

# Continuous Fractionation of Used Frying Oil by Supercritical CO<sub>2</sub>

L. Sesti Osséo<sup>a</sup>, G. Caputo<sup>a</sup>, I. Gracia<sup>b</sup>, and E. Reverchon<sup>a,\*</sup>

<sup>a</sup>Dipartimento di Ingegneria Chimica e Alimentare, Università degli Studi di Salerno, 84084 Fisciano (SA), Italy, and <sup>b</sup>Departamento de Ingeniería Química, Universidad de Castilla-La Mancha, 10 13004 Ciudad Real, Spain

**ABSTRACT:** Fractionation by supercritical carbon dioxide (SC-CO<sub>2</sub>) might be a way to purify used frying oils, since a selective separation of the oil components based on their polarity and M.W. can be attained. In this work, we studied the purification of peanut oil used for frying by SC-CO<sub>2</sub> continuous fractionation in a packed column. The influence of pressure (15–35 MPa) and temperature (25–55°C) on the yield and on the composition of products was determined. The composition of the top and bottom products was evaluated by using size-exclusion chromatography and other accepted chemical methods. Process conditions were selected to separate TG from degraded compounds. Experimental results indicated that the operating conditions leading to maximal TG recovery in the extract were 35 MPa, 55°C, and a solvent-to-feed ratio of 53. By operating at these conditions, it was possible to recover 97% of the TG placed on the column and about 52% by weight of the used frying oil. The composition of the purified top stream was very similar to that of fresh frying oil.

Paper no. J10778 in *JAOCS* 81, 879–885 (September 2004).

**KEY WORDS:** Carbon dioxide, continuous extraction, oil purification, supercritical fluid fractionation, used frying oil.

The food industry uses a large quantity of fats and oils for frying processes. During deep-frying, oils are exposed to temperatures up to 200°C in the presence of air for prolonged heating cycles. At these severe conditions, oils undergo many chemical changes that lead to the formation of substances that compromise the quality of fried foods and pose potential human health hazards. The main reactions occurring during deep-frying are hydrolysis, oxidation, and polymerization of TG. After several hours of deep-frying, the oil contains many degradation compounds such as cyclic monomers, dimers, trimers, and polymers of TG; polycyclic aromatic hydrocarbons (PAH), dioxin, and dioxin-like compounds; oxidized FA; and oxidized TG.

Currently, the main use of used frying oils is in animal feed and, in lesser quantities, in the manufacture of soaps and biodegradable lubricants and in energy recovery by combustion in industrial plants (1). The use of recycled cooking oils in formulated feed for animal production poses some risk for animal health and, as a consequence of bioaccumulation, for human health. In particular, some degradation products such as polymers, PAH, and dioxins causes serious problems to animal and human health because they tend to accumulate in the

body tissues, increasing their concentration along the food chain. Moreover, there is some evidence of direct noxious effects of fried oils to animal health (2). All these considerations indicate the need for purification of fried oils before their use for animal feed.

Used frying oil (coming from waste collection companies) still contains a large proportion of valuable compounds, in particular, 40–70% of unchanged TG. Thus, environmental and economical reasons can justify the idea of a regeneration process.

The technology for the purification of used frying oils is still not well developed. In the last 10 years, several attempts have been made to purify used frying oil, especially using adsorbent-based treatments (3). These methods have the advantage that solvents are not required, but the efficiency of these processes is low, particularly for the removal of high-M.W. compounds.

Supercritical fluid extraction may be an alternative for the purification of used frying oils, on the basis that the solubility of a compound of a chemical family in a supercritical fluid depends on its molecular mass when pressure, temperature, and composition are fixed. In particular, the use of supercritical carbon dioxide (SC-CO<sub>2</sub>) as a solvent in the food industry has some advantages since CO<sub>2</sub> has a low critical temperature (31°C) and pressure (7.4 MPa) and can be easily removed from products; moreover, it is nontoxic, nonflammable, and inexpensive.

Processes based on the use of SC-CO<sub>2</sub> for the extraction and purification of vegetable oils have been developed. Extraction and refining of vegetable oils have been proposed for the purpose of obtaining extracts with lower contents of phospholipids and metals, a higher tocopherols content, a lighter color, and a better flavor (4,5). Selectivity between TG and waxes has been achieved for substances with a high level of fatty material (5). SC-CO<sub>2</sub> extraction has also been used in refining olive oils (6,7) to show that a wide variation in oil quality parameters can be obtained depending on the operating conditions.

Oil fractionation with SC-CO<sub>2</sub> has also been proposed. In some cases, oils characterized by different polarity and M.W. have been obtained when working in discontinuous or in continuous countercurrent extractors (8–12). Yoon and coworkers (13) tested the separation of used frying oil with supercritical CO<sub>2</sub> in a batch extractor. They proposed a two-stage extraction: In the first step the pressure was set at 15 MPa, and in the second, at 30 MPa. The oil still contained 8% of low-M.W. compounds. A continuous process performed in a

\*To whom correspondence should be addressed at Dipartimento di Ingegneria Chimica e Alimentare, Università degli Studi di Salerno, Via Ponte Don Melillo, 84084 Fisciano (SA), Italy. E-mail: ereverchon@unisa.it

mixer-settler unit has recently been patented (14). The authors fractionated used frying oil by SC-CO<sub>2</sub>, with ethanol as co-solvent. The SC phase coming from the settler was sent to three separators, characterized by different pressure and temperature; the liquid phase coming from the settler was simply flashed to separate CO<sub>2</sub> from heavy oils. An overall recovery up to 58% of the fried oil was obtained. No details were given about TG recovery. Another interesting patent, applied in a similar field, described the fractionation of FA TG using SC-CO<sub>2</sub> and ethanol in a continuous tower. A selective recovery of PUFA from the glyceride mixture is possible (15).

Continuous countercurrent SC-CO<sub>2</sub> processing in a packed tower can have several advantages over batch processes. First, this steady-state process affords a fixed composition in the top and bottom products. Moreover, large quantities of fried oil can be treated; therefore, this process can be more interesting from an economical point of view. Thus, the aim of this work has been to check whether SC continuous countercurrent fractionation is a suitable technique to fractionate peanut oil used for frying. The influence of pressure, temperature, and solvent-to-feed flow ratio on the fractionation process has been investigated with the goal of regenerating the TG fraction.

## MATERIALS AND METHODS

**Materials.** Peanut oil that had been used for 36 h of frying at 150°C in an industrial frying machine was obtained from the university canteen. The properties of the oil, analyzed with the methods described in the next section, are indicated in Table 1, together with those corresponding to the fresh oil. Carbon dioxide (purity 99%) was supplied by S.O.N. (Naples, Italy).

Methylene chloride (HPLC grade) was bought from Sigma-Aldrich (Milan, Italy). Potassium hydroxide (1 mol/L in ethanol) and sodium thiosulfate (0.1 mol/L) were supplied by Riedel-de Haën (Seelze, Germany); diethyl ether (99.8%), petroleum ether (99.8%), and acetic acid glacial (99.9%) were supplied by Carlo Erba Reagenti (Milan, Italy); chloroform (99.9%), potassium iodide (99%), and starch from maize were supplied by Fluka (Buchs, Switzerland).

**Analytical methods.** Vegetable oil is substantially a mixture of saturated and unsaturated TG (triacylglycerols of FA). TG are characterized by carbon number, which is the total number of carbon atoms in the three constituent FA. Triolein, with carbon number 57, is the most abundant TG in vegetable oils (>90%).

**TABLE 1**  
**Properties of Peanut Oil<sup>a</sup>: Fresh and Used for 36 h for Frying**

	DPTG, %	TG, %	LMWC, %	TPM, %	Acidity, %	PI, meq O <sub>2</sub> /kg
Frying oil	3.6	93.0	3.4	8.1	0.11	5.59
Fried oil	39.7	59.6	0.7	28.5	0.8	12

<sup>a</sup>DPTG, dimeric and polymeric TG; LMWC, low-M.W. compounds; TPM, total polar material; PI, peroxide index.

Used frying oil, as a consequence of oxidation, polymerization, and hydrolysis reactions, contains a variety of undesired substances such as oligopolymers, oxidized TG, sterols, and FA. The level of degradation of fried oil can be evaluated using several chemical parameters linked to the concentration of compounds formed during frying. The analysis of dimeric and polymeric TG (DPTG) by high-performance size-exclusion chromatography (HPSEC) and the determination of total polar material (TPM) are widely recognized as the most accurate methods for assessing the degradation of used frying oil (16). These are official AOCS methods and are useful since some countries have established regulatory limits for TPM and DPTG in used frying oils. For example, in many European countries the limit for TPM has been set to 25 wt% and the limit of DPTG to 16 wt% (16). In this work, the quality of oil after purification was analyzed using these two methods. In addition, acidity and peroxide indexes (PI) were evaluated. The acidity is the percentage of free oleic acid and gives a measure of the degree of degradation of the oil. A limit of 5% is fixed in many countries. The PI is a measure of the peroxide derivatives in the oil.

(i) *Chemical analyses.* The acidity and PI were determined according to standard methods (17).

(ii) *Chromatography.* Determination of TPM was conducted according to AOCS Official Method Cd 20-91 (18). This method is based on the separation of used frying oil between polar and nonpolar compounds by preparative chromatography with a silica gel column.

Oil composition has been evaluated on the basis of the M.W. of three major classes of components: TG, DPTG, and low-M.W. compounds (LMWC). HPSEC was used to determine the quantity of these compounds in the oil. An HP 1100 Chemstation equipped with a 20- $\mu$ L injector loop, UV detector set at 230 nm, and two PLGel columns (PerkinElmer, Beaconsfield, United Kingdom), 30  $\times$  0.75 cm, was used. The two columns were packed with 5- $\mu$ m cross-linked styrene-divinylbenzene copolymer particles having pore diameters of 100 and 500 Å, respectively. The elution solvent was methylene chloride at 0.8 mL/min flow rate. A sample having a concentration of 1.75% wt/vol was injected at T = 25°C. The elution time of each class of compounds was determined against three standards supplied by Supelco (Bellefonte, PA). The composition of DPTG, TG, and LMWC in the samples was determined by calculating the relative area of each peak.

*Experimental apparatus.* The column was 1920 mm long and had an internal diameter of 17.5 mm. All parts were made in AISI 316 stainless steel and were designed to withstand up to a maximum internal pressure of 70 MPa at 30°C. The column was filled with stainless steel berl packings, 5-mm nominal size, with 1600 m<sup>-1</sup> specific surface and 0.9 voidage. Temperature along the column was controlled by five automatic controllers. Similar temperature-controlling techniques were also adopted for the liquid feed. Carbon dioxide was fed to the column by a high-pressure diaphragm pump that could deliver flow rates up to 12 kg/h. The oil mixture was withdrawn directly from a reservoir and fed to the column by a piston pump.

The stream exiting from the top of the column was heated at 80–90°C before being depressurized to 2 MPa by a micrometering valve and fed to the first separator kept at a temperature around 0°C. A second separator was provided to collect volatile compounds. The total quantity of the solvent was measured at atmospheric pressure and then the flow rate was checked by a dry test meter. Oil fractions were collected at the bottom of the tower and at the bottom of the first and second separators. Extract and raffinate samples were weighed and analyzed according to the analytical procedures already described. The product masses were calculated by weighing the samples collected at the top and bottom of the column.

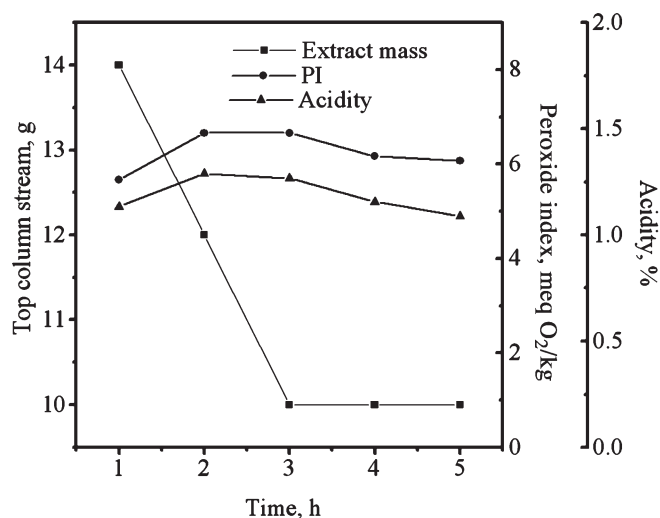
## RESULTS AND DISCUSSION

In this report, used frying oil is considered to be a mixture of three classes of compounds: LMWC, TG, and DPTG. On this basis, fried oil can be treated to obtain a product chemically similar to fresh oil by separating DPTG and LMWC from TG. The goal of fractionation is to obtain a high TG yield and a composition similar to fresh oil. The feasibility of this target was evaluated by studying the effect of the main process parameters on the composition of the top and bottom product and on the separation yield.

Two different yields were considered in this work: overall yield and TG yield. The former is defined as the ratio between the amount of product in the extract phase (top product) and the amount of oil fed to the column; the latter is defined as the ratio between the amount of TG recovered in the top product and the amount of TG in the feed. Overall yield and TG yield were measured as a function of the three main process parameters: solvent-to-feed ratio, pressure, and temperature of the column.

**Continuous operation.** To ascertain that steady-state conditions had been obtained during the experiments, duration of startup was assessed by measuring composition and flow rate variations of the product. This check was made under several sets of conditions by analyzing product samples withdrawn at different processing times. Five withdrawals of the top and bottom products were made over a period of 5 h. The evolution with time of the extract oil mass at the top of the column is shown in Figure 1. Mass flow rates and concentrations showed negligible variations after the second withdrawal (2 h processing). A similar result has been obtained with citrus peel oil fractionation by using the same column (9). However, to avoid any doubt about the attainment of steady-state conditions in the column, all experiments were carried out for at least 4 h before the withdrawal of the products.

In a first set of experiments, the column was operated in a countercurrent mode with the oil fed from the top as the heavy phase and SC-CO<sub>2</sub> fed from the bottom as the light phase. In this manner, the column worked as a stripping section. None of the results obtained with this configuration were satisfactory: A very small quantity of raffinate was recovered at the bottom of the column. Most of the oil was recovered in the top separator where oil and carbon dioxide formed a rela-



**FIG. 1.** Column startup. Mass of the extract, peroxide index (PI), and acidity of the stream on the top of the column are reported as a function of time. Data refer to a test carried out at 35 MPa, 40°C, and solvent-to-feed ratio of  $R = 53$ .

tively stable dispersion. The dispersion was probably formed by the feed oil with SC-CO<sub>2</sub> near the top of the column, causing the failure of the separation process. To overcome this problem a second set of experiments was performed with the feed inlet point put at 0.6 of the column height (1200 mm from the bottom), with the purpose of introducing a defoaming section in the top of the column and performing the separation mainly in the lower part of the column. This configuration ensured a stable and reproducible operation. Therefore, although the column effective height was reduced, its efficiency was relatively high. All data reported in the following discussion refer to experiments carried out with this configuration: feed inlet, 0.6× column height; 1200 mm effective column height.

**Oil solubility in SC-CO<sub>2</sub>.** A complete set of equilibrium data for a complex mixture such as a used frying oil is not available. Some information on the cumulative yield of used frying oil during supercritical fluid extraction can be found in the literature. According to Yoon *et al.* (13), the solubility of used frying oil varies from  $0.3 \times 10^{-3}$  to  $7.4 \times 10^{-3}$  g oil/g CO<sub>2</sub> depending on temperature, pressure, and composition. The solubility increases with pressure and decreases with temperature. However, the design of a fractionation process requires knowledge of the solubility of the various compounds that are present in the oil rather than the solubility of the oil as a whole. Solubility data at various pressures and temperatures can be found in the literature for some of the components of used frying oil. For example, in the extensive study of Borch-Jensen and Mollerup (19), the partition coefficients of all the components of fish oil in CO<sub>2</sub> are reported. Although the compositions of fish and used frying oil are quite different, we used a selection of these data to obtain qualitative information for a preliminary selection of the fractionation conditions. As shown in Figure 2, we plotted the fish oil partition coefficient ( $K_p$ ) between the two phases (SC and

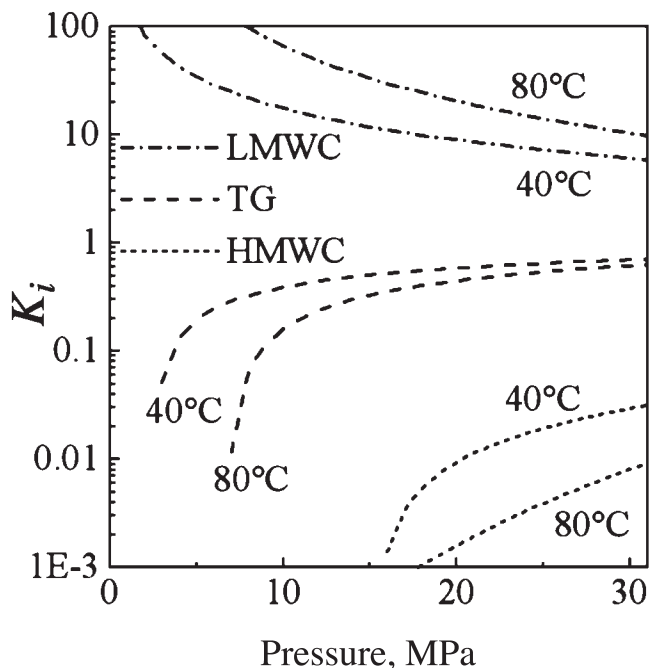


FIG. 2. Equilibrium partition coefficient  $K_i (y_i/x_i)$  of three components of fish oil: triolein (TG), oleic acid (LMWC), and C66-TG (HMWC). Data are adapted from Borch-Jensen and Mollerup (17).

liquid) of triolein as representative of TG (C57), oleic acid as representative of LMWC, and the highest-M.W. TG (C66) as representative of high-M.W. compounds (HMWC). Unfortunately, no experimental data about the solubility of DPTG are available in the literature.

Figure 2 shows that, as expected, TG has an intermediate solubility between LMWC and HMWC. Figure 2 also shows that the partition coefficient of HMWC is negligible at pressures below 15 MPa, and that it rapidly increases at higher pressures. In contrast, the partition coefficient of TG is relatively high starting from 5 MPa, but its increase with pressure is smooth. The partition coefficient increases inversely with temperature for HMWC and TG compounds. The partition coefficient of LMWC has an opposite trend: It decreases with pressure and increases with temperature.

*Effect of the solvent-to-feed ratio.* In a previous work performed on the same column (9), the flooding condition was evaluated as about 10 kg/h of  $\text{CO}_2$ . However, flooding depends on the kind of liquid processed. Therefore, we performed a preliminary solvent flow rate estimation with respect to flooding. In this case, flooding conditions were obtained at  $\text{CO}_2$  flow rates greater than 3 kg/h. Thus,  $\text{CO}_2$  flow rates lower than 3 kg/h were used in all the experiments. The effect of the solvent-to-feed ratio ( $R$ ) has been tested in a series of experiments with  $\text{CO}_2$  flow rates of 1.6, 2.2, and 2.9 kg/h (corresponding to  $R$  values equal to 53, 100, and 148) at a constant feed flow rate (0.03 kg/h). In experiments carried out at  $R = 148$ , fluctuations in the  $\text{CO}_2$  flow rate were observed, and small amounts of oil were entrained by  $\text{CO}_2$ . That is a typical behavior when flooding conditions are approached. Therefore, this unfavorable operating condition was discarded and a

lower  $R$  was chosen ( $R = 53$ ) for all the other experiments. With respect to product fractionation, the main effects of the increase of  $R$  were an increase in top product yield and a decrease in process selectivity. Indeed, in working at  $R = 53$ , the top yield was 39.2% and TG was 39.2%; working at  $R = 148$ , the top yield was 84.5% and TG was 39.2%.

*Effect of pressure and temperature.* The effects of temperature and pressure were tested at an  $R$  value of 53. Temperatures of 25, 40, and 55°C were tested operating at 15, 21, 28, and 35 MPa. The results of these experiments are reported in Figures 3–5 and in Table 2.

Figures 3 and 4 show the effects of pressure and temperature on the overall yield and TG yield, respectively. A continuous increase in both the overall and TG yield can be observed. This effect is due to the increase in  $\text{CO}_2$  density with pressure, which produces an increase in the solubility of both DPTG and TG. For instance, by operating at 25°C and 35 MPa ( $\text{CO}_2$  density 987 kg/m<sup>3</sup>), the overall top yield was 87% and the TG recovery yield was 97.4%. However, at these process conditions the selectivity of the separation was low, because high-density  $\text{CO}_2$  could solubilize a large amount of DPTG (32.7% as reported in Table 2). This result was confirmed by the solubility behavior reported in Figure 2, which shows that at high pressure, the HMWC partition coefficient increased more rapidly than that of TG.

Unlike the TG and DPTG concentrations, the acidity of the top product decreased as the pressure was increased. This trend is shown in Figure 5, where the acidity of the top product, expressed as oleic acid percentage, is reported. In good agreement with the trend in Figure 2 at lower pressures, the acidity value was relatively high and decreased at higher pressures. For example, at 55°C and 15 MPa, the acidity of the top product

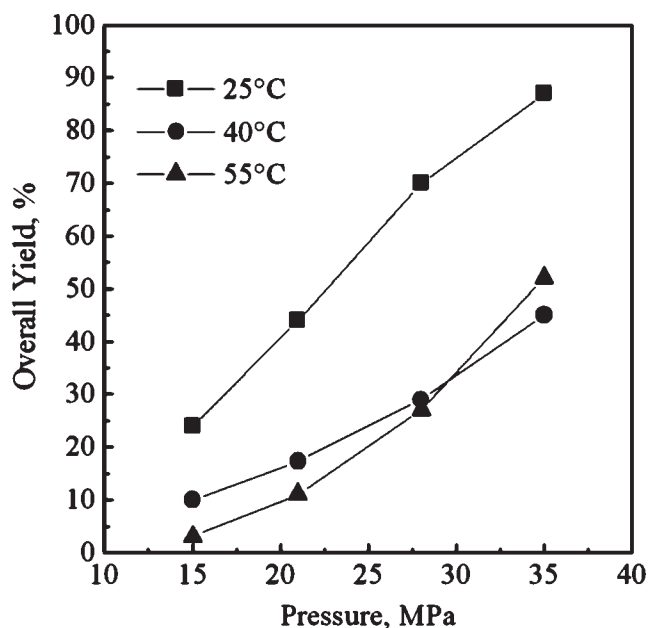


FIG. 3. Effect of pressure and temperature on the overall extraction yield of used frying oil. Data refer to experiments carried out at  $R = 53$ . For abbreviation see Figure 1.

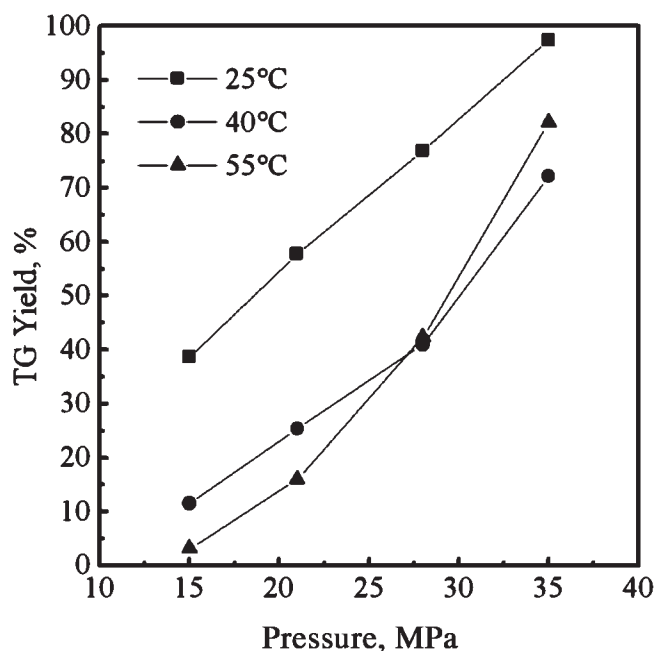


FIG. 4. Effect of pressure and temperature on the TG recovery yield from used frying oil. Data refer to experiments carried out at  $R = 53$ . For abbreviations see Figures 1 and 2.

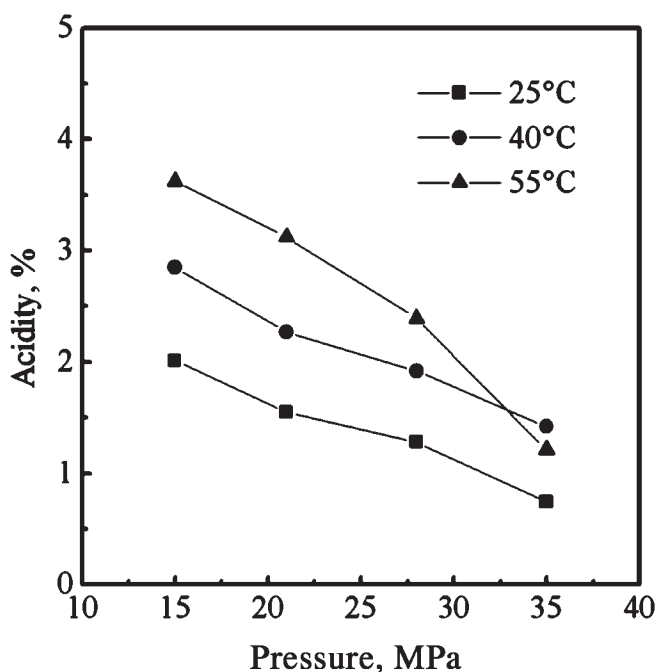


FIG. 5. Effect of pressure and temperature on the acidity of regenerated used frying oil obtained as the top product. Acidity is defined as the percentage of oleic acid.

was about three times higher than that of the used frying oil; at 55°C and 35 MPa acidity it was 1.21%, closer to that of the used frying oil (0.8%). This means that most of the LMWC, which are responsible for the acidity, were extracted at low pressure (about 15 MPa). This result is in agreement with data reported in the literature (6).

The effect of pressure and temperature on the percentage of total polar materials (TPM) was also studied. TPM comprise substances having a polarity greater than unaltered TG. Mainly, they are TG oligomers (dimers, trimers), oxidized TG, partial glycerides, sterols, triterpene diols, and FA (20). TPM analyses are reported in Figure 6 for top fractions obtained at 25 and 55°C. The two curves are very different. When operating at 25°C, the TPM amount increased with pressure up to 17.8%. On the contrary, in operating at 55°C, the TPM amount decreased from 26.6 to 10.5%. The trend of the curve at 55°C is similar to that of the acidity at the same temperature. This fact probably means that the TPM amount is basically related to FA concentration. The increase in the TPM amount observed when operating at 25°C can be related to the DPTG content, which was higher with respect to fractions obtained at this temperature as evidenced in Table 1. Indeed, when operating at 25°C, the DPTG content increased with pressure from 2.4 to 32.7%. However, the TPM amount could be reduced well below the safety limit of 25%.

The lowest DPTG content in the top fraction for which the overall yield was acceptable was obtained working at 35 MPa and 55°C ( $\text{CO}_2$  density =  $881 \text{ kg/m}^3$ ). At these process conditions, the top product had a TG content of 94.5% with a TG yield of 82.1% and a DPTG content of 4.2%. The overall yield was 52%. In comparing the composition data reported in Table 1 for the fresh oil and in Table 2 for the regenerated oil obtained working at 55°C and 35 MPa, it appears that regenerated oil has a composition close to that of the fresh frying oil. The TPM value is also very close to that of the fresh oil. Nevertheless, about 18% of TG remained in the bottom fraction. To recover this TG residue, we performed some experiments at a higher temperature while maintaining the pressure at 35 MPa. Indeed, as shown in Figures 3 and 4, at pressures higher than about 29 MPa an increase in temperature causes an increase in yield. The presence of a crossover among isotherms in the solubility diagram is a well-known phenomenon that is common for various oils (4,21). For this reason, we performed some experiments between 55 and 80°C, setting the pressure at 35 MPa. Unfortunately, the extraction yield was lower than that obtained at 55°C. We speculate that this result is due to the fact that the pressure at which crossover occurs is not the same for all isotherms and that it tends to be higher at higher temperatures. This behavior has been observed with many oils (4,21). Thus, at temperatures higher than 55°C the crossover probably appears at pressures higher than 35 MPa, which was the high-pressure limit of our plant.

Therefore, we made a second attempt to increase the TG yield of the process. The bottom products obtained at 55°C and 35 MPa were mixed and processed in the column as a feed, in the same conditions of the previous experiment. Operating in this manner, we simulated a continuous fractionation with a second column. We obtained an increase in the TG yield up to 97%.

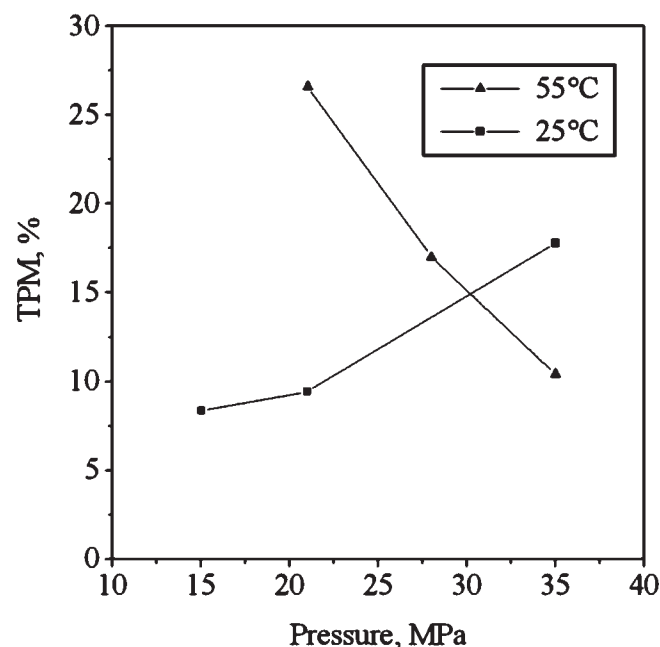
In conclusion, the results indicate that purification of fried oil is possible using SC-CO<sub>2</sub> in a continuous column. The process is very selective with respect to TG and polymerized

**TABLE 2**  
**Experimental Results<sup>a</sup> of Used Frying Oil Fractionation by SC-CO<sub>2</sub>**

T, °C	P, MPa	Product	DPTG, %	TG, %	LMWC, %	PI, meq O <sub>2</sub> /kg
25	15	Top	2.4	94.7	2.9	7.2
		Bottom	51.7	48.3	0.0	5.2
	21	Top	22.3	76.1	0.0	8.3
		Bottom	54	46	1.0	27.0
	28	Top	33.4	46.0	0.0	16.5
		Bottom	54.0	66.5	0.8	30.4
35	Top	32.7	66.5	0.8	5.5	
	Bottom	88.0	12.0	0.0	31.4	
40	15	Top	26.5	66.7	6.8	25.2
		Bottom	41.2	58.8	0.0	22.3
	21	Top	10.8	85.3	3.9	21.3
		Bottom	45.9	54.1	0.0	31.2
	28	Top	4	93.5	2.5	22.2
		Bottom	54	46	0.0	24.3
35	Top	3.2	95.3	1.5	5.3	
	Bottom	69.8	30.2	0.0	9.0	
55	15	Top	11.6	64.3	24.1	25.7
		Bottom	40.5	59.5	0.0	20.6
	21	Top	6.5	87.0	6.4	17.8
		Bottom	43.8	56.2	0.0	32.2
	28	Top	4.8	92.6	2.6	25.7
		Bottom	52.7	47.3	0.0	27.3
35	Top	4.2	94.5	3.0	5.3	
	Bottom	77.8	22.2	0.0	9.4	

<sup>a</sup>All data refer to experiments carried out with a solvent-to-feed ratio of  $R = 53$ . For abbreviations see Table 1.

TG. Pressure and temperature are the main variables that affect the performance of the process. The selection of a proper pair of their values allows the yield and the selectivity of the process to be tuned. The purified oil contains 97% of the TG



**FIG. 6.** Content of total polar material (TPM) in the top fractions as a function of pressure and temperature.

initially present in the feed, with composition and properties very close to that of the fresh frying oil.

On the other hand, the chemical engineering expertise cannot be yet used, because the used frying oil mixture equilibria are not available and DPTG must be better characterized. Some work on equilibria for this mixture are in progress (20). Moreover, the amount of CO<sub>2</sub> necessary to fractionate the oil is relevant and should be minimized to obtain a competitive process. An increase in the operating pressure and/or use of cosolvent could be a suitable technique to reduce the amount of CO<sub>2</sub> for the process.

#### ACKNOWLEDGMENTS

The authors would like to thank Dr. Antonio Maria Rocco for the experimental work and Dr. Marla Cleofe Volpe for TPM analysis.

#### REFERENCES

1. European Parliament, Recycled Cooking Oils, PE nr. 289.889, February 2001.
2. Clark, W.L., and G.W. Serbia, Safety Aspects of Frying Fats and Oils, *Food Technol.* 45:84–94 (1991).
3. Mancini-Filho, J., L.M. Smith, R.K. Creveling, and H.F. Al-Shaikh, Effects of Selected Chemical Treatments on Quality of Fats Used for Deep Frying, *J. Am. Oil Chem. Soc.* 63:1452–1456 (1986).
4. Stahl, E., K.W. Quirin, and D. Gerard, *Dense Gases for Extraction and Refining*, Springer-Verlag, Berlin, 1988.

5. King, M.B., T.R. Bott, M.J. Barr, and R.S. Mahmud, Equilibrium and Rate Data for the Extraction of Lipids Using Compressed Carbon Dioxide, *Sep. Sci. Technol.* 22:1103–1120 (1987).
6. Simoes, P.C., and G. Brunner, Quality Assessment of Refined Olive Oils by Gas Extraction, *J. Supercrit. Fluids* 13:337–341 (1996).
7. Gonçalves, M., A.M.P. Vasconcelos, E.J.S. Gomez de Azevedo, H.J. Chaves das Neves, and M. Nunes da Ponte, On the Application of Supercritical Fluid Extraction to the Deacidification of Olive Oils, *J. Am. Oil Chem. Soc.* 68:474–480 (1991).
8. de Lucas, A., J. Rincón, and I. Gracia, Influence of Operating Variables on Yield and Quality Parameters of Olive Husk Oil Extracted with Supercritical Carbon Dioxide, *Ibid.* 79:237–243 (2002).
9. Reverchon, E., A. Marciano, and P. Poletto, Fractionation of a Peel Oil Mixture by Supercritical CO<sub>2</sub> in a Continuous Tower, *Ind. Eng. Chem. Res.* 36:4940–4948 (1997).
10. Budich M., S. Heilig, T. Hesse, V. Leibkuchler, and G. Brunner, Countercurrent Deterpenation of Citrus Oils with Supercritical CO<sub>2</sub>, *J. Supercrit. Fluids* 14:105–114 (1999).
11. Ruivo, R., M.J. Cebola, P.C. Simoes, and M. Nunes da Ponte, Fractionation of Edible Oil Model Mixtures by Supercritical Carbon Dioxide Column. Part I: Experimental Results, *Ind. Eng. Chem. Res.* 40:1706–1711 (2001).
12. Sato, M., M. Kondo, M. Goto, A. Kodama, and T. Hirose, Fractionation of Citrus Oil by Supercritical Countercurrent Extractor with Side-Stream Withdrawal, *J. Supercrit. Fluids* 13:311–317 (1998).
13. Yoon, J., B.S. Han, Y. Kang, K.H. Kim, M.Y. Yung, and Y.A. Kwon, Purification of Used Frying Oil by Supercritical Carbon Dioxide Extraction, *Food Chem.* 71:275–279 (2000).
14. Devittori, C., M. Perrut, and W. Maiewski, Method for Fractionating Cooking Oils, European Patent EP1261684 (2002).
15. Perrut, M., W. Maiewski, and H. Breivik, Purifying Polyunsaturated Fatty Acyd Glycerides, U.S. Patent 6,204,401 (2001).
16. Takeoka, G.R., G.H. Full, and L.T. Dao, Effect of Heating on the Characteristics and Chemical Composition of Selected Frying Oils and Fats, *J. Agric. Food Chem.* 45:3244–3249 (1997).
17. European Legislation for Olive Oil, no. 2568/91, 5th July 1991.
18. AOCS, *Official Methods and Recommended Practices of the AOCS*, 5th edn., AOCS Press, Champaign, 1997.
19. Borch-Jensen, C., and J. Mollerup, Phase Equilibria of Fish Oil in Sub- and Supercritical Carbon Dioxide, *Fluid Phase Equilib.* 138:179–211 (1997).
20. Gomes, T., and F. Caponio, Effort to Improve the Quantitative Determination of Oxidation and Hydrolysis Compound Classes in Edible Vegetable Oils, *J. Chromatogr. A* 844:77–86 (1999).
21. Sovová, H., M. Zarevúcka, M. Vacek, and K. Stránský, Solubility of Two Vegetable Oils in Supercritical CO<sub>2</sub>, *J. Supercrit. Fluids* 20:15–28 (2001).
22. Sesti Osséo, L., T. Capolupo, and G. Caputo, On the Modelling of the Fractionation of Fried Oil with Supercritical Carbon Dioxide: A First Step, in *9th Meeting on Supercritical Fluids*, ISAFS, Trieste, 13–16 June 2004, published on the Conference CD, E21.

[Received January 9, 2004; accepted July 23, 2004]