

ON THE MODELLING OF FRACTIONATION OF FRIED OIL WITH SUPERCRITICAL CARBON DIOXIDE: A FIRST STEP

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Supercritical fluid fractionation (SCF) has been proposed to purify several liquid mixtures. Particularly, a feed of fried peanut oil has been recently treated in order to re-use the purified oil [1, 2]. Although experiments have been successfully carried out obtaining a product composition similar to the original fresh oil [1, 2, 3], the understanding of the process still needs to be improved. The oil composition, obtained using High Performance Liquid Chromatography (HPLC), is usually lumped in three components groups (pseudocomponents): fatty acids (low molecular weight compounds, LMWC), triglycerides (TG) and dimeric and polymeric triglycerides (DPTG), that have been assumed to be typically triacylglycerol dimers.

To describe overall mass transfer in any continuous device operated with supercritical carbon dioxide (SC-CO₂), local phase equilibria, transfer rate and material balances must be simultaneously solved and integrated along the unit. Unfortunately the fried oil consists of many components and equilibrium data for a part of them are not available. In fact, whereas data between CO₂ and many classical components of vegetable oil are available in literature, the behaviour of mixture solubility of CO₂ and heavier components has not yet been investigated.

For this reason high pressure mixtures of fried oil and CO₂ have been processed, using an equilibrium cell. Particularly, we have used the bottom fraction of a SC fractionation as feed oil, which composition is 77.8% DTG and 22.2% TG (by weight).

Data, obtained in the range 210-380 bar and 40-55°C, show an overall solubility of TG and DPTG in SC-CO₂, and the super critical phase decrease with pressure and increase with temperature. For individual behaviour of TG and DTG a more detailed study, planned for the future, is necessary.

INTRODUCTION

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 class of compounds: LMWC, TG and DPTG [5]. 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 [6].

Tab 1. Fresh oil and fried oil properties.

	DPTG, %	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 DPTG, corresponding to a sharp decrease in TG content; moreover, DPTG 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 valorize the collected material. Within this frame, the fried oil can be treated with SC-CO₂ to be fractionated in a lighter part that can be reused and a heavier fraction that should be differently used [5, 7]. Fractionation by SC-CO₂ might be an effective way for the purification of fried oils since a selective separation of the oil components can be attained. When appropriate operating conditions are set, a recovery of about 97% of TG fed into the column can be obtained, with a composition very similar to the fresh frying oil.

The design of supercritical CO₂ fractionation column requires the knowledge of phase equilibrium data, to estimate the driving force for the material transfer between the phases. Local phase equilibria, mass transfer rate and material balances must be simultaneously solved and integrated along the column. Unfortunately, the fried oil consists of many components and equilibrium data for a part of them are not available. In fact, whereas equilibrium data between CO₂ and the classical components of vegetable oils (LMWC; TG) are available in literature, the data between CO₂ and heavier (DPTG) components has not yet been investigated.

For this reason this study approaches the high pressure CO₂ - DPTG equilibrium.

I - MATERIALS AND METHODS

Peanut fried oil was obtained from our university canteen after 36 hour of frying fish at 150°C in an industrial frying machine. Carbon dioxide (purity 99 %) was supplied by S.O.N. (Naples, Italy).

A bottom fraction (BFR), substantially free of LMWC, see Table 2, is obtained using a SCF, and it is utilized as feed in the cell for equilibrium with SC-CO₂.

Tab 2. Experimental results of bottom fraction (BFR)

T, °C	P, Bar	Product	DPTG, %	TG, %	LMWC, %	P.V.meqO ₂ /Kg
55	350	Bottom	77.8	22.2	0.0	9.4

In Figure 1 is reported a HPLC chromatography for BFR, that show at time of 17.92 min TG peak and at time 15.94 min DPTG peak.

Equilibrium cell is utilized using synthetic method to evaluate solubility of mixture. A known composition mixture is confined in the pressure vessel with two sapphire windows. Temperature and volume of the cell is adjusted until phase separation, visually determined through the transparent window, occurs. In addition, in the static method (not yet possible in our experimental set up) samples of the two phases can be drawn and analysed. This apparatus, sketched in figure 2, is able to describe the performance of phase equilibrium measurements according to both method: static and synthetic.

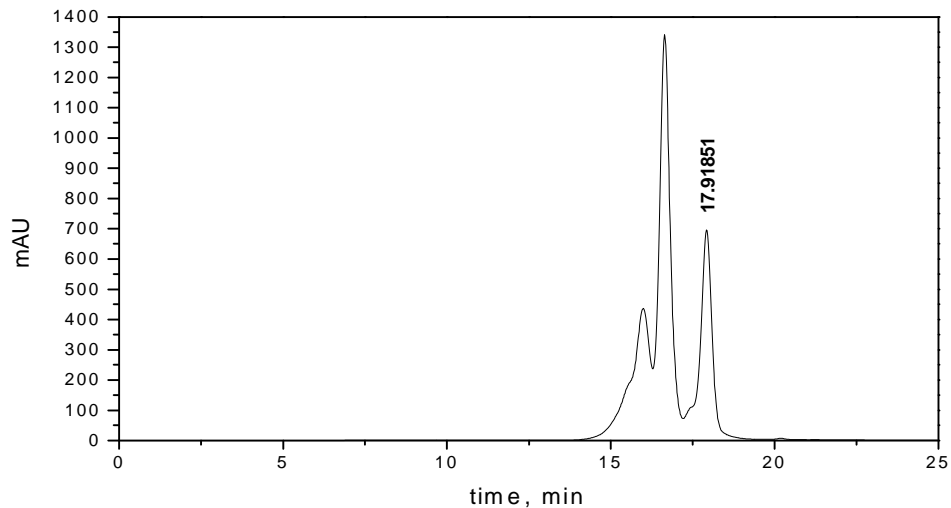


Fig 1. HPLC chromatography for bottom fraction of fried oil.

The apparatus consists of a variable view cell (NWAGmbt, Larrach, Germany) able to operate up to 750 bar and 200 °C. The volume can be changed from 40 to 57 cm³, pneumatically operating an internal movable piston. The cell includes temperature and pressure indicator.

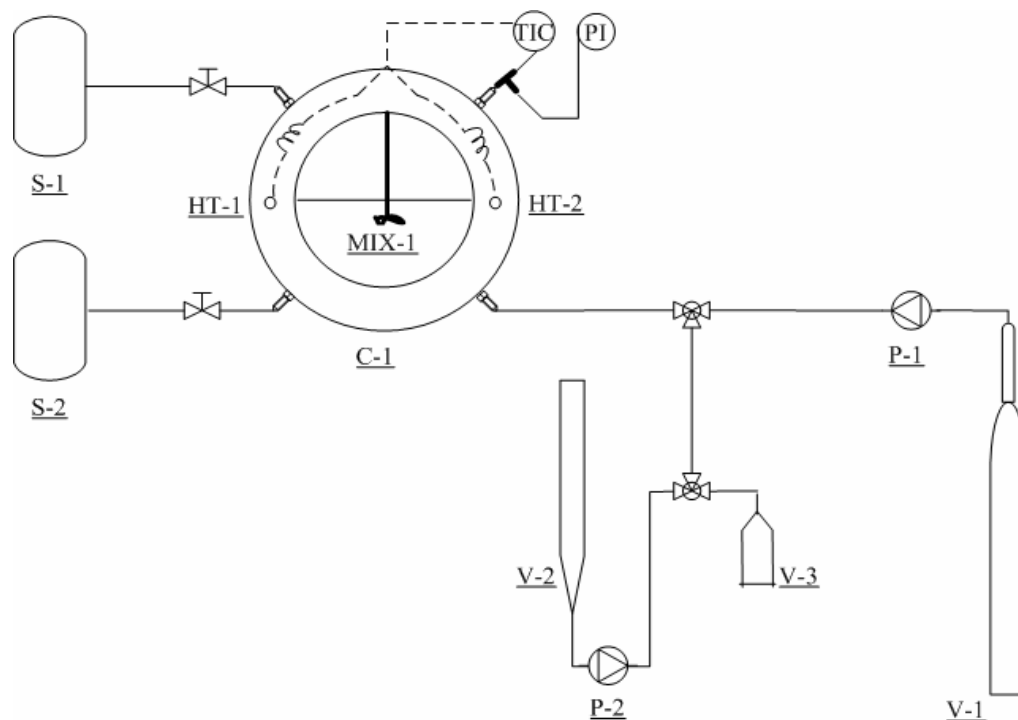


Fig 2. Schematic diagram of apparatus:

C-1 Cell of equilibrium; HT-1, HT-2 Electrical heaters; MIX-1 Stirrer;
P-1 CO₂ Pump; P-2 Liquid pump; S-1, S-2 Separators; V-1 CO₂ vessel; V-2 Liquid vessel;
TIC Temperature indicator and controller; PI Pressure indicator.

The procedure of equilibrium evaluation begins loading the cell with an amount of CO₂ calculated with the Bender equation [8, 9], and with data of cell volume, pressure and

temperature. Thus a known amount of liquid (measured by a graduate capillary) is introduced. The pressure is changed moving the piston and the temperature is set on a PID controller that generate the output to be given by the two electric heaters. After reaching constant pressure and temperature, the cell is stirred for 15 min and the selected temperature and pressure are maintained for 2 hours. After this time equilibrium is supposed to be reached.

A quantity of CO₂ – BFR in ratio 17.58 by weight is processed at temperatures of 40 and 55 °C and pressure of 210, 280, 350 and 380 bar.

RESULTS

At the equilibrium can be observed two phases: the lighter is a supercritical fluid substantially transparent, coloured light yellow; the heavier is a liquid phase coloured from dark yellow to brown, with increase of pressure.

Tab 3. Effect on volume of SC-CO₂

T _{EQUIL} °C	P _{EQUIL} Bar	V _{L,IN} ml	V _{tot, cell} ml	V _{L, EQUIL} ml	ΔV _{oil} ml	Y _{oil} mg _{oil} /gCO ₂
40	210	3.10	54,00	0,94	2,16	39,68
40	280	3.10	52,34	1	2,10	38,54
40	350	3.10	51,08	1,15	1,95	35,73
40	380	3.10	50,71	1,28	1,82	33,46
55	210	3.10	56,96	0,40	2,70	49,62
55	280	3.10	54,47	0,47	2,63	48,20
55	350	3.10	52,58	0,64	2,46	45,16
55	380	3.10	52,06	0,72	2,38	43,61

V_{L,IN} is the liquid mixture fed
V_{tot, cell} is the actual total volume of the cell
V_{L, EQUIL} is the volume of the liquid observable at equilibrium
ΔV_{oil} is the liquid volume difference between fed and equilibrium

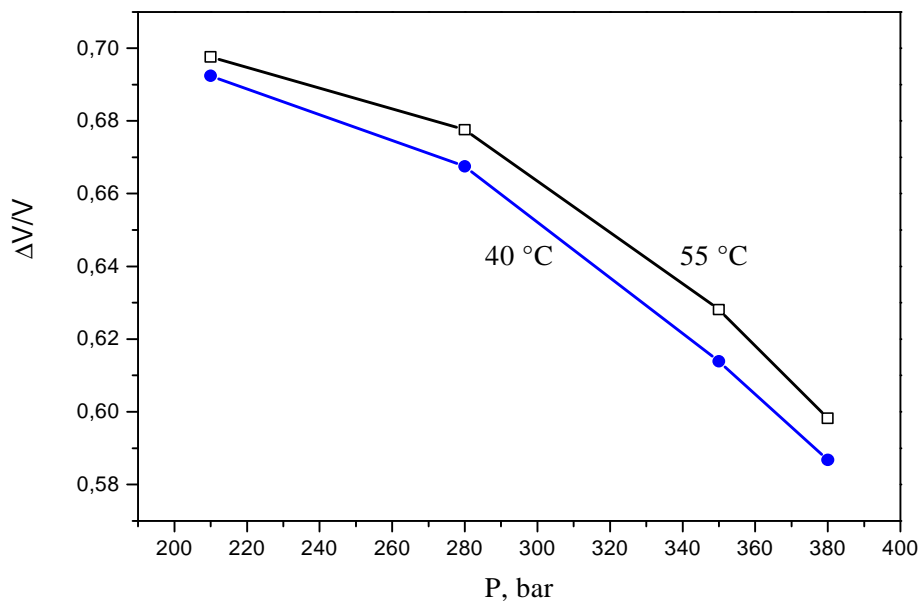


Fig 3. Equilibrium volume ratio of the feed mixture.

During experiments two opposite mass transfer phenomena can be observed: from liquid to supercritical phase and vice versa. The first one is shown when the oil is feed in the cell: the observable liquid volume is considerably reduced because of solubilisation in SC-CO₂ of part of liquid components. The second one is related to the pressure: the liquid volume slightly increases with pressure, probably due to solubilisation of SC-CO₂ in the liquid phase [11]. A temperature increase from 40 to 55 °C slightly increases the solubilised CO₂ into the liquid phase.

CONCLUSION

This first group of experiments performed on SC-CO₂ and BFR showed the existence of only two phases (supercritical fluid and liquid), in the range of 210-380 bars and 40-55 °C.

Limitately to the case of TG-CO₂ equilibrium data available, solubility in supercritical phase of the TG and DPTG mixture seems to be surprisingly about 4 times higher with respect to TG alone. Nevertheless, literature comparison of data is not easy, because of lack of data in our experimental field; moreover, the component mixture classified as DPTG seems to be a very complex one, to be deeper characterised and studied.

Particularly, the solubility of liquid phase components seems to change with pressure. In fact the colour observed for each phase changes with operating condition (see Figure 4). When the pressure increases, supercritical phase colour becomes lighter and liquid phase becomes browner.

This behaviour is suspected to be due to an improvement on TG selectivity. Experiments with static method have been planned for a near future to better define characterization of examined products.

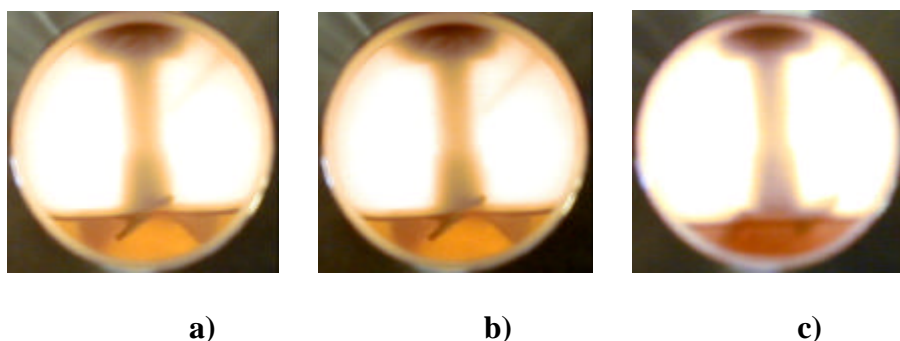


Fig 4. Equilibrium cell images at condition at 55 °C: a) 210 bar; b) 280 bar; c) 350 bar.

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