2 kg^{-1} cork would be necessary. This value was enormously lower than the actual amount of CO_2 that was required to remove the TCA even at the best conditions (Fig. 6). The use of much more CO_2 was due to the slow diffusion inside the cork.

3.6. Study of the mechanical properties of cork

Finally, the impact of supercritical extraction on the mechanical properties of cork was studied. Fig. 7 shows the hardness of the cork after being subjected to a treatment of supercritical CO_2 extraction at different pressures at 40 °C. The cork granules did not suffer any significant reduction of hardness in the medium-low pressure range. But they lost 20% of their hardness operating at high pressures of 45.0 MPa being the deformation permanent. Lagorce-Tachon et al. [2] demonstrated that the stress–strain curves for cork are characterized by three steps: an elastic region up to a strain around 5% followed by a large

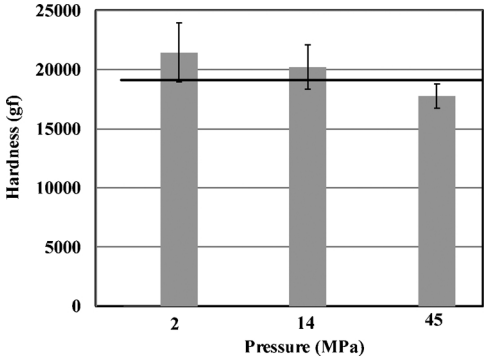

Fig. 7. Hardness of cork after supercritical extraction at increasing pressures. Temperature was 40 °C. The solid horizontal line shows the hardness of the raw material.

plateau between 5% and 60% which corresponds to the progressive buckling of cell walls, and finally above 70% a sharp increase in stress corresponding to the densification of the material. The hardness reduction of the cork granules at the highest pressure may be justified by the fact that the elastic region of the material was exceeded causing densification of the material.

4. Conclusions

Internal mass transport played a significant role in the global rate by which TCA was extracted from cork granules with supercritical CO_2. Thus, a minimum contact time between the CO_2 and the cork was necessary that should be provided by relatively low CO_2 flow rates. TCA extraction from the cork was improved by increasing density because it directly affected solvent capacity, but there was a limit in pressure due to the worsening of the mass transport properties and of the cork hardness; thus, pressure had to be maintained around 12.0–14.0 MPa. Temperature negatively affected extraction above 60 °C. To preserve the mechanical properties of cork during the treatment it was necessary to keep a filling degree of the extractor to about 70% and control the depressurization rate to not more than 0.5 MPa min^{-1}.

References

[1] H. Pereira, Chemical composition and variability of cork from *Quercus suber*, Wood Sci. Technol. 22 (1988) 211–218.
[2] A. Lagorce-Tachon, T. Karbowiak, D. Champion, R.D. Gougeon, J.P. Bellat, Mechanical properties of cork: effect of hydration, Mater. Des. 82 (2015) 148–154, http://dx.doi.org/10.1016/j.matdes.2015.05.034.
[3] A. Sen, M. De Melo, A.J.D. Silvestre, H. Pereira, C.M. Silva, Prospective pathway for a green and enhanced friedelin production through supercritical fluid extraction of *Quercus cerris* cork, J. Supercrit. Fluids 97 (2015) 247–255, http://dx.doi.org/10.1016/j.supflu.2014.12.008.
[4] V. Castola, B. Marongiu, A. Bighelli, C. Floris, A. Laï, J. Casanova, Extractives of cork (Quercus suber L.): chemical composition of dichloromethane and supercritical CO_2 extracts, Ind. Crops Prod. 21 (2005) 65–69, http://dx.doi.org/10.1016/j.indcrop.2003.12.007.
[5] Associação Portuguesa da Cortiça, (2017) https://www.apcor.pt/en/products/cork-stoppers/.
[6] P. Fuller, Cork taint: closing in on an industry problem, Wine Ind. J. 10 (1995) 58–60.
[7] G.J. Soleas, J. Yan, T. Seaver, D.M. Goldberg, Method for the gas chromatographic assay with mass selective detection of trichloro compounds in corks and wines applied to elucidate the potential cause of cork taint, J. Agric. Food Chem. 50 (2002) 1032–1039, http://dx.doi.org/10.1021/jf011149c.
[8] T.H. Lee, R.F. Simpson, Microbiology and chemistry of cork taints in wine, in: G.H. Fleet (Ed.), Wine Microbiology and Bio/Technology, G. Harwood Academic Publishers, Chur, Switzerland, 1993, pp. 353–372.
[9] A.M. Peres, P. Freitas, L.G. Dias, M.E.B.C. Sousa, L.M. Castro, A.C.A. Veloso, Cyclic voltammetry: a tool to quantify 2,4,6-trichloroanisole in aqueous samples from cork planks boiling industrial process, Talanta 117 (2013) 438–444, http://dx.doi.org/10.1016/j.talanta.2013.09.039.
[10] M. Chouchi, D. Maricato, L. Nunes da Ponte, SFE of trichloroanisole from cork, The 4th International Symposium on Supercritical Fluids, Senday, Japan, 1997.
[11] COMMISSARIAT ENERGIE ATOMIQUE, Method for Treating Cork and Extracting Organic Compounds from Cork, with a Dense Fluid Under Pressure, FR2798879, (1999).
[12] AINIA, Procedimiento para extraer del corcho compuestos indeseados diversos, ES2416554 A1, 2011.
[13] G. Sanjuán, Method for Extraction Organic Compounds from Granulated Cork, EP2404647, (2012).
[14] H. Lack, E. Seidlitz, Industrial cleaning of cork with supercritical CO_2, 3rd Int. Meet. High Press. Chem. Eng. Erlangen, Germany, 2006.
[15] Natex, Rice Treatment, New Application for Supercritical Extraction, (2017) https://www.natex.at/fileadmin/content/PDFs/rice_treatment.pdf . (Accessed 1 January 2017).
[16] A.C. Lopes Cardoso, A. Paiva, I.M. Allegro, R.P. Moreira da Silva, J.A.S. Lopes, M. Manic, V. Najdanovic-Visak, M. Nunes da Ponte, Cleaning of wine bottle cork stoppers with high pressure carbon dioxide, 16th European Meeting on Supercritical Fluids, Lisbon, Portugal, 2017.
[17] M. Viguera, J.M. Gómez-Salazar, M.I. Barrena, L. Calvo, The removal of lubricating oils from metallic contacts with supercritical CO_2, J. Supercrit. Fluids 73 (2013) 51–56, http://dx.doi.org/10.1016/j.supflu.2012.09.015.
[18] D.S. Jones, A.D. Woolfson, A.F. Brown, Textural, viscoelastic and mucoadhesive properties of pharmaceutical gels composed of cellulose polymers, Int. J. Pharm. 151 (1997) 223–233, http://dx.doi.org/10.1016/S0378-5173(97)04904-1.
[19] G. Brunner, Gas Extraction, Springer, New York, 1994.
[20] R. Lack, E. Gamse, T. Marr, Extraction from solids, in: G. Bertucco, A. Vetter (Eds.), High Press. Process Technol. Fundam. Appl. Elsevier, Amsterdam, 2001.
[21] L. Maricato, Étude de l'extraction du trichloroanisole par CO_2 supercritique, Universidade Nova de Lisboa, 1996 (Master Thesis).
[22] M. Perrut, Supercritical fluid applications: industrial developments and economic issues, Ind. Eng. Chem. 39 (2000) 4531–4535.