

CONTINUOUS FRACTIONATION OF FRIED OIL BY SUPERCRITICAL CO₂

L. Sesti Osséo^a, G. Caputo^a, I. Gracia^b and E. Reverchon^a

^a Dipartimento di Ingegneria Chimica e Alimentare. Università degli Studi di Salerno. Via Ponte Don Melillo, 84084 Fisciano (SA), Italy. FAX. +39089964057

E-Mail: ereverchon@unisa.it

^b Departamento de Ingeniería Química. Universidad de Castilla-La Mancha. Facultad de Ciencias Químicas. Avda. Camilo José Cela nº 10. 13004 Ciudad Real. España.

ABSTRACT

Fried oils are a waste generated from food industries and restaurants that are usually discarded because oxidized lipids degrade the quality of the fried food. The development of new purification technologies has been of increasing interest over the last years, because the fried oil still contains a large quantity of triglycerides that could be recycled. Fractionation by supercritical Carbon Dioxide (SC-CO₂) might be an effective way for the purification of fried oils because SC-CO₂ can selectively separate oil components on the basis of their polarity and molecular weight. In this work we studied the fractionation of fried peanut oil by SC-CO₂ continuous fractionation. The fractionation has been carried out in a continuous packed column with an inner diameter of 17.5 mm and an effective height of 1920 mm, with the feed at about 800 mm from the top. The content of polymeric compounds (POL), triglycerides (TG) and low molecular weight compounds (LMWC) in the fractionated streams was evaluated by high-pressure size exclusion chromatography. We studied the influence of pressure (in the range 15-35 MPa), of temperature (in the range 25-55 °C), on the process yield and on the composition of extracted streams. Operation conditions were optimised to separate POL and TG fractions in the separation column. Experimental results indicate that the optimal operating conditions leading to maximal TG to POL separation and maximum recovery of TG in the extract were at 35 MPa, 55°C and at solvent to feed ratio of 50.

INTRODUCTION

Food industry uses a large quantity of fats and oils for the preparation various kind of fried foods. During the frying process, fat and oil chemical changes are due to high process temperatures. The main reactions during deep-fat frying include formation of conjugated dienes, formation and decomposition of hydroperoxides, formation of low molecular carbonyl compounds, hydrolysis of triglycerides, and polymerization via complex free radicals. These changes produce a degradation of chemical, physico-chemical and organoleptic characteristics of the oil, and after several heating cycles the oil must be discarded [1, 2, 3]. This residue cannot be reused because of the high content of pollutants; nevertheless the oil still contains a large proportion of valuable compounds. Thus, environmental and economical reasons justify the hypothesis of a regeneration process.

The target of the regeneration of used-frying oil should be the removal of the low molecular weight (LMWC) and polymer (POL) compounds. In the last ten years, several attempts have been made to purify the used frying oil, especially using adsorbent treatments [4-8].

Supercritical fluid extraction could be an interesting alternative for the purification of used frying oil, being the solubility of a supercritical fluid tunable with respect to a compound family when a proper set of pressure and temperature is fixed.

The use of supercritical CO₂ as a solvent in the food industry has advantages over other solvents because CO₂ is non-toxic and can be easily and completely removed from products; moreover it is non-flammable, non-corrosive and readily available in large quantities.

Taking into account all these advantages in both quality and selectivity, supercritical fluid solubility has been extensively studied in vegetable oils. Extraction and refining of vegetable oils has been used to obtain extracts with lower content of phospholipids, metals, higher tocopherol content, lighter color and better flavor [9, 10]. Selectivity between triglycerides and waxes has also been achieved for substances with high level of fatty material [10]. Carbon dioxide has been used in the refining of olive oils [11,12], showing a wide variation of the oil quality parameters depending on the operating conditions [13].

Works on oil fractionation have also been reported, that obtain oil characterized by different polarity and molecular weight working in discontinuous or in continuous countercurrent extractors [14-20]. This late technique seems to be very interesting from an economical point of view.

With respect to fried oil, Yoon and coworkers [2] tested the supercritical CO₂ fractionation in a batch extractor. There obtained promising results only when a two-stage operation was performed. They proposed a two-stage carbon dioxide supercritical extraction: pressure in the first stage was 150 bar, and 300 bar in the second stage, obtaining an oil that still contains 8% LMWC. A similar batch process has been recently reported in a patent [21], where ethyl alcohol has to be used as cosolvent.

Therefore, the aim of this work is to check if the supercritical continuous countercurrent extraction could be a suitable technique to fractionate fried peanut oil. In this work we investigate the influence of the most common operating variables on the oil fractionation in order to obtain a regeneration of the triglyceride fraction.

EXPERIMENTAL PROCEDURES

Materials. Exhausted oil was obtained as residual oil after a frying for 36 hour at 150°C in an industrial frying machine. The properties of the oil analysed with the methods described in the next section, are indicated in **Table 1**, together with those corresponding to the fresh oil used in the food industry.

Table 1, fresh and fried oil composition

	POL %	TG %	LMWC %	Acidity %	PV (Meq O ₂ /kg)
Fresh Oil	4	94.8	1.2	0.11	5.59
Fried Oil	42.6	55.3	2.1	0.8	12

POL: Polymer, TG: Triglyceride, LMWC: Low Molecular Weight Compounds, PV: Peroxide Value

Carbon dioxide (purity 99%) was supplied by S. O. N. (Naples, Italy). All analytical reagents were bought by Sigma-Aldrich, Italy.

Analyses: The Acidity and Peroxide Value parameters of the oil were determined according to standard methods specified in European Commission Regulation 2568/91 [17].

Chromatography

Since the analysis of the exact distribution of the different compounds in the oil is out of the scope of this work, we decided to evaluate the oil composition on the basis of the molecular

weight of the three main components of the oil: LMWC, TG, POL. Molecular weights of these compounds were determined by High Pressure Size Exclusion Chromatography (HPSEC). We used a HP 1100 chemstation equipped with a 20 μL injector loop, a UV detector set at 230 nm, and two PLGel columns (Perkin-Elmer, U. K.) 30 cm x 0.75 cm.

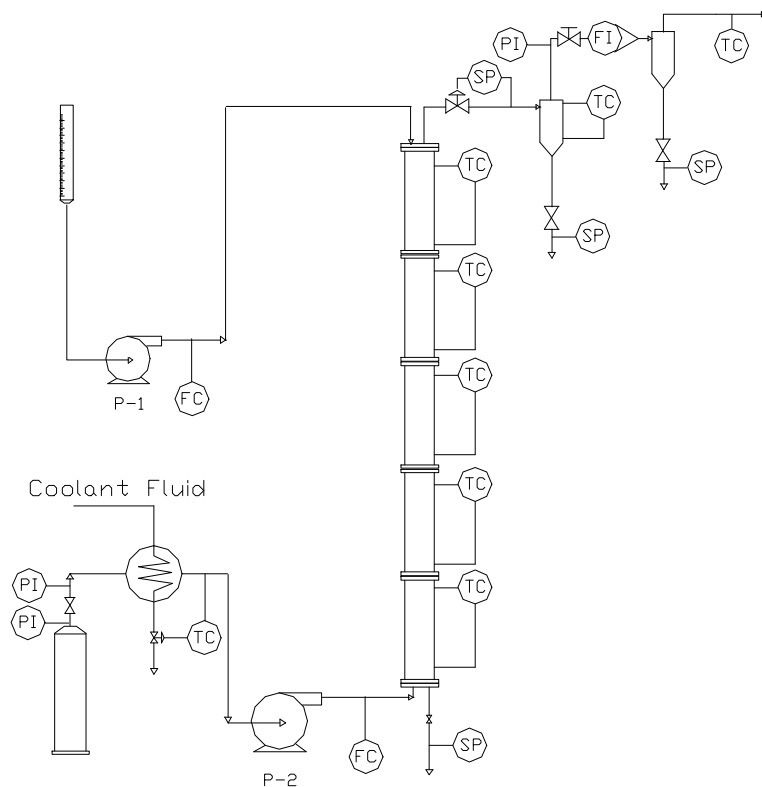


Figure 1. Experimental Apparatus.

P-1 Oil pump	PI Pressure indicator,
P-2 CO ₂ pump	TI Temperature indicator
TC Temperature controller	FI Flow indicator
FC Flow controller	SP sample point.

cooled head. A PID controller controls CO₂ temperature at the column inlet. Similar temperature-controlling techniques are also adopted for the liquid feed. The oil mixture is withdrawn directly from a reservoir, and fed to the column by a piston pump (Milton Roy Model Minipump). The stream exiting from the top of the column is heated to 80-90 °C before being depressurized to 2 Mpa by a micrometering valve, and then it is fed to a separator kept at a temperature around 0 °C by another controller. A second separator collects the eventual part of the most volatile extract. Before the vent, a rotameter and a dry test meter measure the CO₂ flow rate and the total quantity of solvent used, respectively. The oil fractions are then collected at the bottom of the tower and at the bottom of the first and the second separator. Extract and raffinate samples were weighted and analyzed according to the analytical procedures. The product flow rates were calculated by weighing the samples collected at the top and bottom of the column at fixed time intervals.

Apparatus. A scheme of the experimental apparatus is shown in **Figure 1**. The column is 1920 mm long and has an i.d. of 17.5 mm. It consists of 5 cylindrical sections (Autoclave Engineers), 305 mm long and with an O.D. of 25.4 mm, connected to each other and to the process lines by 6 similar 4-port elements. All parts are made in AISI 316 stainless steel and are designed to withstand up to a maximum internal pressure of 70 MPa at 30 °C. The column is packed with stainless steel packing 5 mm nominal size with 1600 m⁻¹ specific surface and 0.9 voidage. The temperature along the column is controlled by five PID controllers (Watlow Model 965). The solvent is fed to the column by a high-pressure diaphragm pump (Milton Roy Model Milroyal B), that can deliver CO₂ flow rates up to 12 kg/h and that is provided with a

RESULTS AND DISCUSSION

In order to approach the fractionation problem, the oil composition has been considered as a mixture of three compounds: the triolein of oleic acid as representative of Triglycerids (TG), the dimer of triolein as representative of Polymers (POL) and oleic acid as Low Molecular Weight Compounds (LMWC). Therefore, fried oil can be treated to obtain a product chemically similar to the fresh oil, performing a separation of the chemical compounds POL and LMWC from TG. These simplifications allow the use of an easier approach for the fractionation problem and the experimental analysis. First of all, the main target of the fractionation is to obtain a high yield of TG and a composition similar to the fresh oil.

With respect to the solubility in supercritical CO₂, TG have intermediate properties between LMWC (highest solubility) and POL (lowest solubility). Thus, a separation of both compounds in a single tower is not possible. In fact, considering TG the light key compounds and POL the heavy key components, the LMWC are certainly mixed in the top product. The separation of TG from LMWC must be done in other equipment, at different operating conditions.

Thus, the fractionator operating conditions must be selected mainly looking at the quantity of TG recovered and at its purity. For these experiments, we selected pressure from 15 MPa up to 35 MPa.

Many studies on fresh vegetable oils solubility indicate that CO₂ density can be the most important parameter. For this reason, we have initially performed the experiments at constant density, selecting first the operating pressure of each experiment and adjusting consequently the relative temperature to generate a set of data at constant density. **Table 2** represents the summary of the oil recovery at the top of the column as a function of the column operation pressure for CO₂ densities respectively equal to 780 and 880 kg m⁻³. It is clear from the data of **Table**

Exp.	T (°C)	P (MPa)	Position	Mass Fraction(%)	Collected Oil (g)
CO ₂ Density 780 kg m ⁻³					
E1	40	15	Top	11.4	13
			Bottom	88.6	101
E4	50	19.6	Top	17.4	19
			Bottom	82.6	90
E5	60	24.4	Top	22	22.5
			Bottom	78	81
CO ₂ Density 880 kg m ⁻³					
E6	25	15	Top	24,3	17
			Bottom	75,7	53
E2	40	25	Top	30.8	36
			Bottom	69.2	81
E7	55	35	Top	60	68
			Bottom	40	45

Table 2: Experimental results at constant density
Conditions: Solvent to feed ratio: 50, CO₂ flow:24.03 g min⁻¹

2 that significant changes –mainly at highest density - in the splitting between the quantity at the top and at the bottom occur. This unexpected behavior can be explained looking at the different compositions: the fresh oil (95% w/w TG) seems to have a behavior similar to a mono compound, whereas the fried oil (only about 55% TG) has a behavior like a real mixture.

However, this group of experiments confirmed that an effective fractionation is possible using a supercritical fractionation tower. Although the top fraction oil composition depends in a complex manner from operating conditions of the column, for all the tested cases TG concentration increases with operating pressure. A particular interest should be devoted to the

fractionation operated at 55°C and 35 MPa, since the top product exhibits a recovery of TG very high (close the total TG fed) and a satisfactory composition (about 93% TG, 3% POL and 4% LMWC).

The consistency of the experimental data has been analyzed with equilibrium data available in literature [23, 24]. Particularly, we used the equilibrium data obtained from Borch-Jensen and Mollerup [23], re-elaborated for our case in **Figure 2**, that reports at two different temperatures the K_i -values on a CO₂ free basis

calculated as the ratio of the CO₂ free mass fraction of component i in the vapor phase y_i to the mass fraction of component i in the liquid phase x_i .

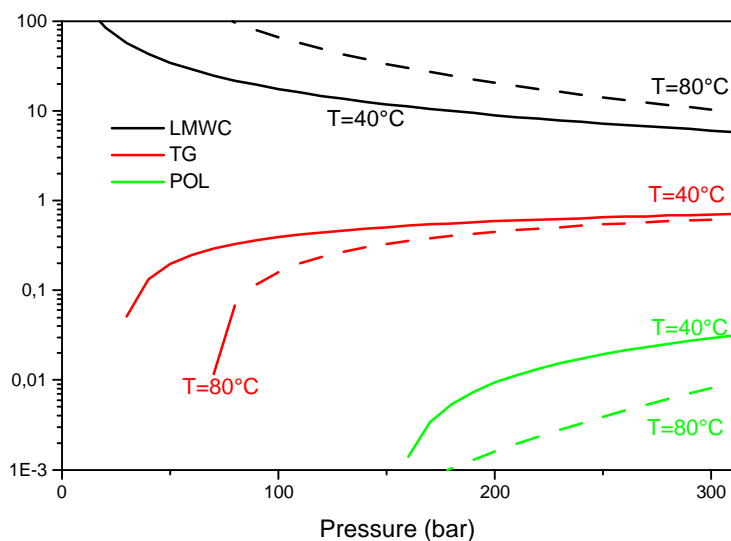


Figure 2. Equilibrium constant of model compounds - adapted from ref. [23]

$$K_i = \frac{y_i}{x_i}$$

Using overall material balances on the fractionation tower and the value of K_i from **Figure 2** and the experimental recovery of product from the top, we show in **Table 3** the evaluation of the equilibrium composition of the top fraction and the experimental composition.

T=40°C P=250 MPa					
		Equilibrium		Experimental	
	Feed	Top fraction (calculated)	Bottom fraction (from balance)	Top fraction (measured)	Bottom fraction (from balance)
TG (w/w%)	55.3	90.4	39.7	83.4	42.8
POL(w/w%)	42.6	2.8	60.3	9.8	57.2
LMWC(w/w%)	2.1	6.8	0.0	6.8	0.0

Above comparison between experimental data and equilibrium provisions shows that – for the case - the equilibrium composition does not seem to be a limiting factor with respect to the fractionation process.

CONCLUSIONS

The operation of a treatment of fried oil in a packed column operated with supercritical CO₂ seems very promising. At pressure above 30 MPa recovery of TG and purity are both satisfying.

Nevertheless, the obtained product still contains a quantity of LMWC that must be treated downstream the tower.

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