Utilization of winery by-products into high added value products – grape seed oil and defatted meal

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Abstract

The aim of this study was to use waste from the wine production process with special accent on grape seeds variety Graševina and Zweigelt and new green technology. Supercritical CO2 was considered as a green solvent in extraction of grape seed oil because it has been proven to be highly desirable solvent in separation processes since it is non-toxic, non-flammable, odorless, tasteless, inexpensive and readily available in large quantities, and because it is an environmentally friendly solvent. The results of this study show the possibility of utilization of grape seeds from wine pomace for the production of good quality grape seed oils with high processing yields.

Key words: winery waste, grape seed oil, supercritical CO2 extraction

Introduction

More than 20% of wine production makes waste in the form of grape pomace (the stems, skins and grape seeds) and sediment from the wine. The biggest problem for winemakers is large quantities of pomace, which can pose a risk to the environment if not properly disposed. In the last ten years in addition there is the problem due to stricter environmental regulations in the EU, which prohibit the disposal of organic waste containing more than 5% organic carbon. (Voća et al., 2009). Dry pomace, as by-product of wine production,
is made of about 38% seed, which can contain 10-15% oil, with differences among white and red grapes (Beveridge et al., 2005). Grape seed oil is very interesting for food industry due to its composition and possibility to be used as nutritive edible oil. It is characterized by a high level of unsaturated fatty acids (90% poly- and monounsaturated fatty acids) (Passos et al., 2010) and the unrefined oils contain some bioactive compounds, like tocopherols and phenolic compounds, which can contribute to their antioxidant activity (Passos et al., 2010).

Supercritical fluid extraction (SFE) has attracted considerable attention in recent years as a promising alternative to the conventional solvent extraction and to mechanical pressing in food processing. As a green solvent in the SFE is mainly used supercritical CO₂ which proved to be a highly desirable solvent in the separation processes, since it is non-toxic, non-flammable, no taste or smell, inexpensive and readily available in large quantities, as well as environmentally friendly and GRAS (generally recognized as safe) solvent (Jokić et al., 2014a). The aim of this study was to use waste from the wine production process with special accent on grape seeds and new green technology - SFE. Grape seed oils obtained from white and red grape varieties were compared (oil yield, oil quality parameters and fatty acids).

Material and methods

Material

Grape varieties Graševina and Zweigelt is picked during the harvest 2015 in the vineyards Kutjevo (continental Croatia). After separating the stems, we started pressing mash varieties Graševina, and after maceration and partial fermentation variety Zweigelt (traditional production of white and red wine) with a pneumatic press type Della Toffola PF 16. Grape seeds listed varieties were separated by sieving from grape pomace by using sieves of aperture size of 5mm.

Cleaning and drying of grape seeds

Grape seeds (varieties Graševina and Zweigelt) are dried naturally in the atmospheric conditions within the first two weeks in October 2015 when they were above average temperatures for this time of year.

Determination of initial oil and water content

The initial oil content in grape seeds was measured by automatic extraction systems Soxterm by Gerdhart with n-hexane (Aladić et al., 2014). Moisture content of the seeds was determined according to AOAC Official Method 925.40 (2000).

Supercritical CO₂ extraction of grape seed oil

The experiment was performed in SFE system explained in detail elsewhere (Jokić et al., 2015). The grounded grape seeds of 100 g were placed into extractor vessel. The extracts were collected in previously weighed glass tubes. Each extraction process took 90 minutes. The amount of extract obtained after defined time was established by weight using a balance with a precision of ±0.0001 g. Separator conditions were 15 bar and 25°C. The SFE was performed at extraction of pressure 300 bar and temperature of 40°C at mass flow rate of 1.94 kg/h.

Oil quality parameters

Peroxide value of grape seed oil was determined according to ISO 3960 (1998) and was expressed as mmolO₂/kg of oil. Free fatty acids were determined according to AOAC Official Methods 940.28 (1999). Insoluble impurities were determined according to ISO 663 (1992). All these determinations were carried out in triplicate.

Determination of fatty acids composition

Preparation of fatty acid methyl esters was carried out according to EN ISO 5509:2000 standard. Prepared fatty acid methyl esters were analyzed by gas chromatography according to EN ISO 5508:1995. Gas chromatograph 7890B (Agilent Technologies, Lake Forest, USA) with a capillary column HP88 100 m long.
with a diameter of 0.25 mm and the thickness of the stationary phase 0.20 microns (Agilent Technologies, Lake Forest, USA), a split-splitless injector (temperature 250 °C) and a flame-ionization detector (temperature 280 °C) was used. A sample (1 μL) was injected with a split ratio of 1:50. Start column temperature was 120 °C with holding time for 1 minute. The oven temperature was increased with a rate of 10 °C/min to 175 °C/min, holding for 10 minutes, then at a rate of 5 °C/min was heated to 210 °C, holding for 5 minutes, then again at a rate of 5 °C/min was heated up to 230 °C holding for 5 minutes. Carrier gas was helium (99.9999%) at constant flow rate of 2 ml/min. The hydrogen flow was 40 ml/min, air flow was 450 ml/min, and the makeup gas flow (nitrogen) was 30 ml/min. Fatty acid methyl esters were identified by comparison with retention times of 37 fatty acid methyl ester standard compound analyzed at the same conditions. With samples and standards, for every analysis, certified reference material (CRM), was prepared and analyzed at the same conditions. The result is expressed as percentage (%) individual fatty acids to total fatty acids determined. The detection limit method was 0.1%. Values determined in the validation process for parameter truthfulness were compared with the criterion of the Guidelines for the implementation of analytical methods and interpretation of results (N.N 2/2005), that to prove the truth of the proportion by weight > 10 mg/kg may vary from -20% to + 10% as compared to the certified value.

Results and discussion

Extraction of grape seed oil was performed employing the supercritical CO₂ extraction method. Before extraction experiments, the initial oil and moisture content of raw material were determined, followed by milling the grape seeds to enhance the extraction process. The average of the moisture content was 14.83% for grape seeds white variety Graševina and 13.32% for grape seeds red variety Zweigelt (Table 1). Results of moisture content in seeds indicate that the cause of the high moisture content in grape seeds can be found in the natural way of drying. Therefore, in future experiments, we should certainly use some of the types of dryers for drying the grape seeds which would result in a lower moisture content in the grape seeds. The initial oil content was 7.98% for grape seeds white variety Graševina and 9.67% for grape seeds red variety Zweigelt which is in accordance with other the literature data where authors confirmed that oil content in grape seeds varied from 8 to 15% (Baydar and Akkur, 2001; Passos et al., 2010).

Table 1. Oil and moisture content of grape seeds

<table>
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<tr>
<th>Properties</th>
<th>Graševina seeds</th>
<th>Zweigelt seeds</th>
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<tbody>
<tr>
<td>Oil content (%)</td>
<td>7.98</td>
<td>9.67</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>14.83</td>
<td>13.21</td>
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The average particle size of milled grape seeds prepared for extraction was determined to be 0.345 ±0.021 mm and was kept constant during extraction experiments because it is well known that different particle size of grounded grape seeds could also influence the oil yield. Reverchon & De Marco (2006) reported that the average particle size should range between 0.25 and 2.0 mm approximately. If particles are too small, they can pose problems with channelling inside the extraction bed, causing a loss of efficiency and yield decrease. On the other hand, the production costs increase due to milling. The extraction process was performing at pressure of 300 bar and temperature 40°C to avoid thermal degradation of bioactive compounds. In obtained grape seed oil at this extraction conditions the following quality parameters were analysed: peroxide value, free fatty acids and insoluble impurities and the results are given in Table 2. Primary oxidation processes in the oil mainly form hydroperoxides, which are measured by the peroxide value. In general, the lower the peroxide value, the better the quality of the oil. In this study, the peroxide value of grape seed oil was 0.88 mmol O₂ kg⁻¹ (Graševina) and 0.72 mmol O₂ kg⁻¹ (Zweigelt). Free fatty acid content was determined to be 1.54 % in oil from Graševina grape seeds and 3.70% in oil from Zweigelt grape seeds. It is very important that grape seed oil is low in peroxide value, free fatty acids and moisture content to maintain the quality and shelf life of the oil (Teh & Birch, 2013). Obtained grape seed oils had very low value of insoluble impurities (Table 2).
Table 2. Quality parameters of grape seed oil obtained by supercritical CO2.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Graševina seeds</th>
<th>Zweigelt seeds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peroxide value (mmol O2/kg of oil)</td>
<td>0.88</td>
<td>0.72</td>
</tr>
<tr>
<td>Free fatty acids (%)</td>
<td>1.54</td>
<td>3.70</td>
</tr>
<tr>
<td>Insoluble impurities (%)</td>
<td>0.28</td>
<td>0.05</td>
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Table 3. Fatty acids composition of grape seed oil

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>Graševina seeds</th>
<th>Zweigelt seeds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic acid (%)</td>
<td>6.98</td>
<td>7.52</td>
</tr>
<tr>
<td>Stearic acid (%)</td>
<td>4.58</td>
<td>3.82</td>
</tr>
<tr>
<td>Oleic acid (%)</td>
<td>19.50</td>
<td>17.94</td>
</tr>
<tr>
<td>Linoleic acid (%)</td>
<td>68.92</td>
<td>70.72</td>
</tr>
</tbody>
</table>

The obtained grape seed oils obtained by supercritical CO2 in this study were analysed by gas chromatography and mass spectrometry (GC/MS) method to determine the fatty acid composition (Table 3). High level of unsaturated fatty acids (90% poly- and monounsaturated fatty acids), mainly linoleic acid (68.92% - Graševina; 70.72 Zweigelt), then oleic acid (19.50% - Graševina; 17.94 Zweigelt) and low content of saturated fatty acids are responsible for nutritional value of grape seed oil. Fatty acid composition of obtained grape seed oil is very similar to composition of grape seed oil published by others (Baydar and Akkur, 2001). The main fatty acid is linoleic, followed by oleic, palmitic and stearic acids. Content of linoleic acid is higher compared to any other oil (for example sunflower oil), which makes grape seed oil suitable for storage because of its high stability.

Furthermore, comparing extraction yields gained employing soxhlet method (7.98% and 9.67%, respectively) and supercritical CO2 method (7.54% and 9.51%, respectively) it is obvious that oil from grape seeds can be totally extracted by supercritical CO2 if the appropriate extraction conditions are applied. Compared to conventional extraction, using supercritical CO2 extraction the solvent distillation and oil refining stages can be omitted (Molero Gomez et al., 1996). Grape seed oil extracted by supercritical CO2 had a yellow colour with characteristic aroma and can be further used not only like dietary product but also in the pharmaceutical and cosmetic industry (Fernandes et al., 2013). Other very important advantage of this green technology is that the defatted cake which remains after supercritical fluid extraction is free of toxic solvents, opposed to extraction with organic solvents where the presence of traces of residual solvent in the final product makes the process less attractive from health and environmental point of views. Such defatted cake which remained after supercritical CO2 extraction can be used further in other processes, for example, in development of new functional and enriched products because a large amounts of phenolic compounds are left in cake (Jokić et al., 2014a).

Conclusion

Because the grape pomace for the winery is waste, there are various requirements that are listed waste used as raw material for production of new high-value products and no longer being treated as waste. Through the results of this research shows that in order to further research the seeds should be dried in a dryer to reduce the moisture content of the seeds, and later in oil. Wineries make additional investments in equipment for drying and processing of grape seed could realize additional income producing high-quality products and at the same time contribute to reducing the negative impact of waste disposal in the ground.
References


