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Short communication

Recovery of grape seed oil by liquid and supercritical carbon dioxide extraction: a comparison with conventional solvent extraction

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Abstract

In this work the extraction of grape seed oil by means of liquid and supercritical carbon dioxide as solvent is described. The operating conditions to determine the maximum extraction yield were studied. The efficiency of supercritical fluid extraction (SFE) was similar to that obtained by conventional liquid extraction, but the quality of the supercritically extracted oil was higher, equivalent to a degummed, liquid-extracted oil. It is considered that SFE is competitive with conventional liquid extraction, because the solvent distillation and oil refining stages can be omitted.

Keywords: Grape seed oil; Liquid/supercritical carbon dioxide extraction; Conventional solvent extraction

1. Introduction

The application of supercritical fluid extraction (SFE), particularly the use of liquid and supercritical carbon dioxide, has received much attention in the food industry in the last few years. This separation technique offers extraction yields comparable with those obtained by conventional extraction methods using organic solvents. Moreover, in contrast with organic solvents, carbon dioxide is non-toxic, non-flammable, non-corrosive, cheap and readily available in large quantities with high purity. Since CO_2 also has a relatively low critical pressure (73.8 atm) and critical temperature (31.1 °C), it can be considered an ideal solvent for the treatment of natural products.

A variety of processes involving extraction with supercritical fluids (SFs) have been developed as promising alternatives to the current separation processes, and industrial applications of SFE using carbon dioxide have increased in the last few years, e.g. the decaffeination of coffee [1,2], the extraction of hops [1,2] and spices [3], etc.

Grape seed is a byproduct of the wine fermentation industry and is generally disposed of by burning, although it is sometimes used for cattle feed. However, grape seed oil has many advantages for human consumption owing to its high level of unsaturated fatty acids [4,5]. In this work we aim to show that it is possible and economically attractive to extract oil from grape seeds by using supercritical carbon dioxide as solvent.

The operating conditions for effective extraction of grape seed oil using liquid and supercritical carbon dioxide have been studied both for the process itself (pressure, temperature and flow rate of solvent) and for the pretreatment of the grape seeds (humidity and size). Finally the physicochemical characterization and fatty acid composition of the supercritically extracted oil are discussed.

2. Materials and methods

The grape seeds (type *airen*) used in this study had previously been treated in the wine fermentation industry with hot water in order to recover all the remaining sugars, since this wash water is normally fermented and distilled to obtain alcohols. As a consequence of the hot water treatment, the total oil content of treated grape seeds is always lower than that of untreated grape seeds [6–10].

The seeds were treated under a range of conditions whereby their grinding size and subsequent drying time were modified. The milling was carried out in a Futurmat model FP coffee mill and the drying in a Heraeus heater at 70 °C. To determine the conditions leading to the optimum extraction yields, a size range of 0.35–2.83 mm and a humidity range of 0.35%–6.50% were studied.

Conventional extraction was carried out using hexane in a Soxhlet apparatus for 20 h (with a fraction grape seed size of 0.75 mm and humidity less than 0.35%) to guarantee the maximum extraction efficiency.

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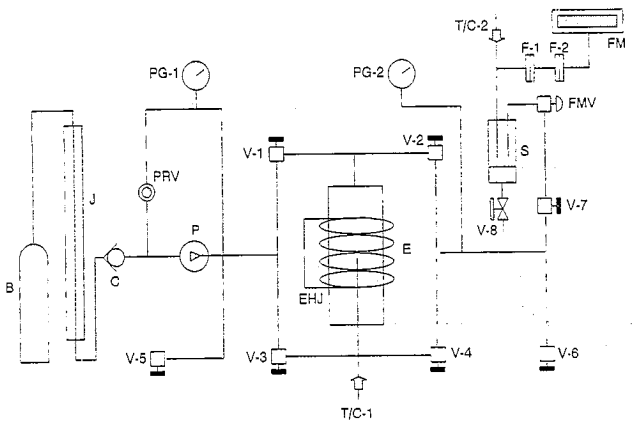

Fig. 1. Schematic diagram of supercritical CO_2 extraction apparatus: B, liquid CO_2 cylinder; J, cooler; C, check valve; P, pump; PRV, pressure regulating valve; E, extraction vessel; S, separator; EHJ, electrical heating jacket; FMV, flow micrometer valve; T/C-1,2, thermocouples; V-1,8, shut-off valves; PG-1,2, pressure gauges; F-1, coalescing filter; F-2, carbon absorption filter; FM, flowmeter.

The flow diagram of the equipment used for supercritical extractions is shown in Fig. 1. Liquid CO_2 was cooled (J) to prevent its gasification and introduced into a pump (P) of 46–460 ml h^{-1} capacity with a cooling head. The extraction vessel (E) was a 75 ml capacity, 316 stainless steel (SS) high pressure cylinder with an electrical heating jacket (EHJ). A sample of about 40 g mass was placed in the extractor vessel. The pressure of the CO_2 cylinder was maintained throughout the system by opening valves V-1, V-2, V-3 and V-4 and closing the other valves (V-5, V-6 and V-7). Before the pump was switched on, valves V-1, V-2, V-3 and V-4 were closed. Then the pump was switched on and its output pressure increased by the pressure regulating valve (PRV) to reach the required processing pressure. Subsequently the compressed CO_2 was introduced into the extractor vessel by opening valves V-3 and V-2. When the desired pressure had been reached by adjusting the pressure regulating valve, the heating jacket was used to reach the processing temperature. When both the desired pressure and temperature had been reached, the extraction was started by opening valve V-7. The flow rate of carbon dioxide through the extractor vessel was regulated by the flow micrometer valve (FMV). The oil dissolved in the supercritical CO_2 was separated from the carbon dioxide and collected in the separator (S) at ambient temperature and pressure. The CO_2 was passed through two filters (F-1 and F-2) to remove the entrained oils and then through an in-line volumetric flowmeter (FM) which controlled the quantity and flow rate of CO_2 used. The flowmeter used was a model FC-70 by EG&G Flow Technology.

The operating condition ranges studied to optimize the extraction processes were: pressure, 50–350 bar; temperature, 10–60 °C; solvent flow rate, 0.5–2.0 l min^{-1} (at standard temperature and pressure (STP)). For liquid extractions at 10 °C the heating jacket was replaced by a brass mantle through which a cooling liquid was passed.

The amount of extracted oil was determined gravimetrically after separation from the solvent. The extraction yield is expressed as the ratio of the amount of extracted oil to the amount of grape seed placed in the extractor vessel.

To characterize the extracted oils, the following parameters were determined: refractive index (refractometer, Atago model 88141), density (densimeter, Paar model DMA 48), viscosity (drop ball viscosimeter, Haake model B/BH), absorption at 290 nm (UV–visible spectrophotometer, Shimadazu model MPS-2000), unsaponifiable and free fatty acid fractions and iodine, peroxide and saponification indices. All these parameters were determined according to the Association of Official and Analytical Chemists' Society procedures [11].

The fatty acid composition of the oils after saponification [12] was determined by gas chromatography (GC). A Hewlett–Packard chromatograph, model 5890, equipped with a flame ionization detector and a Carbowax 20M fused silica capillary column of 0.2 mm internal diameter (i.d.) and 30 m length was used.

The water content (humidity) of the grape seeds was determined using a model MicroKF 2025 Crison titration apparatus by Karl-Fisher.

All products and chemicals employed were "analytical reagent" grade. Commercial grade (99.95%) CO_2 was used.

3. Results and discussion

3.1. Operating conditions for extraction processes

Fig. 2 shows the effect of pressure on the extraction yield of grape seed oil at 10, 40 and 60 °C. Sharp changes in the amount of oil extracted were observed around the critical pressure of carbon dioxide. The changes seem to correspond to changes in the physical properties of CO_2 such as density, which closely relates to its dissolving capacity. At pressures below 150 bar the amount of oil extracted was higher with liquid carbon dioxide, whereas above 150 bar the amount of oil extracted was higher with supercritical carbon dioxide.

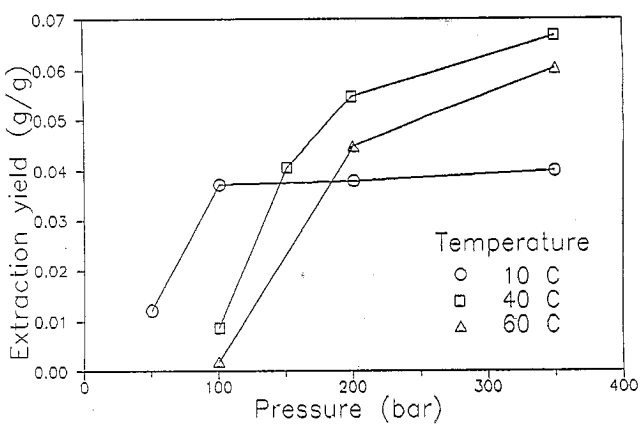

Fig. 2. Effect of pressure on extraction yield of grape seed oil using liquid and supercritical carbon dioxide at three different temperatures (operating conditions: extraction time, 5 h; STP solvent flow rate, 2.0 l min^{-1}; grape seed size, 0.75 mm; drying time, 6.5 h).

Similar results have been reported by other authors working with other seeds [13,14].

From Fig. 2 it can be seen that the best extraction yield is reached at an operating temperature of 40 °C. At this temperature some 90% of the highest oil recovery yield is achieved at 200 bar, much greater pressure being needed to increase the yield significantly. Consequently, 40 °C and 200 bar are considered to be the efficient operating conditions.

Fig. 3 shows the effect of supercritical CO_2 flow rate on the extraction yield at the above temperature but at a considerably higher pressure. The amount of grape seed oil extracted per unit of carbon dioxide used was closely dependent on the flow at rates up to 1.5 l min^{-1}. The yields at flow rates of 1.5 and 2.0 l min^{-1} appeared to be very similar, reaching 96% of their maximum levels within 3 h of operation. Lower solvent flow rates needed longer operating times to reach lower maximum extraction yields. From these figures and taking account of the probable process economics, 1.5 l min^{-1} (at STP) should be considered the minimum efficient supercritical carbon dioxide flow rate.

Fig. 4 shows the effect of grape seed humidity (measured by length of drying time) on the extraction yield. As can be seen in the figure, the extraction yield is not significantly affected by the relative grape seed humidity. The longer the grape seed drying time, the lower is the yield, owing to the evaporation of constituents during the drying process.

Fig. 5 shows the effect of grape seed size on the extraction yield. Milling of the raw materials greatly improved the extraction efficiency, as can be seen in this figure, and the smaller the particle size, the greater is the yield. Therefore the milled grape seed size should be 0.35 mm or smaller for process efficiency. The particle size modification by milling of the physical structure of the grape seed is considered to affect the extraction efficiency by supercritical carbon dioxide very significantly. These results are similar to those for supercritical carbon dioxide extraction from soy bean [13,15] and rice bran [16] but different from wheat germ [14], which can be satisfactorily extracted without any prior milling. The presence of skin with the grape seeds and differences in the location of oil within these seeds are presumed to be responsible for this phenomenon.

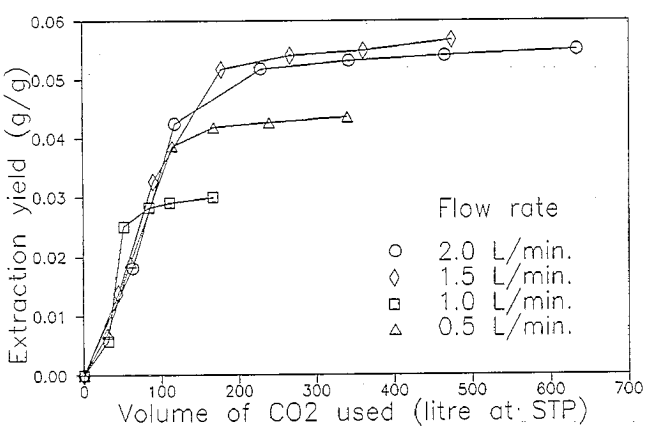

Fig. 3. Effect of supercritical carbon dioxide flow rate on extraction yield of grape seed oil (operating conditions: pressure, 350 bar; temperature, 40 °C; grape seed size, 0.75 mm; drying time, 6.5 h).

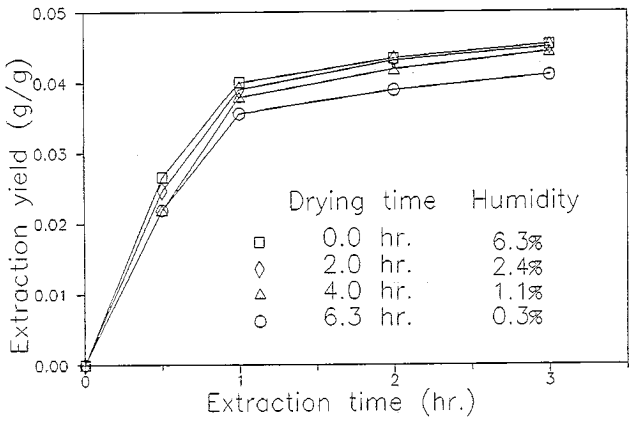

Fig. 4. Effect of grape seed humidity (by drying time) on oil extraction yield (operating conditions: pressure, 350 bar; temperature, 40 °C; STP solvent flow rate, 2.0 l min^{-1}; grape seed size, 0.75 mm).

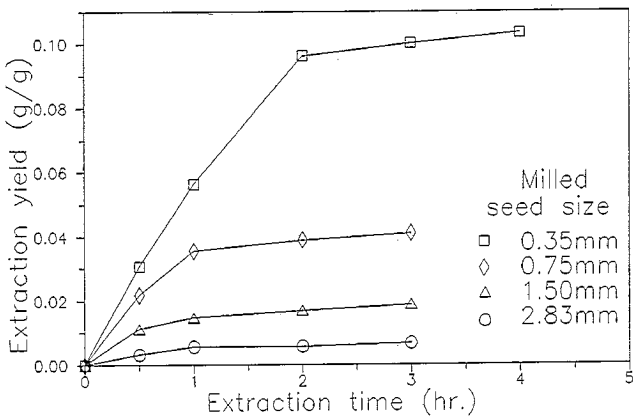

Fig. 5. Effect of grape seed size on oil extraction yield (operating conditions: pressure, 350 bar; temperature, 40 °C; STP solvent flow rate, 2.0 l min^{-1}; drying time, 6.5 h).

Table 1
Comparison of edible oil extraction yields obtained using hexane and supercritical carbon dioxide for various vegetable seeds

Seed	Yield (wt.%)	
	SFE using CO_2	Extraction using hexane
Grape seed (this work)	6.9	7.5
Wheat germ [14]	9.6	10.1
Soy bean [15]	19.9	20.0
Rice bran [16]	22.0	23.0
Soy bean [13]	16.4	19.9
Sunflower seed [13]	36.0	38.4
Grape seed [13]	39.3	40.1

3.2. Characterization of extracted oils

Table 1 gives a comparison of the SFE and conventional hexane extraction yields from grape seeds together with similar yield comparisons for other types of seeds. The following were the operating conditions for the SFE process: pressure,

Table 2
Comparison of properties of extracted grape seed oils obtained using hexane and supercritical carbon dioxide

Physicochemical parameter	Extraction method		Standard for refined oil [17]
	CO_2, 350 bar, 40 °C, 3 h	Hexane, Soxhlet, 20 h	
Refractive index	1.475	1.474	1.473–1.475 (25 °C)
Density (g ml^{-1})	0.924	0.928	
Viscosity (cP)	69	66	
Absorbance at 290 nm (IgE)	2.730	3.177	
Free fatty acid (%)	3.4	33.8	⩽0.2 (oleic acid)
Iodine index (g per 100 g)	98	124	125–150
Saponification index	259	289	185–196
Unsaponifiable fraction (%)	0.27	2.89	
Peroxide index (meq per kg)	383	101	⩽10

Table 3
Fatty acid composition of oil extracted using hexane and supercritical carbon dioxide

Oil	Fatty acid composition (%)					
	Palmitic C16:0	Palmitoleic C16:1	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3
Hexane, Soxhlet, 20 h	8.12	0.15	5.60	19.59	66.16	0.37
CO_2, 350 bar, 40 °C, 3 h	8.03	0.15	5.07	19.06	67.39	0.30
Refined oil [17]	5–10	⩽1.2	3–5	12–26	58–77	⩽1

350 bar; temperature, 40 °C; solvent flow rate at STP, 2.0 l min^{-1}; extraction time, 3 h, milled seed size, 0.75 mm; seed humidity, 0.35%.

The best SFE yield for grape seeds was 6.9%, some 92% of the best hexane extraction yield of 7.5%. Similar results have been found by other authors for other vegetable oils [13–16]. In all extractions the yield was higher for extraction by hexane irrespective of the physical nature of the seeds. This is due to the fact that hexane, unlike carbon dioxide, is non-selective for triglycerides, extracting free fatty acids, phospholipids, pigments and unsaponifiable substances together with triglycerides. Hence the amount of matter yielded by using organic solvents will be always higher than that by using supercritical fluids [13–16].

In Table 2 the properties of the grape seed oil extracted by SFE using carbon dioxide (at the selected operating conditions) and by conventional extraction using hexane are given. The oils are not significantly different when the main physicochemical parameters are considered, but saponification, peroxide and iodine indices show a high concentration of triglycerides in the oil extracted by SFE owing to the higher selectivity of the supercritical solvent.

The main differences between oils are related to the free fatty acid concentration and the unsaponifiable fraction, whose values are much lower for carbon-dioxide-extracted oil than for hexane-extracted oil. Considering both the physical nature of grape seeds and the characteristics of the two extractive processes, these differences could be due to the following reasons.

(1) Supercritical carbon dioxide is selective for triglycerides and does not extract the free fatty acids in the grape seed.

(2) The grape seeds used as raw material were previously washed in hot water. The high temperature involved in this process leads to an increase in the free fatty acids in the grape seeds, because triglycerides break down into fatty acids. Hence the amount of free fatty acids in the washed grape seeds was higher and that of triglycerides lower than in the unwashed seeds. For this reason the SFE yield for the washed grape seeds is always slightly lower than that for the unwashed seeds and the acidity of the hexane-extracted oil is higher than that of the oil extracted by SFE. These effects have also been reported by other authors [6–10].

(3) The operating temperatures of the two extraction processes were significantly different: 40 °C for SFE and 69 °C for hexane extraction using a Soxhlet apparatus. The higher temperature of hexane extraction resulted in considerable free fatty acid formation from triglycerides during extraction, which was not the case with SFE.

When free fatty acids were removed from both oils, both the iodine and saponification indices showed similar amounts of triglycerides. Grape seeds were totally extracted by supercritical carbon dioxide over 3 h. The low value of the unsaponifiable fraction shows that the supercritical carbon dioxide, being more highly selective, extracts only a minimal fraction of unsaponifiable compounds.

Finally, on the basis of the characteristics and composition of the oil described, the supercritical carbon dioxide extraction process is simpler than the conventional extraction pro-

Table 4
Fatty acid composition of oil extracted using supercritical carbon dioxide according to extraction time of process

Time (min)	Fatty acid composition (%)					
	Palmitic C16:0	Palmitoleic C16:1	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3
30	10.52	0.22	5.32	27.60	56.34	
60	9.94	0.19	6.15	26.53	56.84	0.36
120	7.86	0.12	7.54	24.00	60.22	0.34
180	8.03	0.15	5.07	19.06	67.39	0.30

cess, because the final refining stage of edible oil processing can be omitted [14–16].

3.3. Fatty acid composition of extracted oils

As can be seen in Table 3, there were no significant differences between the oils extracted by supercritical carbon dioxide and by hexane. However, as can be seen in Table 4, in which the fatty acid composition of grape seed oil extracted by supercritical carbon dioxide at 30, 60, 120 and 180 min is given, SFE causes a fractionation of the oil by depressurization, which permits the production of various grades of oil with different fatty acid contents.

4. Conclusions

As detailed in the above discussion, the following conclusions have been reached.

Supercritical carbon dioxide gives higher extraction yields than liquid carbon dioxide. The efficient operating conditions proposed for the carbon dioxide SFE of grape seed oil are: pressure, 200 bar; temperature, 40 °C; solvent flow rate, 1.5 l min^{-1} (at STP); milled seed size, 0.35 mm; initial humidity of seed, 0%–6.5%; process time, 2 h.

Under these operating conditions, SFE yields are similar to those of conventional extraction with hexane. Since the oil extracted by SFE is solvent free, the distillation process to recover solvent, which is necessary in conventional extraction, is not needed.

The quality of grape seed oil extracted by SFE is similar to that of oil extracted by organic solvent and then refined. Consequently, the refining process is not needed with SFE.

It is considered that, in spite of the high operating costs, SFE of grape seed oil could be more economical than conventional liquid extraction, because the last two stages of oil refining and solvent distillation, which consume most of the energy, can be eliminated. An industrial scale plant design and costing comparison are required to confirm this last conclusion.

Acknowledgments

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