

CORK TREATMENT - A NEW INDUSTRIAL APPLICATION OF SUPERCRITICAL FLUIDS

Dr. Eduard Lack¹⁾, H. Seidlitz¹⁾, Moaad Bakali²⁾, Rudolf Zobel²⁾

1) NATEX Prozesstechnologie GesmbH, Werkstrasse 7, 2630 Ternitz, Austria, e-mail: office@natex.at, Fax: +43-2630-38163

2) Diamant Techoenologie S.A., Corchos de Mérida, Carreterra de la Estación, km.1, 06500 San Vicente de Alcántara, Spain

Microorganisms produce secondary metabolites like trichloroanisole (2,4,6-TCA), but also other unpleasant substances, which cause the typical “cork taint” in wine. This has led to serious problems for the cork industry in recent years and market share of cork stoppers decreased continuously. Conventional processes to reduce TCA content were only partly successful. Therefore a research program was started using supercritical CO₂ in order to reduce the TCA content below the detectable limit. The R&D project was successful in achieving this target and consequently the results were patented. After pilot tests and scale-up an industrial project was realized in San Vicente de Alcántara at the end of 2005. Soon it was recognised that supercritical CO₂ also eliminates other substances responsible for certain off-tastes of wine.

1. INTRODUCTION

The cork oak (*Quercus suber*), an evergreen oak species reaching a height of 20 m, is the raw material for the production of cork stoppers. It is mainly grown in the southwest of Europe and northwest of Africa. Cork stoppers produced from the bark of the cork oak are resilient and tight closures for wine and sparkling wine bottles. [1] [2] [3]

Nowadays mainly in Portugal, Spain, Tunisia, Morocco, Italy, France and Algeria cork oaks are grown. The European cork industry produces about 340.000 tons of cork per year, which represent a value of 1.5 billion EURO, and employs directly around 30.000 employees.

Portugal is number one of the cork producing countries with a share of 31 % of the cork oaks. 190.000 tons of cork or 51 % of the world production are produced in Portugal’s cork forests. Spain is one of the main producers of cork products.

The stems of the cork oaks show a shining red colour after peeling. The year when the peeling took place is marked on the stems (for example no. 2 for 2002). So the farmers can calculate when they can peel the trees again. The first cork of young oak trees has a low quality and cannot be used for cork stoppers. The bark should be removed very carefully from the stem in order to avoid any damage of the underlying phloem. From the age of 20 years up to around 200 years the stem can be peeled every 10 - 12 years. In this way a good quality of cork material can be obtained and thickness is sufficient to produce cork stoppers.

For centuries cork stoppers have been used to seal wine bottles, even in ancient times wine amphoras were closed with cork. In western society people expect the typical sound “blob” when opening a bottle of wine, which is part of the drinking culture. Worldwide around 20

billion cork stoppers are used every year. Cork is a natural polymer foam based on the substance suberine. [5]

The average chemical composition of cork is:

- Suberine (45%) - the main component of the cell walls and responsible for the resilience of cork
- Lignin (27%) – a cross-linked aromatic polymer
- Polysaccharides (12%) – the structural component of the cell walls
- Tannins (5%), terpenoids and steroides (5%)

Like most other natural raw materials cork can contain secondary metabolites produced by microorganisms. The worst one is TriChloroAnisole (2,4,6-TCA) which is primarily responsible for the typical “cork taint”. Good wine specialists can recognize a TCA content in wine of about 2 ng/l already, while usual consumers notice concentrations between 5-10 ng/l.

The cork industry made a lot of efforts to solve this problem because it became very serious during the recent years. Quite a number of different processes with steam or alcohol were developed to reduce the TCA concentration in cork, but these processes usually don't achieve more than 85 % efficiency at industrial scale.

In 1997 one of the leading cork producers, Sabaté, later Oeneo Bouchage, started the development of a cork cleaning process with supercritical gases in cooperation with CEA. The tests were very successful and consequently the process was patented. Supercritical CO₂ allows a reduction of the TCA content below the detectable limit, which is at the moment 0.5 ng/l. Furthermore CO₂ has special properties regarding reduction of pesticides and inhibition of fungus growth.

In 2003 the Austrian based company NATEX Prozesstechnologie, a well recognized leading specialist for scale-up and supply of supercritical processes was selected for the exploitation of the patent and for scale-up purposes. Several test series were executed first on the 80 litres pilot plant owned by NATEX and later on industrial size in order to proof and confirm the theoretically calculated scale-up factors. Cork has a very low bulk density (around 60 kg/m³), which makes special equipment necessary for loading and unloading of the extractors.

Cork in its natural form has a relatively precise bubble size distribution. The gas bubbles have a diameter of around 25-35 µm as can be seen in Fig. 1.

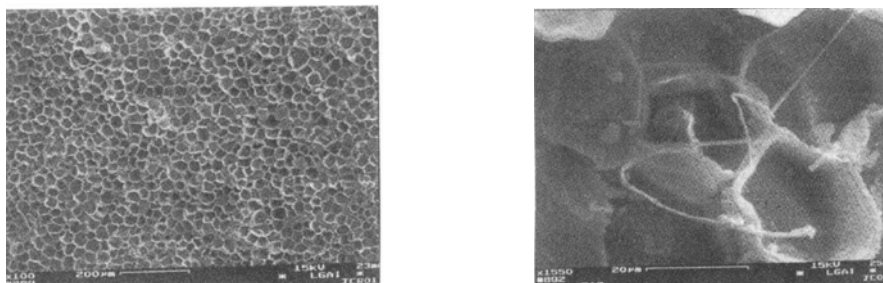


Figure 1: Electron microscope picture of cork. The left picture shows a cork in good condition and the right one a cork cell with fungi infection.

2. EXPERIMENTAL SECTION AND THEORY

Raw cork granules start to shrink above 15 bar during pressurization in the extraction vessel. This shrinking continues up to about 90 bar. Above this pressure no further major deformation could be recognized. During the depressurization step the original shape of the raw material is slightly changed. It is difficult to extract whole cork stoppers and more recommendable to extract cork granulate first and to produce the final cork stoppers by compacting the treated cork granulate afterwards. For the tests extraction pressures between 100-300 bar and temperatures between 40-60°C were selected. The extraction conditions are mainly influenced by the cork material itself. Young trees have larger bubbles, the cork material is softer and consequently the diffusion is faster. Older trees (100 years and older) have a more solid bark with small bubbles, which reduces mass transfer due to the higher diffusion resistance. Further the climate in the area, where the trees are grown, influences the cell structure of the cork bark. Very important is the moisture content of the raw material and the degree of moisture during the extraction process.

3. ENGINEERING AND SCALE-UP OF THE PRODUCTION PLANT [6]

After obtaining enough information regarding the scale-up factors and the extraction behaviour the engineering of the industrial plant started. A production capacity of 2500 tons per year, which corresponds to 500 million cork stoppers, was the basis for the design. In order to optimize energy consumption a careful comparison between the pump- and the compressor process was executed. Larger industrial processes with supercritical CO₂ were only designed as pump processes until today. The evaluation showed economical advantages for the compressor process and in consequence design engineering was adjusted accordingly.

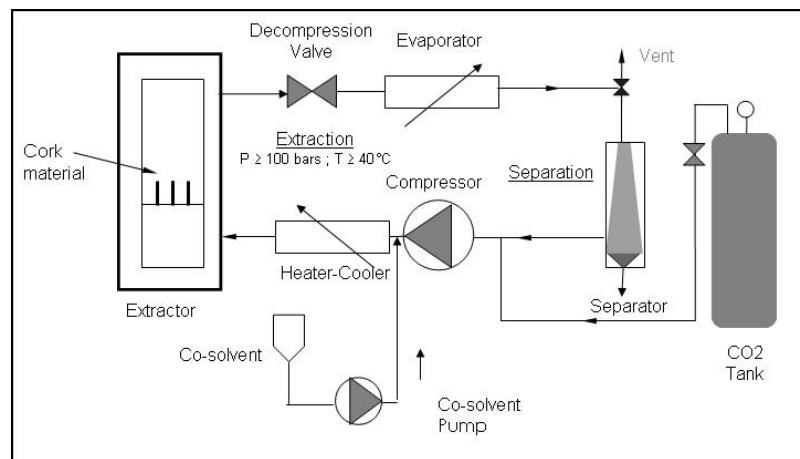


Figure 2 shows the schematic CO₂ process for cork cleaning

A circulation compressor increases the CO₂ pressure from separation conditions to the required extraction pressure. After the compressor a heat exchanger adjusts the CO₂ to the corresponding extraction temperature. As the discharge temperature of the compressor is higher than the necessary extraction temperature, the heat exchanger must be able to operate as cooler and heater. While flowing through the cork bed the CO₂ is loaded with the soluble substances, mainly TCA, but also resins and other organic components. After passing the extractor the supercritical fluid is depressurized by means of a control valve and routed through an evaporator, in which the liquid part of CO₂ is evaporated. The gaseous CO₂ with

the liquid extract reaches the separator, where the extracted substances are precipitated. The extract, mainly an oil and wax emulsion with an unpleasant smell, must be treated as waste.

Big efforts were made for the design and manufacturing of the compressors. As a compressor process was used for an industrial supercritical CO₂ extraction plant for the first time, careful analysis regarding safety and piping design was necessary. In spring 2005 the construction of the plant was started and it was already commissioned at the end of the same year.



Figure 3: Cork cleaning plant in San Vicente de Alcántara, Oeneo Bouchage



Figure 4a: Extractors with cork filling system



Figure 4b: Compressor station

4. RESULTS

Very soon it was recognized that the DIAM closure gives excellent results regarding sensorial neutrality with emphasis on fruit aromas in fresh wines. Starting with 2005 Oeneo Bouchage led an extensive research program to verify whether the sensorial nature of wine closures with

DIAM is only related to the extraction of 2,4,6-trichloroanisole or if the extraction of other aromatic substances is important for the quality of the cork stoppers.

Due to the fact that the Diamant Process was already in operation on industrial scale enough treated cork flour and cork extract was available for the research program. The cork raw material showed an average TCA content of 11-25 ng/l. The extracts obtained in the separators of the production plants showed a TCA content of 70 - 200 ng/l.

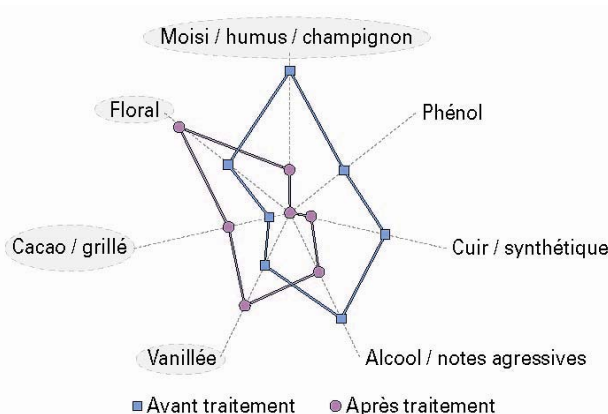


Figure 5: Sensory differences between treated and non-treated cork flour tested in the cork flour macerate [4]

As shown in Fig. 5 it is most important to eliminate mould flavour and reduce substantially humus and mushroom, leather/synthetic phenol and alcohol/aggressive type notes. Quite positive is the increase of floral notes. The results also showed an increase of the cocoa grill and vanilla notes. The reason of this enhancement is not really clear and cannot be caused by temperature in the CO₂ process, which is around 50C°.

Further a series of tests was performed, in which white wine (chardonnay) was contaminated with liquid or solid fractions of the CO₂ extracts. Even after adding small quantities of extracts to white wines, notes of humus, mushrooms synthetic, leather and mould were rising immediately.

Chromatographic analysis [4]

The following chromatographic analysis carried out on treated and untreated cork demonstrated the reduction of extracted substances besides TCA.

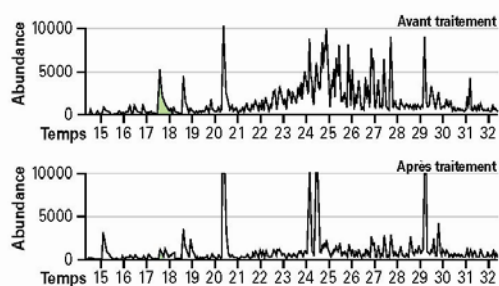


Figure 6: Chromatogram of 1-octen-3-ol substances in the cork granulates before and after the Diamant Process (These substances are associated with the humus/mushroom descriptor)

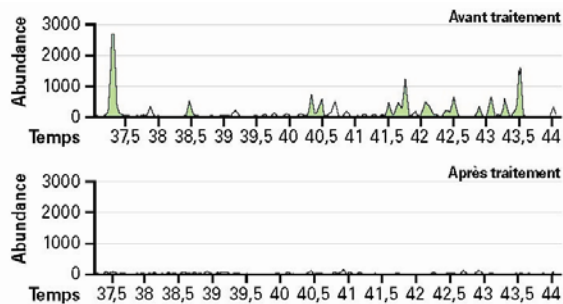


Figure 7: Chromatogram of the content of the sesquiterpenes in the cork granulates before and after the Diamant Process. (These substances are associated with the phenol/leather/synthetic descriptor)

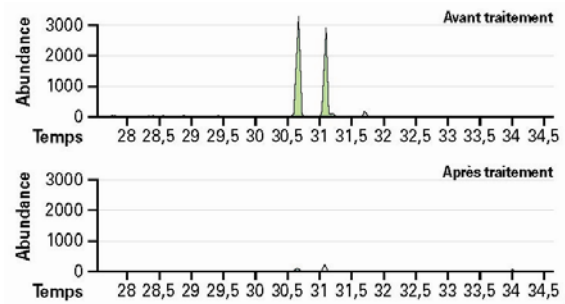


Figure 8: Chromatogram of the content of isomers of anisole isopropyl methylen before and after the Diamant Process

During the chromatographic analysis around 150 substances were detected by GC-MS and a great number of substances could be identified. Most of the substances belong to different chemical families, like alcohol, ketones, aldehydes, acids, esters, phenol compounds, anisoles, furans, furanones, pyranones, alkylbenzenes, hydrocarbons, terpenes, sesquiterpenes, etc.

5. PRODUCTS

As mentioned above cork granules extracted with supercritical CO₂ have an absolutely neutral taste and are nearly free from microbiological contamination. Most of the wooden parts are already removed during the grinding process and the final cork stoppers have a very homogeneous structure. During the SFE process elasticity behaviour of the cork is not changed and if the final stopper is deformed, 97% of the original shape is reached again within 30 sec. Further gas diffusion through the stopper can be adjusted by the moulding process of the cork stopper.

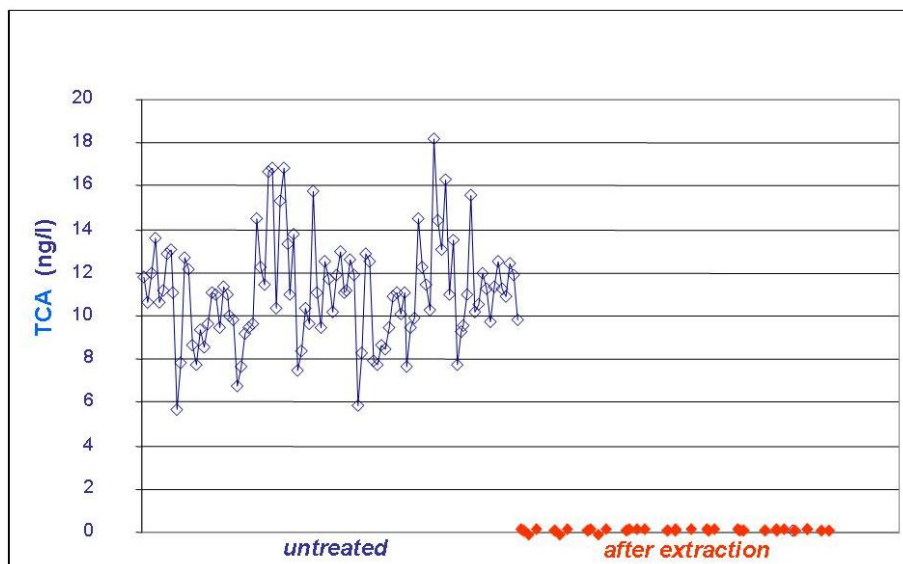


Figure 9: Efficiency of the Diamant Process

With the Diamant Process a secured and reproducible reduction of the TCA content can be reached on industrial scale. After three years of industrial practice no reduction of the efficiency of the process is recognizable.

6. CONCLUSIONS

“Cork taint” in wine is a serious problem and has led to increased use of alternatives to cork stoppers. A research program was carried out to eliminate TCA by means of dense CO₂. Because of the very successful results of this research program an industrial scale SFE plant was realized in Spain. This plant can process up to 2500 tons of cork granules per year. During CO₂ extraction also other substances besides TCA are removed. Cork flour treated with supercritical CO₂ can therefore be characterised by significantly improved sensorial neutrality along with an expression of certain positive aromatic notes, such as floral, vanilla, cacao (grilled), which are naturally present in cork but are normally masked by other less positive notes. This was proved by comparative sensorial analyses and chromatographic analyses. With this innovation the conservative cork industry stepped into a new era and gave hope to the cork farmers. Furthermore it was a genuine European project, because most of the cork is produced in Europe, mainly in Portugal and Spain, and also the final cork stoppers are produced mainly in Europe.

7. REFERENCES

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