

FRYING OIL RECYCLING WITH DENSE CARBON DIOXIDE

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ABSTRACT

Waste frying oils are a pollution source that may be eliminated by oil recycling. A possible technology to recycle this oil is extraction with dense gases. In this work we investigate the use of sub and supercritical carbon dioxide to recover the undegraded triglycerides fraction from the waste oil. The experiments have been performed in a semicontinuous extraction system. The effects of pressure (300-400 atm) and temperature (25-80°C) on the extraction yield have been investigated. In order to study the characteristics of the oils recovered under different operating conditions, the concentrations of the polar components coming from the oxidation, hydrolysis, and/or polymerisation of triglycerides have been measured in the extracted oils.

The results obtained in the experimental range investigated showed several findings. Extraction yields obtained with liquid CO₂ slightly increased with pressure at constant temperature. With supercritical CO₂ the extraction yields increased with increasing pressure and decreasing temperature (while keeping constant temperature and pressure, respectively); besides, the yield increase with pressure was more significant than with liquid CO₂. As regards to the polar compounds concentrations, it has been found that the effect of pressure and temperature on this variable followed a trend similar to that observed with the extraction yield and that the effect of pressure was also more noticeable with the solvent at the supercritical state.

INTRODUCTION

A large proportion of fats and oils is used in the world for the preparation of fried foods. During the frying process many chemical complex reactions occur so the fat begins to degrade. The principal reactions taking place include formation of conjugated dienes, formation and decomposition of hydroperoxides, formation of low molecular weight carbonyl compounds, hydrolysis of triglycerides, and polymerisation via complex free radical processes at elevated temperatures [1].

As frying continues, the concentration of degradation products increases until the oil is unfit for use and it must be discarded [2]. This residue can not be reused because of its high content of pollutants but, since it still contains a large proportion of triglycerides, not only environmental but also economical reasons justify its regeneration.

Then, the objective of the regeneration process is the separation of the triglycerides fraction from the polar compounds (oxidized low molecular weight material and polymers) formed during the degradation process.

In the last decade several studies have been made to purify the used frying oil by adsorbent and high pressure extraction treatments [3-9]. This last technology presents several advantages over adsorption processes (such as continuous operation, low temperature separation, good and easy adjustable selectivity) and it has been successfully applied to extract and separate lipid components from different food products [10-12]. Therefore, it seems interesting to analyse its use in waste frying oil recycling. As regards to the extraction solvent to be used, CO₂ should be recommended since in the food industry it has advantages over other solvents because it is non-toxic and can be easily and completely removed from products; furthermore, it is non-flammable, non-corrosive and readily available in large quantities.

The regeneration of used frying oil with supercritical carbon dioxide was first proposed by Perrut and Majewski [7] to improve the results obtained when applying the more classical adsorption technology. Then, several works have been published about this recycling process [8-9], but more detailed information is needed about the operating conditions and the characteristics of the influent and effluent process streams in order to assess its viability at the industrial scale. Accordingly, the major aim of this paper will be to analyse the high pressure extraction of used frying oil in order to select the best extraction conditions leading to both high yield and quality of the oil recovered.

EXPERIMENTAL SECTION

Materials

Carbon dioxide (purity 99%) was supplied by Praxair (Madrid, Spain). The used frying oil was obtained by heating sunflower oil during 14 hours at 195 °C in a frying machine. Simulating the frying process in this way allowed to obtain a degraded oil (Triglycerides: 70%, Polar compounds: 30%) with no food particles that may interfere in the extraction study. Once the oil was degraded, it was stored in topaz glass bottles, in a nitrogen atmosphere, in order to avoid further oil degradation by light, oxygen, and/or humidity.

Apparatus and extraction procedure

A schematic diagram of the extraction system used in this study is presented in Figure 1. It consists of three main sections: the carbon dioxide supply system, the extractor assembly, and the separator assembly. Basically the supply system was a steel cylinder (SC) that provided liquid CO₂. After cooling and filtering the CO₂ was compressed by a membrane pump. The pressure was regulated by a back pressure regulator (BPR) and checked by a manometer (M). The compressed fluid was passed through an autoclave extraction cylinder which had been previously filled with the used oil. As indicated in the figure, the extractor design allowed the CO₂ to enter through a 8 mm i. d. tube and, as it went upwards through the extractor, to intimately mix with the used oil and to separate the CO₂ soluble base oil (triglycerides) from the rest of non-soluble used oil components (degradation products). A type J thermocouple was inserted in the extractor to indicate its operation temperature. This variable was controlled by immersing the extractor in an oil bath at the desired temperature. The oil-laden CO₂ from the extractor was passed through a heated metering valve (MV)

where the CO₂ was depressurized and the separated oil was collected in a cool receiver (RE). The CO₂ flow through the extractor was measured by a turbine flow meter (FM) and totalized by a flow computer (FC).

Analyses

The separation of the polar y non polar fractions was performed by column chromatography [13]. The analysis of the polar fraction composition was carried out by Gel Permeation Chromatography (GPC) according to the method specified in reference [14].

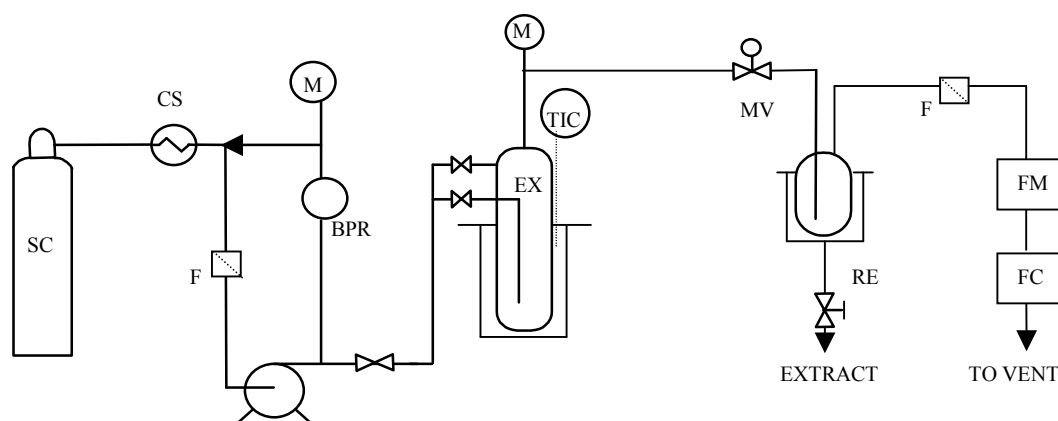


Figure 1. Experimental extraction system: SC, CO₂ cylinder, CS: Cooling System; BPR: Back Pressure Regulator; EX: Extractor; MV: Metering Valve; RE: Cool Receiver; FM: Flow Meter; FC: Flow Computer.

RESULTS AND DISCUSSION

Experimental conditions of experiments performed in this work are summarised in Table 1. The results obtained are discussed below.

Table 1. Summary of the experiments carried out with liquid and supercritical CO₂.

Experiment Number	1	2	3	4	5	6	7	8	9
Pressure, atm	300	300	300	350	350	350	400	400	400
Temperature, °C	25	40	80	25	40	80	25	40	80
Solvent state ¹	L	SC	SC	L	SC	SC	L	SC	SC
Density (ρ_i $i=1$ to 9), Kg/l	0,967	0,910	0,746	0,987	0,935	0,789	1,005	0,957	0,823

¹ L = Liquid. SC = Supercritical.

Extraction Yields

Figure 2 shows the effect of the solvent state, pressure and temperature on the extraction yield. It can be observed that yields are always higher with liquid than with supercritical CO₂. On the other hand, it can also be seen that with liquid CO₂, at a given

temperature, the yield slightly increase with pressure. With supercritical CO₂ the yield increases with increasing pressure (at constant temperature) and decreasing temperature (at constant pressure), being the effect of pressure more noticeable in this case than with the solvent in the liquid state.

These results are mainly related to the solvent density, since it is larger for liquid than for supercritical CO₂ and shows a smaller variation with pressure and temperature in the liquid than in the supercritical region [10]. As regards to the effects of pressure and temperature, the variation of the solvent density with both variables is similar to that observed with the extraction yields, indicating a direct correlation between both variables. Nevertheless, as it can also be seen in Figure 2, the extraction yields depend also on the solutes vapour pressures since, in some experiments performed at experimental conditions leading to very close values of the solvent density, the variation of the yields with the variable inverts with regard to the normal trend (increasing yield with increasing density).

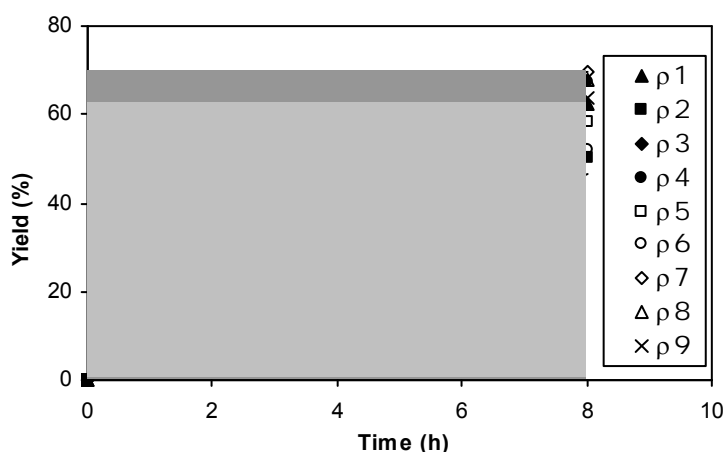


Figure 2. Effect of the solvent density on the extraction yield.

Percentage of polar compounds in the recovered oil

Figure 3 shows the evolution with time of the percentage of polar compounds in the oil recovered with CO₂ at 400 atm. It can be seen that the percentage of polar compounds in the oil decreases as the extraction progresses. In other words, both liquid and supercritical CO₂ extract selectively used frying oil polar compounds from its mixture with triglycerides. Similar results were found at the other pressures tested.

This experimental finding, the selectivity of a non-polar solvent as CO₂ for the polar fraction of the used oil, can be explained only if the molecular weights of the polar compounds extracted are smaller than those of the triglycerides, non-polar compounds that, in principle, would dissolve more easily in a non-polar solvent than the polar matter. Therefore, this result could suggest that the molecular weights of the polar compounds in the used frying oil are smaller than those of the triglyceride fraction. It could also indicate that both liquid and supercritical CO₂ may dissolve only the polar compounds of low molecular weight and that, as these components are exhausted, the extraction of polar components decreases due to that also decreases the capacity of the supercritical solvent to dissolve the remaining polar

compounds (those with larger molecular weight). This last hypothesis was confirmed by analysing by Gel Permeation Chromatography (GPC) the evolution with time of the polar fraction composition of the recovered oil [15].

As regards to the effect of pressure and temperature on the percentage of polar compounds in the oil recovered, it was observed that it followed a trend similar to that of yields and, as in such case, although it mainly depended on the solvent density, the used oil components vapour pressure also affected to the variable [15].

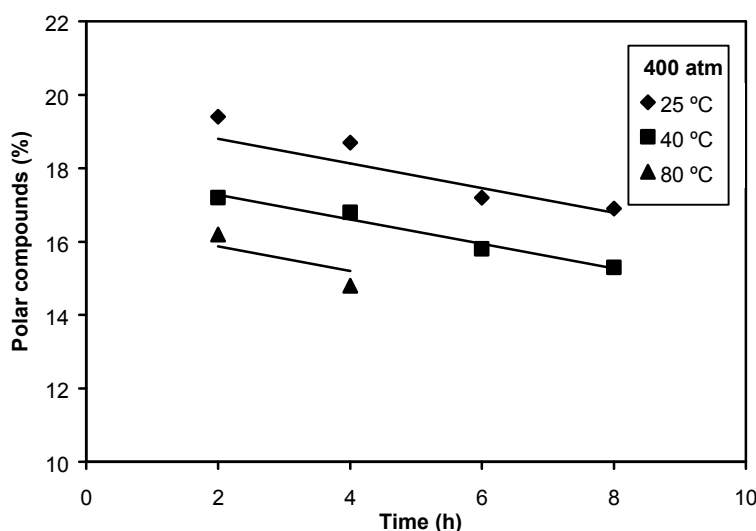


Figure 3. Effect of the solvent density on the percentage of polar components in the recovered oils.

CONCLUSIONS

The high pressure extraction of used frying oil seems very promising. In the experimental range analysed it has been observed that with liquid CO₂ yields slightly increase with pressure (at constant temperature) and with supercritical CO₂ they increase with increasing pressure and decreasing temperature (while keeping constant temperature and pressure, respectively); besides, the yield increase with pressure was much more important than with liquid CO₂. As regards to the polar compounds concentrations, it has been found that the effect of pressure and temperature on this variable followed a trend similar to that observed with the extraction yield and that the effect of pressure was also more noticeable with the solvent at the supercritical state. These results may be explained by considering both the solvent density and the solutes vapour pressure.

In order to assess the viability of the process at the industrial scale an effort has been made to select the best extraction conditions. It has not been a simple task since the percentage of undesirable polar compounds in the recovered oil was larger at those conditions leading to higher yield. Nevertheless, operating at 300 atm and 40 °C the extraction yield was 50% and the product recovered contained only about 10% of polar matter.

ACKNOWLEDGEMENTS

This research has been financially supported by the Junta de Comunidades de Castilla-La Mancha (Spain) through Contract PBI-05-048.

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