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SUPERCRITICAL CO_2 EXTRACTION OF OILS FROM RED GRAPE VARIETIES: YIELDS AND EXTRACTION PARAMETERS

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Abstract. *In this work, the extraction by supercritical carbon dioxide of grapeseed oil from five red grape varieties was investigated. Apart from an indigenous variety Prokupac, as the domestic, and Merlot and Cabernet Sauvignon, as international grape varieties the most represented in the Republic of Serbia, Pinot Noir and Gamay were studied as well. Extraction conditions were: temperature of 50 °C, 250 bar pressure, and 0.3 kg/h flow rate of CO_2. It was shown that the extraction kinetics of international grape varieties, mutually similar differ significantly from the domestic one. The obtained oil yields were in the range of 8.3% w/w (Gamay) to 10.4% w/w (Pinot Noir) for the international varieties and 5.0% w/w for the domestic variety. The mathematical model "Sovova" was applied to define transport parameters regulating the oil mass transfer inside the seed particles and determine the agreement between experimental and model curves. The interpretation of results took into account the differences of grade seed morphologies (outer surfaces and inner layers) which was investigated by SEM analysis.*

Key words*: grape seed oil, supercritical carbon dioxide extraction, extraction kinetics, seed morphology*

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1. INTRODUCTION

Grape seeds are one of the parts of a grape berry that occur as waste. It was found that 10-12 kg per 100 kg of the wet residues is generated in the winemaking process (Matthäus, 2008).

Solid waste from the winery is the potential resource of valuable constituents, which possess nutritive and health benefits. Lavelli et al. presented promising developments for the conversion of winemaking by-products into novel food ingredients, as well as their use in innovative foods (Lavelli et al., 2016).

In recent years, extraction with gases in a liquid and supercritical state as a new technique had a broad application in the chemical, pharmaceutical, and food industries. Many scientific papers are published which refer to applying supercritical carbon dioxide extraction to oil isolation from the grape seed because this method is ecologically friendly (Barba et al. 2016; Machado et al. 2013).

Supercritical extraction uses a supercritical fluid as a solvent. The physical properties of supercritical fluids, which are between gases and liquids, make them suitable solvents (Žižović, 2009).

It is considered that extraction with gases in a liquid state is superior for extracting valuable substances from agricultural resources. As a non-toxic solvent with critical point (T_C = 31.1 °C, P_C = 7.38 MPa), carbon dioxide allows extraction in mild operational conditions so that thermally labile constituents remain unchanged and the extracts better resemble the natural material than extracts obtained by conventional solvent extraction where the solvent is usually separated from the extract under increased temperature (Skala et al., 2002; Sovova and Stateva, 2011). In addition, supercritical carbon dioxide possesses a high affinity for lipophilic compounds (Ghaderi, 2000; Mićić et al., 2011) and its high hydrophilic selectivity allows to obtain extract free of unwanted compounds: sugars, organic and inorganic salts, tannins, amino acids (Da Porto et al., 2009).

Fluids in a supercritical state possess higher solubility and it implies higher process selectivity under classical solvents extraction. The physical and chemical properties of supercritical fluids can vary significantly without change at the molecular level (Sovilj, 2004). A minor variation of pressure and/or temperature cause variation in constituents solubility. The supercritical fluid has a higher diffusion coefficient, even 100 times higher than common solvents, lower viscosity, and surface tension, which leads to a more favorable mass transfer (Abbas et al., 2008; Sovilj, 2004).

For successful extraction, specific location in the raw material and mass transfer resistance is very important. In this sense information about material particle size and solvent retention time are significant (Reverchoni et al., 2006).

For oil extraction from the different plant material apart from compressed carbon dioxide which is the most studied extraction agent, compressed propane was also used. For sesame seed oil results indicated that extraction with propane was much faster than that with carbon dioxide because propane is a better solvent for vegetable oils compared to carbon dioxide (Corso et al., 2010). Sunflower oil was isolated in higher yield when extracted with compressed propane in comparison with supercritical carbon dioxide (Nimet et al., 2011). Compressed carbon and propane were examined as solvents for oil isolation from the grape seeds. Very fast kinetic and higher yield were achieved with propane. Pressure and temperature are the main parameters that influenced the obtained yield (Freitas et al., 2008).

Using a response surface method, Barriga-Sánchez et.al (2018) optimized the extraction yield, and significant effects of pressure, temperature, and CO_2 flow on the oil yield were reported. The same methodology was used to optimize solvent extraction of phenolic compounds from red grape marc (*Vitis vinifera* L., Da Porto et al., 2018).

Supercritical extraction was used to compare the yield and the chemical composition of the oil from different varieties of *Vitis* sp. obtained from wine waste from two distinct harvests: three varieties of *Vitis vinifera* (Moscato Giallo, Merlot, and Cabernet Sauvignon) and two of *Vitis labrusca* (Bordo and Isabel; Agostini et al., 2012).

Beveridge et al. (2005) investigated the yield and composition of oils obtained from eight grape varieties using supercritical carbon dioxide and petroleum ether as solvents. Total phytosterol content was higher with SCE than with PE in seven of eight variety extractions. In both extracts, linoleic acid was indicated as a major component ranging from 67.56 to 73.23% of the fatty acids present.

Oils from red grape seed (mixture of C. Sauvignon, Merlot and Pinot Noir with an approximate ratio of 65:30:5 (m/m/m) and white grape seed (blend of Chardonnay, Sauvignon blanc Riesling, 60:30:10 (m/m/m), were extracted by modern techniques, ultrasound-assisted (UAE), microwave-assisted (MAE) and supercritical fluid extraction (SFE), and compared to the Soxhlet extraction (SE). The effect of operating parameters on total extraction yield was reported. The highest yield was achieved by supercritical CO_2 extraction at the optimal conditions. A similar fatty acid profile was obtained for different techniques. However, SFE technology was favorable for the high tocopherols content and UAE for the highest antioxidant potential (Dimić et al., 2020).

Many researchers have examined the extraction of vegetable oils and developed mathematical models that can predict extraction flow and apply to optimize extraction parameters. Detailed reviews about these models were already reported (De Melo et al., 2014; Oliveira et al., 2011; Sovova et al., 2011). BIC model (broken and intact cell) proposed by Sovova (1994) is the most used model which considers the physical structure of the solid matrix. This model was successfully applied to SFE of various seeds such as grape (Duba et al., 2015; Fiori et al., 2014; Sovova et al., 1994), sunflower (Nimet et al., 2011), sesame seed (Corso et al., 2010).

For extraction of different constituents from natural raw materials using supercritical fluid extraction (SFE) model based on the concept of broken and intact cells were proposed. This is especially suitable to fit experimental data. The model simulates two extraction periods, the first period is equilibrium dependent phase, and the second one undergoes internal diffusion in particles (Sovova, 2005).

To describe the kinetic extraction, Nimet et al. (2011) used the “Sovova” mathematical model, which showed a high precision in all the conditions investigated. The mathematical modeling of the kinetic extraction using a second-order kinetic presented good results for the extraction of sesame seed oil with compressed propane and supercritical carbon dioxide (Corso et al., 2010).

2. Materials and Methods

Seeds of four international red grape varieties (Cabernet Sauvignon, Merlot, Pinot Noir, Gamay) and indigenous variety, Prokupac cultivated in the vineyard of wine producer “Rubin” Kruševac, Serbia, and harvested in 2013, were used in this study. Seeds were separated during the fermentation process using a special valve on the vessel. Clean seeds were dried on the ambient air to a moisture content below 10%. Dry seeds were ground with a horizontal coffee grinder (Elektron Dublje) and sifted through standard laboratory sieves with 0.3 mm and 0.5 mm pore size. The fraction with an average particle diameter of 0.4 mm collected between sieves was used for the experiments.

Carbon dioxide (99.9%) and synthetic air were purchased from Messer Technogas A.D., Novi Sad, Serbia, *n*-Hexane, was purchased from Merck KgaA, Darmstadt, Germany.

Laboratory-scale equipment (Autoclave Engineers SCE Screening Systems, USA) was used for the extraction of the grapeseed oil, which simplified scheme is presented in Figure 1. The system is fitted with a 150 cm^3 classic filter vessel extraction cell for solid samples. Oil isolation was performed with a 25.0 g seeds sample, at a temperature of 50 °C, with a pressure of 25.0 MPa and 0.3 kg CO_2/h flow rate.

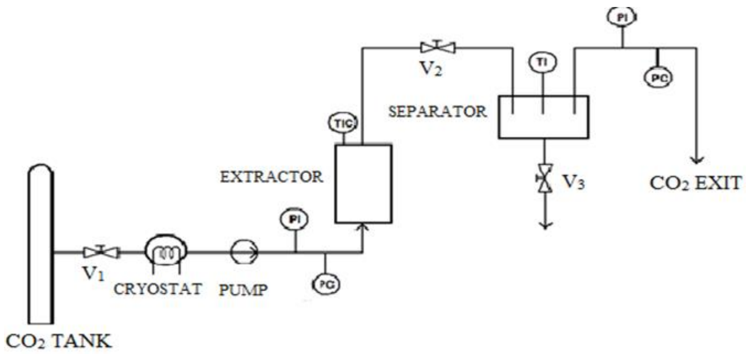

Fig. 1. Schematic presentation of equipment for supercritical extraction (Žižović, 2009)

Seed morphology was investigated by Scanning electron microscopy (SEM JOEL JSM-6390 LV). Samples (the parts of seed) were coated with Au, using Spater coater device Baltec SCD 005.

2.1. Total oil content - Soxhlet method

Soxhlet method was used to determine total oil content according to standard method SRPS EN ISO:2011. Extraction was conducted at 80 °C for 6 h. Solvent removal was performed on rotary vacuum evaporator „Senco“, at 50 °C, 0.8 bar, and 150 r/min, to the constant weight.

2.2. Oil yield

Oil yield was calculated by measuring the mass of the seed samples before extraction and the mass of the obtained oil. The following equation was used:

$$Y\,(\%) = \frac{\text{mass of extracted (pressed) oil}}{\text{mass of seed sample}} \times 100$$

2.2. Statistical analysis

All the experiments (extraction procedures and chemical analyses) were done in triplicate. Statistical Package for Social sciences (IBM SPSS Statistics 20, Chicago, IL, USA) was used. The differences between the mean values were evaluated by a Tukey test with significant levels set at $p \leq 0.05$. Results given as mean values ± SD (standard deviation) were further subjected to one-way analysis of variance (ANOVA). For those parameters for which the significance of mean values differences by samples was shown, the Duncan test for post hoc analysis was used.

3. RESULT AND DISCUSSION

Preliminary experiments were carried out to define process variables for CO_2 extraction. Experimental conditions were selected based on the oil mass yield, fatty acid profile, and total phenolic composition. As a result, the temperature of 50 °C, pressure and flow rate of 250 bar 0.3 kg CO_2 /h was selected as operational conditions.

The obtained oil yields (%, w/w) and isolated oil contents are presented in Table 1. The yield was calculated as the ratio between the mass of extracted oil and the mass of initial grape seeds, and the isolated oil content was calculated as the ratio between the mass of extracted oil and the total oil content determined by the Soxhlet method.

Table 1 Grapeseed oil yields

Grape variety	Total oil content (%, w/w)	Oil yield content (%, w/w)	Isolated oil (%, w/w)
Pinot Noir	$15.22_D \pm 0.04$	$10.04_D \pm 0.25$	66.0
Gamay	$14.25_C \pm 0.03$	$8.3_B \pm 0.18$	58.2
Prokupac	$11.84_A \pm 0.05$	$4.96_A \pm 0.15$	41.9
C. Sauvignon	$15.77_E \pm 0.04$	$6.27_C \pm 0.15$	39.8
Merlot	$12.84_B \pm 0.03$	$8.98_C \pm 0.20$	69.9
Average	13.98	8.26	58.7

Values in the same column with the different labels in the subscript are statistically significantly different ($p < 0.05$). All measurements are performed three times and dates are expressed as average value ± SD

Supercritical extraction used in this study can be presented as an overall kinetic curve: the plot of the cumulated extract is presented versus the amount of solvent passed through the extractor, as it has been already reported in the literature (Sovova, 2005).

This type of extraction includes two phases; they are characterized by accelerated and slow or very slow oil extraction, respectively. The fast phase occurs from the surface and the layers just below the surface where the cell walls are damaged by seeds pretreatment (Sovova and Stateva, 2011) In fact, the cells are broken during grinding and the extraction from thus broken cells is fast. In contrast, the central parts of the seeds contain intact cells, so the extraction from these deeper layers requires CO_2 to enter into these solid matrices, to dissolve oil and exit from the solid matrices (Beveridge et al., 2005). As a result of the difference in CO_2 transfer through the intact cell wall and the broken cells, there are differences in extraction rates from these layers (Sovova, 2005). The extraction curve presented as a plot of oil yield versus a specific amount of solvent carbon dioxide is given in Figure 1.

It can be seen that extraction kinetic for four grape varieties is very similar while there is a significant difference for the Prokupac variety.

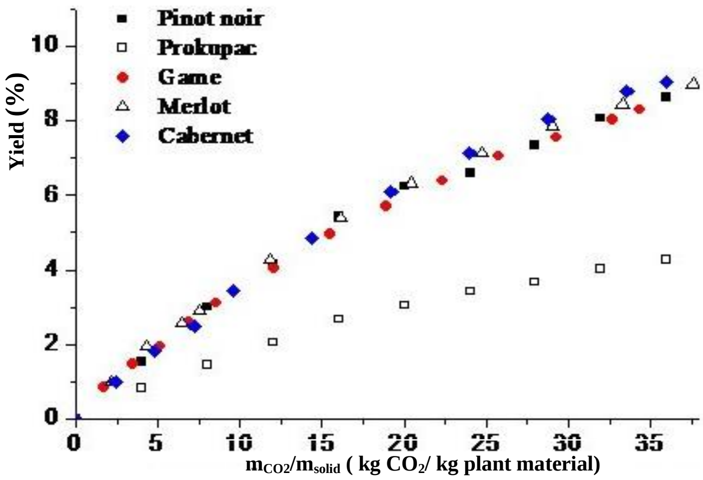

Fig. 1 Dependency graph of oil yield investigated grape varieties and the specific amount of carbon dioxide [m_{CO2}/m_{solid} (kg CO_2/kg plant material)]

The values of achieved extraction yields (presented in Table 1), found in the range from 4.96 (Prokupac) to 10.04% w/w, express statistically significant differences ($p < 0.05$) among investigated varieties. It can be seen that this method of extraction is less efficient for the seeds of the Prokupac variety where isolated oil content is 41.9%, nearly as obtained by cold pressing of the same seeds. The obtained results show that the applied extraction method is the most efficient for the seeds of the Merlot variety (69.9% w/w of isolated oil recovery). Oil yield obtained in this study is lower than it was reported by Agostini et al (2012), who used the same grape variety (Merlot, 14.66% w/w) but different extraction conditions (higher temperature -80 °C and higher CO_2 flow–4.14 kg/h). At the same pressure (25.0 MPa) and 40 °C Perez et al. (2015) achieved the yield of 8.21% w/w, while with increasing temperature the yield was found to increase–at 60 °C it reaches 21.6% w/w.

Beveridge et al. (2005) investigated the possibility of using supercritical extraction with carbon dioxide or petrol ether from seeds of eight red grape varieties and obtained the yields in the range from 5.85% ± 0.33 to 13% ± 0.46 for supercritical extraction and petrol ether extraction from 6.64% ± 0.16 to 11.17% ± 0.05. Four varieties among the eight investigated (Pinot Noir, Gamay, Merlot, and C. Sauvignon) are used in our study; the yields achieved differ compared to the results of the aforementioned authors: they are lower for the Merlot and C. Sauvignon varieties and slightly lower for the Pinot Noir variety, while for the Gamay variety significantly higher yield (8.3 ± 0.18% to 5.85 ± 0.33%) was found. Different cultivation localities and different extraction conditions (65 ˚C, 37 MPa, flow rate CO_2 60 g/min, 6 hours duration; freeze-drying of seed are possible factors that caused these differences.

Passos et al. (2009) reported the effects of enzyme pretreatment of seeds on oil yield enhancement. The supercritical fluid extraction of grape seed oil (grape variety Touriga National) using carbon dioxide has been carried out at constant temperature (313.15 K) and solvent flow rate (1.7×10^{-4} kg s^{-1}), while pressure was varied (160, 180 and 200 bar), using both untreated and enzymatically pre-treated seeds. For untreated seed the maximum extraction yield obtained was 11.5%, whereas the enzymatic pre-treatment increased this value by 43.5%, attaining 16.5%. Such results confirm the validity of the hypothesis of the broken-intact cells model. Pretreatment increases the ratio of broken to intact cells by increasing the oil availability in the milled seed. These results also confirmed that pressure has a large impact on the extraction: CO_2 necessary to reach a maximal extraction yield decreases at higher pressures.

Comparing extraction curves obtained by Passos et al. (2009) with those presented in Figure 1, it can be noticed that experimental curves obtained in our study are similar to those collected for untreated seeds and pressure of 160 bar. This leads to the conclusion that an increase in pressure could lead to a decrease in CO_2 consumption required to achieve maximum oil yield.

Hence, it can be concluded that the oil yield is closely affected by extraction parameters, grape growing areas as well as the way of seeds treatment before extraction.

The "Sovova" model (2005) was applied to calculate extraction parameters for oil seed extraction using supercritical carbon dioxide extraction. Determination was carried out for the indigenous Prokupac variety and the international Pinot Noir variety, which showed similar kinetics and the highest yield among investigated international varieties.

Experimental curves in Figure 1, representing the dependence of oil yield and specific solvent consumption (kg CO_2 per kg plant material), show markedly lower yield for Prokupac variety in comparison with other studied varieties. That was the reason this variety was taken in model parameters calculation.

Values of physical parameters necessary for calculating model parameters are average particle size diameter, the main component of the extract, solvent flow rate, viscosity, and density, and they are given in Table 2.

Table 2 Values of physical quantities for Model "Sovova" (2005)

Grape variety	P(MPa)/T(K)	d_p (mm)	Flow CO_2 (g/s)	E (Bed porosity)	Main component
Prokupac	25/ 323.15	0.40	0.3	0.545	Linoleic acid
Pinot Noir	25/ 323.15	0.40	0.3	0.43	Linoleic acid

For particle size determination (mean particle size) sieving method was used and for porosity measurement standard dropping method.

Experimental curves (•,◦) and curves resulting from modeling (−), which represent oil yield in the function of specific solvent consumption are given in Figure 2.

As it can be seen from Figure 2 there is a high agreement of the experimental and model curve. Two extraction periods are noticed:

- the first (linear), obtained at the beginning of extraction. The content of the easily accessible oil is the highest, the process is fast and is limited by the free oil solubility in the solvent. That period is characterized by a high oil/solvent concentration gradient, as a driving diffusion force and it can be recognized by a higher slope of the initial part of the curve;

- the second period of slow extraction, which is controlled by diffusion inside the solid particles. Total available oil quantity decreased with time of extraction, driving force is lower, as well as extraction rate. This period can be recognized by slower yield change.

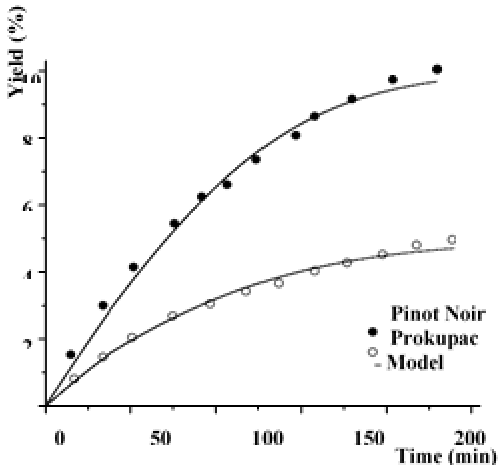

Fig. 2 Kinetic curves (line) using model "Sovova" to supercritical CO_2 extraction of the seeds of grape variety Prokupac and Pinot Noir

Model parameters are calculated by optimizing data for mass transfer coefficient through solid-phase k_s (m/s), equilibrium oil solubility in supercritical carbon dioxide y_r (kg oil/kg CO_2) proportion of tied oil x_k (kg oil/kg insoluble solid phase after free oil isolation). Optimized values for calculated parameters are reported in Table 3.

The curve slope in the first extraction period is correlated with oil solubility and the slope is higher as the quantity of the free oil increases. The equilibrium solubility coefficient for extraction from Prokupac variety seeds (0.12×10^{-2}) is significantly lower compared with that of the Pinot Noir variety (0.17×10^{-2}) which gives a lower curve slope in the first extraction phase.

Table 3 Calculated parameters according to the "Sovova" model (2005)

Grape variety	Model parameter		
	$x_k \times 10^2$	$k_s \times 10^8$ (m/s)	$y_r \times 10^2$ ($kg_{extract}/kg_{CO2}$)
Prokupac	0.4	4.5	0.12
Pinot Noir	0.86	5.5	0.17

k_s – solid-phase mass transfer coefficient (m/s); y_r – equilibrium oil solubility (kg oil/kg CO_2); x_k – limiting value of the mass of the soluble substances per mass insoluble solid phase (kg oil/kg insoluble solid phase)

The Prokupac variety seeds contain a lower quantity of free available oil, consequently, in the first 50 minutes of extraction, the yield of isolated oil is half the yield from the seeds of the Pinot Noir variety. If the extraction rate is expressed as the mass of extracted oil per unit time, the extraction of oil from Prokupac variety seeds of grape of Prokupac variety is far slower than extraction from the seeds of Pinot Noir variety.

The extraction rate is determined by the oil diffusion rate from the interior part of the particles to the supercritical fluid. Interior diffusion rate depends on temperature, the contact surface, and concentration gradient between material and extraction solvent. Taking into account that extraction is accomplished at the same temperature, the difference in extraction rate between two varieties comes from the two remaining factors; the amount of contact surface and differences in the rate of changing the concentration of the oil in plant material and insolvent.

In the case of the average diameter of the seeds, extraction is carried out with material ground and sieved under the same conditions. However, there are differences in the morphology (porosity and density) between the two considered seed types. and could be important factors determining the kinetics of extraction. Higher density and lower porosity were found in the seeds of the Prokupac variety, meaning that more time is required for making a layer of solvent around the particle and to provide good contact for mass transfer. From the values for mass transfer coefficient through solid-phase k_s (Table 3), it can be seen that they are expectedly different, and smaller value belongs to variety Prokupac (4.5×10^{-8} m/s). This coefficient refers to an interior diffusion, from the interior to the outside particle surface. To reach the solvent layer outside the particle, oil crosses a longer path, and consequently, the extraction rate is lower.

Very different values of model parameters may be explained by different seeds morphology which is evident from the SEM images of the outer surface of grape seeds (Figure 3).

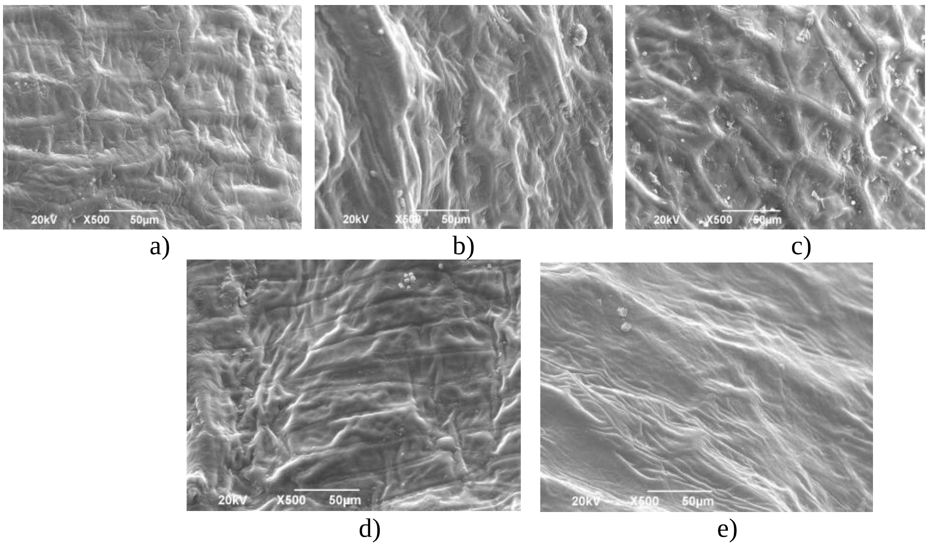

Fig. 3 SEM images of the inner layers of seeds of different varieties of grape: a) Cabernet Sauvignon, b) Gamay, c) Merlot, d) Pinot Noir, e) Prokupac; magnification: (x500)

It is noticeable that grapes of the Prokupac variety (e) have the most compact and flattest surface. Inner morphology is presented on the SEM images of the vertical section of the seeds (Figure 4).

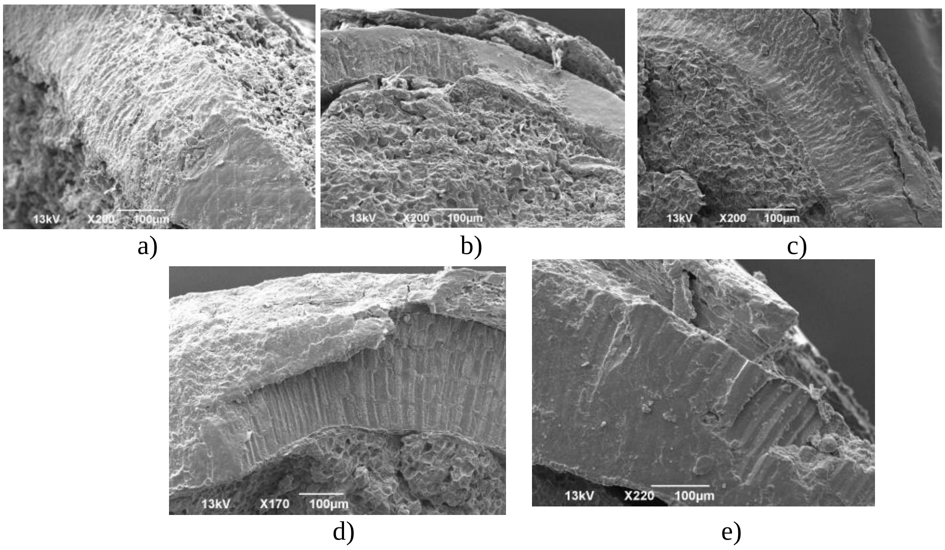

Fig. 4 SEM images of the outer surface of seeds of different varieties of grape a) Cabernet Sauvignon, b) Gamay, c) Merlot, d) Pinot Noir, e) Prokupac.

The images show differences in the thickness of the epidermis and seminal vesicles and morphology of the inner layers. (Figure 4). The Prokupac variety (e) has the thickest central part of the seeds and an extremely compact structure compared to other varieties.

CONCLUSION

In this study supercritical CO_2 extraction from the seeds of five different red grape varieties was carried out. It was shown that the obtained oil yields and oil recoveries depend on the grape variety and applied experimental conditions. Extraction kinetics were monitored; from these data, it was concluded that the rate of extraction from the seeds of the Prokupac variety is significantly slower. Extraction conditions do not suit seeds of that grape variety. Surface morphology and seed anatomy visible on the SEM images of the section layer show that seeds of the Prokupac variety have the most compact and flattest surface. Additionally, different content of total phenolics may affect reduced oil solubility which is important in the extraction process. The “Sovova” model used in this study fitted to the experimental results.

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EKSTRAKCIJA ULJA IZ SEMENKI CRVENIH SORTI GROŽĐA NATKRITIČNIM CO_2. PRINOSI I PARAMETRI EKSTRAKCIJE

U ovom radu je ekstrakcija natkritičnim ugljen-dioksidom primenjena za dobijanje ulja iz semenki crvenih sorti grožđa koje su najzastupljenije u Republici Srbiji, od kojih je sorta Prokupac autohtona, a ostale sorte su internacionalne. Ekstrakcija je izvedena na temperaturi od 50 °C, pritisku od 250 bar i protoku od 0,3 kg CO_2 */h. Pokazano je da je kinetika ekstrakcije slična za internacionalne sorte grožđa, a da se značajno razlikuje od kinetike ekstrakcije ulja iz autohtone sorte Prokupac. Prinosi ulja su se kod internacionalnih sorti grožđa kretali od 8,3% (Game) do 10,4% w/w (Pinot Noir), dok je kod domaće sorte Prokupac ostvaren prinos od 4,96% w/w. Za definisanje parametara ekstrakcije koji regulišu transport mase unutar čestica semenki primenjen je matematički model "Sovova". Snimanje unutrašnje i spoljašnje morfologije semenki SEM metodom je korišćeno za interpretaciju rezultata dobijenih primenom matematičkog modela.*

Ključne reči*: ulje iz semenki grožđa, ekstrakcija natkritičnim ugljen-dioksidom, kinetika ekstrakcije, morfologija semenki grožđa*