

**CONTINUOUS FRACTIONATION OF FRIED OIL
BY SUPERCRITICAL CO₂ AND HEXANE
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ABSTRACT

Fractionation of fried oils by Supercritical Carbon Dioxide (SC-CO₂) might be a suitable purification technique, since a selective separation of the oil components can be attained [1, 2, 3]. Unfortunately, the specific quantity of CO₂ with respect to the oil is fairly high [2, 3] and thus the operating cost is estimated to be high [4]. The use of hexane as cosolvent has been tested to reduce it.

The influence of the hexane concentration at selected operating condition (P = 35 MPa and T = 50°C) has been tested at constant ratio oil-hexane (60% vol). Ratio between CO₂ and oil has been reduced from 52 down to a 22 kg/kg at constant CO₂ flow rate. Fractionation yields and composition of products has been analysed and discussed.

Experimental results indicate that the use of hexane can allow a significant CO₂ flow rate reduction maintaining the oil composition and recovery substantially constant at column top. Nevertheless, the presence of some percentage of hexane residue in the oil has been detected and further treatments are necessary.

INTRODUCTION

Fractionation of fried oils to recover triglycerides components is receiving an increase of interest because of the recent availability in many countries of collected fried oils. A large part of fats and oils in the world is used for the preparation of fried foods. During deep fat frying a significant quantity of oil is heated for a long period and a complex series of chemical changes during frying occur. Fried oil, as a consequence of oxidation, polymerisation and hydrolysis reactions, contains a variety of undesired substances such as oligopolymers, oxidized triglycerides, sterols and fatty acids. The discharged fried oil still has a large portion of triglycerides, but there are also volatile compounds, that include hydrocarbons, aldehydes and ketones, and polymers, that include mostly triglycerides dimers (DPTG), which were not even detectable in fresh oil [4].

Oil composition is usually considered as a mixture of three classes of compounds: Low Molecular Weight Components (LMWC), Triglycerides (TG) and Higher Molecular Weight (POL) [1, 2, 3]. Moreover, Acidity and Peroxide Value (PV) parameters are often used to characterize the oil, these are determined according to standard methods specified in European Commission Regulation 2568/91 [5].

Tab 1. Fresh oil and fried oil properties.

	POL %	TG %	LMWC %	Acidity %	PV meq O ₂ /Kg
Fresh Peanuts Oil	3.6	93.0	3.4	0.11	5.59
Fried Peanuts Oil	39.7	59.6	0.7	0.8	12

Table 1 shows a fresh and a fried oil. Fried oil exhibits a strong increase in the POL, corresponding to a sharp decrease in TG content; moreover, POL increases both values, Acidity and PV. The recent availability of recovered fried oil, now possible in many countries because of environmental protection law, encourages to find new techniques able to valorise the collected material.

The fried oil can be treated with supercritical carbon dioxide (SC-CO₂) to fractionate TG; LMWC and POL. This technique allows a very interesting TG recovery and purity [2, 3]. Nevertheless the specific quantity of CO₂ with respect the oil that is fairly high and thus the operating cost is expected to be high [4].

Hexane has been selected as cosolvent because this is an excellent solvent for the vegetable oils, well accepted in oil processing. Moreover the hexane was the original solvent and oil separation is easy and almost quantitative in SC-CO₂ packed tower [6, 7].

MATERIALS AND METHODS

Peanut fried oil was obtained from our university canteen after 36 hours (three cycles of 12 hours) of frying fish at 150°C in an industrial frying machine. Carbon dioxide (purity 99 %) was supplied by S.O.N. (Naples, Italy) and hexane (purity 95 %) by Sigma Aldrich.

The Acidity and Peroxide Value parameters of the oil were determined according to standard methods specified in European Commission Regulation 2568/91 [5]. All analytical reagents were bought by Sigma-Aldrich, Italy.

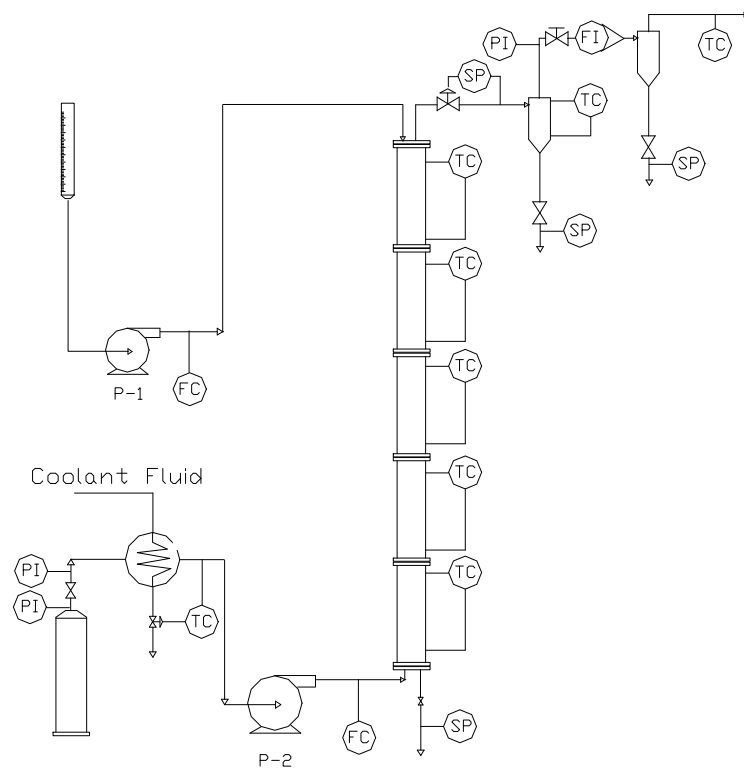
Since the analysis of the exact distribution of the different compounds in the oil is out of the scope of this work, we decided to evaluate the oil composition on the basis of the molecular weight of the three main components of the oil: LMWC, TG, POL. Molecular weights of these compounds were determined 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.

A HP 1100 Chemstation equipped with a 20 µL injector loop, UV detector set at 230 nm, and two PLGel columns (Perkin-Elmer, U. K.) 30 cm x 0.75 cm, was used. The two columns were packed with 5 µm cross-linked styrene-divinylbenzene copolymer particles having a pore diameter 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% w/v was injected at T = 25 °C. The elution time of each class of compounds has been determined against three standards supplied by Supelco. The composition of DPTG, TG and LMWC in the samples was determined by calculating the relative area of each peak.

The hexane content has been determined through static headspace gas chromatography. Adsorbent column was Agilent 19091J-413, 30 m long and 0.3 mm of diameter, support was HP 95-5% Phenyl Methyl Siloxane. Vial volume was 20 µl, heated at 170 °C and equilibration time 15 min. The loop temperature was 175 °C / 180°C, duration 7 min. Transfer line between vial and headspace has been set at 180 °C. Gas carrier are H₂ (30.0 ml/min) and Air (400 ml/min).

A scheme of the experimental apparatus is shown in **Figure 1**.

The column, 1920 mm long, is cylindrical, i.d. of 17.5 mm, O.D. of 25.4 mm. It consists of 5 sections (Autoclave Engineers), 305 mm long connected to each other and to the process lines by 6 similar 4-port elements.



Two ports (17.5 mm ID) are utilized for column connection, two (6.35 mm) are for piping or and instrumentation use. 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). CO_2 is fed to the column by a high-pressure diaphragm pump (Milton Roy Model Milroyal B), that can deliver CO_2 flow rates up to 12 kg/h and that is provided with a cooled head. The CO_2 temperature at the column inlet is controlled by a PID controller. Similar temperature-controlling techniques are also adopted for the liquid feed. The oil, mixed with hexane, 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 depressurized to 8

MPa by local pressure control valve and 30°C and then the top stream is fed to a second separator, kept 2 MPa and 30°C . The oil fractions are collected at the bottom of the tower and at the first and second separator bottom.

A rotameter and a dry test meter measure approximately at atmospheric pressure the CO_2 flow rate (before oil/hexane feeding) and during normal operation, the total quantity of CO_2 and cosolvent flowing.

Extract and raffinate samples were weighted and analyzed according to the analytical procedures. The product yields are calculated by the ratio of target product with respect of the total amount of liquid from the two separators and bottom of the column.

RESULTS AND DISCUSSION

Experiments have been carried out maintaining constant the main flows in the column. Because CO₂ flow rate is largely higher with respect to fried oil, during experiments this flow rate has been kept constant, whereas oil and cosolvent flow has been changed.

The first set of measurements was realized in order to test the hexane co-solvent effect.

For this reason the packed tower has been operated maintaining constant the pressure at 35 MPa, the temperature at 50°C, the CO₂ flow rate at 24 g/min and the oil flow rate at 0.45 g/min. Fractionation at this condition was tested in a previous work [2]. With respect to this experiments, hexane flow rate has been progressively added to feed, starting from 0 up to 0.44 g/min of hexane, corresponding to the range 0-60% vol for oil-hexane mixture and to 0-2.5% wt of ratio hexane- CO₂.

Thus CO₂ flow rate has been continuously reduced from 53 down to a 23 kg of CO₂/kg of oil, when the ratio oil/hexane feed is constant (60% vol of hexane). Top and bottom fractionation and their products composition has been analysed.

Fig. 3 shows the top oil recovery as total and fractional in the first and in

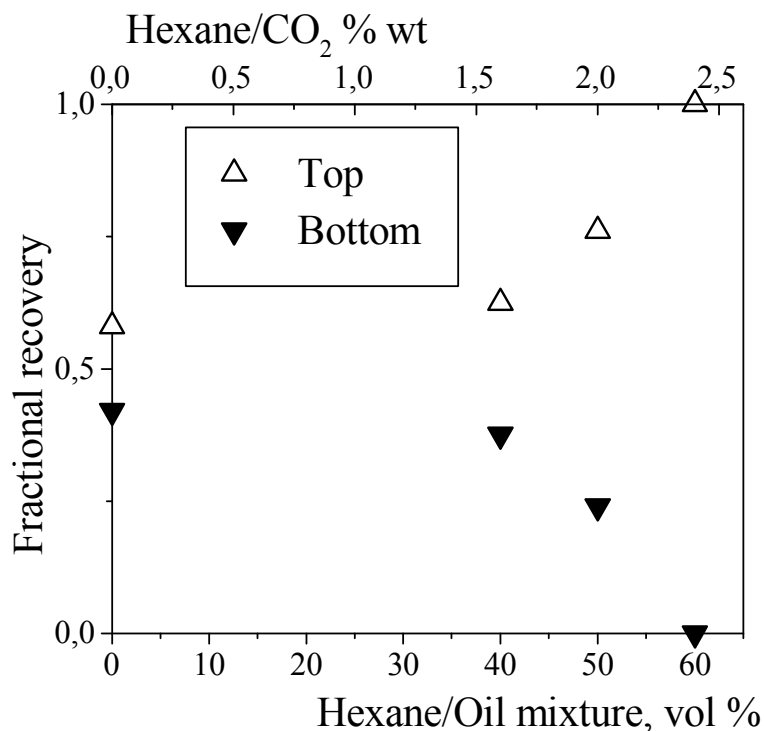


Figure 2. Recovery at top (open triangle) and bottom (filled triangle) fraction as a function of hexane to CO₂ ratio.

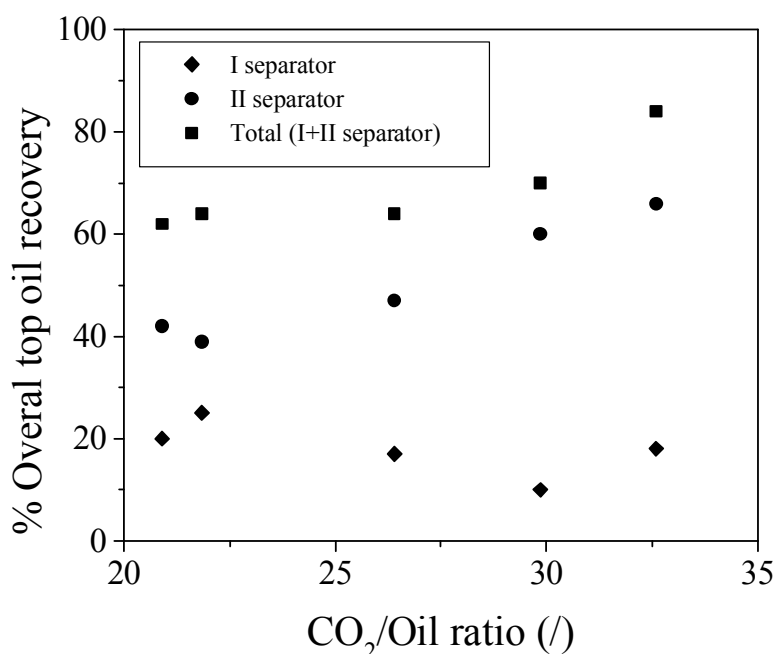


Fig 3. Overall oil recovery on top of tower at 35 Mpa and 323°K (60% vol of hexane in oil/hexane mixture).

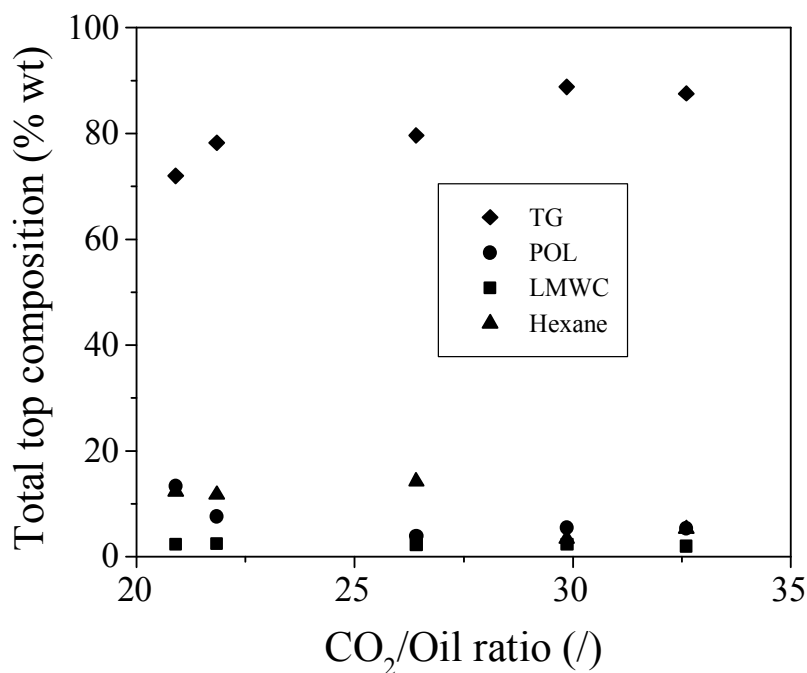


Fig. 4 Overall composition in the top fraction of the column operated at 35 MPa and 323 °K, 60% hexane in the feed.

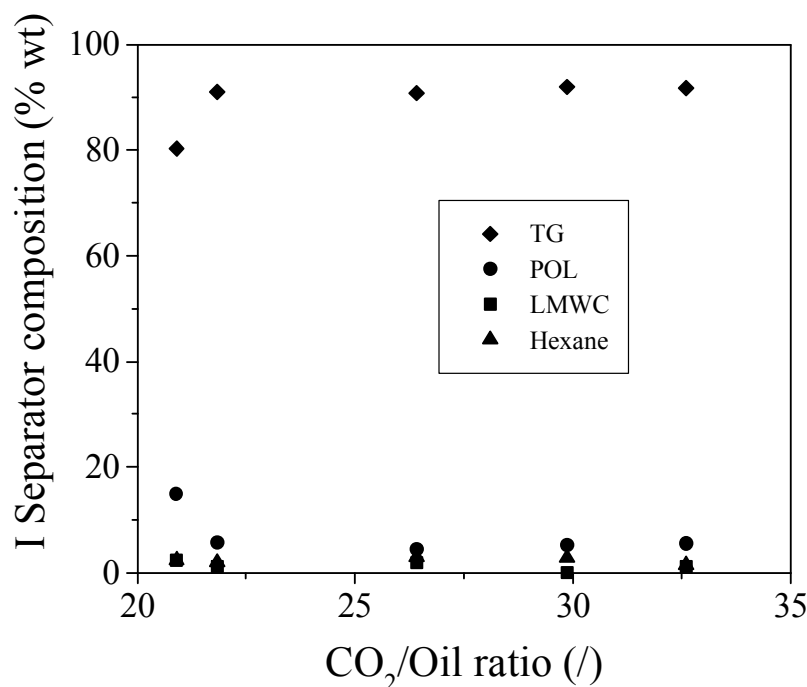


Fig. 5 Composition of the liquid collected at the first separator. Column is operated at 35 MPa and 323 °K, 60% hexane in the feed, separator is at 8 MPa and 303°K

the second separator, as a function of the flow rates ratio CO₂/oil. Coming down from value 1 corresponding to ratio oil/hexane 53 (not shown in **Fig. 3**), a progressive reduction of total top recovery can be observed in the range experimentally investigated (limited by feed oil pump capacity).

The value of top oil recovery is consistent with TG content in the feed; and the first separator (pressure at 8 MPa, T=30°C) collect the greater part; the second separator (pressure at 2 MPa, T=30°C) collects the remaining, in the range from 10% to 20%.

Fig. 4 shows the composition of the oil collected at the first and second separator, as a function of CO₂/oil ratio.

With respect to the most valuable components, i.e. TG, composition ranges from about 70% corresponding to a CO₂/oil ratio of about 22, up to 90% at greater values of **Fig. 4**.

Fig. 5 shows the liquid composition collected at the first separator, set at temperature of 303°K and pressure of 8.0 MPa. The results of TG concentration Vs CO₂/oil ratio are higher than 90% and substantially constant. Hexane contents ranges between 1.5 and 2.9% wt. So, if hexane is removed, TG, POL and LMWC composition are not far from the original values (see **Tab.3**).

Tab 3 – Oil composition at first separator, base free of hexane			
CO ₂ /Oil Ratio (/)	POL % wt	TG % wt	LMWC % wt
32.60	5.54	93.22	1.23
29.86	5.33	94.67	0
26.41	4.54	93.52	1.94
21.84	5.81	92.93	1.26
Fresh oil	3.6	93.0	3.4

CONCLUSION

Hexane has been demonstrated an effective cosolvent for fried oil in supercritical fractionation using CO₂. The experiments carried out in this work show that cosolvent can reduce in two possible way operating cost of the separation:

1. reduction CO₂ flow rate
2. maintaining at high level the separator pressure

With respect to the first point, it is clear that operating costs are well approximated by a linear dependence to CO₂ flow rate. So, CO₂ flow rate reduction higher than 50% as here shown has an high impacts on operating cost.

With respect to the second point, it should be noted that a separation above CO₂ critical pressure could have a positive impact on cost, avoiding the CO₂ condenser need.

Nevertheless, the hexane presence makes the flow sheet more complicated (and more expensive) also using supercritical CO₂ techniques.

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