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Extraction of lipids and essential oils from vegetable matrix by liquid carbon dioxide

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Carbon dioxide (CO_2) is particularly advantageous for processing food materials. It can easily be removed from the solutes by mere expansion to ambient pressure. The olive paste and the lemon peel are rich in lipids and essential oil respectively. The aim of this work was to examine the effect of operating conditions on the extraction of essential oils as well as the whole oil fraction from olive paste, and evaluate qualitative characteristic of this extracts. Olive paste and lemon peel were extracted with liquid CO_2 at 50 bar and 15°C. Extraction yield was observed, and extraction curves for each were obtained. High resolution gas-chromatographic (HRGC) analyses of fatty acids (FA) and identification peaks with mass spectrometer detector (MS) of essential oils were performed.

1. Introduction

The extraction of solids by liquid solvents is a well-known process which is used in various industries. Natural substances are conventionally extracted by liquid solvents at normal pressure as, for example, in the extraction of hops, spices or oil seeds (Kikuchi and Kawamura, 1999; Monteiro et al., 1997; Moyler, 1993; Ferreira et al., 1993). General problems are residues in products and the need for additional processing steps to remove the solvent from the mixture and from the extracted solid. Alongside conventional solid/liquid extraction, the compressed fluid extraction of natural substances has recently become established (Stahl et al., 1988; Johnston and Penninger, 1989; Bruno and Ely, 1991). This process employs unproblematic, innocuous fluids as the solvent and yields practically solvent-free products in a thermally gentle manner (Gomez Molero et al., 1996). Simple fractionation of the products is possible by a variation of pressure and/or temperature. To date, this process has become particularly familiar in the foodstuffs, coffee and tabacco industries. The extraction of the natural substance, lemon peel (Carlson et al., 2001) and olive paste, are taken as an example. The extraction of lemon peel is nothing other than the transfer of the desired substances (essential oils as flavour) from the solid phase into the liquid phase. In the ideal case, this is a purely physical process without any chemical change to the constituent substances. Conventional extraction for olive was carried out by a phase of crushing,

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one of kneading and one of centrifugation. For the essential oils extraction, commonly, it use ethanol as solvent. Pilot and production plants for the compressed fluid extraction of both matrix, in this experimentation, use liquid CO_2, a solvent which is physiologically innocuous. Processes are known where CO_2 is in the compressed state during extraction, as are others where CO_2 is in the liquid state (Hubert et al., 1980; Wilson, 1984). This technique offers extraction yields comparable with those obtained by conventional extraction methods using organic solvents. Moreover, in contrast with organic solvents, carbon dioxide is non-toxic, non-flammable, non-corrosive, cheap and readily available in large quantities with high purity.

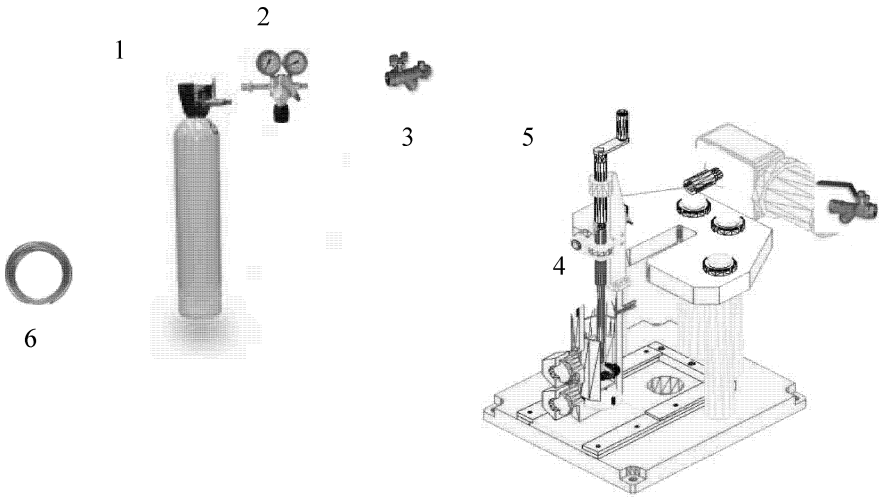

Fig. 1*- Component of laboratory-scale extraction unit: 1) CO_2 liquid cylinder; 2) pressure reducing valve; 3) valve on-off CO_2 in; 4) valve on-off CO_2 out to rycicle; 5) jacketed extraction vessel; 6) serpentine.*

The aim of this experimentation was to examine the effect of operating conditions on the extraction of essential oils from lemon peel as well as the whole oil fraction from olive paste, and evaluate qualitative characteristic of this extracts.

2. Materials and methods

The extractions with liquid CO_2 were performed in a pilot unit schematically represented in Fig. 1. The extractor was a stainless steel jacketed vessel of 980 cm^3 and 7.50 cm internal diameter (ID). Its temperature was maintened by thermostatic water bath. The extracts were collected in a beaker (positioned in the vessel) after expansion to atmosferic carbon dioxide. The extracts obtained at different time intervals were subjected to following determination:

- Free acidity according official method (NGD C 10-1976)
- Peroxide values (Reg. CE 1989/03)

- Spectrofotometric index
- Fatty acids composition by trans-esterification reaction. Peaks identification was made by external standard (Supelco TM 37 component FAME mix) by comparison of retention time of pure standards peak.
- Triglycerides concentrtion (Reg. CE n° 213/2001)
- Essential oils by GC-MS. The composition of the extracts was analyzed using a GC-MS system *(*HP-6890 5-MS AGILENT) equipped with a column HP-5MS (30m lenght and 0,25mm film thickness Agilent). The carrier gas was helium (1.2 mL/min) and 1µL of the sample was injected. For the oven programme, the temperature was fixed at 50°C for 5min, then was raised from 50°C to 250°C at 7°C/min where stop for 5min. The mass spectra were generated at 70 eV with a Mass Spectometer ranging 35-400 UMA. The identification of the chemical constituents was based on comparison of the mass spectrums of the substances with the GC-MS system data library (NIST 02 and WILEY 275)
- Phenolic concentration. The phenolic compounds were extracted in hydroalcoholic solution. 10g of olive oil, dissolved in n-hexane (10 mL) were extracted, for three times, with 7 mL H_2O/methanol mixture (40/60 v/v). The hydroalcoholic extract obtained was washed with n-hexane to eliminate fat contamination and was centrifuged for 10 min at 3500 rpm. The total poliphenols were valutated by colorimetric reaction with Folin- Ciocalteau (C. Erba Reagent) reactive.

All determinations and experiments were performed in triplicate and the present results are the average values of three determinations.

3. Results and discussion

The experimental conditions of liquid CO_2 extractor were maintained constant, at a pressure of 50 bar and at a temperature of 15 °C.

3.1 Extraction of oil from olive paste

The olive paste was obtained by olives crushing and kneading phases.

In this experimentation olive paste was subjected to solvent extraction with n-hexane and then centrifuged. The maximum solvent extraction yields was 16 wt%, and this value was taken as theoretical fat content of the olive paste which it obtained by solvent.

For the extraction by liquid CO_2, the sample undergoes to the following phases:

Compression
Solubilisation
Expansion
Extract separation
Gas-solvent recovery

To establish the time corresponding to the maximum extraction yield, the samples (50g olive paste) were subjected to the extraction at regular time break of 30 minutes.

Figure 2 presents extraction yield for total extract and shows that the extraction of oil seems to have a linear trend until 180 min. From these results it can be observed that extract amount become stable when reach the equilibrium between liquid CO_2 and olive paste. The extractor pressure was 50 bar and the temperature was fixed at 15 °C. After only 30 min of contact between liquid CO_2 and olive paste it reach an yield of 7.21% which increase, with a linear trend, of 2-3% every 30 min., until 150min. Between 150 and 180 min the extraction yield raise only of 0.2%.

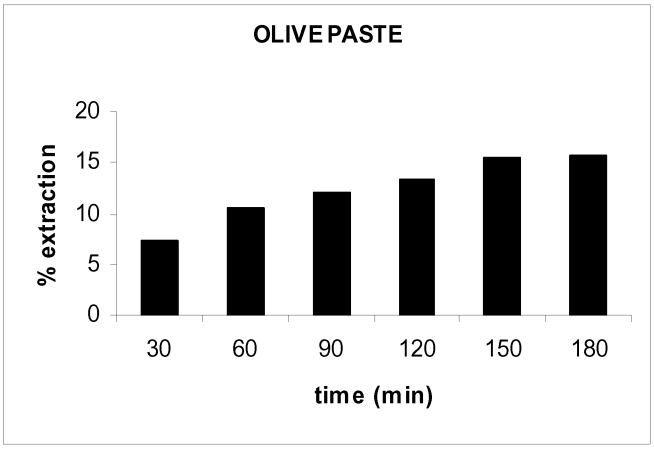

Fig. 2- *Extraction yield of oil (% on vegetable matrix) from olive paste by liquid CO_2*

The equilibrium concentration depends on the quantity of solute available in the solid-fluid interface and on interactive forces within the solid substrate, and its value may be lower from solubility values obtained for pure extract components (Brunner, 1994).
The oils obtained by both method show similar acidity values, 0.46% for the oil extracted by solvent (n-hexane) and 0.49% for the oil obtained by liquid CO_2.
Peroxide values in the oil extracted by liquid CO_2 was 6.61 $mEqO_2/kg$ and in the oil obtained by solvent was 8.87$mEqO_2/kg$ of oil. This is probably due to the fact that liquid CO_2 in the density range 0.8-1.1 g/ml exhibits high extraction selectivity.
The extinction index K232, K270 and ΔK didn't show significant differences.
The total polyphenols were 596 mg/L (as gallic acid) in the oil obtained by hexane extraction and 919mg/L in the oil extracted by liquid CO_2.
The fatty acids and triglyceridic composition didn't show important differences between the two oil.

3.2 Extraction of essential oils from lemon peel

In this experimentation lemon peel were subjected to liquid CO_2 extraction at 50 bar of pressure and at 15°C. The lemon peel were grounded and putted in the CO_2 apparatus and subjected to cycles of 30min. The maximum extraction yield was reached at 300 min (Fig. 3). Fig. 4 and 5 show HRGC-MS spectra of the essential oils fraction obtained during 300 min of liquid carbon dioxide extraction. By comparison with alcoholic extract the one obtained by CO_2 show a complex profile. From this results it can be

observed that CO_2 extract had minor concentration of limonene and terpinene (peaks 1 and 2 in fig 4 and 5) and major concentration of cumarano, cis-geraniol , and nerol (peak 3, peak 4 and peak 5 respectively in fig.5).
The liquid CO_2 is fully miscible with low molecular weight hydrocarbons and many organic compounds oxygenated, and therefore is a good solvent for many organic products: the low solubility in water allows the extraction of organic compounds by aqueous solutions. .
There are some advantages that make preferable the use of CO_2 compared to other solvents in the case of simple extraction: non-flammable, non-toxicity, low viscosity, high capacity to spread, the easy of separation for high volatility.

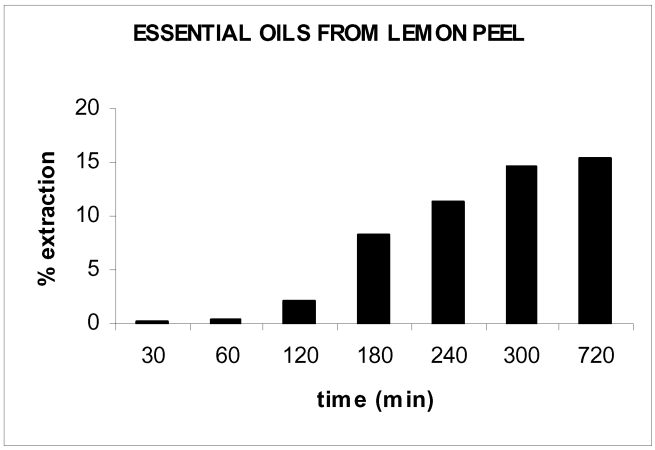

Fig. 3*- Extraction yield of essential oils (% on vegetable matrix) from lemon peel by liquid CO_2*

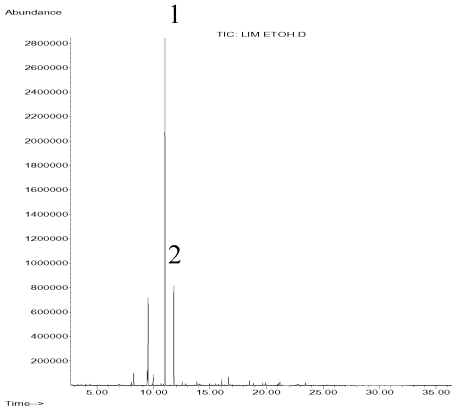

Fig.4*- HRGC-MS profile of essential oils obtained by ethanol extraction*

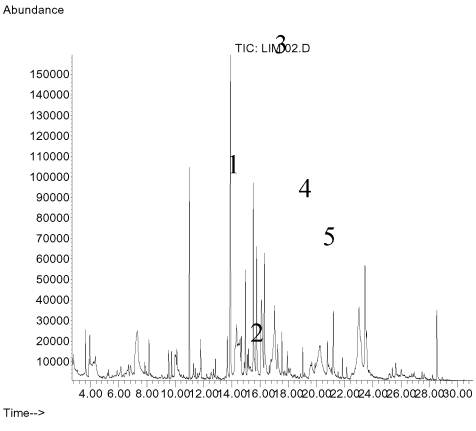

Fig.5*- HRGC-MS profile of essential oils obtained by CO_2 liquid extraction*

Although we obtained extracts are excellent in terms of quality, both time-consuming to extract that anti-cost of a plant on an industrial scale could be a limiting factor for effective implementation of this innovative technology. However the installation of a chamber of liquid CO_2 under pressure is useful for the preservation and transportation of fresh food products as well as frozen food products. In summary, the results presented contribute to our knowledge of the complex chemistry of olive paste and of lipophilic CO_2 plant extracts, opening new applications for their use.

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