On the Application of Supercritical Fluid Extraction to the Deacidification of Olive Oils

M. Gonçalves, A.M.P. Vasconcelos, E.J.S. Gomes de Azevedo[1], H.J. Chaves das Neves and M. Nunes da Ponte*
Departamento de Quimica, Faculdade de Ciencias e Tecnologia, Universidade Nova de Lisboa, 2825 Monte da Caparica, Portugal

A recent suggestion on the applicability of supercritical fluid extraction to the deacidification of olive oils of high acid content was based on solubility data in clear disagreement with the results of other authors. In this work, we measured the solubilities of substances chosen for their importance in that extraction process, namely pure glycerol trioleate, the most abundant triglyceride in olive oil, and of a husk oil with a high acid content. Our results agree well with some of the previous reports on this subject. These seem to be a trustworthy data base, but more results are needed for a definite conclusion about the technical feasibility of the process.

KEY WORDS: **Deacidification, husk oil, olive oil, supercritical carbon dioxide.**

The use of supercritical fluid extraction in the vegetable oil industry has been suggested by several authors. For example, Friedrich *et al.* (1) and List *et al.* (2) compared the composition and stability of vegetable oils either obtained by supercritical carbon dioxide (SC-CO_2) extraction or recovered and purified by conventional methods. Stahl and collaborators (3–5) performed extensive studies on the solubilities of soybean oil up to very high pressures. Processes for deacidification and deodorization of natural fats and oils have been described in patents by Zosel (6) and by Coenen and Kriegel (7). Brunner and Peter (8) describe a deacidification method of palm oil using supercritical carbon dioxide as the solvent and ethanol as the entrainer.

Brunetti *et al.* (9) have recently suggested the use of SC-CO_2 extraction as a deacidification method for olive and husk oils. Olive oil is a vegetable oil extracted by mechanical means from olives. Large quantities of oil are unsuitable for immediate consumption, due to a high free fatty acid content, and require refining. Conventional refining processes, however, may alter the nutritional qualities of the oil, resulting in a lower price product. On the other hand, about 15% of the triglyceride content of olives remains trapped in the solid matrix, from where it is usually extracted with organic solvents. The end product is husk oil, which has a triglyceride composition slightly different from olive oil, and a much higher acid content. If supercritical carbon dioxide could extract the acid without affecting the triglyceride content of the oils, this could become an economically interesting process.

In their work, Brunetti *et al.* (9) measured solubilities of some of the main components of these oils. Their data are, however, in notorious disagreement with other results reported in the literature, like those of Chrastil (10) and King *et al.* (11). On the other hand, Di Giovacchino *et al.* (12) report preliminary measurements that seem to show that SC-CO_2 is not selective towards the free fatty acids present in olive oil.

Lack of agreement between literature reports of the solubilities in supercritical fluids of vegetable oil components is still quite frequent, reflecting the difficulties inherent to these measurements. The need remains, therefore, for additional work to be performed in this field.

At the time of publication of Brunetti's paper, we were conducting a study on SC-CO_2 of olive husk oils. The striking differences between their solubilities and our own led us to a literature survey and comparison of published results.

In this work, we present measurements of the solubility in SC-CO_2 of a pure triglyceride—glycerol trioleate, usually known as triolein, the main component of olive oil—and compare our results and Brunetti's with analogous results from other authors. The solubility behavior of triolein and oleic acid contained in a husk oil of high acidity was also investigated and a comparison of reported solubilities of oleic acid is presented.

Additionally, the SC-CO_2 extraction of husk oil directly from the corresponding solid (husk flakes) was also performed and results are compared with similar data of King *et al.* (11) for rapeseed.

EXPERIMENTAL PROCEDURES

Materials. The CO_2 used in this work was 99.5% (w/w) pure and supplied by Air Liquide (Paris, France), and glycerol trioleate (triolein) was 99% (w/w) pure, purchased from Sigma Chemical Co. (St. Louis, MO). All solvents used in the chromatographic analysis were of analytical grade and obtained from E. Merck (Darmstadt, Germany). The husk flakes were milled to a thickness of 0.5–1.5 mm prior to use.

Solubilities in supercritical carbon dioxide. The solubility measurements were performed in an apparatus which is an improved version of the one used in previous studies (13), and is similar to the apparatus described by Matos *et al.* (14). The main piece of equipment is a static vapor-liquid equilibrium cell, approximately 30 cm^3, immersed in a thermostatted water bath.

A typical experiment starts with filling of the cell, at atmospheric pressure, with a small amount (about 2.5 cm^3), of liquid (crude husk oil or triolein) or solid (husk flakes). The CO_2 is then pressurized by a diaphragm compressor into the cell. After about 60 min of stirring (using a magnetic bar) and about the same time of rest, the pressure is read on a Bourdon tube manometer, with an accuracy of ± 100 kPa, and the temperature is measured with a mercury thermometer of 0.1 K precision. A sample is then taken from the top of the cell.

The samples are collected in the thermostatted bath by depressurization and expansion into a glass trap connected to a large steel bottle of calibrated volume. When the valve is open, the solute condenses in the cold trap, while the solvent gas expands into the steel bottle (with

---

[1] Permanent address: Centro de Quimica Estrutural, Instituto Superior Tecnico, P — 1096 Lisboa, Portugal.
*To whom correspondence should be addressed.

a volume of approximately 1 dm^3, calibrated to ± 0.1 cm^3). The pressure of the gas is read in a mercury manometer with a precision cathethometer, and is used to calculate the amount of gas present in the sample. The amount of liquid is measured by weighing.

The accuracy of the composition results obtained is limited by disturbances introduced in the phase equilibrium by the sampling procedure itself. A sufficient amount of the fluid phase has to be withdrawn from the cell to deposit a measurable amount of liquid in the cold trap. Observed pressure drops in the cell were between 0.2 and 1 MPa, depending on the pressure at which the sampling is performed. The mass taken out in each sample is no more than 3% of the total mass inside the cell.

Another source of error in this procedure is the existence of a dead volume between the sampling valve and the cold trap, where some solute may condense. To minimize these errors, a series of samples were successively taken in the same operating conditions and the average value of solubility was estimated.

The standard deviations for each of the sets of measurements vary from 0.7 mg/nL to 3.2 mg/nL; the average value is 1.8 mg/nL (1 nL = 1000 cm^3 at 1 bar, 0°C = 1.977 g of CO_2).

Capillary gas chromatography. Gas chromatography (GC) of SC-CO_2 extracted husk oil, and of other oil samples we used for reference, was performed with a Carlo Erba instrument of the Mega Series, model 5300, equipped with a Carlo Erba MFA 515 injector and a flame ionization detector (FID). Quantitative calculations were made with a Shimadzu CR3A computing integrator equipped with a floppy disk unit and a CRT display.

GC analysis of the samples were carried out in a homemade glass capillary, 25 m long, 0.25 mm i.d. column, coated with OV-17-OH.

A detailed description of the method used here was given by Chaves das Neves *et al.* (15), following Geeraert and Sandra (16). The injection was performed at programmed temperature under the following conditions: FID temperature, 400°C; injector temperatures—initial temperature 100°C, final temperature 390°C; split of the solvent (*n*-pentane) during a period of 300 seconds. After the split period, the injector was ballistically heated to 390°C, and followed a splitless period of 180 seconds at this temperature. The split valve flow rate was 340 mL/min. Aliquots 0.1-mL of the nonextracted oil samples and 3-mL aliquots of the SC-CO_2 extracted oil samples were injected. Hydrogen at a pressure of 100 kPa was the carrier gas.

The oven temperature was programmed as follows: initially set at 150°C and after ballistic heating to 280°C, it was linearly programmed at a heating rate of 8°/min until the final temperature of 370°C was reached.

The reproducibility of injection was tested with samples of nonextracted oil; aliquots of different concentration were injected with eight replicates each, and the mean value deviation was of 1–2.5% at the higher concentrations and of 4–5% at the lower concentrations.

RESULTS

We measured the solubility of glycerol trioleate in SC-CO_2, at 308.1 ± 0.2 K, over a pressure range of 9.6–22 MPa. The results are given in Table 1, where the solubility units are mass of solute per normal liter of gaseous carbon dioxide (= 1.977 g of CO_2), and are shown in Figure 1.

TABLE 1

Solubility (S) of Glycerol Trioleate in Carbon Dioxide, at Pressure P and at 308.15 K (1 nL of CO_2 = 1.977 g)

P MPa	S mg/nL	P MPa	S mg/nL
9.6	1.1	12.2	3.8
9.9	1.9	14.0	4.4
10.0	2.2	15.0	5.6
10.3	1.9	18.9	6.2
11.3	3.6	22.0	7.7

The solubility in SC-CO_2 of crude husk oil (previously extracted with hexane from husk flakes) was measured at 308.6 ± 0.3 K and 313.6 ± 0.1 K, in a pressure range of 9–22 MPa. Extraction of the husk oil from the husk flakes was performed in a pressure range from 10–18 MPa and at 308.6 K. The results of these measurements are presented in Table 2, and are shown, at 308.6 K, in Figure 2.

We used capillary gas chromatography to obtain the composition profiles of some of the samples extracted from liquid husk oil. By the same method, we analyzed the composition of the crude husk oil from which the SC-CO_2 extraction was performed, and additionally a husk oil obtained by traditional refining processes and two olive oils with a good market acceptance. Integrating the peak areas corresponding to the major groups of compounds present in the several samples analyzed, we obtained their relative concentration in the samples. In all cases, these groups were triglycerides and free fatty acids.

The composition data thus obtained and the corresponding results for the oil solubility enabled us to calculate the solubilities of the free fatty acid and of the triglyceride fractions of the oil, as a function of pressure. These are given in Table 3 and shown at 313.6 K in Figure 3. In Figure 4, the solubilities of the free fatty acid fraction are plotted together with results of other authors for oleic acid.

The composition of the free fatty acid and the triglyceride fractions of the SC-CO_2 extracted husk oil were separated into their individual elements. The triglycerides are identified by a group of three letters corresponding to the fatty acid moieties, present in the triglyceride molecule, for instance, PLO refers a triglyceride that results from the esterification of glycerol with palmitic acid, linoleic acid and oleic acid, respectively at the first, second and third carbon atoms of the glycerol molecule. The most abundant triglycerides in the crude oil are OOO and POO, in concentrations of approximately 45 and 30 w% of the triglyceride fraction, respectively. Within the precision of the analysis, there is no discernible effect of the extraction process in the relative abundance of the triglycerides in the pressure and temperature ranges of our study, as is shown in Figure 5. The same applies for the relative abundances of the acids in the free fatty acid fraction, containing approximately 65% oleic, 10% palmitic, 9% linoleic and 4% stearic acids.

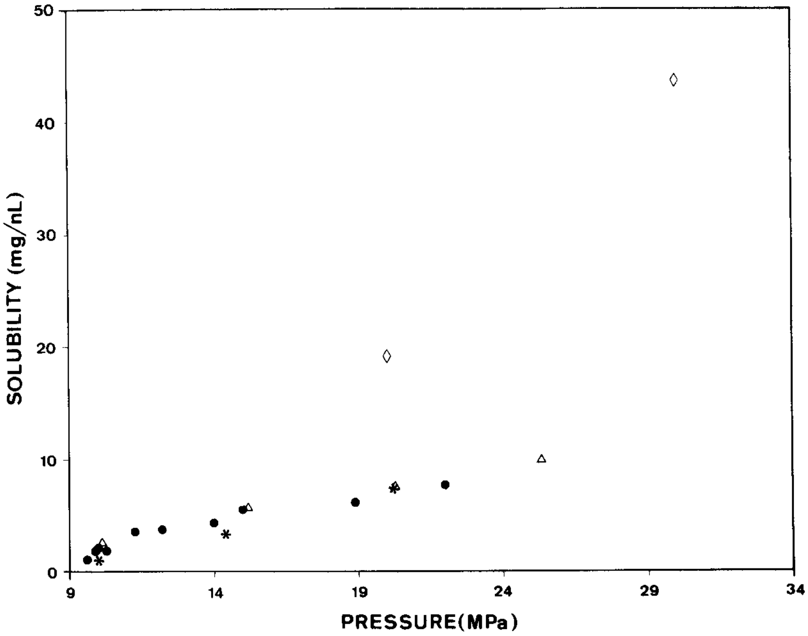

FIG. 1. Solubility of glycerol trioleate in SC-CO_2, at 308.6 K (●). Comparison with measurements reported by: King *et al.* (*), at 308.15 K; J. Chrastil (△) and Brunetti *et al.* (◊), at 313.15 K.

TABLE 2

Solubility of Husk Oil in Carbon Dioxide, at Pressure P and Temperature T[a]

P	308.65 K		313.65
MPa	Solid	Liquid	Liquid
9.0		5.0	
10.0	4.7	5.5	
10.5		6.1	5.5
11.3		7.5	7.3
12.0	6.2	8.9	7.8
12.5		9.3	
13.0		10.0	10.5
14.2		11.7	11.2
15.3		11.9	13.7
16.0	6.4	12.3	
16.8		13.4	15.9
17.6		14.6	17.0
18.0	8.1	15.8	
18.6		16.9	
19.5		18.8	17.5
19.8		19.1	
20.7			17.5
21.7			18.4

[a]The oil was extracted from: Solid phase, husk flakes; and liquid phase, crude husk oil.

DISCUSSION

Although olive oil had not been, as far as we know, subject to any SCF extraction study previously to Brunetti's, triolein is a major component of another important vegetable oil, rapeseed oil. Studies of the solubility of this compound were already available before the publication of their paper. Brunetti *et al.* (9) mention the work of Chrastil (10), although they erroneously classify their method as a single pass flow technique, when, in fact, Chrastil worked with a batch system. King *et al.* (11), using a flow technique with recirculation, have also published results, that extend to three temperatures and pressures to 20 MPa.

The solubility of triolein, measured in this work at 308.6 K, is compared in Figure 1 with data of other authors. Our results are in very good agreement with the

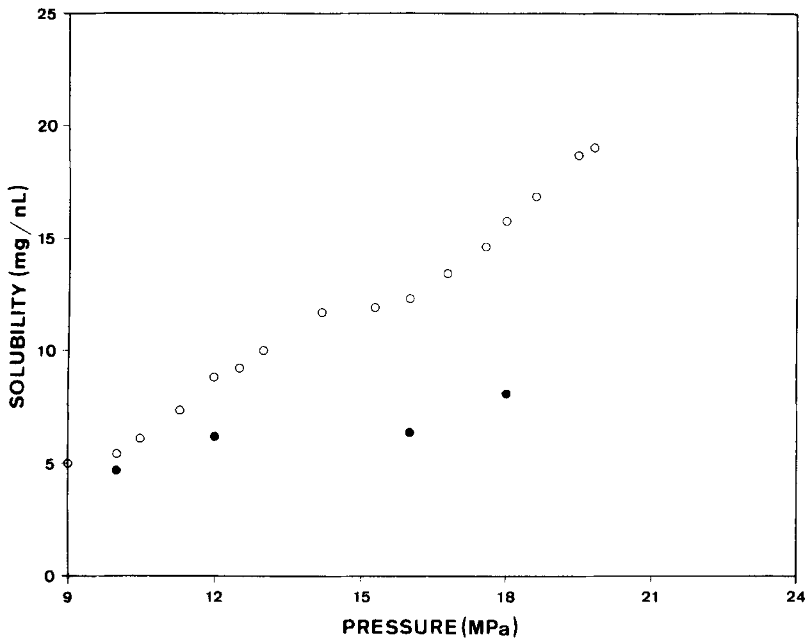

FIG. 2. Solubility of husk oil in SC-CO_2, at 308.6 K, when extraction is performed from crude husk oil (○) or from olive husk flakes (●).

TABLE 3

Comparison Between the Solubility S, in Carbon Dioxide, of Crude Husk Oil (S_{Oil}), and of the Corresponding Triglyceride (S_{Tri}) and Free Fatty Acid (S_{FFA}) Fractions, at Pressure, P, and at Temperatures of 308.6 K and 313.6 K

	P	S mg/nL		
T/K	MPa	S_{Oil}	S_{Tri}	S_{FFA}
308.6	11.3	7.5	3.7	3.4
	12.5	9.3	4.2	4.6
	14.2	11.7	3.5	7.1
	15.3	11.9	3.4	7.1
	17.6	14.6	3.6	9.2
	19.8	19.1	3.4	14.3
313.6	10.5	5.5	1.7	3.4
	13.0	10.5	1.6	7.4
	14.2	11.2	2.0	8.2
	15.3	13.7	3.7	8.8
	17.6	17.0	5.3	10.3
	20.7	17.5	3.9	12.1
	21.7	18.4	6.0	10.7

solubility values obtained by King *et al.* at 308.15 K. The results of Chrastil are also within experimental error of our results. Although they were obtained at a 5 K higher temperature, 313.15 K, interpolation between results at different temperatures of King *et al.* (11) suggest that this increase in temperature should lower the solubility by only about 0.6 mg/nL. It should be mentioned, however, that the data of Chrastil shows a peculiar increase with temperature, and not only for triolein, but for several other triglycerides and fatty acids. Bamberger *et al.* (17) have recently suggested that Chrastil's results might be severely affected by volatile impurities eventually contained in the samples he used. They report, for instance, one order of magnitude increase in the solubility of tripalmitin when the purity of the sample decreased from 99% to 90%.

Relevant for comparison with the above mentioned results are the data of Klein *et al.* (18) for vapor-liquid equilibria of carbon dioxide and rapeseed oil, obtained in a vapor recirculation apparatus. They give vapor phase oil concentrations in carbon dioxide at 313.15 K, that are only slightly lower than our results for triolein. Although the oil is a complex mixture, triolein is its major compo-

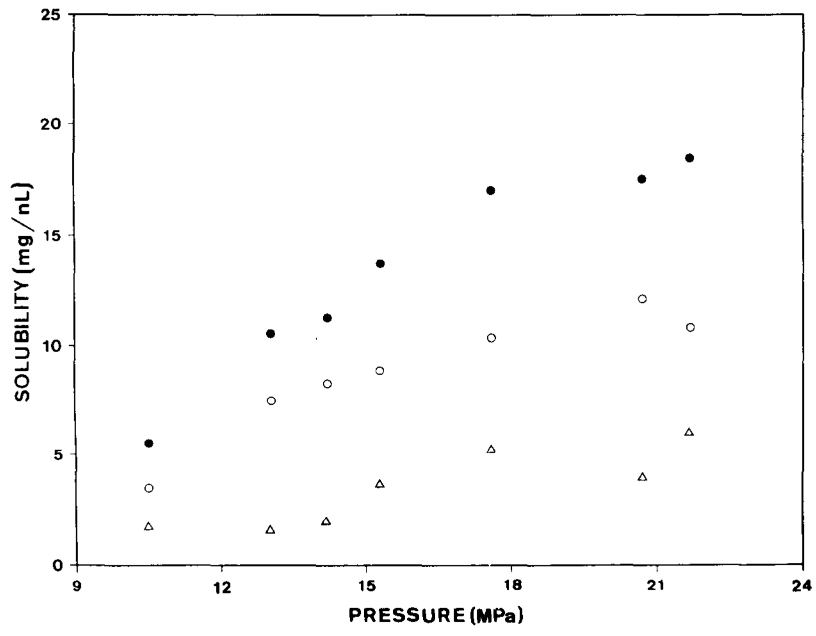

FIG. 3. Solubility of: Crude husk oil (●), the free fatty acid (○), and the triglyceride (△) fractions from the same oil, in SC-CO_2, at 313.6 K.

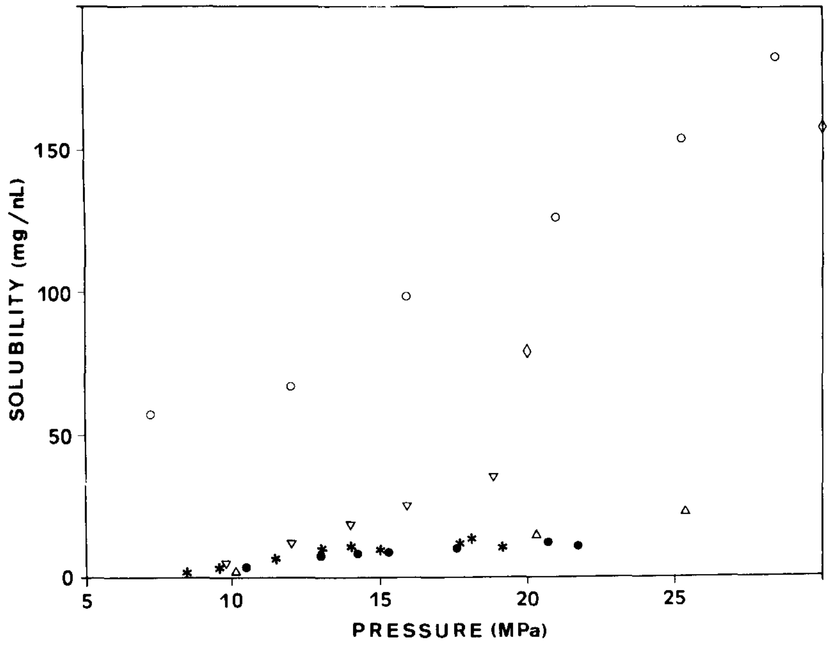

FIG. 4. Comparison between: Solubility in SC-CO_2 of free fatty acids from husk oil (●), at 313.6 K; other authors reports on the solubility in SC-CO_2 of oleic acid—Chrastil (△), Peter *et al.* (▽), Brunetti *et al.* (◇), Zou *et al.* (○), at 313.15 K; and King *et al.* (*) at 308.15 K.

nent, and therefore this kind of agreement would be expected.

The data reported by Brunetti *et al.* at 313.15 K, that are also shown in Figure 1, diverge strongly from the above mentioned results. Their solubilities are much higher than all the others for triolein and also than other published values of the solubilities of oils mainly composed by triglycerides, like those of Friedrich *et al.* (1)

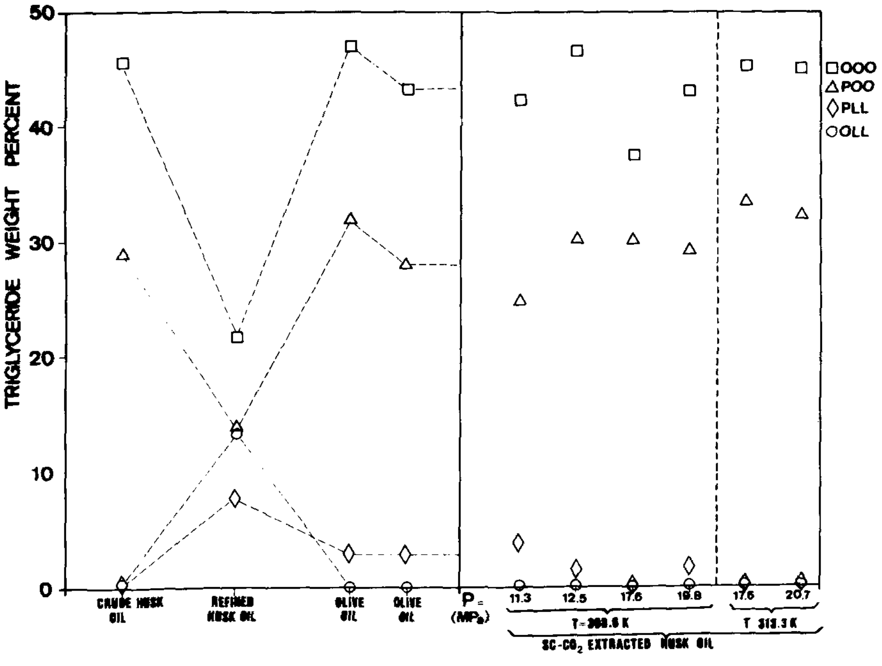

FIG. 5. Triglyceride composition of SC-CO_2 extracts from crude husk oil obtained in different pressure and temperature conditions; comparison with olive and husk oils.

and Stahl *et al.* (4) for soybean oil. It is difficult to assess the cause of these discrepancies. We speculate, following Bamberger *et al.* (17), that impurities in the reportedly 65% pure triolein used by Brunetti *et al.* might be partly responsible. Another possibly important source of error in their experimental method might be the measurement of the quantity of carbon dioxide circulated.

In addition to the solubilities of triolein, we measured husk oil solubility in carbon dioxide from previously hexane extracted crude husk oil and also from solid olive husk flakes.

Our results of the SC-CO_2 extraction from the husk flakes are very similar to those of King *et al.* (11) on rapeseed. Their conclusions should therefore be at least partially applicable to the olive husk oil case.

We verify that, in both cases, solubilities are slightly higher than the solubility of triolein in identical pressure and temperature conditions. This probably means that the seed extracted oil contains compounds other than triglycerides—King reports the presence of small amounts of free fatty acids in the rapeseed oil extracts. However, these are smaller than the total acid contents of hexane extracts.

When SC-CO_2 extraction is performed from the husk flakes, the solubility values are lower than when similar measurements are done on liquid husk oil. This difference is shown in Figure 2 and indicates that some of the compounds extracted with hexane can be solubilized by carbon dioxide when they are in the lipid form, but not when they are bound to the solid matrix.

The SC-CO_2 extracts from the hexane extracted husk oil (crude husk oil) were analyzed by capillary chromatography and high contents of free fatty acids were found. The chromatographic analysis allowed the separate calculation of solubilities of the free fatty acid and triglyceride fractions, as shown in Figure 3, at 313.6 K.

As the major constituent of the free fatty acid fraction is by far oleic acid, with about 65% in weight, we compared our results of the free fatty acid fraction solubilities with data of several authors for pure oleic acid. Although the solubility of a component in a mixture can be very different from its solubility as a pure substance, it is usually the heavier compounds (triglycerides in this case) that are affected. The lighter components (fatty acids in our case) may act as entrainers, increasing the overall solubility of the mixture. It can be seen in Figure 4 that, as for triolein, the results of Chrastil (10) and of King *et al.* (19) are in close agreement with our own. The measurements of Peter *et al.* (20) give somewhat higher solubilities.

As to the results of Brunetti *et al.* (9), they are once again higher than those of most other authors, as found previously for pure triolein. For oleic acid, however, a recent paper by Zou *et al.* (21) gives solubilities in carbon dioxide that are even higher, using a double recirculation (vapor and liquid) technique. This last paper, however, consistently reports very high solubilities at lower pressures, close to the critical pressure of CO_2, where the density of the solvent is quite low, and it is very unlikely that it can solubilize any significant amount of acid. Therefore, their results might not be very reliable.

As to the triglyceride fraction of our husk oil extracts, solubilities at 308.65 K and 313.65 K are similar but slightly lower than the solubility of pure triolein, as measured in this work.

Triolein is not as prevailing among triglycerides in husk oil as oleic acid is among free fatty acids. After triolein (with about 45% weight), the most abundant constituent of the triglyceride fraction is 1-palmityl diolein (approximately 30% weight); other triglycerides are present in amounts lower than 10% weight. We do not have data on the solubility of pure 1-palmityl diolein, but since it is reported (10) that tripalmitin has a lower solubility in SC-CO_2 than triolein, it is reasonable to suppose that the presence of a palmitic acid group in 1-palmityl diolein will be associated with a lower solubility of this triglyceride.

In Figure 3 we can see how free fatty acids are more easily extracted than triglycerides from the oil, at 313.6 K. This difference between the solubility of free fatty acids and triglycerides was also detected at 308.6 K. Application of SC-CO_2 extraction to deacidify husk and olive oil seems, therefore, to be feasible in relatively mild operational conditions. This is the same conclusion as reached by Brunetti *et al.*, but based on substantially different results.

The conventional refining processes used to deacidify either olive and husk oils may introduce changes in the triglyceride composition, producing a decrease in the nutritional qualities of the oil. The results in Figure 5 show that the SC-CO_2 extracted husk oil, the crude oil and the two olive oils have a similar triglyceride composition; refined husk oil presents some considerable differences from all others, particularly in the weight percent of triglycerides that contain oleate or linoleate groups. As no detectable differences were found between the crude oil and the extracts, it is reasonable to assume that contact with high pressure carbon dioxide, in opposition to classic refining processes, does not affect the organoleptic qualities of husk oil.

We conclude that the results obtained in this work lend partial support to the previous suggestion by Brunetti *et al.* (9) of the applicability of SC-CO_2 extraction to the deacidification of olive oils. They also indicate that, in this process, the oils retain their triglyceride composition, consequently preserving their nutritional characteristics. The work of Brunetti *et al.* is based, however, in solubility data in such disagreement with values obtained by other authors that more work is needed before a definite conclusion can be reached.

ACKNOWLEDGMENTS

We thank J.N.I.C.T., Lisbon (grant no. 886•86•119), A.I.D. Washington, D.C. (grant no. DPE-5542-G-SS-7048-00) and I.N.V.O.T.A.N. (N.A.T.O. grant PO-837-Lisbonfood) for financial support. M. Gonçalves thanks J.N.I.C.T. for a grant (BIC no. 185).

REFERENCES

1. Friedrich, J.P., G.R. List and A.J. Heakin, *J. Am. Oil Chem. Soc. 59*:288 (1982).
2. List, G.R., and J.P. Friedrich, *Ibid. 66*:98 (1989).
3. Stahl, E., E. Schutz and H.K. Mangold, *J. Agri. Food Chem. 28*:1153 (1980).
4. Stahl, E., K.W. Quirin and D. Gerard, *Fette. Seifen. Anstrichm. 85*:458 (1983).
5. Stahl, E., K.-W. Quirin and D. Gerard, *Gense Gases for Extraction and Refining,* Springer-Verlag, 1987.
6. Studiengesellschaft Kohle Zosel, K., German Patent DAS 23 32 038 (1973).
7. Coenen, H., and E. Kriegel, German Patent DOS 2843 920 (1978).
8. Brunner, G., and S. Peter, *Ger. Chem. Eng. 5*:181 (1982).
9. Brunetti, L., A. Daghetta, E. Fedeli, I. Kikic and L. Zandrighi, *J. Am. Oil Chem. Soc. 66*:209 (1989).
10. Chrastil, J., *J. Phys. Chem. 86*:3016 (1982).
11. King, M.B., T.R. Bott, M.J. Barr and R.S. Mahmud, *Separation Science and Technology 22*:1103 (1987).
12. Di Giovachino, L., M. Solinas, V. Brandani, G. del Re and G. Di Giacomo, *Ind. Alim. 28*:925 (1989).
13. Vasconcelos, A.M.P., . Gonçalves, E.J.S. Gomes de Azevedo, M. Nunes da Ponte and H.J. Chaves das Neves, *J. High Resol. Chromatogr. Chromatogr. Comm. 12*:244 (1989).
14. Matos, H.A., E. Gomes de Azevedo, P.C. Simões, M.T. Carrondo and M. Nunes da Ponte, *Fluid Phase Equilibria 52*:357 (1989).
15. Chaves deas Neves, H.J., and A.M.P. Vasconcelos, *J. High Resol. Chromatogr. Chromatogr. Comm. 2*:226 (1989).
16. Geeraert, E., and P. Sandra, *Ibid. 7*:431 (1984).
17. Bamberger, T., J.C. Erikson, C.L. Cooney and S.K. Kumar, *J. Chem. Engn. Data 33*:327 (1988).
18. Klein, T., and S. Schulz, *Ind. Eng. Chem. Res. 28*:1073 (1989).
19. King, M.B., D.A. Alderson, F.H. Fallaha, D.M. Kassim, J.R. Sheldon and R.S. Mahmud, in *Chemical Engineering at Supercritical Fluid Conditions,* edited by M.E. Paulaitis, J.M.L. Penninger, R.D. Gray, Jr., P. Davidson, 1983, Chapter 2, p. 31.
20. Peter, S., M. Seekamp and A. Bayer, in *Proceedings of the International Symposium on Supercritical Fluids,* Nice, 1988, p. 99.
21. Zou, M., Z.R. Yu, P. Kashulines, S.S.H. Rizvi and J. Zollweg, *J. Supercritical Fluids 3*:23 (1990).

[Received August 20, 1990; accepted March 16, 1991]