SUPERCRITICAL FLUID EXTRACTION OF GRAPE SEED OIL: EXTRACTION KINETICS AND FATTY ACID PROFILE

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ABSTRACT

The current research for the valorization of residues coming from the wine industry using sustainable technologies such as supercritical fluid extraction, has promoted the research on the suitable operating conditions which maximize the extraction performance in terms of yield and bioactive concentration. In this work, a kinetic study of the supercritical extraction of the grape seed with carbon dioxide at 45 MPa and temperatures of 40, 50 and 60°C for 6 hours has been carried out. The studies indicated that extraction temperature of 60°C resulted in the highest extraction yield. The potentiality of grape oil as a source of unsaturated fatty acids was demonstrated, obtaining linoleic acid in a greater proportion, followed by oleic acid, and palmitic acid. It was found that extraction temperature of 50°C resulted on the highest concentration of unsaturated fatty acids present in the oil.

Keywords: high pressure extraction, grape seed, fatty acid

1. INTRODUCTION

The current trend towards the consumption of healthy products with functional and nutraceutical properties are the main study of the industries for the design and development of alternatives to satisfy the needs of the market. The constant search for new products has led industries to emphasize on the recovery of high value added products that meet these characteristics from residues which were previously considered as waste. (Prado *et al.*, 2012).

The wine industry generates solid and liquid residues that present a high demand for storage, transformation and/or disposal, which constitutes a serious problem in ecological and economic terms. For this reason, in the last decades, alternatives for a transformation of these residues are being evaluated, encouraging a sustainable agriculture to mitigate the environmental impact of its activities. These residues are currently used as animal feed, organic fertilizer for soils, or filling material (González-Centeno *et al.*, 2010).

The principal solid residue of this industry is the pomace, which is made up of grape husks and grape seeds. This residue is a source of high-value added products such as dietary fiber, phenolic compounds and grape seed oil (González-Centeno *et al.*, 2010). Specifically, grape seeds are already used as dietary supplements and natural food additives in the USA, Australia, Japan, Korea and some European countries (Bakkalbasi *et al.*, 2005). In the cosmetics industry, grape seed oil is also widely used in the manufacture of skin moisturizers, and, the food industry benefits from the antioxidant qualities of this oil (Navas, 2010).

The current technologies for the process of elaboration of products with high functional and nutraceutical composition make reference to the use of clean technologies such as the supercritical fluid extraction that avoids the use of organic solvents and use of high temperatures to prevent the degradation of the interest compounds by consumers. Extraction by supercritical fluids consists on the separation of a compound of interest (solute) present in a solid matrix through contact with a supercritical solvent. The most widely used solvent in the food industry is carbon dioxide (CO_2) due to its moderate temperature and critical pressure, availability in high purity and approval in food processing (Brunner, 1994).

For this reason, the main objective of this work was to conduct a study of the supercritical extraction of grape seed oil from Malbec variety (one of the most cultivated varieties in Perú) by evaluating the extraction kinetics in function of the extraction global yield and the fatty acid profile in order to assess the behavior of this sustainable extraction technique at different operating conditions.

2. MATERIAL AND METHODS

2.1. Chemical and Reagents

Carbon dioxide (99.9%) was obtained from Praxair White Martins Inc. (Lima, Perú). The analytical reagents used in fatty acid analysis were of HPLC grade and obtained from JT Baker (New Jersey, USA). The FAMEs standard was obtained from Restek (Code 35078, USA).

2.2 Raw Material Preparation

The grape residues, containing seeds and husks of Malbec variety, were donated by Santiago Queirolo Company (Lima-Perú). The seeds were separated from husks manually and then, this raw material was dried at 40°C in a home-made convective drying oven until humidity of 10%. Then, the material was comminuted using a knife mill (Bosch, model MKM-6003, USA) to homogenize the sample. Particles smaller than 80 mesh were separated using sieves (Series Tyler, W.S. Tyler, Wheeling, USA) in a vertical vibratory shaker.

2.3. Supercritical fluid extraction (SFE)

The extraction experiments were performed in a commercial SFE unit (Supercritical Fluid Inc., Model SFT-150, Delaware, USA) equipped with a cooling bath, supercritical fluid pump, a heating oven up to 200°C, extraction vessel of 100 cm^3, block valve, restrictor valves and a flowmeter (Dwyer, model DR220282, USA). Supercritical CO2 was used as the extracting solvent. An apparent density of 400 kg/m^3 and CO2 flow rate of 0.142 m^3/h was considered for all experiments. In a preliminary work, the effect of extraction pressure of 15, 25 and 45 MPa on the global yield was studied. The results showed that pressure of 45 MPa resulted on highest global yield. Based on these results, the extraction kinetics at pressure of 45 MPa, and temperature of 40, 50 and 60°C were studied in this work. For the supercritical extraction experiments, the vessel was assembled and placed inside the oven at the operating temperature and CO_2 was pumped into the system until reaching the operating pressure. A static period of 30 min was used before the dynamic extraction step. The extract was collected inside a sealed 100 cm^3 amber glass flask immersed on an ice bath. The samples were collected at the extraction time of 15, 30, 45, 60, 90, 180 and 360 min, and stored under freezing (−4°C) in the absence of light for further analyses. The experiments were performed in duplicate.

2.4 Extract Characterization

2.4.1 Global Yield

The global yield X_0 was determined as the ratio of the total mass of soluble material extracted at each time ($m_{extract}$) to the initial mass of grape seed (m_{GS}) on a dry basis, according to Eq. (1).

$$X_0 = \frac{m_{extract}\ (g)}{m_{GS}\ (100\ g)} \quad (1)$$

2.4.2 Analysis of fatty acids (FAMEs)

Transesterification of supercritical grape oil was performed according to the methodology proposed by Fiori et al., 2017. 0.3 g of extract reacted with 5 mL of 0.5 M solution of KOH in methanol for 3 hours. Then, the mixture was acidified with HCl and partitioned with hexane. The organic phase was dried with Na_2SO_4 and evaporated to obtain a dried sample. Chromatographic separation was performed on an Agilent GC system (USA) equipped with a FID detector and a cianopropil/dimetilpolisiloxane (50%/50%) chromatographic column (DB-26, USA). The column temperature was set with the following gradient: 50 - 100°C (12 min) at 5°C/min, 100 – 150 °C (5 min) at 10°C/min, and 150 – 230°C (18 min) at 20°C. Injection volume was 1 µL with a split of 1:10. FAMEs were identified by comparing retention times with a FAMEs standard solution (NLEA Mix, Restek, USA) (R^2 = 0.999). The results were expressed as mg of fatty acid/g of extract (supercritical fluid oil).

3. RESULTS AND DISCUSSION

Figure 1 shows the extraction kinetic curve of SFE for grape seed at pressure of 45 MPa, and temperature of 40, 50 and 60°C. The extraction kinetic followed an initial constant extraction period (CER) up to 60 min, followed by a falling extraction period (FER) up to 180 min, and a final diffusion-controlled period (DC) for all operating conditions. The increasing of temperature from 40 to 50 °C resulted in an increment of the extraction yield, while the increment from 50 to 60°C presented similar yields due to deviation. The highest yield value was obtained at the temperature of 60°C and it was of 7.4 ± 0.8 g extract/100 g of grape seed in dry basis. These results have the same tendency as the described by Passos *et al.* (2010) for supercritical extraction at 220 MPa.

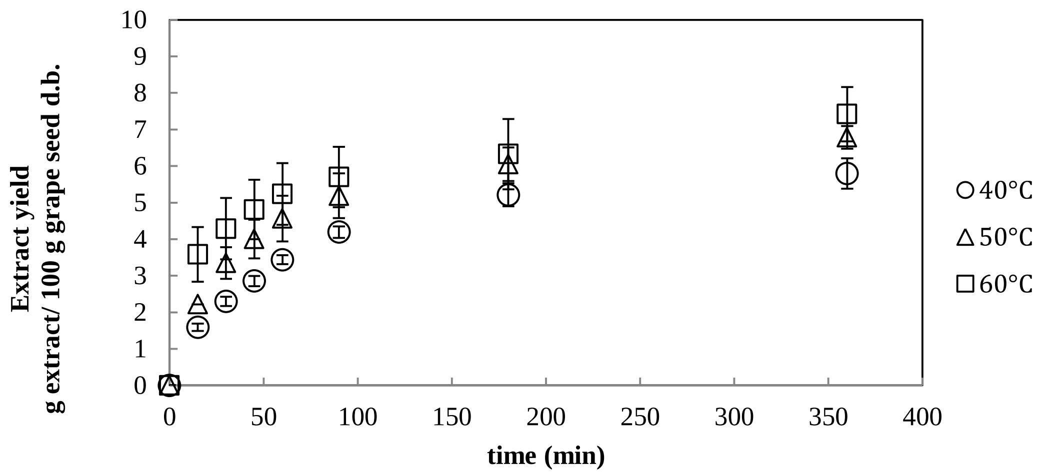

Figure 1. Kinetic extraction curve of grape seed oil obtained by SFE at 45 MPa, and temperature of 40, 50 and 60°C

Figure 2 shows a chromatogram for the supercritical oil obtained at the pressure of 45 MPa, temperature of 50°C and extraction time of 15 min. An identification of the fatty acids was performed by comparison of retention times with a 28 components - standard solution of FAMEs. It was found that linoleic acid, oleic acid, palmitic acid and stearic acid were identified by the chromatographic method, and quantified using a standard calibration curve. Similar chromatograms were obtained for the other conditions.

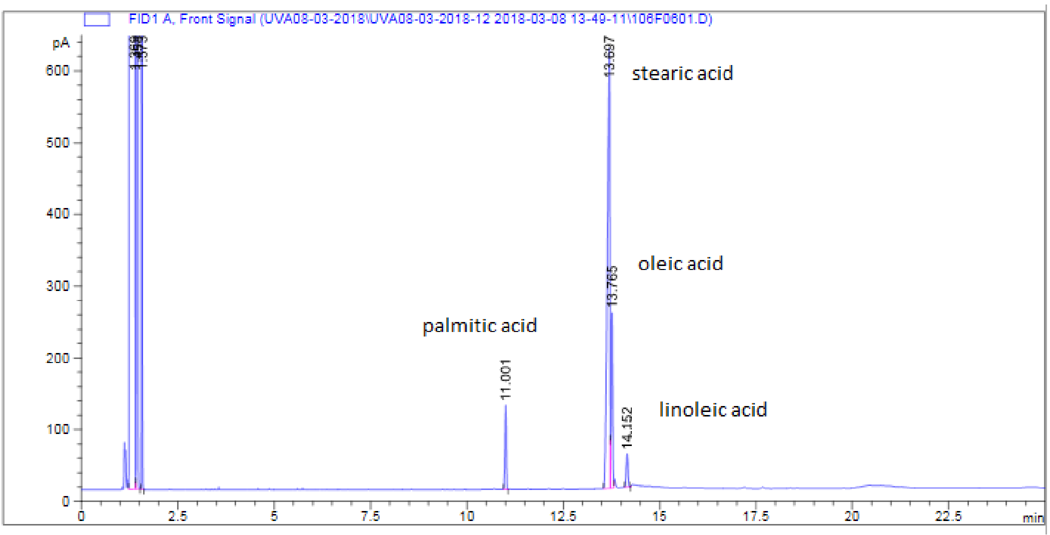

Figure 2. Chromatograms of SFE at 45 MPa, 50°C and extraction time of 15 min

Figure 3 shows the kinetic extraction curve for the fatty acid profile in supercritical extracts: linoleic, oleic, palmitic and stearic acid. The recovery of fatty acids increased with increment of time for all conditions. After extraction time of 90 min, there was no appreciable increment on the fatty acid recovery. The temperature of 50°C resulted on the highest fatty acid content in extract, and the linoleic acid was around the 90% of the total fatty acid content. Similar behavior was found for extraction at 40°C and 60°C. This behavior was also found by Fiori et al., 2014. The fatty acid content in extracts obtained at 60°C presented lowest values. One explanation would be that higher temperatures promote the recovery of additional compounds and promote the degradation of unsaturated fatty acids. If we take into consideration that there is no substantial difference on the extraction yield between 50 and 60°C, we can recommend the supercritical fluid extraction at 50°C led for the recovery of highest unsaturated fatty acid in extract.

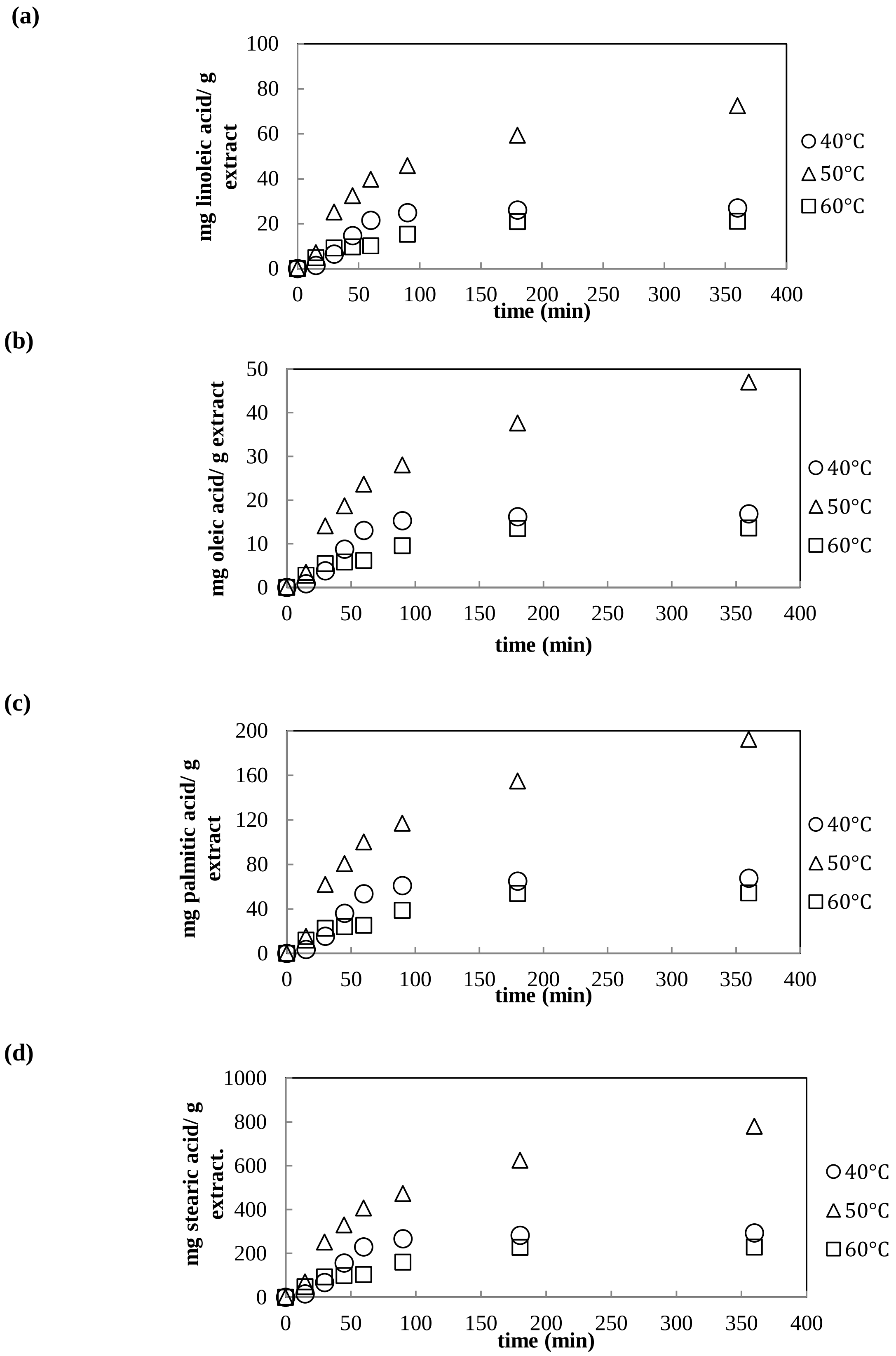

Figure 3. Kinetic extraction profile of a) palmitic acid, b) stearic acid, c) oleic acid and d) linoleic acid obtained by SFE at 45 MPa, 40, 0 and 60°C

4. CONCLUSIONS

In this work, a kinetic study of the supercritical fluid extraction from grape seed was conducted at the pressure of 45 MPa, and temperatures of 40, 50 and 60°C. From the results we can conclude that supercritical fluid extraction at 50°C led in to the highest fatty acid content in extract that can be considered as a potential operating condition when scaling up at 45 MPa.

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