Influence of Operating Variables on Yield and Quality Parameters of Olive Husk Oil Extracted with Supercritical Carbon Dioxide

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ABSTRACT: Supercritical fluid extraction is a viable alternative process for extracting oil from olive husk, a residue obtained in the olive oil production. We analyzed the effects of pressure (P) (100–300 bar), temperature (T) (40–60°C), solvent flow (1–1.5 L/min), and particle size (D) (0.30–0.55 mm) on extraction yield, and three oil-quality parameters: acidity (OA), PV, and phosphorus content (PC). A response surface methodology based on the statistical analysis of the experimental data permitted us to obtain mathematical expressions relating the operational variables and parameters studied. At the best extraction condition of the experimental range analyzed ($P = 300$ bar, $T = 60°C$, $D = 0.30$ mm, and solvent flow = 1.25 L/min at standard conditions), the oil yield was 80% (w/w) with respect to hexane extraction, whereas the quality parameters OA, PV, and PC were 14% (w/w), 8 meq/kg, and $2.3 \cdot 10^{-3}$% (w/w), respectively. These results were compared to those obtained by hexane Soxhlet extraction. The quality of the supercritical extract was superior, requiring only simple refining. This advantage may result in improved economics of the supercritical process in relation to the conventional extraction with hexane.

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KEY WORDS: Carbon dioxide, olive husk, olive oil, quality parameters, response surface methodology, supercritical extraction.

Olive husk is a residue obtained from the industrial process for olive oil production. Its main constituents are water, oil, olive peel, and kernels. Crude olive husk oil is obtained by treating olive husk with organic solvents, usually hexane. The industrial process consists of different successive steps such as drying, grinding, extraction, and distillation of the solvent. This process causes several problems: the use of organic solvents (toxic, expensive, generate residues, and have low selectivity) and the necessity of recovering the solvent, an energy-intensive operation. Furthermore, the crude husk oil obtained in this process must be refined to be in accordance with the values established by food normatives for quality (1). This refining step is expensive, and thermal degradation and loss of valuable compounds usually result (2).

The main advantages of supercritical fluids over classical solvent extraction agents are that their high diffusivity, low viscosity, and low surface tension can favor mass transfer phenomena, and that solute solubilities may be modified by altering pressure and/or temperature. The use of supercritical CO_2 as a solvent in the food industry has advantages over other solvents because CO_2 is nontoxic, nonflammable, noncorrosive, inexpensive, and readily available in large quantities. In addition, owing to its relatively low critical pressure (73 bar) and critical temperature (31.1°C), CO_2 is easy to handle as a solvent and easily removed from solutes with low energetic input (3).

Taking into account these advantages in quality and selectivity, supercritical fluid extraction (SFE) has been applied to the extraction and refining of vegetable oils, producing extracts with lower contents of phospholipids and metals, higher tocopherol content, lighter color, and better flavor (2,3). Moreover, FFA are obtained in the initial stages of extraction, whereas phospholipids are recovered at the final stages. Selectivity between TG and waxes has also been achieved for substances with high levels of fatty materials (3,4).

In the case of olive oil, little has been reported in the literature. Brunner and Simoes (5) applied SFE to continuous countercurrent extraction of virgin olive oil. Nunes da Ponte and Gonçalvez (6) reduced the FFA content of olive husk oil by applying SFE to olive husk flakes and to olive husk oil previously extracted with hexane. Esquivel and Bernardo-Gil (7) studied olive husk extraction rates and acidities of the extracts at pressures from 10 to 18 MPa and temperatures from 40 to 60ºC. Lucas *et al.* (8) and Gracia (9) determined the effects of pressure, temperature, and other variables such as solvent flow and particle diameter on extraction yield. These earlier works, however, lack information about the effects of operation variables on the olive oil quality parameters established by the European Community normative for human consumption (10).

To eliminate the possibility of confusing olive oil with mixtures of pomace and seed oils, the European Community has promulgated Regulation 2568/91. In this regulation (10), classification of olive oils based on strict limits related to quality and purity, defined as *parameters*, is also established (10). Among others, the following parameters and their analytical methods are specified in this regulation: volatile matter, acidity, PV, UV absorption, trace metals, and phosphorous content.

In this work we studied the supercritical CO_2 extraction of olive husk oil. The aim was to determine the effects on extraction yield and oil quality of some operational variables such as pressure, temperature, solvent flow, and particle size.

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This information will be necessary to evaluate SFE as an alternative extraction process and for further scaleup steps.

EXPERIMENTAL PROCEDURES

Materials. Olive husk, provided by Aceites Pina Bajo Aragón, S.A. (Villarta de S. Juan, C. Real, Spain), was milled and dried to a final moisture content of 6% (w/w). The dried husk was sieved to obtain several size fractions with average diameters, 0.108, 0.175, 0.240, 0.300, 0.425, 0.550, 0.610, 0.845, 1.500, and over 2.000 mm. These fractions were frozen and stored in N_2 atmosphere. Liquid CO_2 (purity 99.5%) was supplied by Carburos Metalicos S.A. (Madrid, Spain).

Apparatus and extraction procedure. The flow diagram of the extraction equipment is shown in Figure 1 and has been previously described (11). Liquid CO_2 was provided from a steel cylinder. After cooling and filtering, the CO_2 was compressed by using a positive displacement HPLC pump. The pressure was regulated by a back-pressure regulator and checked by using a manometer. The compressed fluid was passed from the bottom through a vertically mounted extractor. The extractor was a 75-mL stainless-steel cylinder (17.48 mm i.d. × 304.8 mm). To keep the extractor at the desired temperature, a digital controller regulated the electric current through a resistor that surrounded the extractor cylinder. The temperature in the extractor was displayed. The oil-laden gas from the extractor was passed through a heated metering valve where the supercritical CO_2 was depressurized, and the extracted oil was collected in a cooled receiver at 0ºC. The gas flow through the extractor was measured by a turbine flow meter and totaled by a digital flow computer. The extractions were run on 25-g olive husk samples, which were placed in the extractor between two layers of glass wool to prevent loss of small particles. The experiments were accomplished in 2.5 h because longer extraction times did not significantly increase oil yield.

Soxhlet extractions. To compare the supercritical extracts to those obtained with hexane, samples of 25 g of olive husk flakes were extracted in a 250-mL Soxhlet apparatus with analytical-grade hexane (Panreac, Montplet & Esteban, S.A., Barcelona, Spain) for 2.5 h, using the industrial particle-size distribution of 0.55 mm average diameter. After extraction, the solvent was evaporated and the oil content was determined gravimetrically. The residual hexane content in the extract was less than 1 mg/kg, determined according to European normative (10), corresponding to AOCS Official Method of Analysis Ca 3b-87 (11).

Analyses. The quality parameters of the oil were determined according to standard methods specified in European Commission Regulation 2568/91 (10), in accordance with the AOCS Official Methods of Analysis.

RESULTS AND DISCUSSION

Response surface methodology (RSM) (13) is commonly used in the study of empirical relationships between measured responses and independent variables (also called factors), minimizing experimentation and leading to correlations that can be used for optimization purposes. The responses studied in this work were oil yield (*Y*), defined as the weight percentage of oil extracted at supercritical conditions with respect to that obtained by hexane Soxhlet extraction, and three quality parameters included in the normative: oil acidity (OA), PV, and phosphorus content (PC).

The operation variables selected were pressure, temperature, solvent flow, and particle size. The levels of each factor are indicated in Table 1. Pressure ranges were determined, taking into account that pressures below 100 bar lead to low extraction rates, whereas over 300 bar compression costs become uneconomical. Temperature levels were selected over the critical temperature of the solvent (31.1ºC) but excluding temperatures over 60ºC to avoid oxidative degradation of the extracts. The 0.55 mm particle size was chosen as the upper limit value because it is approximately the mean diameter employed in the industrial hexane extraction process. Since oil

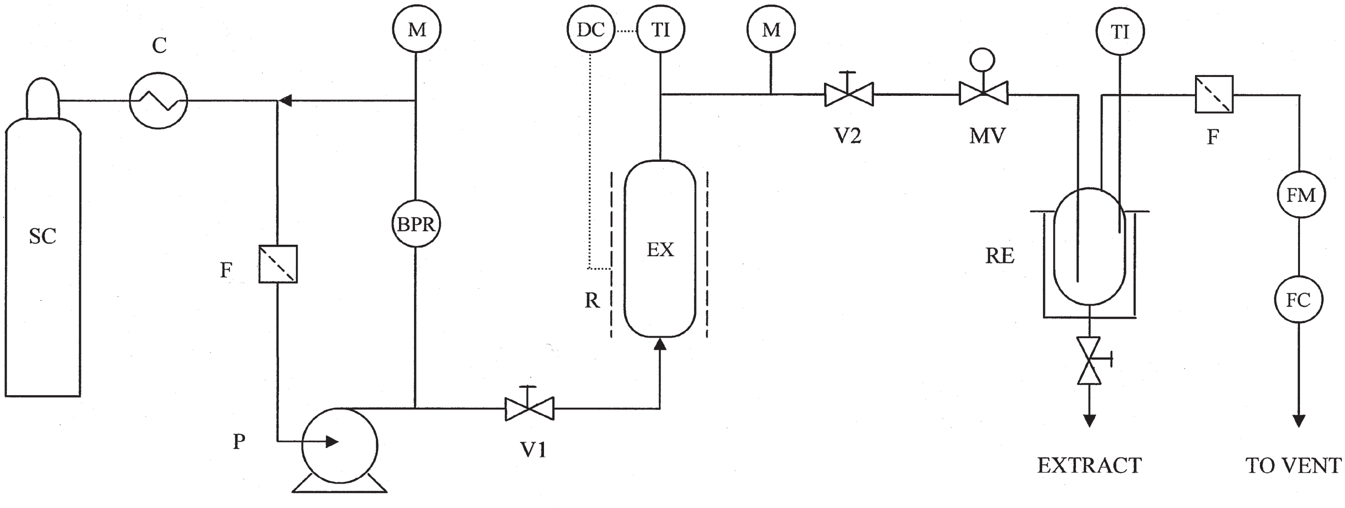

FIG. 1. Extraction apparatus. Steel cylinder (SC), cooler (C), filter (F), pump (P), back-pressure regulator (BPR), manometer (M), extractor (EX), digital controller (DC), resistor (R), temperature indicator (TI), metering valve (MV), receiver (RE), flow meter (FM), flow computer (FC).

TABLE 1
Levels of Factors

Factor	Lower level (–1)	Higher level (+1)
Temperature, *T* (°C)	40	60
Pressure, *P* (bar)	100	300
CO_2 flow, *Q* (L/min)	1.0	1.5
Particle diameter, *D* (mm)	0.30	0.55

yield increases with increasing particle diameter (14), we set the lower value at 0.30 mm. Smaller particle sizes were discarded to avoid particle agglomeration and losses of the oil when sieving. The solvent flow range was set, taking into account that CO_2 flows lower than 1 L/min (at standard conditions) produce very low yields (15), whereas above 1.5 L/min dragging or channeling situations can be produced.

For direct comparison of each variable, the independent variables were normalized in the range −1 to +1 according to:

$$x_i = 2\,(X_i - X_{\min})/(X_{\max} - X_{\min}) - 1 \qquad [1]$$

where x_i is the normalized value of variable X at condition i, X_i is the dimensional value, and $X_{\min}$ and $X_{\max}$ represent the dimensional inferior and superior limits, respectively.

The first step of RSM analysis consisted of a full-factorial 2^4 experimental design to which two central points were added in order to evaluate the curvature effect. The standard experimentation matrix is shown in Table 2. Columns 3 to 6 give the ±1 coded variable levels in the dimensionless coordinate, and columns 7 to 10 give the dimensional variable levels. Experiments were run at random. Column 2 indicates the number of the replications performed in each experiment to obtain significant oil quantity for the required analyses according to the European normative (10). Table 2 also shows the experimental values obtained for the selected responses.

A statistical analysis using these results and the commercial software Statgraphics 5.0 (Manugistics, Inc., Rockville, MD) was performed. The analysis of the main effects and interactions for the chosen responses, together with the curvature check results, are shown in Table 3. The test of statistical significance, *P* value, was determined according to the total error criteria considering a confidence level of 95%. The influence of a factor will be significant if the value of critical level (*P*) is lower than 0.05; parameters for *P* values over 0.05 are discarded as meaningless (13).

Table 3 shows that there was significant curvature in the responses for *Y* and OA. For these parameters, it was therefore necessary to consider a different design, which allowed us to fit the experimental data to a second-order model including quadratic terms in the mathematical correlations. On the other hand, those curvature effects were not significant for responses in PV and PC (Table 3). This result indicated the validity of the pure factorial design in the experimental range analyzed.

For PV, data from Table 3 show the only significant influence of pressure (*P*) and the pressure–temperature (PT) interactions. Fitting the data to a first-order model gave the following relationship, where the independent variables were codified:

$$\text{PV (meq/kg)} = 16.27 - 5.35\,P - 2.60\,\text{PT} \qquad [2]$$

The effect of pressure and temperature on this quality parameter cannot be separately discussed, because the PT interaction was significant. Figure 2A shows the influence of those variables on PV. Peroxide extraction was favored at 100 bar and 60ºC. This selective extraction of hydroperoxides and dienes compared to glycerides is observed in conditions where extraction of compounds with high solubility in CO_2 prevails (16). When using extraction conditions that increased the solvent power of CO_2, TG were co-extracted and peroxides were diluted in the oil. This finding is seen more clearly in Figure 2B,

TABLE 2
Experimental Matrix and Results for the Full 2^4 Factorial Design[a]

Exp.	Number of extractions	*P*	*T*	*Q*	*D*	*P* (bar)	*T* (°C)	*Q* (L/min)	*D* (mm)	*Y* (%)	OA (%)	PC (%)	PV (meq/kg)
1	5	−1	−1	−1	−1	100	40	1.0	0.300	21	32	$2.4\cdot10^{-3}$	22
2	3	+1	−1	−1	−1	300	40	1.0	0.300	59	13	$2.6\cdot10^{-3}$	15
3	5	−1	+1	−1	−1	100	60	1.0	0.300	9	43	$2.5\cdot10^{-3}$	29
4	3	+1	+1	−1	−1	300	60	1.0	0.300	57	10	$2.0\cdot10^{-3}$	8
5	5	−1	−1	+1	−1	100	40	1.5	0.300	17	30	$2.2\cdot10^{-3}$	18
6	3	+1	−1	+1	−1	300	40	1.5	0.300	72	10	$2.2\cdot10^{-3}$	10
7	5	−1	+1	+1	−1	100	60	1.5	0.300	7	34	$2.4\cdot10^{-3}$	26
8	3	+1	+1	+1	−1	300	60	1.5	0.300	75	6	$2.7\cdot10^{-3}$	9
9	5	−1	−1	−1	+1	100	40	1.0	0.550	11	19	$2.8\cdot10^{-3}$	19
10	3	+1	−1	−1	+1	300	40	1.0	0.550	53	6	$2.8\cdot10^{-3}$	16
11	5	−1	+1	−1	+1	100	60	1.0	0.550	10	30	$2.7\cdot10^{-3}$	18
12	3	+1	+1	−1	+1	300	60	1.0	0.550	52	7	$1.8\cdot10^{-3}$	8
13	5	−1	−1	+1	+1	100	40	1.5	0.550	14	23	$1.9\cdot10^{-3}$	16
14	3	+1	−1	+1	+1	300	40	1.5	0.550	45	6	$2.2\cdot10^{-3}$	11
15	5	−1	+1	+1	+1	100	60	1.5	0.550	4	36	$2.2\cdot10^{-3}$	25
16	3	+1	+1	+1	+1	300	60	1.5	0.550	52	5	$2.2\cdot10^{-3}$	10
17	4	0	0	0	0	200	50	1.25	0.425	55	22	$2.0\cdot10^{-3}$	14
18	4	0	0	0	0	200	50	1.25	0.425	51	24	$2.0\cdot10^{-3}$	15

[a] Conditions: Time of extraction, 2.5 h; weight of olive husk, 25 g. *Y*, oil yield; OA, oil acidity; PC, phosphorus content. See Table 1 for other abbreviations.

TABLE 3
Main Effects and Interactions from 2^4 Factorial Design[a]

Factor or interaction	Effect *Y*	*P* value	Effect OA	*P* value	Effect PV	*P* value	Effect PC	*P* value
P	46.6	0.000	−23.2	0.000	−10.7	0.000	$-9.5 \cdot 10^{-5}$	0.507
T	−3.4	0.010	4.0	0.018	1.0	0.334	$-7.5 \cdot 10^{-5}$	0.597
Q	1.8	0.201	−1.0	0.432	−1.0	0.321	$-2.1 \cdot 10^{-4}$	0.164
D	−9.3	0.007	−5.6	0.005	−1.6	0.154	$-3.7 \cdot 10^{-5}$	0.790
PT	4.9	0.563	−5.9	0.004	−5.2	0.003	$-2.0 \cdot 10^{-4}$	0.168
PQ	4.2	0.030	−0.8	0.529	−0.4	0.678	$-2.1 \cdot 10^{-4}$	0.164
PD	−6.0	0.000	2.0	0.143	2.8	0.065	$-9.2 \cdot 10^{-5}$	0.517
TQ	0.8	0.903	−0.9	0.485	3.0	0.057	$3.1 \cdot 10^{-4}$	0.062
TD	−1.8	0.262	2.0	0.138	−0.9	0.393	$-1.2 \cdot 10^{-4}$	0.417
QD	−4.5	0.394	3.0	0.051	1.3	0.221	$-1.8 \cdot 10^{-4}$	0.208
Curvature	−20.1	0.001	−11.0	0.001	4.2	0.144	$3.6 \cdot 10^{-2}$	0.083

[a] See Tables 1 and 2 for abbreviations.

which represents the total amount of extracted peroxides, instead of PV, as a function of pressure and temperature. Peroxide extraction increased with increasing pressure, obviously due to the increased CO_2 density and its solvent power. However, it slightly decreased with temperature, probably due to the opposite effect that the increase in this variable produced on the two factors affecting solute solubilities. The decrease in CO_2 density and the increase in solute vapor pressure is more noticeable for the former in the experimental range analyzed (2,3).

From Table 3 one can see that there was no significant effect of any operation variables on PC. The mean value in the experimental range analyzed was 0.00232%.

This result means that the differences observed in Table 2 were not due to the effect of the variables but to the deviation of experimental results. This fact could be attributed to the low sensitivity of the analytical method when determining very low PC. The chemical structure of phospholipids of high polarity and M.W. was responsible for the low solubility in supercritical CO_2, two or three orders of magnitude lower compared to the corresponding treatment in hexane (17,18). This is the reason why TG are preferentially extracted over phospholipids, which are extracted in traces or not at all (3,19). This fact results in economic advantages in degumming treatment.

A second-order model was required for those responses with significant curvature in the first-order model, *Y* and OA. Additional experiments (star points) must be incorporated into the two-level factorial design. The new experiments must be performed over a wider range. The distance from the middle of the range (0) to the new normalized limits was defined, in dimensionless coordinates, by the α value (13). Table 4 shows the standard orthogonal central composite design matrix, including coded levels, dimensional values, and experimental results. The α value was calculated from:

$$\alpha = [k\,(1 + n_{s\,0}/\,n_s)/(1 + n_{c\,0}/n_c)]^{1/2} \qquad [3]$$

where *k* represents the number of variables, $n_{s\,0}$ the number of replications in the central point in the star design, $n_{c\,0}$ the number of replications in the central point in the factorial design, n_s the number of experiments in the star design, and n_c the number of experiments in the pure factorial design (13). In this design, a

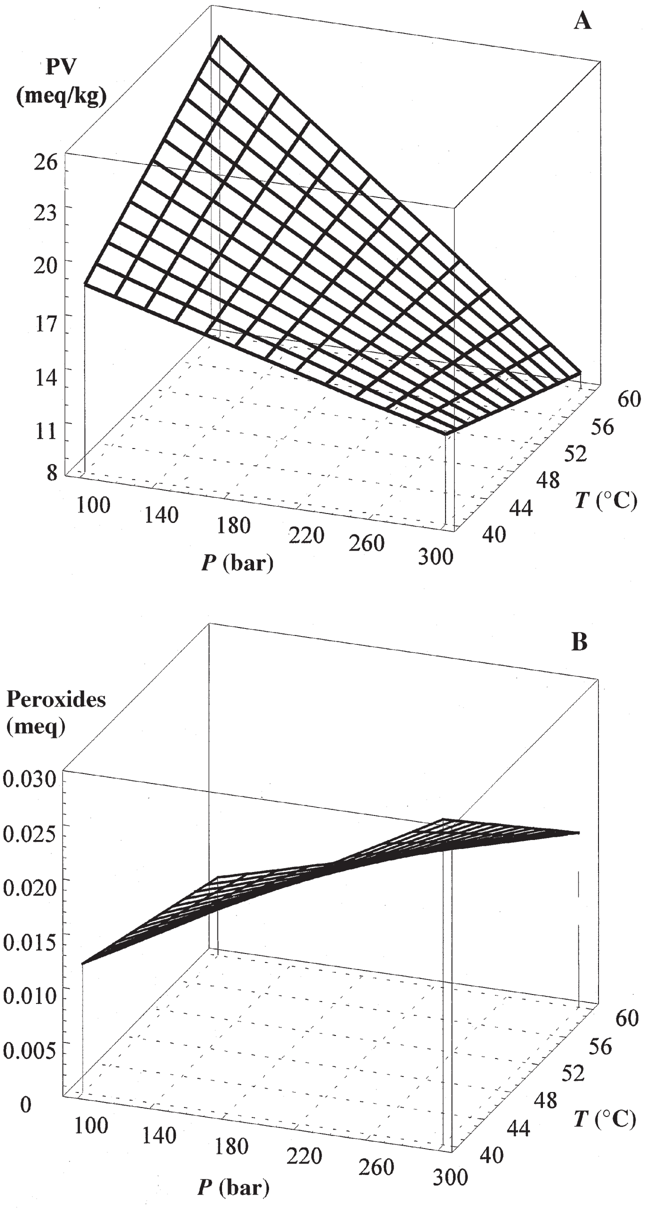

FIG. 2. Pure factorial design. Pressure–temperature interaction: (A) PV, (B) mass of peroxides extracted.

TABLE 4
Full Central Composite Design for Experimental Matrix and Results[a]

Exp.	Number of extractions	*P*	*T*	*Q*	*D*	*P* (bar)	*T* (°C)	*Q* (L/min)	*D* (mm)	*Y* (%)	OA (%)
1	5	−1	−1	−1	−1	100	40	1.0	0.300	21	32
2	3	+1	−1	−1	−1	300	40	1.0	0.300	59	13
3	5	−1	+1	−1	−1	100	60	1.0	0.300	9	43
4	3	+1	+1	−1	−1	300	60	1.0	0.300	57	10
5	5	−1	−1	+1	−1	100	40	1.5	0.300	17	30
6	3	+1	−1	+1	−1	300	40	1.5	0.300	72	10
7	5	−1	+1	+1	−1	100	60	1.5	0.300	7	34
8	3	+1	+1	+1	−1	300	60	1.5	0.300	75	6
9	5	−1	−1	−1	+1	100	40	1.0	0.550	11	19
10	3	+1	−1	−1	+1	300	40	1.0	0.550	53	6
11	5	−1	+1	−1	+1	100	60	1.0	0.550	10	30
12	3	+1	+1	−1	+1	300	60	1.0	0.550	52	7
13	5	−1	−1	+1	+1	100	40	1.5	0.550	14	23
14	3	+1	−1	+1	+1	300	40	1.5	0.550	45	6
15	5	−1	+1	+1	+1	100	60	1.5	0.550	4	36
16	3	+1	+1	+1	+1	300	60	1.5	0.550	52	5
17	4	0	0	0	0	200	50	1.25	0.425	55	22
18	4	0	0	0	0	200	50	1.25	0.425	51	24
19	7	−α	0	0	0	50	50	1.25	0.425	2	28
20	3	+α	0	0	0	350	50	1.25	0.425	93	15
21	4	0	−α	0	0	200	35	1.25	0.425	51	25
22	4	0	+α	0	0	200	65	1.25	0.425	52	24
23	4	0	0	−α	0	200	50	0.88	0.425	30	30
24	4	0	0	+α	0	200	50	1.62	0.425	49	29
25	4	0	0	0	−α	200	50	1.25	0.240	51	31
26	4	0	0	0	+α	200	50	1.25	0.610	52	25

[a] Conditions: Time of extraction, 2.5 h; weight of olive husk, 25 g. See Tables 1 and 2 for abbreviations.

value of α equal to 1.485 was found. Table 5 summarizes the results obtained for the new statistical analysis, including the main effects and first- and second-order interactions, considering the total error criteria with a confidence level of 95%.

For oil yield, the significant factors were pressure, particle diameter (*D*) and the quadratic terms of pressure and solvent flow, according to the following mathematical model with codified independent variables:

$$Y\,(\%) = 57.05 + 24.87\,P - 3.73\,D - 5.48\,P^2 - 9.07\,Q^2 \qquad [4]$$

TABLE 5
Main Effects and Interactions for the Full Central Composite Design[a]

Factor or interaction	Effect *Y*	*P* value	Effect OA	*P* value
P	49.7	0.000	−20.1	0.000
T	−2.5	0.500	3.0	0.234
Q	4.0	0.265	−0.9	0.708
D	−7.4	0.044	−5.3	0.059
PT	4.9	0.231	−5.9	0.055
PQ	4.2	0.305	−0.8	0.777
PD	−6.0	0.149	2.0	0.481
TQ	0.8	0.842	−0.9	0.753
TD	1.8	0.657	2.0	0.475
QD	−4.5	0.271	3.0	0.295
PP	−11.0	0.042	−7.8	0.047
TT	−6.8	0.200	−4.6	0.214
QQ	−18.1	0.004	−0.1	0.980
DD	−7.3	0.173	−1.9	0.603

[a] See Tables 1 and 2 for abbreviations.

where *Y* = yield, *P* = pressure (bar), *D* = particle diameter (mm), and *Q* = CO_2 flow (L/min). This expression shows that oil yield strongly increased with pressure. This result was not unexpected, since increasing *P* increases CO_2 density and its solvent power (3).

The effect of solvent flow is shown in Figure 3, representing the oil yield at different values of this variable. In the

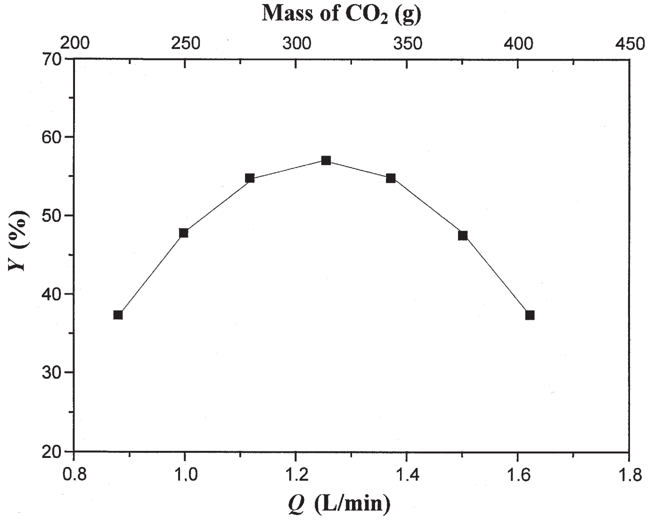

FIG. 3. Oil yield (*Y*) at different values of solvent flow and the total mass of CO_2 introduced into the extractor [pressure (*P*) = 200 kg/cm^2, temperature (*T*) = 50°C, particle diameter (*D*) = 0.425 mm].

experimental range analyzed, the oil yield is maximal for a solvent flow of 1.25 L/min. From 0.875 to 1.25 L/min, the increased oil yield was due to the increased CO_2 total mass introduced in the extractor (see secondary x axis). The approximately linear relationship between these two values seems to indicate that the CO_2 remained saturated with oil up to the upper limit of this range. However, the decline observed from 1.25 to 1.625 L/min could indicate that, over 1.25 L/min, the CO_2 residence time (the average time spent by a CO_2 molecule to cross the bed of husk particles) in the extractor is not enough to reach equilibrium conditions (20).

The slight decrease in oil yield with increasing particle diameter can be explained by taking into account that increasing this variable (14,21) (i) decreases the amount of easily accessible oil located in the outer part of the particles, (ii) decreases oil flow transferred by external diffusion, and (iii) increases the internal diffusion mass transfer resistance. Obviously, these three effects negatively influence extraction yield.

That no effect of temperature was found may indicate the temperature range was not wide enough to observe the influence of this variable. Other possible explanations are that the two factors (namely, CO_2 density and solute vapor pressure) affecting the solubility of the main oil components, TG, are balanced in the experimental range analyzed.

For OA, the only significant operational variable was pressure, and the mathematical expression relating both variables was:

$$\text{OA}\ (\%) = 27.62 - 10.04\ P - 3.91\ P^2 \qquad [5]$$

Figure 4 shows the variation with pressure of OA and extraction yield. OA slightly decreased with pressure up to 150 bar and then declined sharply up to 350 bar. Taking into account that TG are the main components of oil and that in this experimental range (Fig. 4) the extraction yield increases with increasing pressure, this experimental finding indicated that FFA were preferably extracted at lower pressure than TG. This result was similar to that obtained by other investigators (21,22) and may be due to the higher solubility of FFA in CO_2 compared to TG (6,19).

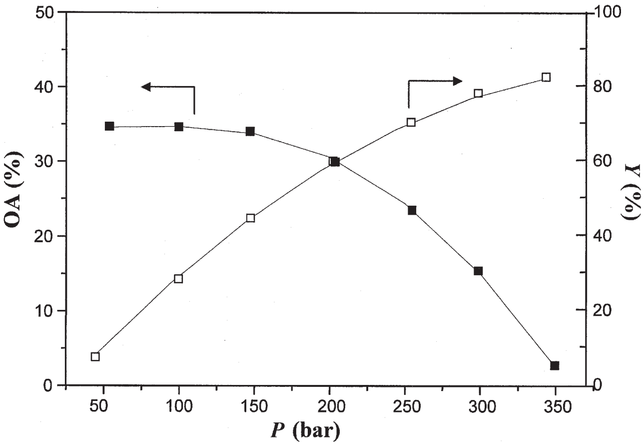

FIG. 4. Variation of oil acidity (OA) and Y with pressure [T = 50°C, CO_2 flow (Q) = 1.25 L/min, D = 0.425 mm]. See Figure 3 for abbreviations.

Comparison with hexane extracts and optimal extraction conditions. Table 6 shows the extraction yield and the quality parameters of the oil obtained by extracting olive husk with hexane. Table 6 also summarizes the results obtained for these parameters in the SFE of olive husk oil (columns 3 to 7). Columns 3 to 6 show both maximal and minimal experimental and calculated values of such variables in the experimental range studied. The best values determined from the mathematical correlations derived are shown in column 7. Operating conditions leading to optimal responses are presented in columns 8 to 11. Finally, in order to compare the quality of the oil with the specifications given in the European Community Regulations (10), these are included in column 13 of the table.

From data in column 2, it can be observed that the hexane extract did not comply with the OA and PV European regulations. Furthermore, PC values were high. Hence, commercializing this oil will necessitate refining the crude oil in a severe and expensive refining process.

For the supercritical extracts, the notable difference between results in columns 3 to 6 (Table 6), obtained at different conditions, confirms the possibility of modifying the

TABLE 6
Comparison of Hexane and Supercritical Extracts

1[b]	2	3	4	5	6	7	8	9	10	11	12	13
	Soxhlet extraction	Supercritical extraction					SFE best operation conditions					
	Experimental	Experimental values		Calculated values								
Response	value	Min.	Max.	Min.	Max.	Best	P (bar)	T (°C)	Q (L/min)	D (mm)	Equation[d]	Normative[a]
Y (%)	100	3	75	3	80	80	300	—[c]	1.25	0.30	[4]	—
OA (%)	16	5	43	14	34	14	300	—	—	—	[5]	≤0.5
PC (%)	$3\cdot10^{-2}$	$1.61\cdot10^{-3}$	$2.86\cdot10^{-3}$	$2.3\cdot10^{-3}$	$2.3\cdot10^{-3}$	$2.3\cdot10^{-3}$	—	—	—	—	[e]	—
PV (meq/kg)	14	8	29	8	24	8	300	60	—	—	[2]	≤5

[a] CEE/2568/91 (Ref. 10). See Tables 1 and 2 for abbreviations.
[b] 1–13 = column numbers for text reference.
[c] —, not applicable.
[d] For equations see text.
[e] Equation: PC = 2.32×10^{-3}.

selectivity of the extraction of the different oil compounds by varying the operating conditions. Under the best extraction conditions, the extraction yield and characteristics of the oil obtained are these: $Y = 80\%$, OA = 14%, PV = 8 meq/kg, and PC = $2.3 \cdot 10^{-3}\%$. The OA is still far from the value required by the European Regulations (10), but the PV is very close to the normative specifications. Besides, the supercritical extract presents a very low content of phosphorus. In this case, all quality parameters are superior to those oils extracted with hexane, and, therefore, a simpler refining process is required. This fact suggests an important economic savings can be achieved with the alternative supercritical process.

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