Statistical Analysis of the Supercritical Fluid Oil Extraction from Grape Seed

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Abstract

Traditional methods for the extraction of edible oils from natural matrices regularly require more than one extraction step with organic solvents. Furthermore, additional process steps are necessary during the refining. Consequently, faster processing methods that are compatible with food production are extremely important. Supercritical carbon dioxide extraction of edible oils is an alternative to solvent extraction because it provides a high-speed extraction process with a simple purification stage. In the study, the effect of the main operating variables during the supercritical fluid extraction (SFE) of oil from grape seeds was statically analysed. For this, the oil extraction yield oil was determined as a function of pressure (200 bar and 300 bar), temperature (40 °C and 60 °C), solvent flow (1 g/min and 5 g/min) and particle size (0.4 mm and 0.80 mm). The statistical analysis showed that the extraction yield increased with an increase in pressure and mass flow, and on the contrary, with a reduction in temperature and size; pressure and temperature being the most influential factors, in that order. The results demonstrate that it is necessary to work at a pressure of 300 bar and a temperature of 40 °C to obtain a significant yield in the extraction of seed oil.

Keywords: p-value, analysis of variance, factorial design, Vitis labrusca, statistical effects
1. Introduction

Grapes are one of the fruit crops grown widely in many areas of the world and 46\% of the fresh grapes produced are accounted for in wine production [1]. Since about 80\% of the total amount is used in winemaking, some 10 million tons of grape pomace arise within a few weeks of the harvest campaign. The seeds constitute a considerable proportion of the pomace, amounting to 38\%–52\% on a dry matter basis [2].

Grape seed oil is a product resulting from the processing of grape marc. It is ever more appealing for the cosmetic and pharmaceutical industries: the pharmaceutical activities concern its antioxidant properties, due to the large content of unsaturated fatty acids [3], which represents positive benefits on the human health, such as antimutagenic and antiviral activity or inhibition of the oxidation of low-density lipoproteins [4]. Apart from being a rich source of a high-value fatty oil, grape seeds have also been appreciated because of their content of phenolic compounds such as gallic acid, catechin and epicatechin, and a wide variety of procyanidins. The latter is also referred to as condensed tannins. Grape seed extracts and procyanidins have been a matter of intense investigations with respect to their potentially beneficial effects on human health [2].

Usually, the production of edible oils from vegetable seeds comprehend several stages during the industrial processes, where the extraction with n-hexane is an important one [5]. However, this organic solvent is non-selective and simultaneously removes non-volatile pigments and waxes, giving rise to dark coloured and viscous extracts contaminated with solvent residues [6].

The application of supercritical carbon dioxide (sc-CO$_2$) has received much attention in the food industry in the last few years, taking into account that this procedure offers extraction yields comparable with those obtained by conventional extraction methods using organic solvents [7]. Additionally, differently than with organic solvents such n-hexane, CO$_2$ is non-toxic, non-flammable, non-corrosive, cheap and readily available in large quantities with high purity. Furthermore, CO$_2$ also has a relatively low critical pressure (73.77 bar) and critical temperature (30.98 °C), it can be considered an ideal solvent for the treatment of natural products [8].

Finally, the statistical analysis is a scientific approach to analysing numerical data in order to enable us to maximise our interpretation, understanding and use [9]. This means that statistics help us turn data into information; that is, data that have been interpreted, understood and are useful [10]. Therefore, considering that statistics is the systematic collection and analysis of numerical data, to investigate relationships among phenomena so as to explain, predict and control their occurrence [11], the aim of this study was to analyse statistically the effect of the main operating variables during the supercritical fluid extraction (SFE) of oil from grape seeds.
2. Methodology

2.1 Raw material

Grape (Vitis labrusca) from southwest Colombia were used for this work. At the begging, stalks were separated from the seeds and skins at the winery. The mixture of seeds and skins was stored at −20 °C before drying. The samples were dried at 60 °C for 48 h, and then the skins and seeds were separated by means of sieves and further cleaned manually. The seeds were stored in dark under vacuum at ambient temperature and finally, dried grape seeds were milled for two cycles of 10 s and then sieved [5,12].

2.2 Installation and operation procedure

All the extractions resulted from the experimental design were done in a homemade semi-continuous flow apparatus that consisted of a pure CO₂ feed line and an SFE equipment with 50 mL. Complete details of the equipment used were described in a previous report [12]. A heating jacket was placed around it to control the temperature inside. The CO₂ flow rate was fixed with a pump, while pressure was controlled by a backpressure regulator. The quantity of CO₂ was measured using a mass-flow meter that was placed at the end of the line. An approximate amount of 5 g of sample was introduced in the vessel forming a fixed. A wire mesh was placed on top of the bed to prevent particles entrainment. The extractor was then closed and pre-heated. After that, the CO₂ was pumped in, and, once the desired pressure was reached, the back-pressure regulator (BPR) was opened to provide a continuous flow of the CO₂ through the bed. The CO₂ was distributed through the bed and after the BPR, this was depressurized; the solvent power of the supercritical fluid dropped, and the oil was precipitated in a previously weighed glass flask. The amount of CO₂ circulated was read by the mass flow meter. When the operation was over, the apparatus was depressurized and the exhausted sample unloaded. After each treatment, lines were cleaned before to start the next experiment. The experimental error was deduced from selected tests that were repeated six times. The maximum standard deviation in extraction yield was 1.5 %.

For a better comparison of the oil yield extractions, the operation was over at the same consumption of CO₂ (3000 g) for all the treatments. This, to recollect the sample at the end of the line stage of extraction. For this, a previous extraction curve was done at the highest pressure (300 bar), the lowest temperature (40 °C), a mass flow of 5 g/min and a particle diameter of 0.40 mm.

2.3 Experimental design

A general factorial design $2^4$ was carried out. Pressure (200 bar and 300 bar), temperature (40 °C and 60 °C), solvent flow (1 g/min and 5 g/min) and particle diameter (0.4 mm and 0.80 mm) were considered as the design factors. A total of
16 experiments and its duplicates resulted. The only response variable was the oil extraction yield, expressed as milligram of dry oil extract per gram of dry sample. Table 1 shows the factorial experimental design, levels, density values at the conditions tested and the results obtained for all the experiments.

2.4 Statistical analysis

Statistical analysis was made by using the Statgraphics Centurion XVII® software with analysis of variance (ANOVA). All mean values were analysed by a multifactorial ANOVA. When a factor had a p-value smaller than 0.05, its influenced the process in a significant way for a confidence level of 95%.

4. Results

The oil extraction yields are shown in Table 1 and are expressed as percent dry weight/initial weight. These values were obtained for the same consumption of CO₂ (3000 g) for the different extraction conditions studied. For information, a column including the CO₂ density has been included.

<table>
<thead>
<tr>
<th>Run</th>
<th>P (bar)</th>
<th>T (°C)</th>
<th>CO₂ density (kg/m³)</th>
<th>Mass flow (g/min)</th>
<th>Particle diameter (mm)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>0.40</td>
<td>59.01</td>
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<tr>
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<td></td>
<td>40</td>
<td>839.81</td>
<td></td>
<td></td>
<td>53.96</td>
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<tr>
<td>3</td>
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<td>40</td>
<td></td>
<td>5</td>
<td>0.40</td>
<td>65.99</td>
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<tr>
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<td></td>
<td></td>
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<tr>
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<td>80.99</td>
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</table>

On the other hand, the estimated effects between the range of variables studied and the analysis of variance of the extraction process are given in Table 2. The sign associated with each of the effects indicates a positive or negative influence on the yield of the dependent variable. The degree of significance of each factor is represented in the table by its p-value. When a factor had a p-value smaller than 0.05 it influenced the process in a significant way for a confidence level of 95%.
Table 2. Estimated effects and the analysis of variance of the process for the oil extraction yields with supercritical carbon dioxide

<table>
<thead>
<tr>
<th>Variable</th>
<th>Effects</th>
<th>( p )-Value</th>
</tr>
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<tbody>
<tr>
<td>Pressure</td>
<td>0.98</td>
<td>0.01</td>
</tr>
<tr>
<td>Temperature</td>
<td>-0.56</td>
<td>0.02</td>
</tr>
<tr>
<td>Mass flow</td>
<td>0.12</td>
<td>0.04</td>
</tr>
<tr>
<td>Particle diameter</td>
<td>-0.23</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The results obtained in Table 2 show that pressure, temperature, mass flow and particle diameter had a statistically significant influence on the oil extraction process (\( p < 0.05 \)). Pressure and mass flow had a positive influence on the yield. On the other hand, temperature and particle size had a negative influence on the extraction yield. This influence was increasing by the order: pressure > temperature > particle diameter > mass flow.

It could be observed in Table 1 that, for a given temperature, the oil extraction yield increased with pressure. The effect of sc-CO\(_2\) pressure on the yield extraction is well known and there is an agreement in the research community that increasing operating pressure has a positive effect on the oil yield extraction [4,13]. The reason is that an increase in pressure at constant temperature makes the density of sc-CO\(_2\) increase, which enhances its solvent power and, ultimately, the oil yield extraction if all the other parameters are kept constant. However, it should be taken into account that the economic viability of working at high pressure has to be evaluated because any increase in pressure is related to a rise in energy consumption [5]. In the case of seed oil extraction, it seems convenient to use the sc-CO\(_2\) according to some works [5–7,12,14–16].

It should also take into account that the cellular walls of the sample used had not a great resistance to the mass transfer. This phenomenon explains the lack of variation observed in the yields obtained in the oil extraction within the pressure range selected for each of the temperatures studied.

On the other hand, it could be seen that, for each pressure, an increase in the temperature generally produced a reduction in the yield of the oil extraction. This yield depended on the decrease caused in the density of the sc-CO\(_2\), which was expected [17].

The higher was the flow rate, the higher the extraction yield, in line with an increase in both the external and internal mass transfer parameters. This means that the higher is the flow rate, the lower could be the extraction time. Nevertheless, the specific consumption of the solvent increased at increasing sc-CO\(_2\) flow rate, which would imply that, for commercial purposes, the solvent flow rate should be optimized in terms of extraction time and solvent volume used per operation [5].
Finally, in particles with lower diameter was higher the yield extraction, because they had a large surface area per unit volume, contain a high percentage of “free oil” and require less distance for the “tied oil” to reach the surface, which reduces the internal mass transfer resistance [5].

5. Conclusions

The effect of the main process variables affecting the supercritical carbon dioxide extraction of oil from grape seeds was investigated experimentally and analysed statically. The statistical analysis showed that the extraction yield increased with an increase in pressure and mass flow, and on the contrary, with a reduction in temperature and size; pressure and temperature being the most influential factors, in that order. The most appropriate operating conditions to obtain the best yield in the extraction were 300 bar, 40 °C, 5 g/min and a particle size of 0.4 mm.

References


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