Lampante Olive Oil Refining with Supercritical Carbon Dioxide

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Lampante olive oil has been treated in a supercritical CO_2 extraction plant operating in a continuous countercurrent mode. We report the results of a systematic investigation to define the optimal operative parameters. We also have examined the compositional variation of lampante olive oil samples with different characteristics and of different geographic origins before and after refining at optimal conditions. Although practical feasibility of the proposed procedure can be questioned, the results demonstrate the possibility of fractionating components contained in the starting oil even if present at trace levels.

KEY WORDS: Carbon dioxide, countercurrent column, fractionation, liquid liquid extraction, olive oil, refining, supercritical fluids.

The use of supercritical fluids, carbon dioxide in particular, for production of foodstuffs has been studied throughout the world for over ten years. For fatty substances, many examples exist of seed oil extraction (1–5), extraction of olives in their natural or dehydrated states (6), fractionation of glycerides in castor oil as described by Stahl in his classic experiments (7), or the fractionation of Karitè butter (*Butirrospermum parkji*) (8). Supercritical fluids also have been used for the preparation of concentrates of ethyl esters from fish oil with a high level of fatty acids of nutritional interest (9), as well as for trial preparations of animal fat fractions with low cholesterol levels (10).

In the field of vegetable oil refining, with particular reference to the separation of fatty acids from triglycerides with a simultaneous improvement of organoleptic characteristics, there are patents (11,12) and publications (13,14) that demonstrate the feasibility of the process. We have recently carried out an experiment which, notwithstanding the limitations connected with the use of batch equipment of modest dimensions and flexibility, confirmed the validity of this idea (15).

Lampante oil is a cold-pressed oil with more than 4% free fatty acid (FFA) and an unpleasant flavor, which is sold only after refining. The reason for the choice of lampante oil as a starting material for our trials was based upon the following considerations: i) Approximately 50% of the cold-pressed Italian olive oil is unsuitable for immediate consumption and must be refined (16) due to the presence of excessive levels of free acid, taste defects or contamination with volatile organic substances; ii) notwithstanding the need for refining, lampante olive oil has a market value three to four times higher than that of seed oil. This value differential allows us to consider applying a supercritical CO_2 refining method to olive oil, but we must remember that such methods are generally more capital-intensive than the more traditional methods.

EXPERIMENTAL PROCEDURES

Materials. The oil samples used came from Italian industrial sources. Specifically, for trials relative to research towards optimal processing conditions, we used a Spanish oil with a free acidity level of 6.3%, expressed in terms of oleic acid. For the subsequent trials (designed to characterize the oils obtained) three other samples of Italian, Spanish and Tunisian origin were used. Their acidities were 1.73%, 3.38% and 3.93%, respectively (in terms of oleic acid).

Extraction equipment. The pilot plant, designed and constructed by Muller Extract Co. GmBH (Coburg, Germany) is shown schematically in Figure 1. The column consists of three sections (A,C,E) joined by intermediate segments and is packed with Sulzer mod. EX packing material. The column is 3 m high and has an internal diameter of 30 mm. Each section of the plant has thermostated water jackets. Because the three sections are independent, it is possible to create different temperatures along the length of the column. The high-pressure pump (P1) transfers the supercritical fluid at the desired pressure to the lower part of the column. The flux of supercritical CO_2 is therefore directed from the bottom to the top of the column. The crude liquid process material is injected in the middle of the column (section C) by means of a high-pressure volumetric pump (P2) and follows a descending course. The top product (extracted by supercritical fluid) passes through a pressure reduction valve (VR), then through the heat exchanger (H1) and reaches the separator (S), which is maintained at a pressure of 50 bar and a temperature of 40°C. The liquid carbon dioxide is then separated from the extracted product by evaporation, condensed in the condenser (H2), sent to the holding tank (L) and held prior to recirculation.

Methods of analysis. Method NGD C 42-1976 (17) was used for UV spectrophotometric analysis. Free fatty acid analysis was carried out by method NGD C 10-1976 (17). Partial glyceridic forms were determined by the gas liquid chromatography (GLC) method proposed by Mariani *et al.* (18). Minor nonglyceridic components were analyzed by the method of Grob *et al.* (19).

RESULTS

The first phase of our research was a systematic study to define the optimal conditions of temperature, pressure and flux ratio that would maximize the deacidification of lampante olive oil, while optimizing the yield at the same time.

To evaluate the samples prepared during this phase of the research, we took three different parameters into consideration: i) The free fatty acid content in the processed oil with particular reference to its final absolute value; ii) the yield in the refined product; and iii) the free fatty acid content of the extract.

The finished product must be in compliance with Italian and European Economic Community (EEC) laws, which allow the sale of refined olive oil only if its FFA content is lower than 1.5%. However, because pure olive oil for the U.S. market is a mixture of virgin and refined olive oil, and virgin oil generally used for these purposes normally contains 3% FFA, we decided to accept only samples with less than 1% FFA (as oleic acid) as suitable for use.

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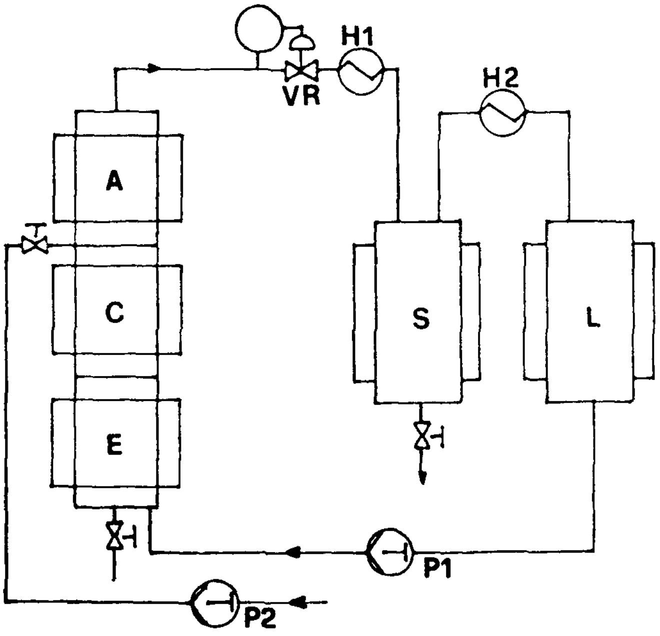

FIG. 1. Flow sheet of supercritical CO_2 extraction plant. A,C,E = column sections; P1 = CO_2 high-pressure pump; P2 = oil high-pressure volumetric pump; VR = pressure reduction valve; H1 = heat exchanger; S = separator; H2 = condenser; L = holding tank.

TABLE 1

Influence of Pressure on Fatty Acids/Triglyceride Separation[a]

P (bar)	Refined oil yield (%)	FFA in refined oil[b]	FFA in extract[b]
80	99.3	6.00	35.22
90	94.7	5.01	27.47
110	93.8	3.57	46.06
130	84.8	0.70	36.88
140	71.7	2.20	16.33
150	68.7	2.07	15.26

[a] T = 40°C, Flux ratio = 100 kg CO_2/kg oil. FFA in starting material 6.3% as oleic acid.

[b] As oleic acid %.

TABLE 2

Influence of Temperature on Fatty Acids/Triglyceride Separation[a]

T (°C)	Refined oil yield (%)	FFA in refined oil[b]	FFA in extract[b]
40	84.8	0.70	36.88
60	94.8	4.11	44.42

[a] P = 130 Bar, flux ratio = 100 kg CO_2/kg oil. FFA in starting material 6.3%) (as oleic acid %).

[b] As oleic acid %.

TABLE 3

Influence of CO_2/Oil Flux Ratio on Fatty Acids/Triglyceride Separation[a]

Flux ratio (kg CO_2/kg oil)	Refined oil yield (%)	FFA in refined oil[b]	FFA in extract[b]
10	85.5	5.08	12.78
20	91.9	4.34	27.30
30	89.5	4.34	22.05
40	88.7	3.97	23.72
50	90.6	3.60	31.30
60	88.9	2.91	32.52
70	80.6	1.55	25.52
80	87.5	1.49	39.18
90	85.8	1.12	36.92
100	84.8	0.68	36.98
150	77.9	0.62	25.87
170	77.3	0.50	25.62

[a] P = 130 Bar, T = 40°C. FFA in starting material 6.3% (as oleic acid %).

[b] As oleic acid %.

TABLE 4

Influence of Injection Site on Fatty Acids/Triglyceride Separation[a]

Injection site	Refined oil yield (%)	FFA in refined oil[b]	FFA in extract[b]
Middle	84.8	0.70	36.88
Top	80.4	1.30	25.27
Bottom	83.5	1.82	28.43

[a] P = 130 Bar, T = 40°C, flux ratio = 100 kg CO_2/kg oil. FFA in starting material 6.3% (as oleic acid %).

[b] As oleic acid %.

TABLE 5

Temperature Gradient Tests[a]

Temperature gradient[c]	Refined oil yield (%)	FFA in refined oil[b]	FFA in extract[b]
40/40/40	84.8	0.70	36.88
50/40/30	89.8	0.80	54.60
60/50/40	92.8	3.42	43.75
70/60/50	96.9	5.23	37.45

[a] P = 130 Bar, T = 40°C, flux ratio = 100 kg CO_2/kg oil. FFA in starting material 6.3% (as oleic acid).

[b] As oleic acid %.

[c] Temperature of different section in °C (top/middle/bottom).

Influence of pressure. In the first series of trials we investigated the effect of pressure at a constant temperature of 40°C with a flux ratio of 100 kg CO_2/kg oil. Table 1 shows that for pressures below 130 bar satisfactory reduction of acidity was not attained. The FFA content of the extract reached a maximum at 110 bar and decreased at higher pressures. By increasing the pressure we increase the solvent power of the supercritical fluid with an evident reduction in the yield of refined oil. Thus, only the test carried out at 130 bar gives a refined oil that is suitable for use.

Influence of temperature. Another point requiring investigation regarded the influence of temperature on extraction behavior. For results obtained when a sample was treated at P = 130 bar with a flux ratio of 100 kg CO_2/kg oil, Table 2 shows that an increase of 20°C seriously com-

TABLE 6

Olive Lamp Oil Refining—Composition Differences Between Crude and Refined Oil[a]

	Sample A (Italy)		Sample B (Spain)		Sample C (Tunis)	
	Crude	Refined	Crude	Refined	Crude	Refined
FFA (%)	1.73	0.20	3.38	0.38	3.93	0.92
Monoglycerides (%)	0.04	0.03	0.05	0.05	0.06	0.03
Diglycerides (%)	2.90	2.22	4.22	3.17	4.52	3.97
Squalene (ppm)	5200	400	2500	<200	3200	<200
Aliphatic alcohol (ppm)	76.1	12.1	88.7	23.2	80.4	22.7
Tocopherol (ppm)	n.d.[b]	n.d.	144	57	43	15
Free sterols (ppm)	1104	811	1545	1185	1096	887
Free terpenes (ppm)	819	611	948	726	848	706
Waxes (ppm)	150	132	233	193	323	280
Sterol esters (ppm)	632	787	1081	1244	1117	1248
Terpene esters (ppm)	514	601	749	798	723	736

[a] P = 130 Bar, flux ratio = 100 kg CO_2/kg oil, temperature gradient 50/40/30°C (top/middle/bottom).
[b] n.d., Not determined.

TABLE 7

Observed Enrichment Ratios Expressed as Concentration Extract/Refined Ratios (average of calculated values)

Squalene	168
Fatty acids	85
Free aliphatic alcohols	60
Monoglycerides	22
Free terpenes	10
α-Tocopherol	9
Free sterols	7
Diglycerides	4
Waxes	2
Sterol esters	0.4
Terpene esters	0.2

promised the outcome of the processing. We could have avoided the decrease in density of the supercritical fluid due to the temperature increase to 60°C by increasing the pressure in a parallel manner, but that would not be economical.

Influence of flux ratio of CO_2/oil. In this series of tests, all carried out at set conditions of pressure and temperature, we investigated the influence of the flux ratio on the final product. Table 3 shows that, for flux ratios higher than 100 kg CO_2/kg oil, we obtain the desired reduction of acidity, while the FFA content in the extract reaches a maximum at a flux ratio of 80 kg CO_2/kg oil. The yield of refined product remains acceptable. The situation tends to improve for values higher than 80 kg CO_2/kg oil, reaching a balance between yield, reduction of acidity in the product and acidity of the extract at a flux ratio of 100 kg CO_2/kg oil. This indicates that values higher than this flux ratio cause only a limited increase of fatty acid removal and a notable reduction in yield.

Influence of injection point. The pilot plant used in this study allowed us to inject the crude oil at any of three different points along the length of the extraction column. Therefore, we investigated the dependence of yield and purity of the finished product upon injection at the middle or the top of the column. We also tried to inject the oil at the bottom of the column but, as expected, we obtained modest results, as shown in Table 4. Injection of the oil in the middle part of the column gives a refined product of lower acidity and results in higher FFA content in the extract, while the yield of refined oil remains more or less constant.

Temperature gradients. In the final test we investigated whether it would be possible to increase process performance by introducing a temperature gradient along the length of the column. Data reported in Table 5 compare the results from tests with three gradient combinations to data obtained isothermally with all three sections held at 40°C. The gradient, in which the top, middle and bottom sections were held at 50, 40 and 30°C, respectively, gave a product of nearly identical acidity when compared to that of the isothermal run but in larger yield. The FFA content in the extract also is increased, allowing us to reduce refining losses.

Characteristics of the refined product. Once we had unequivocally established the optimal conditions for the proposed procedure, we began to study the characteristics of the resulting products, with particular reference to product distribution of the different components, both major and minor. For this purpose we took three different samples of lampante olive oil from different sources with different grades of acidity, and refined them under optimal conditions, *i.e.*, P = 130 bar, temperature gradient 50/40/30°C (top/middle/bottom), and a flux ratio of 100 kg CO_2/kg oil. Table 6 shows the compositional characteristics of the three crude oils and of the corresponding refined products.

DISCUSSION

As is apparent from the results reported above, by variation of parameters such as pressure, temperature and flux ratio, it is possible to obtain fraction that are different from the standpoint of product quality and yield. Of particular interest are the results obtained from varying the injection point where we demonstrate the efficacy of dedicating a part of the extraction column to washing of the extract to minimize the loss of neutral oil. Also of interest is the temperature gradient study. In the most favorable case, where the 50/40/30°C gradient was used, the conditions of major solvent power are met in the central portion of the column (40°C), while the stripping area processes at 50°C. Next to the exit of the refined oil the process is active at near-subcritical conditions.

TABLE 8

Main Triglycerides Composition (expressed as percent area)

	Sample A			Sample B			Sample C		
	Crude oil	Extract	Refined oil	Crude oil	extract	Refined oil	Crude oil	Extract	Refined oil
C_{50}	3.5	6.9	3.4	9.9	14.2	9.7	4.5	11.2	4.4
C_{52}	29.7	37.8	28.7	41.8	44.4	41.7	31.7	45.3	31.6
C_{54}	66.9	55.4	67.9	48.4	41.2	48.6	63.8	43.5	64.8

TABLE 9

UV Absorption Analysis, Comparison Between the Characteristics of Crude and Refined Oils

	Sample A[a]		Sample B[a]		Sample C[a]	
	Crude	Refined	Crude	Refined	Crude	Refined
K_{232}	3.547	2.744	4.098	3.222	3.881	3.348
K_{270}	0.321	0.237	0.272	0.237	0.319	0.231
Delta K	0.014	0.011	0.010	0.011	0.018	0.016

[a] Samples prepared by gradient temperature solution 50/40/30°C, P = 130 bar, flux ratio = 100 kg CO_2/kg oil.

Data obtained were used to calculate the average concentration ratios in the extract and the refined product for several minor components present in the crude oil. The results (Table 7) allow us to formulate some hypotheses concerning the selectivity and solvent power of supercritical carbon dioxide at the conditions stated above. For example, comparing the obtained values for squalene and fatty acids, even though of greater molecular weight and lower volatility, squalene is particularly concentrated in the extract, possibly due to its hydrocarbon nature. The fatty acids, in turn, are extracted preferentially when compared to the triglycerides, even though they possess a higher polarity, because they have an higher vapor pressure. Under the conditions used, the vapor pressure is greater by some orders of magnitude. Under these experimental conditions we also have verified the selective extraction of triglycerides of lower molecular weight, as indicated by the differences in composition of the main triglycerides present in the extract and in the refined oil as compared to those of the crude oil (Table 8). The refined oils obtained have composition characteristics similar to those oils prepared in the conventional way.

Finally, UV absorption data (Table 9) indicate a reduction of the absorption coefficient for refined oils relative to the crude. This is probably due to the extraction of minor components, such as phenol and carotenes, during the extraction process.

This contribution presents an alternative method for the preparation of refined olive oil that has been freed of all its negative characteristics while maintaining the absolute integrity of its natural components. High production costs might discourage application of this procedure for the production of pure olive oil, but we believe that such costs may not rule out the market possibility of a product that, for its intrinsic characteristics, has an image of high quality, even though it possesses characteristics similar to conventionally refined oil.

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