TECHNICAL

Deacidification of Olive Oils by Supercritical Carbon Dioxide

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An investigation of the application of supercritical carbon dioxide (SC-CO_2) extraction to the deacidification of olive oils has been made to verify that the nutritional properties of the oil remain unchanged when this technique is applied.

Preliminary runs at 20 and 30 MPa in the temperature range of 35–60°C were performed on fatty acids and triglycerides as pure compounds or mixtures, to determine their solubility in SC-CO_2. The solubility data obtained show that CO_2 extracts fatty acids more selectively than triglycerides under specific conditions of temperature and pressure (60°C and 20 MPa). It has been noted that the physical state of the solutes plays an important role in determining the solubility trends as a function of temperature and pressure.

Extraction of free fatty acids from olive oil was performed on samples with different free fatty acid (FFA) contents at 20 and 30 MPa and at 40 and 60°C. Experimental data suggest that the selectivity factor for fatty acids is higher than 5 and increases significantly as the fatty acid concentration of the oil decreases. For a FFA content of 2.62%, the selectivity reaches a value of 16.

In order to evaluate any variations in the composition, several SC-CO_2 extractions of husk oil with high FFA content (29.3%) were made. The results show that selectivity is still significant ($\approx$5) and the composition in the minor component of the deacidified oil has not changed. On the basis of the experimental results and preliminary process evaluations, the authors conclude that SC-CO_2 extraction could be a suitable technique for the deacidification of olive oils, especially for oils with relatively high FFA (<10%).

The extraction of oil from vegetable seeds by using a fluid at temperatures and pressures above the critical point of the solvent (1) is known as supercritical fluid extraction (SCFE). Several researchers (2–8) have demonstrated the suitability of supercritical carbon dioxide (SC-CO_2) as a solvent for the extraction of seed oils. These oils do not contain phospholipids and other complex substances, unlike hexane extracted oils; therefore, they do not require a degumming refining step.

Chrastil (9) measured the solubility of certain fatty acids and triglycerides in SC-CO_2 within the pressure range 8–25 MPa and the temperature range 40–80°C. The solubility data presented by this author show that at certain temperatures and pressures, CO_2 has a higher solvent power for fatty acids than for the corresponding triglycerides.

Peter (10) reported on the deacidification of palm oil using SC-CO_2 as solvent and ethanol as entrainer.

Biological, meteorological and agricultural factors result in large quantities of olive oil obtained using expression processes to have high free fatty acid content (4–15%). This confers an unacceptable flavor and causes the oil to be of poor quality. Large quantities of olive oil have to be refined to get a saleable product. Modification of the nutritional constituents of the oil takes place during refining (11), which explains why refined olive oil has a lower market value.

Preliminary runs at different temperatures and pressures were performed to determine the solubility of fatty acids and triglycerides in SC-CO_2, as pure compounds or as mixtures, in order to get data on the solvent selectivity and its variation with operating conditions. Based on the results of this preliminary study, the deacidification of the samples of olive oil, with different free fatty acids (FFA) content, was carried out.

The aim of the experimental program was (i) to measure the solubility of pure fatty acids, triglycerides and their mixtures in SC-CO_2; (ii) to investigate the variation in extraction selectivity as a function of the fatty acid content of the olive oil, and (iii) to gather data for a feasibility study of the deacidification process using SCFE.

Moreover, in order to evaluate any variations in the composition, several SCFE of husk oil with high FFA content were made.

EXPERIMENTAL

Materials. The solubility of fatty acids and triglycerides was measured for the following compounds: myristic acid, RLE Grade Carlo Erba, 90% min, mp 54°C; palmitic acid, RLE Grade Carlo Erba, 96% min, mp 63°C; stearic acid, RLE Grade Carlo Erba, 95% min, mp 70°C; oleic acid, CodexErba Carlo Erba, 68% min, mp 13°C; tristearin Technical Grade Fluka AG, 65% min, 61°C; triolein, Technical Grade Fluka AG, 65% min, −18°C; stearic:palmitic acid, 1:1 (w/w), and triolein:tristearin, 1:1 (w/w).

The olive oil samples used for deacidification were hexane-extracted husk oil with FFA content of 29.3% (w/w evaluated as oleic acid) and commercial olive oils containing 20.19%, 5.14% and 2.62% (w/w) oleic acid. The latter samples were prepared by mixing a commercial olive oil of FFA content of 0.30% with a weighed amount of the oleic acid.

EXTRACTION EQUIPMENT

SC-CO_2 extractions were performed in a Muller Extract Co. GMbH-BRD laboratory extractor. The scheme for the extraction apparatus is shown in Figure 1.

EXTRACTION PROCEDURES

A weighed amount of sample was put inside the extractable cylinder, which was then introduced into the

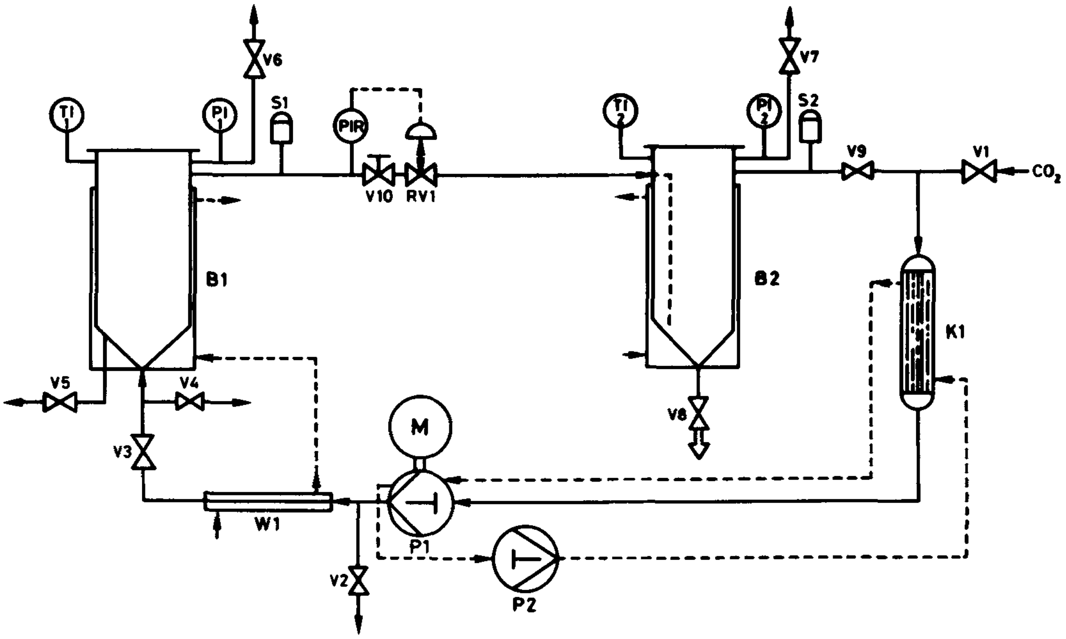

FIG. 1. Scheme for the extraction apparatus. B1 is an insulated 200-ml jacketed extractor into which there is an extractable cylinder containing sintered metal disks at the top and the bottom. An insulated 200-ml jacketed separator, B2, supplied with internal dip tube, affords improved separation of the extract from the solvent. RV1 is a back pressure regulating valve between the extractor and the separator. This on-off valve is feedback-regulated by a pressure controller on the extractor outlet line. An insulated vessel, K1, provides for the condensation of gaseous CO_2, with an internal heat exchanger, refrigerated by freon fed by the pump (P2). P1 is a piston pump whose capacity may be regulated manually. W1 is a tubular heat exchanger. Hand regulated high pressure needle valves provide for feed (V1) and recycling (V9 and V3) of CO_2; extractor (V4 and V5) and separator (V8) product outlet; venting of noncondensable products (V2), and venting of extractor and separator (V6 and V7).

extractor, B1 (Fig. 1). Stainless steel coils were introduced to prevent entrainment of the sample and assure proper contact between the samples and the solvent (CO_2). After steady state conditions were reached, the extraction cycle proceeded as follows: solvent at the operating temperature and pressure was allowed to flow into the extractor B1 and to come into contact with the sample for the time required to reach equilibrium solubility. The outlet flow passed through the back-pressure regulating valve RV1 into the separator, which is operated at pressures and temperatures to allow coexistence of liquid and gaseous CO_2. Due to the decrease in solubility, the extract may be separated from the CO_2 and collected at the bottom of the separator, whereas the gaseous CO_2 is recycled and subsequently condensed in the vessel K1. After condensation, liquid CO_2 is compressed to extraction pressure by pump P1 and heated to operating temperature by heater W1; hence, the CO_2 enters the extractor for an additional extraction cycle. The extract collected inside the separator B2 was discharged at fixed intervals, but the residue was removed only at the end of each extraction run.

The separator was operated at 5.5 MPa pressure and at a temperature of 27°C.

The fluid dynamics of the system was studied by measuring the solubility of the reference triglyceride in SC-CO_2 at different values of CO_2 flow rate. From these results, it was possible to determine the optimal operating flow rate of CO_2 as 11.16 g/min for extraction at 20 MPa and 8.44 g/min for extraction pressure of 30 MPa. For a CO_2 flow rate equal to or lower than these values, the solubility is not influenced by the fluid dynamics of the system.

Solubility of fatty acids and triglycerides. Solubilities were measured at extraction pressures of 20 and 30 MPa and in the temperature range 35–60°C. The solubilities of fatty acid and of triglyceride mixtures were determined at 20 MPa and 40°C.

Extraction of FFA from olive oil. Four extraction runs at pressures of 20 and 30 MPa and temperatures of 40 and 60°C were performed for samples with FFA of 20.19 and 5.14%. Olive oil having a fatty acid content of 2.62% was extracted at 20 MPa and 60°C.

Deacidification of husk oil. Nine extractions were performed at pressures of 10, 20 and 30 MPa and temperatures of 40, 50 and 60°C. A CO_2 flow rate of 100 g/min was used to simulate a process flow-rate; extraction time was 20 min in all cases. In contrast to the above experiments, the extract and residue were collected at the end of every run.

ANALYTICAL METHODS

Solubility of fatty acids and triglycerides. The amount extracted was determined by discharging the extract from the separator at predetermined intervals, collecting and weighing it.

TABLE 1

Solubility (S^0) in SC-CO_2 of Tested Fatty Acids and Triglycerides in the Pressure and Temperature Range Investigated

Sample	Temperature (°C)	$S^0 \times 10^{2a}$ at 20 MPa	$S^0 \times 10^{2a}$ at 30 MPa
Myristic acid	40	9.4 ± 0.6	
	50	8.3 ± 0.6	
Palmitic acid	35	0.91 ± 0.08	1.2 ± 0.1
	40	2.2 ± 0.3	2.0 ± 0.2
	45	4.1 ± 0.9	
	50	4.2 ± 0.4	
Stearic acid	40	0.9 ± 0.3	0.8 ± 0.3
	50	1.9 ± 0.4	3.9 ± 0.6
	60	2.0 ± 0.1	6.0 ± 0.7
Oleic acid	40	4.0 ± 0.2	8.0 ± 0.6
	60	2.6 ± 0.5	7.4 ± 0.9
Triolein	40	0.97 ± 0.04	2.2 ± 0.1
	60	0.4 ± 0.1	1.8 ± 0.2
Tristearin	40	0.38 ± 0.04	1.0 ± 0.2
	50	0.38 ± 0.01	1.4 ± 0.2
	60	0.17 ± 0.02	1.4 ± 0.2
Stearic and Palmitic acids (1:1, w/w)	40	2.9 ± 1.0	
Triolein-tristearin (1:1, w/w)	40	0.6 ± 0.1	

[a] S^0 is expressed in g solute/g CO_2.

Extraction of free fatty acids from olive oil. As with determining the solubility of fatty acids and triglycerides, the extract was collected at predetermined intervals and weighed. The residue was collected and weighed only at the end of the extraction run. The extracts and the residues were analyzed for FFA contents by titration according to method NGD C10-1976 Norme Grassi e Derivati, (Specifications for Fats and Derivatives) (12).

Deacidification of husk oil. Extracts and residues were analyzed for:

- FFA content by titration according to NGD C10 1976 method (12).
- Composition of unsaponifiable matter, sterols and eritrodiol according to NGD C51-1984 and NGD C52-1976 (12). Sterols were analyzed by high resolution gas chromatography (HRGC) using a Carlo Erba Fractovap 2960 gas chromatograph equipped with FID detector and split-splitless injection system. Column: 25 m × 0.3 mm i.d. (fused silica) WCOT, SE-52 liquid phase (df = 0.1–0.15 μm). Column temperature 245°C, carrier gas (H_2) flow-rate 1.8 ml/min, split 1/40 (detector and injector temperature, 299°C).
- Composition of fatty acids by analysis of the methyl esters prepared according to NGD C41-1976 (12) method. HRGC was performed under the following

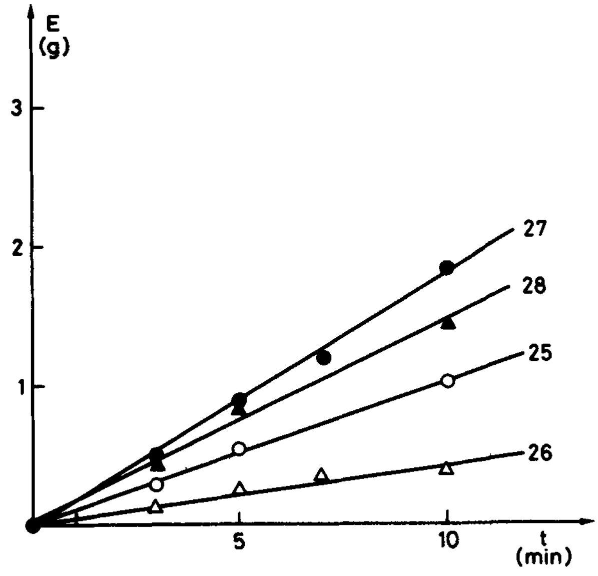

FIG. 2. Amount of triolein extracted (E) at various time intervals. Operating conditions: run 25 at 40°C and 20 MPa; run 26 at 60°C and 20 MPa; run 27 at 40°C and 30 MPa; run 28 at 60°C and 30 MPa.

conditions: column 25 m × 0.3 mm i.d. (glass) WCOT, Carbowax 20M liquid phase (df = 0.4–0.45 μm). Column temperature was programmed from 170 to 200°C at 7.5°C/min, carrier gas (H_2), flow rate 1.5 ml/min, split 1/60. Injector temperature 240°C, detector temperature 260°C.

RESULTS

Solubility of fatty acids and triglycerides. The amounts of extract (E) for triolein at different extraction times for P = 20 and 30 MPa; T = 40°C and 60°C are shown in Figure 2. Similar plots were obtained for all the other compounds investigated. The solubilities (S^o) were calculated from the plots as the ratio of the total amount extracted, at steady state conditions, in a known time interval to the quantity of CO_2 that flowed through the apparatus in the same time interval.

The data for fatty acids and triglycerides are shown in Table 1. The solubilities of pure compounds relative to triolein (S^o_R), the most abundant triglyceride in olive oil (ca. 40%) (11), are reported in Table 2. As may be observed, CO_2 extracts fatty acids more selectively than triglycerides only under certain conditions of temperature and pressure; the relative solubilities are higher at 60°C and 20 MPa.

The data of the solubility of mixtures of stearic and palmitic acid, and of triolein and tristearin, at 20 MPa and 40°C are also shown in Table 1.

Extraction of free fatty acids from olive oil. In Figure 3 the total extract (E), the total FFA content of the extract (acidity of extract A_E) and the distribution coefficient of the mixture (S^M_R) are reported vs the extraction time, at 60°C and 30 MPa, for a sample with a 20.19% FFA content. S^M_R values were calculated for each run according to the following equation:

$$S^M_R = \frac{W^A_E}{W^T_E} \; \frac{W^T_R}{W^A_R}$$

where W^A_E and W^A_R are the weight fraction of the acids in the extract and in the residue, and W^T_E and W^T_R the weight fraction of triglycerides in the extract and in the residue.

For the calculation of the weight fraction, the olive oil was assumed to be composed of only two classes of compounds, namely FFA and triglycerides. Because only relatively small quantities of minor constituents are present in the oil, they have no significant effect on the phase equilibria of the main compounds.

A linear relationship between total extract and extraction time was observed for all extraction runs. For extracted FFA, linearity does not exist over the time interval; that is, only for a slight variation in the amount of FFA of the oil during the run. In all cases the rate of extraction v (g/min) for the total extract and for the FFA may be calculated from the slope of the extracted amount vs time.

The data for the solubilities in CO_2 of total extracts, of FFA and of the triglycerides are reported in Table 3 for the temperature and pressure ranges investigated. The amount of the extracted triglycerides was evaluated as the difference between the total extract

TABLE 2

Relative Solubility (S^o_R) for Pure Compounds

P = 20 MPa	S^o_R at 40°C	S^o_R at 60°C
S^0 Myristic acid / S^0 Triolein	9.7	
S^0 Palmitic acid / S^0 Triolein	2.2	
S^0 Stearic acid / S^0 Triolein	1.0	4.9
S^0 Oleic acid / S^0 Triolein	4.1	6.3
P = 30 MPa	**S^o_R at 40°C**	**S^o_R at 60°C**
S^0 Palmitic acid / S^0 Triolein	0.9	
S^0 Stearic acid / S^0 Triolein	0.4	3.4
S^0 Oleic acid / S^0 Triolein	3.6	4.2

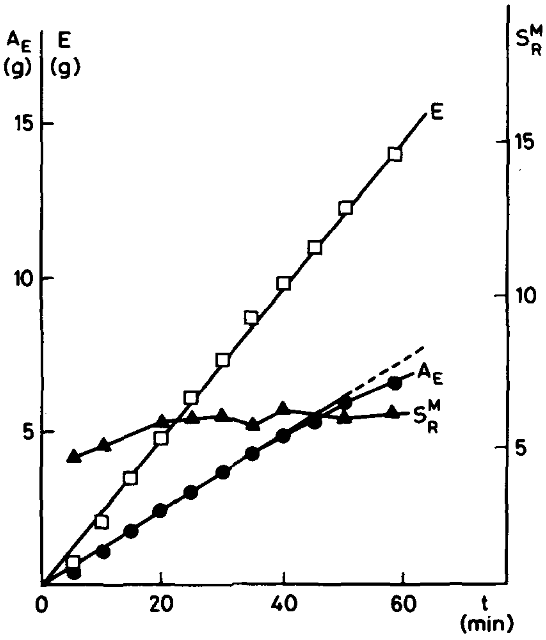

FIG. 3. Extraction of free fatty acids from olive oil: trend of total extract (E), free fatty acids in the extract (A_E), and of distribution coefficient (S^M_R) at various extraction times. Sample: olive oil with FFA content of 20.19%. Operating condition, 30 MPa, 60°C.

and the amount of FFA extracted, as previously described.

Deacidification of husk oil. Table 4 shows the total amounts of extract and residue obtained at different temperatures and pressures by extraction from 100 g of husk oil with an acidity of 29.3%. At pressures less than or equal to 10 MPa and at temperatures of 50 and 60°C, no extract was obtained. FFA in the extract varies from 42% (run 1) to 59.2% (run 9), whereas FFA content in the residue oil was reduced from the initial value of 29.3% to 21.4% at 20 MPa and 40°C (run 3) and to 21.9% at 20 MPa and 50°C (run 6). The extraction yield of FFA was about 50%.

The distribution coefficient (S^M_R), which is a measure of solvent selectivity, was higher at 20 MPa (Table 4). At 50 and 60°C, S^M_R decreased with increasing pressure.

Table 5 shows the acidic composition of feed oil and of extraction residues; the variation of operating conditions (temperature and pressure) does not affect the composition of refined oils significantly.

Extraction residues were also analyzed for total unsaponifiable fraction, sterol and triterpenic dialcohol composition (eritrodiol and uvaol) (Table 6). No significant variation was observed for the total unsaponifiable fraction and sterol composition. Triterpenic dialcohols vary from 13.94% in the feed oil to 9% in the residue of run 3 at 40°C and 20 MPa and up to 25.7% in the residue of run 5 at 50°C and 30 MPa.

DISCUSSION

Solubility values for fatty acids and triglycerides in CO_2 determined in this work are one order higher than those presented by Chrastil (9). Chrastil's experiments were performed using a single pass flow technique at a flow rate which allowed CO_2 saturation. It is likely that the data presented by Chrastil were not determined under equilibrium conditions (13).

From the data shown in Table 1, it follows that the solubility in CO_2 of the pure acids and triglycerides seems to increase with pressure, the increase being more pronounced at higher temperatures. All of the tested compounds show this trend, even though the increase in solubility varied from compound to compound. The influence of temperature on solubility at constant pressure is rather complex: the solubility increases with temperature for palmitic acid and stearic acid, but it decreases for myristic acid, oleic acid, triolein and tristearin.

It should be noted that substances whose solubility increases with temperature are solid under the described experimental conditions, while those which experience a decrease are liquid. Myristic acid and tristearin have melting points near the temperatures used in these experiments and therefore may be liquid at the operating conditions due to the solvent effect of CO_2.

For the described equilibria, the solubility in the

TABLE 3

Extraction of Free Fatty Acids from Olive Oil: Solubility (g solute/g CO_2) for Total Extract (S_E), Triglycerides (S_T) and FFA (S_A) in the Temperature and Pressure Range Investigated

		40°C			60°C	
Sample[a]	$S_E \times 10^2$	$S_T \times 10^2$	$S_A \times 10^2$	$S_E \times 10^2$	$S_T \times 10^2$	$S_A \times 10^2$
20 MPa 1	1.84 ± 0.03	0.89	0.95 ± 0.03	0.97 ± 0.05	0.31	0.66 ± 0.03
2	1.01 ± 0.04	0.78	0.23 ± 0.01	0.48 ± 0.03	0.27	0.21 ± 0.01
3				0.37 ± 0.02	0.26	0.11 ± 0.04
30 MPa 1	3.1 ± 0.1	1.54	1.57 ± 0.08	3.05 ± 0.07	1.47	1.58 ± 0.07
2	2.13 ± 0.04	1.81	0.32 ± 0.01	1.97 ± 0.06	1.56	0.41 ± 0.01

[a] FFA content of sample: (1) 20.19%; (2) 5.14%; (3) 2.62%.

TABLE 4

Husk Oil Deacidification: Characteristic of the Products Obtained by SC-CO_2 Extraction of 100 g of Husk Oil at Various Operating Conditions

Run number	Temp. (°C)	Pressure (MPa)	Extract Amt (g)	Residue Amt (g)	Extract FFA %	Residue FFA %	S^M_R
1	40	10	9.2	90.8	42.1	28.0	1.87
2	40	30	28.6	71.4	47.3	22.1	3.16
3	40	20	28.6	71.4	49.0	21.4	3.53
4	50	10	—	100.0	—	29.3	—
5	50	30	21.7	78.3	45.9	24.7	2.59
6	50	20	22.9	77.1	54.2	21.9	4.22
7	60	10	—	100.0	—	29.3	—
8	60	30	24.4	75.6	50.0	22.6	3.42
9	60	20	11.8	88.2	59.2	25.3	4.28

vapor phase is different for solids and liquids: the CO_2 may be considered insoluble in solids, although it has a finite solubility in liquids. The equilibrium condition between the solid and the fluid, at constant temperature and pressure, is as follows:

$$f^S_2 = f^F_2 \qquad [1]$$

where 1 is carbon dioxide, 2 is solid solute, S is the solid phase and F is the fluid phase. The fugacity of the pure solid at constant temperature (T) and pressure (P) is expressed by:

$$f^S_2 = P^{sat}_2\ \varphi^{sat}_2 \exp\int_{P^{sat}_2}^{P} V^S_2 dP/RT = f^{sat}_2 \exp\int_{P^{sat}_2}^{P} V^S_2 dP/RT \qquad [2]$$

where P^{sat}_2 is the vapor pressure of pure solid at temperature T; φ^{sat}_2 is the fugacity coefficient at saturation pressure P^{sat}_2 and V^S_2 is the molar volume of the solid. The following equation holds for the fugacity of the fluid phase:

$$f^F_2 = y_2\ \varphi_2\ P \qquad [3]$$

where y_2 is the molar fraction of solid in the fluid phase, and φ_2 is the fugacity coefficient of solid compound dissolved in the fluid phase at temperature T and operating pressure P. Substitution of equations [2] and [3] into [1] yields:

$$y_2\ \varphi_2\ P = P^{sat}_2\ \varphi^{sat}_2 \exp\int_{P^{sat}_2}^{P} V^S_2\ dP/RT \qquad [4]$$

$$y_2 = \frac{P^{sat}_2}{P}\ E = y^{id}_2\ E \qquad [5]$$

$$E = \frac{\varphi^{sat}_2}{\varphi_2} \exp\int_{P^{sat}_2}^{P} V^S_2\ dP/RT \qquad [6]$$

where E is the enhancement factor of the solubility of the solid in the fluid phase and y^{id}_2 is the ideal solubility. The temperature dependence of solubility may be deduced as follows:

TABLE 5

Husk Oil Deacidification: Fatty Acids Composition (GC%) of Feed Oil and Residues for Extraction Runs 1 to 9

Fatty acid	Feed oil	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9
Myristic	tr	tr	0.11	tr	tr	tr	tr	0.08	0.14	tr
Palmitic	14.00	13.58	13.73	13.54	13.60	15.88	16.34	13.90	13.60	18.79
Palmitoleic	0.81	0.80	0.78	1.08	0.92	1.10	1.20	0.84	0.83	1.36
Eptadecanoic	0.14	0.14	0.14	0.17	0.17	0.17	0.17	0.15	0.13	0.21
Eptadecenoic	0.22	0.22	0.20	0.25	0.23	0.24	0.27	0.22	0.21	0.36
Stearic	2.45	2.47	2.42	3.36	3.03	2.78	2.91	2.51	2.33	3.65
Oleic	62.38	72.67	73.41	72.72	71.51	71.84	69.84	72.66	72.99	63.39
Linoleic	8.63	8.53	7.90	5.76	8.43	6.59	8.06	8.54	8.24	11.10
Linolenic	0.60	0.59	0.50	0.27	0.55	0.38	0.55	0.55	0.55	0.74
Arachidic	0.32	0.32	0.35	0.61	0.51	0.38	0.30	0.35	0.36	0.52
Gadoleic	0.27	0.13	0.15	1.01	0.59	0.49	0.35	tr	0.30	0.61
Behenic	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr
Others	0.18	0.54	0.31	1.23	0.45	0.14	—	0.20	0.32	0.27

TABLE 6

Husk Oil Deacidification: Unsaponifiable Percent, Sterol and Triterpenic Diols Content (GC%) of Feed Oil and Residues for Extraction Runs 1 to 9

	Feed oil	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9
Unsaponifiable (%)	1.99	1.99	2.01	1.89	2.00	1.91	1.86	2.04	1.97	1.66
Sterol Composition										
Campesterol	3.57	3.62	3.44	3.21	3.21	2.90	2.91	3.48	3.75	2.84
Stigmasterol	2.65	2.27	2.60	2.37	2.46	2.38	2.39	2.59	2.59	2.30
β Sitosterol	88.00	88.05	88.28	90.78	91.42	90.95	89.35	88.18	89.05	90.80
Δ 5-Avenasterol + X (RRT=1.02)	5.78	6.06	5.68	3.65	2.92	3.77	5.35	5.76	4.62	4.07
Diols composition										
Eritrodiol	11.43	9.00	14.44	7.14	17.12	20.08	19.82	12.89	13.55	9.25
Uvaol	2.51	1.25	3.14	1.89	3.15	5.64	3.74	3.03	3.00	1.45
Eritrodiol + Uvaol	13.94	10.26	17.58	9.03	20.27	25.72	23.53	15.92	16.55	10.70

$$d \ln y_2 / dT = d \ln P^{sat}_2/dT + d \ln E / dT \qquad [7]$$

From Clausius-Clapeyron's equation one gets:

$$d \ln P^{sat}_2/dT + \Delta H/RT^2 = (H^F_2 - H^S_2)/RT^2 \qquad [8]$$

where H^F_2 is the enthalpy of component 2 in the physical state as it is present in the fluid phase, and H^S_2 is the enthalpy of the pure solid 2 at the same temperature and pressure. To evaluate the variation of the solubility with temperature, it is necessary to know the variation of the enhancement factor with temperature. From (6):

$$d \ln E/dT = d \ln \varphi^{sat}_2/dT - d \ln \varphi_2/dT + d/dT \int_{P^{sat}_2}^{P} V^S_2\, dP/RT \qquad [9]$$

For the second term of (9) the following equation holds:

$$d \ln \varphi^{sat}_2/dT = -(H^F_2 - H'_2)/RT^2 \qquad [10]$$

$$d \ln \varphi_2/dT = -(\overline{H}^F_2 - H'_2)/RT^2 \qquad [11]$$

where H^F_2 is the enthalpy of the solid in the fluid phase; H'_2 is the enthalpy of the solid in the ideal state, and $\overline{H}^F_2$ is the partial molar enthalpy of the solid in the fluid phase. By assuming the volume of the solid is independent from temperature T and the vapor pressure of the solid is insensitive to small temperature variation, i.e., $P^{sat}_2(T) \approx P^{sat}_2\,(T + dT)$:

$$d/dT \int_{P^{sat}_2}^{P} V^S_2 dP/RT \approx - \int_{P^{sat}_2}^{P} V^S_2 dP/RT^2 \qquad [12]$$

and substituting the various terms in equation (7), one obtains:

$$d \ln y_2/dT = 1/RT^2 \,[\overline{H}^F_2 - H^S_2 - \int_{P^{sat}_2}^{P} V^S_2 dP] = A/RT^2 \qquad [13]$$

that is:

$$\ln y_2 = C - A/RT \qquad [14]$$

where C is the integration constant and

$$A = (\overline{H}^F_2 - H^S_2) - \int_{P^{sat}_2}^{P} V^S_2 dP$$

Two cases may occur: (i) When $A > 0$, solubility increases with the temperature; (ii) when $A < 0$, solubility decreases by increasing the temperature. The sign of A depends on the relative values of the solubilization enthalpy ($\overline{H}^F_2 - H^S_2$) and the value of the Poynting term. At low pressure, the Poynting term is low, and therefore:

$$|\overline{H}^F_2 - H^S_2| >> \int_{P^{sat}_2}^{P} V^S_2\, dP > 0 \qquad [15]$$

and the sign of A results positive for endothermic processes ($\overline{H}^F_2 > H^S_2$) and negative for exothermic ones ($\overline{H}^F_2 < H^S_2$). At high pressure, when the Poynting term is greater than the enthalpy variation, the value of A is always negative. The relations (14) and (15) explain the solubility variations of a substance in a SCFE process.

In the reported pressure range, the value of the Poynting term is ca. 10 cal/g. This value is lower than the latent heat of fusion and of evaporation, which in the case of stearic acid are 40 cal/g and 70 cal/g, respectively. This seems to indicate a minor effect of the Poynting term compared to that of solubilization enthalpy, in the experimental pressure range. By modeling the fluid phase as an expanded liquid phase and using the reference state for component 2 in the fluid phase as liquid state, equation [14] may be rewritten as follows:

$$\ln y_2 = A\,(1 - T_m/T) \,/\, (RT_m) \qquad [16]$$

where T_m is the melting point of the solid, and $A/T_m = -\Delta S$ is the variation of entropy associated with the solution process (14).

For liquid substances the decrease of solubility in the fluid phase caused by increasing the temperature may be due partially to the solubility of the CO_2 in the liquid phase. The phase equilibria equation for the liquid component 2 is:

$$y_2\, \varphi_2\, P = P^{sat}_2\, \varphi^{sat}_2\, (1 - x_1) \exp \int_{P^{sat}_2}^{P} V^L_2 dP/RT \qquad [17]$$

$$y_2 /(1 - x_1) = P^{sat}_2\, E_1/P \qquad [18]$$

where

$$E_1 = (\varphi^{sat}_2 / \varphi_2) \exp \int_{P^{sat}_2}^{P} V^L_2\, dP/RT \qquad [19]$$

and x_1 is the molar fraction of supercritical compound in the liquid phase. Proceeding as before, one gets:

$$d \ln y_2/dT = A/RT^2 - 1/(1 - x_1)\, dx_1/dT \qquad [20]$$

The solubility of the component 2 in the supercritical phase decreases by increasing the temperature when:

$$A/RT^2 - 1/(1 - x_1)\, dx_1/dT < 0 \qquad [21]$$

If the solubility of the supercritical component in the liquid phase is low, as normally may be assumed, $(1-x_1) \approx 1$, the previous relation becomes:

$$(A/RT^2) < dx_1/dT \qquad [22]$$

For $A/RT^2 > 0$ (this situation occurs for solid substances) the result is $dx_1/dT > 0$, which means that the decrease in solubility of the component 2 in the supercritical phase depends upon the increase of the solubility of the supercritical component in the liquid phase. It is worthwhile to emphasize that the experimental range in which this phenomenon occurs is restricted and depends upon the values of the terms A which will not be high and in many cases lower than those for solids. For the other case the solubility of component 2 in the supercritical phase increases with temperature when:

$$A/RT^2 - 1/(1 - x_1)\, dx_1/dT > 0 \qquad [23]$$

or:

$$(A/RT^2) > dx_1/dT \qquad [24]$$

This relation is always verified when the solubility of the SCF in the liquid phase decreases by increasing the temperature or when the increase in solubility is very low and has practically no effect on the composition of the liquid phase, the behavior of which is determined by the solubilization enthalpy of the liquid in the SCF.

As for the effect of the pressure on solubility, at constant temperature, for all cases reported in Table 1 an upward trend in solubility is observed when pressure is increased. Nevertheless, when the variation of the solubility associated with the Poynting effect is calculated, a threefold increase results while the observed variation in solubility is lower than expected, except at higher temperatures. This seems to indicate that the increase in the density of the solvent and molar or partial molar volumes of the solute play a determinant role in the definition of the variation of solubility with pressure (15).

For mixtures of fatty acids and triglycerides (Table 1), it is interesting to note that, at 40°C, stearic and palmitic acid are solid. Thus, the experimental run was performed on an immiscible mixture of the two components. For an heterogeneous system, the solubility of the mixture may be calculated by adding the solubilities of the pure compounds. From the calculation, a value of $3\ 10^{-2}$ g/g CO_2 is obtained, which agrees well with the experimental value of $2.9\ 10^{-2}$ g/g CO_2.

Tristearin and triolein are miscible because tristearin is a solid, but triolein is a liquid at the operative extraction temperature. As these two compounds are chemically and structurally similar, it is reasonable to assume the mixture behaves ideally according to Raoult's law. The value 0.7 g/g CO_2 thus calculated is close to the experimental value of 0.6 g/g CO_2. Because the aim of this study was to verify the feasibility of the deacidification process for olive oil, the solubilities of fatty acids relative to triolein were calculated. From the data in Table 2, it follows that relative solubilities greater than or equal to 5 occur at 20 MPa and 60°C. Hence, selectivity is influenced favorably by temperature and not by pressure. The solubility of the mixture may be described by the following equation:

$$S_E = S_T + S_A = S_T^o x_T \gamma_T + S_A^o x_A \gamma_A \qquad [25]$$

where E = total extract; T = triglyceride; A = FFA; x_i = molar fraction; γ_i = activity coefficient, and S^o_i the solubility of the pure compound. Equation (25) may be obtained either from Raoult's equation, by taking into account the nonideality of the mixture through the activity coefficients γ_i, or by the phase equilibria equations. Because molar fractions are unknown, equation (25) can be written in the following form:

$$S_E = S_T^o W_T \gamma'_T + S_A^o W_A \gamma'_A \qquad [26]$$

where W_i are the weight fractions and $\gamma' = \gamma\, \overline{MW}/MW_i$; MW_i is the molecular weight of component i and $\overline{MW}$ the mean molecular weight of the mixture.

By dividing the solubilities of FFA (S_A) and of triglycerides, (S_T), reported in Table 3, by the respective weight fractions, the values of $S^o_i\ \gamma'_i$ are obtained (Table 7). Moreover, by dividing these values by the solubility of pure oleic acid (S^o_A) and of pure triolein, the activity coefficients γ' can be calculated. From the ratio of γ'_A/γ'_T, taking into account the molecular weights

TABLE 7

Extraction of Free Fatty Acids From Olive Oil: Calculated Value for $S_i \times \gamma'_i$; Activity Coefficient (γ'_i) and γ_A/γ_T Ratio at the Pressure and Temperature Range Investigated

		40°C					60°C				
P_E	Sample[a]	$S^o_T \times \gamma'_T \times 10^2$	γ'_T	$S^o_A \times \gamma'_A \times 10^2$	γ'_A	γ_A/γ_T	$S^o_T \times \gamma'_T \times 10^2$	γ'_T	$S^o_A \times \gamma'_A \times 10^2$	γ'_A	γ_A/γ_T
20 MPa	1	1.11	1.14	4.70	1.17	0.33	0.38	0.93	3.27	1.27	0.44
	2	0.82	0.85	4.47	1.12	0.42	0.28	0.69	4.09	1.59	0.73
	3						0.27	0.65	4.20	1.63	0.83
30 MPa	1	1.93	0.86	7.78	0.97	0.36	1.84	1.03	7.83	1.05	0.32
	2	1.91	0.86	6.23	0.78	0.36	1.64	0.92	8.17	1.09	0.30

[a] FFA content of sample: 1, 20.19%; 2, 5.14%; 3, 2.62%.

TABLE 8

Extraction of Free Fatty Acids From Olive Oil: Mean Distribution Coefficient of Compounds in Mixture $(\bar{S}^M)_R$ Under Various Operating Conditions[a]

Sample[b]		$\bar{S}^M_R$ at 40°C		$\bar{S}^M_R$ at 60°C	
20 MPa	1	5.0	(4.1)	8.7	(6.3)
	2	6.3		14.8	
	3			16.0	
30 MPa	1	4.3	(3.6)	5.2	(4.2)
	2	4.3		6.0	

[a] In brackets the relative solubility of pure compounds (S^o_R) are reported from Table 2 for oleic acid and triolein.

[b] FFA content of sample: 1, 20.19%; 2, 5.14%; 3, 2.62%.

of oleic acid and triolein, one obtains γ_A/γ_T, that is, the ratio of the effective activity coefficients.

It is obvious that, because a mixture of homologous components has been considered, the calculated value gives only an approximate indication of the nonideality of the mixture. In the temperature and pressure range investigated, the activity coefficients for the triglycerides are always higher than those for FFA. This seems to indicate that free fatty acids, in the range of concentrations tested, are present in the liquid phase in an associated form. This behavior is widely observed for acids.

The solvent selectivity or the mean distribution coefficient $(\overline{S^M}_R)$ was calculated for different operating conditions (Table 8). $\overline{S^M}_R$ is higher than the relative solubility of pure compounds (S^o_R), at the same temperatures and pressures. The solvent selectivity shows an increase with temperature and decreases as pressure increases. This trend is also observed for S^o_R. The distribution coefficient, $\overline{S^M}_R$, also increases significantly with the decrease of FFA content of samples, probably due to the lower association of the acid at low concentration. The data obtained for the test mixture were confirmed by the extractions runs on a sample of husk oil with natural FFA content of 29.3%.

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