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(54) **METHOD FOR DIRECT TREATMENT OF CORK STOPPERS, USING SUPERCRITICAL FLUIDS**

VERFAHREN ZUR DIREKTBEHANDLUNG VON KORKSTOPFEN MIT ÜBERKRITISCHEN FLÜSSIGKEITEN

PROCÉDÉ POUR LE TRAITEMENT DIRECT DE BOUCHONS DE LIÈGE AU MOYEN DE FLUIDES SUPERCRITIQUES

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Description

FIELD OF THE INVENTION

[0001] The present invention refers to a method which permits implementation of supercritical fluids treatment directly to natural cork stoppers without losing their shape and maintaining their sealing properties, using a separating device. This method eliminates or reduces a quantity of cork contaminants, namely 2,4,6-trichloroanisole which is the main compound responsible for off - aromas occurring in wine.

BACKGROUND OF THE INVENTION

[0002] Traditionally, cork has been used as stoppers for wine bottle sealing. The most important application of cork is as stoppers in the preservation of wines. The natural cork stopper has unique physical properties such as elasticity, hydrophobicity and impermeability to gases and liquids. To date, there are no other natural or artificial products that possess such desirable characteristics. Besides an efficient sealing, these properties ensure adequate wine maturation or aging., and therefore natural cork stoppers are frequently used for storage of wines for long periods of time (Fischer, 1997; Insa, 2006). However, this application is being challenged due to the so-called "mouldy taint" problem, which leads to the rejection of the product by consumers, thus provoking considerable losses in the wine industry. Soleas et al. (2002) showed that about 6.1% of wine bottles were affected by the "mouldy taint" problem. Another study (Quercus (1996)) revealed that between 0.1 and 10% of European wine bottles are contaminated.

[0003] The problem of sensory deviations caused by cork stoppers, which frequently occurs in wines, has been related with the presence of chloroanisoles, especially 2,4,6-tricloroailisole (TCA), but also with 2,3,4,6-tetracloroanisole (TeCA) and pentachloroanisole (PCA) (Insa, 2006). TeCA and PCA are more related with contaminants from the cellar environment. For the first time in 1982 Tanner et al. identified TCA as the main compound responsible for the "mouldy taint" problem.

[0004] Even though other aromatic compounds have been related to the same problem (Simpson, 2004; Pena-Neira 2000; Chatonnet, 2004), TCA is generally considered the main indicator (Hervé, 2000). According to the European project "Quercus", the presence of TCA was detected in at least 80% of wine with undesirable sensory deviation. Additionally, TCA is a compound with a sensory detection limit at very small concentrations, in the order of a few nanograms per litre of wine (Amon, 1989; Tanner, 1982).

[0005] The presence of TCA in wines is associated with cork stoppers and its appearance in stoppers has been the subject of numerous studies (Silva Pereira, 2000). Direct precursors of chloroanisoles are chlorophenols, which are converted into chloroanisoles via a methylation reaction provoked by microorganisms, especially fungus at certain conditions of temperature and pressure (Insa, 2006). In this way, chlorophenols constitute a potential source of TCA and their appearance in the cork oak can occur through the use of certain insecticides and fungicidal products, as well as from certain materials used in storage, transport and packing (Czaplicka, 2004, Alvarez-Rodríguez, 2002). Although the cork industry has developed preventive procedures in order to avoid the presence of these compounds, residual chloroanisoles continue to be detected in cork stoppers.

[0006] TCA removal is a difficult process due to a combination of various factors such as:

1. impermeable characteristics of cork;
2. need to reach values of concentration in the order of ppt, an extraordinarily low value, due to the low concentration threshold of perception;
3. great chemical stability of the compound.

[0007] Since the identification of TCA as the main compound responsible for undesirable taste of wine, processes of treatment and minimization have been developed (Gil, 2006).

[0008] Industrially, cork stoppers are cleansed using hydrogen peroxide or peracetic acid. The aim of this process is to wash and disinfect the stoppers. There are also other methods such as implementation of microwaves (Jager, 1999). Washing/disinfection is followed by stabilization of the humidity level, optimizing the performance of the cork as a sealant and simultaneously reducing microbiological contamination. However, these methods are not sufficient for volatile compounds (Gil, 2006).

[0009] Other processes for removal of cork stopper contaminates have been proposed. The most prominent are sterilization of cork using gamma-radiation (PT103006), ozone treatment (Vlachos, 2007), an ultra-sound method (Penn, C, 2004), steam extraction (WO03041927), photodegradation (Vlachos, 2008) and extraction with supercritical CO2 (FR19990012003, published as US2007/0017550 and WO 01/23155).

[0010] Supercritical CO2 is recognized as a very efficient solvent for extraction of cork contaminates, namely TCA. This fact was reported originally in 1997 by Chouchi et al. The authors reported that "supercritical extraction of cork

contaminants which provoke undesirable wine taste is efficient and much faster than conventional method".

[0011] In 2000 Taylor et al. confirmed that yields of supercritical extraction of TCA have similar values compared to Soxhlet extraction, being however much more efficient in terms of time.

[0012] The patent FR19990012003 illustrates a process for extraction of cork contaminants using supercritical fluids, namely supercritical CO2. In the examples presented in the description of the invention, it is clear that the cork treated by supercritical extraction is always in granulated form or as planks and not in the form of cork stoppers. As a matter of fact, there is no known application directly to the natural cork stoppers.

[0013] The publication of Eduard Lack in 2006 at the 3rd Chemical Engineering and High Pressure International Meeting is especially relevant. The author, representing NATEX, the Austrian company responsible for the design and construction of the industrial facilities for the patented process of supercritical extraction, claims that cork stoppers do not return to their original form during the depressurization step. Therefore, the author has concluded that it is impossible to implement supercritical extraction to natural cork stoppers. The author also states that treatment with supercritical fluids should be applied directly to granulated cork and stoppers should be produced afterwards.

SHORT DESCRIPTION OF THE DRAWINGS

[0014] This invention can be illustrated using the attached drawings. These drawings show the devices and processes used to accomplish this invention:

Figure 1: It shows a model of a separating device with attached shelves. Figure 1A is a front view of the said separating device, which is composed of one central rod (1) and three side rods (2) with a base composed of hole-bored metallic sheet, to which the shelves that support the cork stoppers to be treated are attached. The shelves are organized one above the other and attached to the above-mentioned rods up to a number limited by the height of the rods. Figure 1B is a plan view of the separating device, having a cover lid with a hook to allow pulling up the whole structure.

Figure 2: A model of shelf used in the separating device is shown. Figure 2A is a perspective view of the said shelf, composed of a perforated plate (5), having attacking holes (4), a side ring in a flat plate (6) with a rod attached on the top (7). Figure 2B represents a plan view of the said shelf.

Figure 3: It shows a scheme of the process in which the solvent stored in a cylinder is compressed by a liquid pump (8) and introduced into the high-pressure pressurized vessel (9) containing the cork stoppers to be treated according to this invention. During the process, the solvent is recycled after decompression, TCA separation (10) and passing through an adsorption filter (11). At the end of the process, the solvent is substituted with nitrogen stored in a cylinder.

SUMMARY OF THE INVENTION

[0015] To date, although the known supercritical extraction process is very efficient for cork contamination removal, it has only been possible to apply it to granulated cork. It is not possible to directly treat cork stoppers using this extraction technology. The present invention permits the application of supercritical extraction in the treatment of cork stoppers.

[0016] The present invention refers to a new method, which employs a separating device, permitting direct supercritical fluid extraction from natural cork stoppers without damaging their shape and maintaining their sealing properties.

[0017] Taking into consideration all the known facts and publications to date, the success obtained by the process using the separating device is totally unexpected. This process will solve a technical problem that until now is not resolved.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The novelty of the present invention consists of using a separating device which permits direct treatment of natural cork stoppers without damaging their form and maintaining their sealing properties using supercritical fluids.

[0019] The present invention is a supercritical extraction method applied directly to natural cork stoppers with the objective of eliminating/reducing contaminant compounds, namely 2,4,6-trichloroanisole (TCA), using supercritical fluids in a high-pressure vessel comprising a separating device. It allows shrinking and expanding of the cork stoppers with minimal contact between them, avoiding significant distortion of their original shape and maintaining their sealing properties.

[0020] Preferentially, in the high-pressure vessel (9) the supercritical fluid or mixture of supercritical fluids, with or without addition of co-solvent, is directly contacted with natural cork stoppers.

[0021] In one embodiment according to Figure 3, the method can be carried out through the following steps:

a) Introduction of a compressed fluid or mixture of compressed fluids through a compressor or liquid pump (8) into a sealed high-pressure vessel (9) immersed in a temperature-controlled bath, containing cork stoppers distributed within the shelves of the separating device. The method can optionally use an inert and non-toxic co-solvent which can be introduced by a compressor/liquid pump (8) or placed in the high-pressure vessel (9) prior to extraction;

b) Circulation of the compressed fluid, mixture of compressed fluids or mixture of compressed fluids and co-solvent through the high-pressure vessel (9) under predetermined conditions of pressure, temperature and time, with predetermined velocity - preferentially low;

c) Removal of compressed fluid, mixture of compressed fluids, or mixture of compressed fluids and co-solvent, by decompression and, optionally, by substitution with a permanent gas, like nitrogen.

[0022] Preferentially, the supercritical extraction step is carried out in a temperature range from 30°C to 120°C and at pressures between 6 MPa and 40 MPa. This step can take 1 to 24 hours, preferentially between 4 to 24 hours.

[0023] Any fluid or mixture of fluids in the supercritical state or in the sub-critical liquid state can be used to carry out this invention. Preferentially, the compressed fluid or mixture of these fluids should be very volatile or be in gas state at atmospheric conditions, in order to facilitate its removal by expansion and/or evaporation after treatment. For safety reasons, the compressed fluid, or a mixture of these fluids, should be non-toxic and not flammable, as well as recyclable. Preferentially, the fluid used is carbon dioxide.

[0024] Co-solvents can be added, preferentially inert and non-toxic compounds, in order to increase solubility of cork stopper contaminants in compressed fluids.

[0025] According to Figures 1 and 2, in one specific embodiment, the separating device for carrying out the invention consists of:

- A metallic structure comprising four rods, a central one (1) and three side ones (2) with a base made of perforated metallic sheet, where the shelves (3) that support the cork stoppers to be treated are attached;
- Shelves (3) made of perforated sheets (5), with four attaching holes (4) where the above-mentioned rods are secured, a side lid made of metallic sheet (6) with a rod soldered at the top (7); the shelves are attached to each other up to a maximum number limited by the height of the rods;
- A cover lid made of metallic sheet, where a hook is attached to allow pulling up the whole structure.

[0026] Preferably, the metallic structure is made of stainless steel.

[0027] In an even more specific embodiment, the four said rods are metallic and 12 mm thick. The shelves have 3 cm of useful height while the perforated metallic sheet is 2 mm thick. The holes have a diameter of 2 mm and the distance between them is 5 mm.

[0028] The second aim of the method of the present invention is maintaining the original form and sealing properties of the cork stoppers after treatment.

EXPERIMENTAL PART

[0029] One of the ways to carry out the invention is given in Figure 3. The solvent is stored in a cylinder and introduced into a high-pressure vessel (9) up to the desired pressure through a compressor (8). The vessel contains the cork stoppers to be treated using the separating device according to the method of the present invention. In the first phase, the fluid in the high-pressure vessel is retained at desired operational conditions of temperature ranging from 30°C to 120°C and pressure ranging from 6 MPa to 40 MPa during a predefined time period ranging from 1 to 24 hours, typically between 4 and 8 hours. Next, the fluid circulates at predetermined velocity, preferentially low. The TCA is collected in the separator (10) while CO_2 is decompressed and filtered (11), being reused after new compression. Finally, a substitution of the solvent with nitrogen stored in a cylinder is carried out, in order to avoid temperature decrease.

[0030] The invention is additionally illustrated by the following non-restrictive examples.

Examples

Example 1: Example of treatment efficiency using supercritical CO_2 applied directly to natural cork stoppers containing different initial concentration of TCA.

[0031] A high-pressure vessel with a capacity of 170 cm^3 and a manual liquid pump were used. One cork stopper and

10% mass of distilled water were placed in the vessel. The system was heated up to 40°C and pressurized with CO_2 up to 100 bar. The cork stopper was left in contact with CO_2 during two periods of time, of two and three hours respectively. The extraction cycle was carried out in the following way:

- Phase 1 - Pressurisation up to 100 bar and retention of CO_2 in the vessel for 2 hours;
- Phase 2 - Slow circulation of CO_2 through the vessel with flow of approximately 0.8 g/min;
- Phase 3 - New retention of supercritical fluid in the vessel for 3 hours :
- Phase 4 - New slow circulation of CO_2 through the vessel with flow of approximately 0.8 g/min;
- Phase 5 - Slow depressurization of the system.

[0032] The total used mass of CO_2 was 100 g/g of cork. The quantity of TCA in the natural cork stoppers was measured before and after the treatment with supercritical CO_2 and the results are shown in Table 1.

Table 1

Sample	$[TCA]_{initial}$ (ng/l)	[TCA] final (ng/l)	% of Extraction
S45	5.2	<1.0	>90
S59	17	1.4	92
S55	215	5.4	98

Example 2: Experiments leading to the unexpected discovery that the use of a separating device in the supercritical treatment of natural cork stoppers allows conserving their shape and mechanical properties.

[0033] Experiments were carried out with the immersion of cork stoppers in CO_2 inside a high-pressure extractor. CO_2 was fed to the extractor up to the desired working pressure, while temperature was kept constant by a thermostat.
[0034] The experiments were carried out in the following conditions:

- temperature: 40°C
- pressure: 100 bar
- time of immersion: 1 hour
- decompression time: 15 minutes
- cork stoppers placed at random inside the extractor.

[0035] After decompression, the cork stoppers were found to have collapsed to the bottom of the extractor, where they accumulated in highly contorted shapes. As a result, the cork stoppers showed highly irreversible deformations.
[0036] The same experiment was repeated, in the same working conditions of pressure and temperature and immersion/decompression. However, the cork stoppers were separated by a metallic grid with holes (to allow homogeneous flow of CO_2 along the extractor).
[0037] Very small deformation of the cork stoppers was observed, with small increases of about 2 mm in height and 1 mm in diameter. Only cork stoppers in the base of the extractor showed slightly greater deformation, but much less than in the initial experiments.
[0038] These deformations in the base of the extractor are caused by compression due to the weight of the stoppers above arid by the joint forces due to the volume expansion of the stoppers upon carbon dioxide decompression.

Example 3: Experiments leaving to confirmation of the unexpected discovery that the use of a separating device in the supercritical treatment of natural cork stoppers allows conserving their shape and mechanical properties.

[0039] Experiments were also carried out where the cork stoppers were placed above the grids, but with freedom to expand in height (but not sideways). The useable volume inside the extractor is therefore decreased.
[0040] The increases in height were now slightly smaller (maximum of 1.5 mm) than in the previous examples. The increases in diameter were slightly higher, due to a smaller free space between stoppers in the packing in comparison with the situation where the cork stoppers are simply piled upon the grids.
[0041] There was no indication of shape effects resulting directly from decompression. It was therefore confirmed that the slight increase of dimensions of the cork stoppers upon decompression only leads to problems of irreversible deformation if they are freely and randomly placed inside the extracting vessel. These problems are soluble in an extractor where each cork stopper is given the freedom to expand upon decompression without interference from other stoppers.

Example 4: Natural cork stoppers and cylinders were subjected to compression/decompression cycles in supercritical CO_2 and they were evaluated in relation to their mechanical properties.

[0042] The compression/decompression cycles consisted of:

- pressurization of the extractor up to 100 bar
- allowing CO_2 to diffuse into the cork for 3 hours
- slow depressurization after 3 hours - depressurization time of 1 hour
- cork stoppers separated by grids in order to be allowed freedom of expansion.

[0043] Evaluation of the compression/relaxation behaviour was carried out following the Portuguese Standard NP 2803 and the dimensional recovery of the diameter 15 minutes after compression (Table 2).

Table 2

Cylinders	Samples	Compression (10 mn) (daN)	Relaxation (12 mm) after 1 min (daN)	Recovery (%)
Natural cork cylinders 45×15 mm	Control	63.7	9.8	93.2
	After SCF*	55.5	9.7	92.5
Cork stoppers	Samples	Compression (16 mm) (daN)	Relaxation (19 mm) after 1 min (daN)	Recovery (%)
Natural cork stoppers of 45×24 mm calibre	Maximum Acceptable Value	80		
	Minimum Acceptable value	60	10	95
	After SCF	65.2	11.8	92.9
* SCF = supercritical fluid extraction cycle				

[0044] An adequate behaviour of the cork stoppers subjected to supercritical extraction is therefore verified, as much in relative terms - by comparison with non-processed samples in the case of cylinders with diameters smaller than 24 mm - as in absolute terms - by comparison with reference values for cork stoppers.

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Claims

1. A method for the treatment of natural cork stoppers, with the objective of eliminating/reducing cork contaminating compounds, namely 2,4,6-trichloroanisole (TCA), **characterized by** the use of supercritical fluids in a high-pressure vessel comprising a separating device that allows, during compression/decompression cycles, contraction and expansion of the cork stoppers with minimal contact between them, without significant distortion of their original shape and keeping their sealing properties intact.

2. A method, according to claim 1, wherein, in the high-pressure vessel (9), the supercritical fluid or mixture of supercritical fluids, with or without co-solvent, is contacted directly with natural cork stoppers.

3. A method, according to claims 1 or 2, which is carried out according to the following steps:

   a) Feeding a compressed fluid, or a mixture of compressed fluids, through a compressor/liquid pump (8), into a sealed high-pressure vessel (9), placed in a temperature-controlled bath or oven, containing the cork stoppers placed in the above-mentioned separating device, optionally using an inert co-solvent, preferably non-toxic, which can be added through a compressor/ liquid pump (8) or previously introduced into the high-pressure vessel (9) ;
   b) Circulating the compressed fluid, the mixture of compressed fluids or the mixture of compressed fluids and co-solvent, through the high-pressure vessel;
   c) Removing the compressed fluid, the mixture of compressed fluids or the mixture of compressed fluids and

co-solvent, by decompression and, optionally, by substitution with a permanent gas, like nitrogen.

4. A method, according to claim 3, wherein the step of supercritical extraction is carried out in the 30°C to 120°C temperature range.

5. A method, according to claims 3 or 4, wherein the step of supercritical extraction is carried out in the 6 MPa to 40 MPa pressure range.

6. A method, according to any of the claims 3 to 5, wherein the step of supercritical extraction is carried out in the time interval of 1 to 24 hours.

7. A method, according to claim 6, wherein the step of supercritical extraction is carried out in the time interval of 4 to 8 hours.

8. A method, according to any of the claims 1 to 7, wherein the fluid used is carbon dioxide.

9. A method, according to any of the claims 3 to 5, wherein the separating device consists of:

- A metallic structure, comprising four rods, a central one (1) and three side ones (2), with a base made of perforated metallic sheet, where the shelves (3) that support the cork stoppers to be treated are attached;
- Shelves (3) made of perforated sheets (5), with four attaching holes (4) where the above-mentioned rods are secured, a side lid made of metallic sheet (6) with a rod soldered at the top (7); these shelves are attached to each other up to a maximum number limited by the height of the rods;
- A cover lid made of metallic sheet where a hook is attached to allow pulling up the whole structure.

10. A method, according to claim 9, wherein the metallic structure is made of stainless steel.

Patentansprüche

1. Ein Verfahren für die Behandlung von natürlichen Korkstopfen, mit dem Ziel verunreinigenden Verbindungen, nämlich 2,4,6-trichloranisol (TCA), zu entfernen/vermindern, **gekennzeichnet durch** die Benutzung von superkritischen Flüssigkeiten in einem Hochdruckbehälter, der eine Trennvorrichtung umfaßt, die es erlaubt während der Verdichtung/Dekompressionzyklen das Schrumpfen und Ausdehnung der Korkstopfen mit minimalem Kontakt zwischen denen, ohne signifikanter Verzerrung der ursprünglichen Form und Bewahrung der ursprünglichen Abdichtungeigenschften.

2. Ein Verfahren gemäß Patentanspruch 1, wobei in dem Hochdruckbehälter (9), die überkritische Flüssigkeit oder Mischung von überkritischen Flüssigkeiten, mit oder ohne Lösungsmittel, in direktem Kontakt mit den natürlichen Korkstopfen kommen.

3. Ein Verfahren gemäß einem der Patenansprüche 1 oder 2, das nach den folgenden Schritten durchgeführt wird:

a) Zuführung von einer komprimierten Flüssigkeit, oder einer Mischung von komprimierten Flüssigkeiten durch eine Kompressor-/Flüssigkeitspumpe (8) in einem hermetischen Hochdruckbehälter (9), eingelegt in einem Bad oder Ofen mit kontrollierter Temperatur, und wo die Korkstopfen in der zuvor gennanten Trennvorrichtung aufgelegt werden, fakultativ mit einem inerten Lösungsmittel, bevorzugt ungiftig, das durch die Kompressor-/Flüssigkeitspumpe (8) beigefügt oder zuvor in dem Hochdruckbehälter (9) zugeführt werden kann.
b) Zirkulierung der komprimierten Flüssigkeit, der Mischung von komprimierten Flüssigkeiten oder der Mischung von komprimierten Flüssigkeiten und Lösungsmittel durch den Hochdruckbehälter,
c) Entfernung der komprimierten Flüssigkeit, der Mischung von komprimierten Flüssigkeiten oder der Mischung von komprimierten Flüssigkeiten und Lösungsmittel durch Dekompression und fakultativ durch Ersetzung mit einem Permanentgas, wie Stickstoff.

4. Ein Verfahren, gemäß Patentanspruch 3, wobei der Schritt der überkritischen Entnahme in einem Temperaturbereich von 30°C bis 120°C durchgeführt wird.

5. Ein Verfahren, gemäß einem der Patentansprüche 3 oder 4, wobei der Schritt der überkritischen Entnahme in einem

Druckbereich von 6 MPa bis 40 MPa durchgeführt wird.

6. Ein Verfahren, gemäß einem der Patentansprüche 3 bis 5, wobei der Schritt der überkritischen Entnahme in einem Zeitraum von 1 bis 24 Stunden durchgeführt wird.

7. Ein Verfahren, gemäß Patentanspruch 6, wobei der Schritt der überkritischen Entnahme in einem Zeitraum von 4 bis 8 Stunden durchgeführt wird.

8. Ein Verfahren, gemäß einem der Patentansprüche 1 bis 7, wobei die Flüßigkeit Kohlendioxid ist.

9. Ein Verfahren, gemäß einem der Patentansprüche 3 bis 5, wobei die Trennvorrichtung besteht aus:

- eine metalische Struktur, die vier Stangen umfaßt, eine zentrale (1) und drei seitliche (2), mit einer Grundlage aus einem perforiertem metallischem Blech, wo die Borde (3), die die zu behandelnden Korkstopfen unterstützen, befestigt sind;
- Borde (3) aus perforieten Blechen (5), mit vier anschliessende Löcher (4), wo die zuvor gennanten Stangen befestigt sind, ein seitlicher Deckel aus metallischen Blech (6) mit einer oben verlöteten Stange (7); diese Borde sind miteinander befestigt bis zu einer maximalen Nummer, die durch die Höhe der Stangen bedingt ist;
- ein Deckel aus metallischen Blech, wo ein Hacken befestigt ist um es zu ermöglichen, die ganze Struktur hochzuziehen.

10. Ein Verfahren, gemäß Patentanspruch 9, wobei die metallische Struktur aus Edelstahl ist.

Revendications

1. Procédé de traitement de bouchons de liège naturel, avec l'objectif de d'éliminer/réduire les composés contaminants du liège, notamment 2,4,6-trichloroanisole (TCA), **caractérisé par** l'utilisation de fluides supercritiques dans une autoclave à haute pression qui enferme une pièce séparatrice, laquelle permet, pendant des cycles de compression/ décompression, la contraction et l'expansion des dits bouchons de liège avec contact minimale entre eux, sans distorsion significative de sa forme originale et maintenant intactes leur propriétés de bouchage.

2. Procédé selon la revendication 1, dans lequel dans l'autoclave à haute pression (9), le fluide supercritique ou mélange de fluides supercritiques, avec ou sans cosolvant, est contacté directement avec des bouchons de liège naturel.

3. Procédé selon les revendications 1 ou 2, qui est réalisé en prenant les pas suivants :

a) Faire passer un fluide comprimé ou un mélange de fluides comprimés par un compresseur/ pompe à liquides (8) et dans une autoclave à haute pression (9), placée dans un bain ou four à température contrôlée, et contenant des bouchons de liège placés sur la dite *pièce séparatrice,* optionnellement utilisant un cosolvent inerte, de préférence non toxique, lequel peut être ajouté par un compresseur / pompe à liquides (8) ou introduit préalablement dans l'autoclave (9).
b) Circuler le fluide comprimé, le mélange de fluides comprimés ou le mélange de fluides comprimés et cosolvant par l'autoclave à hautes pressions ;
c) Retirer le fluide comprimé, le mélange de fluides comprimés ou le mélange de fluides comprimés et cosolvant par décompression ou, optionnellement, par substitution avec un gaz permanent, comme l'azote.

4. Procédé selon la revendication 3, dans lequel le pas d'extraction supercritique est effectué entre les températures de 30 °C et 120 °C.

5. Procédé selon les revendications 3 ou 4, dans lequel le pas d'extraction supercritique est effectué entre les pressions de 6 MPa et 40 MPa.

6. Procédé selon quelqu'une des revendications 3 à 5, dans lequel le pas d'extraction supercritique est effectué dans l'intervalle de temps de là 24 heures.

7. Procédé selon la revendication 6, dans lequel le pas d'extraction supercritique est effectué dans l'intervalle de temps

de 4 à8 heures.

8. Procédé selon quelqu'une des revendications 3 à 7, dans lequel le fluide supercritique est le dioxyde de carbone.

9. Procédé selon quelqu'une des revendications 3 à 5, dans lequel la pièce séparatrice consiste à :

- Une structure métallique, comprenant quatre tiges, une centrale (1) et trois sur les flancs (2), et avec une base de feuille métallique perforée, où sont attachées les étagères (3) qui supportent les bouchons de liège ;
- Étagères (3) faites de feuilles perforées (5), avec quatre trous où les dites tiges sont solidement fixées, une paroi latérale faite de feuille métallique (6) avec une tige soudée en haut (7) ; lesdites étagères sont attachées unes aux autres jusqu'à un nombre maximum limité par l'hauteur des tiges ;
- Une couvercle faite de feuille métallique, où est fixé un crochet qui permet saisir et enlever toute la structure.

10. Procédé selon la revendication 9, dans lequel la structure métallique est faite d'acier inoxydable.

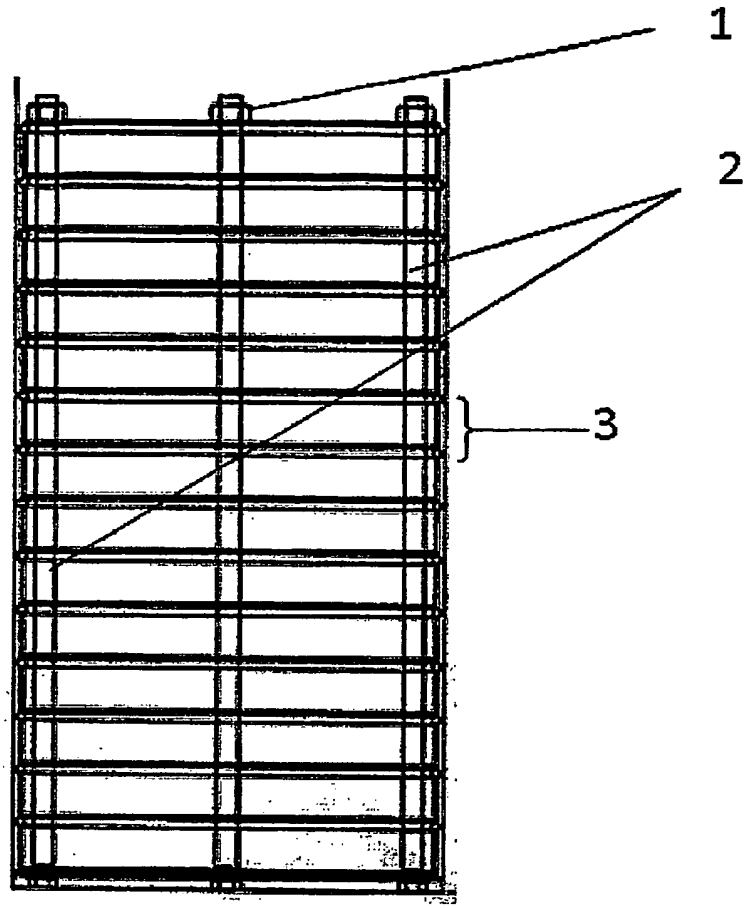


Fig. 1A

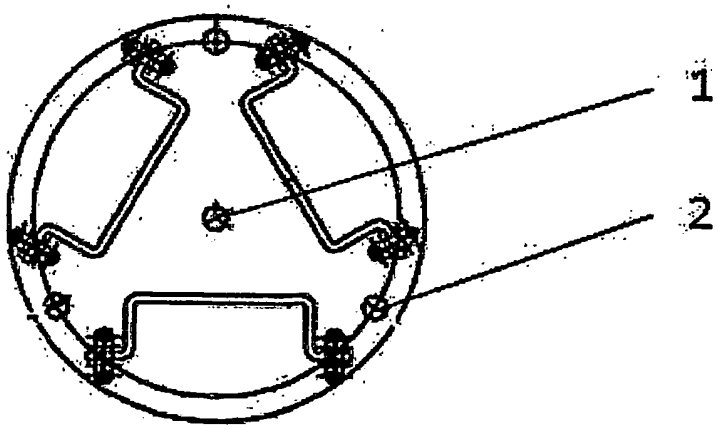


Fig. 1B

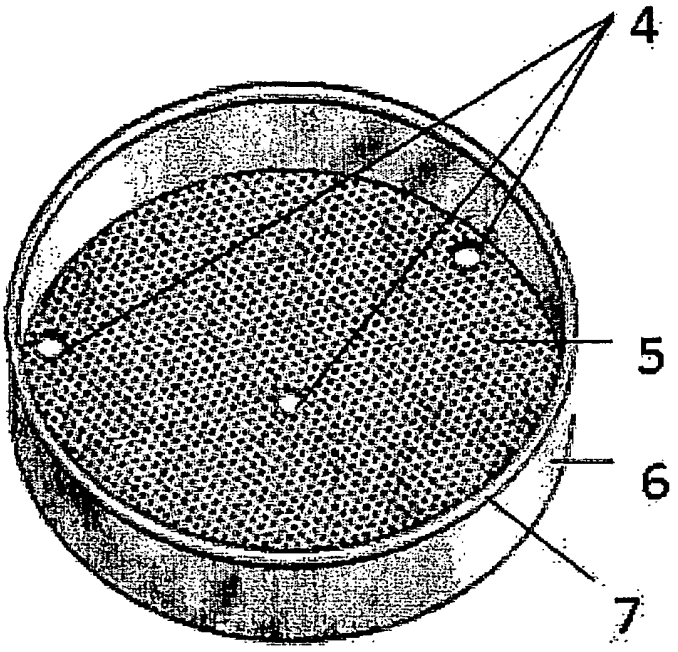


Fig. 2A

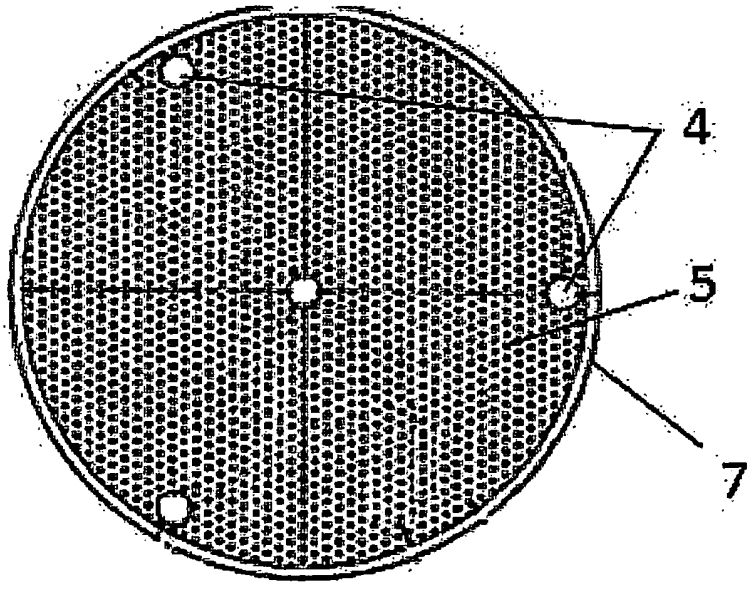


Fig. 2B

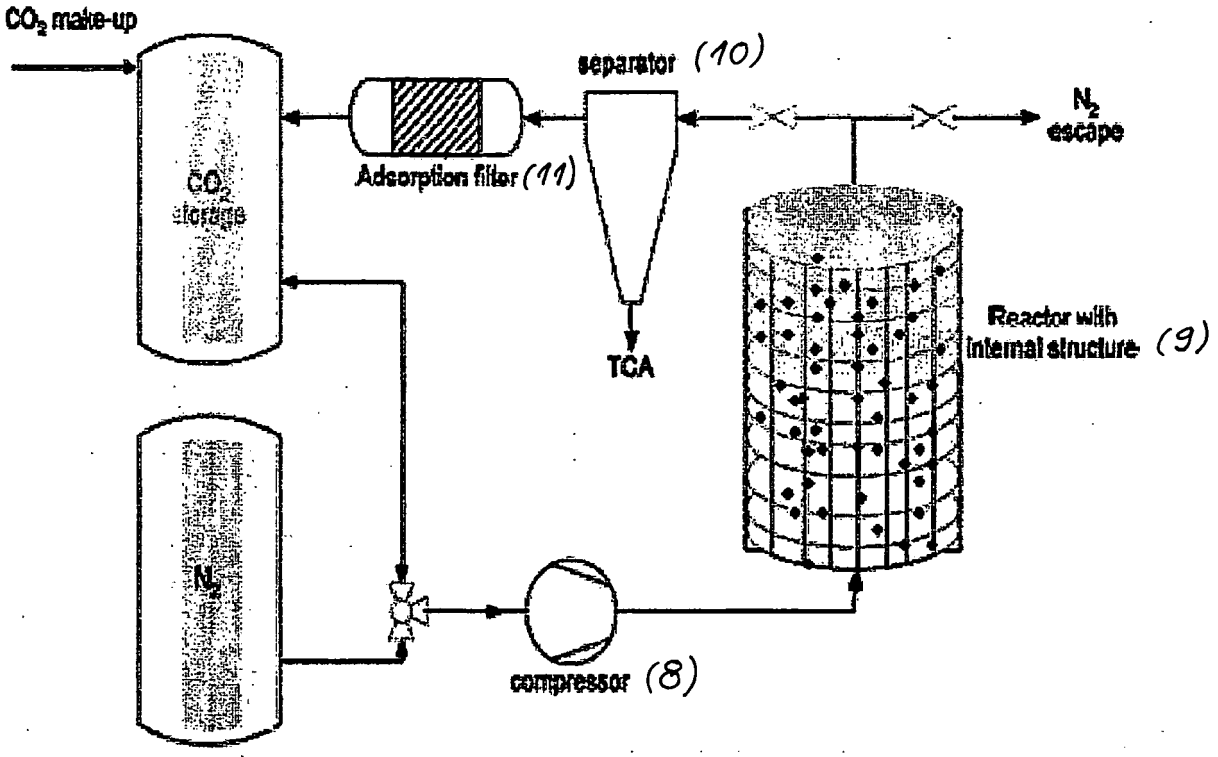

CO_2 make-up
CO_2 storage
Adsorption filter (11)
separator (10)
N_2 escape
TCA
Reactor with internal structure (9)
N_2
compressor (8)

Fig. 3

REFERENCES CITED IN THE DESCRIPTION

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