LIFE TANNINS PROJECT
PREVENTING EXPLOITATION OF FORESTS BY OBTAINING TANNIN EXTRACT FROM GRAPE PIPS THROUGH RECOVERY OF A WASTE PRODUCT OF THE WINE INDUSTRY

Layman’s report
Summary of the project and objectives

The purpose of the project is to avoid or minimise the deforestation of some species of trees, such as quebracho, mimose, chestnut, mirabolan, valonea and tara. Tanning agents extracted from these species are commonly used in leather tanning. The study proposes to replace such vegetable tanning agents by a wine tanning extract obtained from a waste of the wine industry.

The project intends to prove the industrial feasibility of the proposal in terms of quality of the leather obtained using this new “grape” extract.

The developed process in the project provides a positive environment impact by reducing excess of wine waste, valorising this material and making a more sustainable method.

The advantages of the demonstration project can be summarised as follows:

- lower deforestation of some tree species
- maximum valorisation of a low profitable by-product
- reduction of the energetic costs necessary for the concentration of the vegetable tannins
- reduction of logistic costs using local available vegetable extracts and avoiding overseas sources

A health related advantage can be added by avoiding dust formation at workplaces in the tanning industry. A powder-based product would be substituted by a liquid solution.

Participants in the project comprise two alcohol producing companies: La Alcoholera de La Rioja, Ebro y Duero, S.A. (Spain) and Villapana, S.P.A. (Italy); a tannin chemical trader: Comercial Godó, S.L. (Spain); two tanneries producing most of the vegetable tanned leather in Spain: Curtidos Lancina, S.A. (bovine leather), Sociedad Aragonesa de Curtición de ovinos, S.A. (SARCO) (sheepskin); a Leather Research Centre: AIICA (Spain); and the administration D.G. Calidad Ambiental: Consejería de Turismo, Medio Ambiente y Política Territorial of the Spanish Regional Government of La Rioja.

The project started characterising the wine waste from different types, origins and fractions to test possible different tannin content, followed by trials to be carried out at a pilot plant scale with the selected fraction and the industrial scale testing of the whole process. To do that, a prototype for the tannin extraction and concentration process was designed and built up to produce enough quantities of “grape” tannin extract. Then they were applied at industrial level at the two tanneries participating in the project, being the quality of the leather assessed. Waste products generated from the new process were also analysed to assess outlets of the obtained by-product.

The process developed in the project is environmentally friendly because it reduces deforestation and minimises the excess of grape seed in order to obtain a better valorised product.
Techniques, methodology, and results

Europe accounts for 66% of the wine production in the world market.

A mapping of wine production was carried out in order to have the best knowledge about grape waste availability, in terms of the analysis of its economical viability. The most important European wine-producing countries are France, Italy and Spain.

![Pie chart showing wine production in Europe](chart_url)

In the wine process, wine pomace and lees are obtained. The pomace contains stalk, peel and seed.

<table>
<thead>
<tr>
<th>Grape</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wine</td>
<td>70-72%</td>
</tr>
<tr>
<td>Pomace</td>
<td>10-12%</td>
</tr>
<tr>
<td>Lees</td>
<td>3-4%</td>
</tr>
<tr>
<td>Volatile compounds</td>
<td>17-12%</td>
</tr>
</tbody>
</table>

Taking into account the tannin content, the optimal fraction came out from seeds with values ranged from 6 to 16%.

<table>
<thead>
<tr>
<th>Grape pips</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>14-20%</td>
</tr>
<tr>
<td>Tannin content</td>
<td>6-16%</td>
</tr>
<tr>
<td>No tannin content</td>
<td>8-14%</td>
</tr>
<tr>
<td>Insoluble content (fibers)</td>
<td>72-50%</td>
</tr>
</tbody>
</table>

From every 100 kg of grapes, between 1.22 and 2.18 kg of degreased seed flour can be obtained.
Oil extraction

To extract tannins in aqueous medium, the oil content was previously removed with hexane from crushed pips.

This oil was characterised by Thin Layer Chromatography and by Gas chromatography proving mineral oils, cerids, methylc esters, triglycerides and fatty acids, being mainly unsaturated compounds.

Grape oil characteristics are validated in human consumption. Nowadays, grape pips can be sent to oil extraction companies.

Grape seed oil can be used in the leather manufacturing, as alternative to crude oil in the fat-liquoring process on vegetable hide.

Tannin extraction

As grape tannins from seed are insoluble in cold or hot water, the degreased crushed seed was treated with sodium metabisulphite in aqueous medium, under high temperature and pressure in autoclave, in order to introduce sulphonic groups and increase solubility of tannins in water.

The tannin content was analysed by the filter-bell method in which the tannin solution passes through a bell which contains standard absorbent hide powder.

The process conditions to obtain grape oil and tannin extract were optimised to obtain lab-scale tanning extract for the pilot tannery trials.

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated compounds</td>
<td>34%</td>
</tr>
<tr>
<td>Unsaturated compounds</td>
<td>57%</td>
</tr>
</tbody>
</table>

Tannins obtained from grape seed were characterised for their properties in comparison with commercial tannin extracts by chromatography, obtaining a similar behaviour to quebracho.

The tannin structural type was determined by the tannin reaction towards hydrochloric acid and formaldehyde. Condensed tannins (catechin) are not decomposed by acids unlike the hydrolysable tannin (pyrogallic tannin). Grape tannin from seed contains a mixture of structural types.
**Tannin extraction at small scale**

To scale up the process, a small extractive equipment was designed and built up in order to get knowledge about the tannin extraction process with vapour pressure. The tannin extraction process was validated in this equipment, which showed the feasibility to scale up the demonstration prototype with the aim of obtaining enough product for industrial tannery trials.

**Tannin extraction at semiindustrial scale**

The prototype designed and built up includes 3 plants:

- Tannin extraction plant
- Tannin concentration plant, which includes
  - Ultrafiltration section
  - Nanofiltration section
- Waste water treatment plant
Tannin extraction protocol

The degreased and crushed seed is treated with sodium metabisulphite under temperature and pressure in aqueous medium in the extractor. Metabisulphite produces the sulphitation and therefore the solubilisation of tannin molecules. In these conditions 11.4% of grape seed is solubilised.

The treated seed, which remains inside the autoclave, is washed with clean water to reduce its tannin content, and the washed water obtained is collected to be used in the following extraction with new seed.

The washed and treated seed, which contains 60% of humidity, is pressed to increase the amount of washed water collected.
Tannin concentration protocol

The tannin solution obtained is settled and later, it goes through an ultrafiltration membrane to obtain a solution named UF concentrate, and a light brown permeate which contains some tannins. This permeate goes through nanofiltration membranes to obtain a concentrated solution, named NF concentrate, and a permeate, which is the waste water.

Two different grape products are obtained in the prototype: UF concentrate and NF concentrate. The products obtained are well preserved with the biocide 2-(tiocianometiltio)benzotiazol (TCMTB). In spite of running the concentration plant up to a maximum permissible pressure of membranes, low level concentration was achieved, being 14% the dry matter content in the UF product and 20% in the NF product.

![Diagram of tannin concentration process]

<table>
<thead>
<tr>
<th>Product</th>
<th>Dry matter content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrafiltration product</td>
<td>14%</td>
</tr>
<tr>
<td>Nanofiltration product</td>
<td>20%</td>
</tr>
</tbody>
</table>

Management of the remaining waste in the new process

Two waste products were generated in the proposed process to obtain tannin extracts from grape seed: the wet solid waste, which is the treated seed, and the waste water removed out from the tannin concentration process by membranes (permeate).

Treated seed:

- Compost source material
  The treated seed is highly biodegradable and it can be composted

- Active carbons
  The waste can be used in the production of active carbons with good adsorbing properties.
Waste water:

The water removed out from the tannin concentration process was biologically treated in aerobic conditions.

**Industrial applications**

Preliminary trials of leather tanning were carried out in a pilot tannery in AIICA to test the performance of the grape tannin extract.

Later, the participating tanneries, Curtidos Lancina and SARCO, tested the grape products at industrial scale under the conditions of the tanning process with commercial vegetable extracts. The UF product was used to tan cow hides to produce sole leather and the NF product to tan sheepskin to produce lining leather.

**Colour**

- The colour of the leather obtained with NF product was similar to the leather produced with commercial extracts
- The UF product gave a dark brown leather. Consequently, the technical viability of the UF product is limited to the production of dark sole leather.

The leather obtained was assessed by standard physico-chemical analytical tests compared with the standard production of the tannery. Results proved that the leather produced with grape tanning extracts at industrial scale was similar to the standard production. Even more, values in light fastness were improved.

**Other applications of tannins from grape seed**

Furthermore than the tanning properties of tannins from grape seed, other applications in other industries can be considered:

- wood industry: as a dye for wood
- wine industry: as additive for wine, to stabilize the red colour and to increase the astringent properties.
Assessment of the environmental impact of the project

The environmental advantages using the process to obtain tannins are as follows:

- Deforestation is the major problem and it could be reduced using grape seed as renewable source to obtain tannin extracts for the leather industry. A tannin producer company with a treatment capacity of 22830 tons a year of grape seed flour, could obtain 2625 tons a year of grape tannin extract (supplied as a liquid product at 35% concentration). The substitution of the commercial extracts for this amount of grape tannin extract would avoid the cutting down of approximately 551.250 trees a year among the most common species used, quebracho, mimose, and chestnut.

- The reduction of wine waste and its valuation as a raw material is an environmental benefit. From every 100 kg of grapes, between 1.22 and 2.18 kg of degreased seed flour can be obtained. As tannins are extracted from this flour, the amount of seed flour in Europe as raw material could range from 287 to 514 million kilos annually.

- Maximum valorisation of a low profitable by-product that is currently used for energetic and compost uses.

- Reduction of logistic costs using local available vegetable extracts and avoiding overseas sources

- A health related advantage can be added by avoiding dust formation at workplaces in the tanning industry. A powder-based product would be substituted by a liquid solution.

Cost-benefit discussion on the results

The concentration method by membranes was not the most appropriated for grape tannins because of the low levels of dry matter 14% (UF product) - 20% (NF product) achieved. Diluted solutions require higher amount of biocide and, on the other hand, an important cost of transportation to tanneries.

The economical evaluation of the process to obtain tannins at industrial scale proved that the extraction system carried out in this project, together with the concentration system by triple effect evaporator, would produce a grape tannin extract at 35% level concentration of dry matter content at a sale price of 450 euros/ton approximately, which is competitive with the current price of commercial tannins.
Transferability of project results

The activity for obtaining tannins from wine waste (grape pip) can be applied in every area with high concentration of wine cellars, connected with distilleries and oil producing companies. The most important European wine-producing countries are France (30%), Italy (29%) and Spain (27%). So, at an industrial level it would be reasonable to collect the grape waste in these countries.

It is expected high reproduction potential on tannin extraction process carried out in this project at industrial scale but not for the concentration process by membranes. However, the alternative proposal, that is the triple effect evaporator, is the current system used for the few tannin extract companies in the world (chestnut, mimose, quebracho) to concentrate the tannin extraction solution which is atomised later to obtain the powder product. The validation of the grape tannin extract concentrated by the triple effect evaporator would have to be required to assure the transferability of the process at industrial scale. In principle, it is not expected significant differences on quality leather because the solution at 35% level concentration would contain the total tannin compounds extracted from grape seed and it would produce leather with intermediate colour between the dark and light brown colour.