Supercritical Fluid Extraction of Fatty Acids From Spent Coffee Grounds

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ABSTRACT

Nowadays, the better utilization of wastes from different technological productions is a key factor for the economical and the environmental issues. The easiest solution is often the choice of their incineration in order to produce energy.
Among the others special focus is spent to wastes derived from food and beverage industries. Looking at the amount of the treated material the coffee production is situated at the same level as the steel and oil industries. For that reason the possible reutilization of several wastes produced during the different treatments of the coffee beans, starting from the plants until the final cup of coffee, is very important.
The aim of this work is the application of supercritical fluid extraction technique for the recovery of lipids from spent coffee grounds. Pressure, temperature and extraction time are considered in order to evaluate the influence of such parameters on the oily fraction yield. The results indicate that the extraction pressure is the most important parameter affecting the process.
A good quality characterization of the extracts is presented in order to verify their possible utilization in the fine and cosmetic industries. These results are compared with those obtained using conventional methodology based on solvent extraction.

Keywords: Spent coffee grounds, supercritical fluids, soxhlet, fatty acids

INTRODUCTION

Spent coffee grounds (SCG) are the residue obtained from the treatment of coffee beans, with hot water or steam for extracting flavour substances there from, that have not been used so far for industrial application, even though they are composed by carbohydrates, lipids, flavonoids and proteins [1,2]. Triglycerides and diterpene alcohol esters are the major lipid classes in coffee brewed from ground coffee beans, and they range from 86.6 to 92.9 and 6.5 to 12.5% of total lipids, respectively [3]. The real value of this material can be assessed, for instance, in the possible use of coffee ground oil to produce high quality cosmetical excipients or active ingredients as well.
Extraction of compounds from natural matrices is one of the most studied applications of supercritical fluids (SCF). Supercritical fluid extraction (SFE) has immediate advantages over

traditional extraction techniques because it is a flexible process due to the possibility of continuous modulation of the supercritical solvent power/selectivity: it allows the elimination of both polluting organic solvents and expensive post-processing of the extracts for solvent elimination.
Carbon dioxide is the most popular SFE solvent because it is safe, not flammable, readily available and not expensive. Moreover, the comparatively low critical temperature (304.25 K) of CO_2 allows the extraction of thermo sensitive substances without degradation. It has been carried out in a commercial scale for more than two decades, in processes like the decaffeination of coffee beans and black tea leaves and the production of hop extracts [4].
The purpose of this work was to assess the feasibility of using supercritical carbon dioxide (SCO_2) to extract the lipid fraction of spent coffee grounds. The influence of the main operating conditions of extraction, namely, the temperature and pressure of extraction on the oil extraction yield was performed.
The total fatty acid (FA) composition of the extracted oil was determined by means of high resolution gas chromatography (HRGC). For this objective the FA of the extracted oil were esterified to methyl esters (FAME).

MATERIAL AND METHODS

MATERIALS

Spent coffee grounds (SCG) of Arabica of 100% were kindly supplied by a coffee shop of Trieste (Italy).
The solvents, n-hexane, acetone, chloroform, dichloromethane, petroleum ether and n-heptane by Merck, and methyl heptadecanoate by Sigma-Aldrich, were purchased, and used as received.

METHODS

SCO_2 extraction

The supercritical fluid extraction experiments were performed using a column type extraction vessel (Separex-France, Autoclave A21 model) depicted in Figure 1. It consists of an extraction vessel of 100 mL, filled with 20 g of SCG dried, at 60 °C, for 48 hours. The extraction pressure was controlled by means of a back pressure regulator (lamination) valve. In order to prevent sample plugging during experiment, the valve's body was warmed electrically. The gas flow-rate and total mass of CO_2 consumed in the experiment were measured with a gas wet test meter (SIM Brunt) at room conditions. The extracts were also precipitated and collected into a glass trap, immersed in an ice bath.
After extraction the samples were weighted (Sartorius BL 210 S) in order to calculate the extraction yield (y):

$$y = \frac{\text{extracted mass}}{\text{starting material mass}} \quad (1)$$

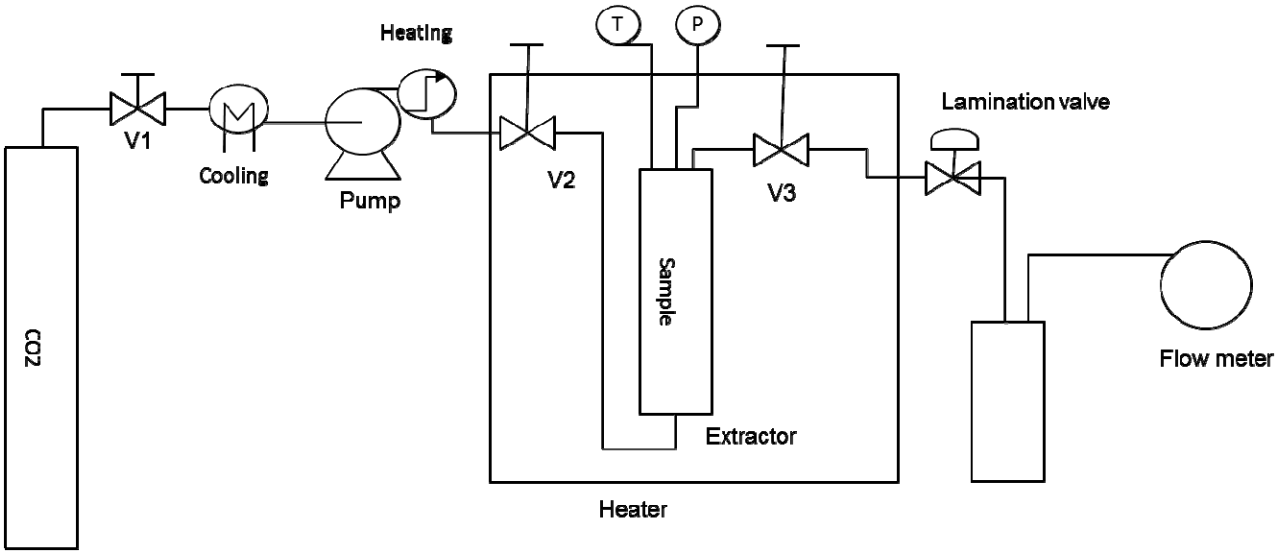

Figure 1: Schematic diagram of SFC extractor. V1, V2 and V3 are on-off valves; T, P are temperature and pressure probes.

Preparation of methyl esters (FAME)

The preparation of the methyl esters of total fatty acids (FAME) was carried out by the AOAC official method [5]. 100 mg of extracted oil were added to 5 ml of a 0.5 M solution of sodium hydroxide in methanol: to the mixture, heated at reflux for about 10 min, were added 5 ml of the complex BF_3/CH_3OH and this solution was maintained at reflux for a further 2 min. Then, 2 ml of heptane were added to the mixture and the solution was heated to reflux for another 2 min. After cooling, 10 ml of a saturated solution of sodium chloride were added, to facilitate the separation of the phases. The separated organic phase was then dried over anhydrous sodium sulfate. 0.1 µl of the clear solution were immediately injected into the gas chromatographic system.

High resolution gas chromatography (HRGC)

The analysis of samples was conducted using a chromatographic system consisting of a Shimadzu GC 14A gas chromatograph equipped with a split/splitless injector (1:20), a flame ionization detector and a capillary column SP 2330 fused silica 30 m x 0.32 mm ID and 0.2 µm film (Supelco).
The used chromatographic conditions were: a starting temperature of 100°C for 2 min, increased to 250°C with a programmed temperature of 10 °C/min and a final isotherm (at 250°C) of 10 min; injector and detector temperatures of 280°C, carrier gas (helium) flow rate of 2,0 ml/min.
The area calculation of the chromatographic peaks was determined using the instrument integrator.

RESULTS AND DISCUSSIONS

Supercritical extraction of spent coffee grounds gave a yellow to yellow/brown viscous oil extract. Table 1 shows the conditions at which the SFE experiments were carried out as well as the oil yield obtained for each extraction of 3 hours. Supercritical carbon dioxide was able to extract, a maximum yield of 10.2 %.

T (°C)	P (bar)	Y(%)
40	150	3.40
40	200	6.74
40	250	10.20
50	150	1.48
50	200	7.80
50	250	8.77
60	150	1.50
60	200	4.55
60	250	10.28

Table 1: SFE experimental conditions and oil extracted yield

Figure 2 depicts the extraction curves, at three different pressures of 150, 200, and 250 bar and temperatures of 313, 323 and 333 K.
Extraction yields increases with pressure at constant temperature, which follows the usual trend in SFE of lipids from food residues [6]. This increase with pressure is explained by the augmented CO_2 density and then the solvent capacity to solubilize the lipids from the coffee grounds.

Temperature's effect on extraction is dual. On one hand, higher temperature can accelerate fluid flow and thus increase the solute of compounds; on the other hand, higher temperature can decrease fluid density and thus reduce extraction efficiency. The overall extraction effect of supercritical fluids usually follows the competition between the increasing in solute of compounds and the reduction in $SCCO_2$ density due to the rise in temperature [7].

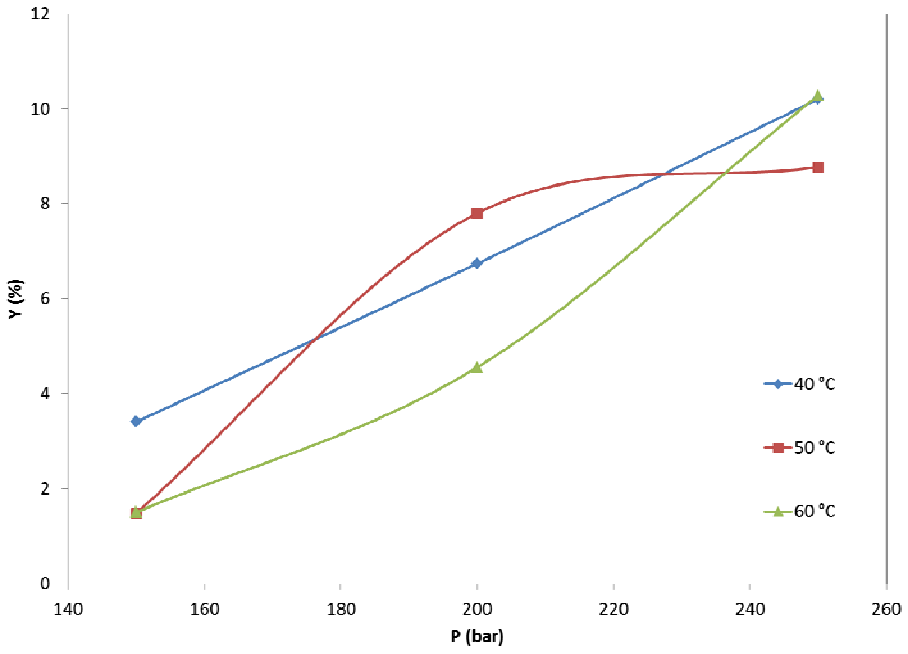

Figure 2: 3 hours coffee grounds extraction yield at different temperatures and pressures

Figure 3 depicts the spectrum of the esterified extracted oil composition detected by ~~means of~~ GC chromatography.

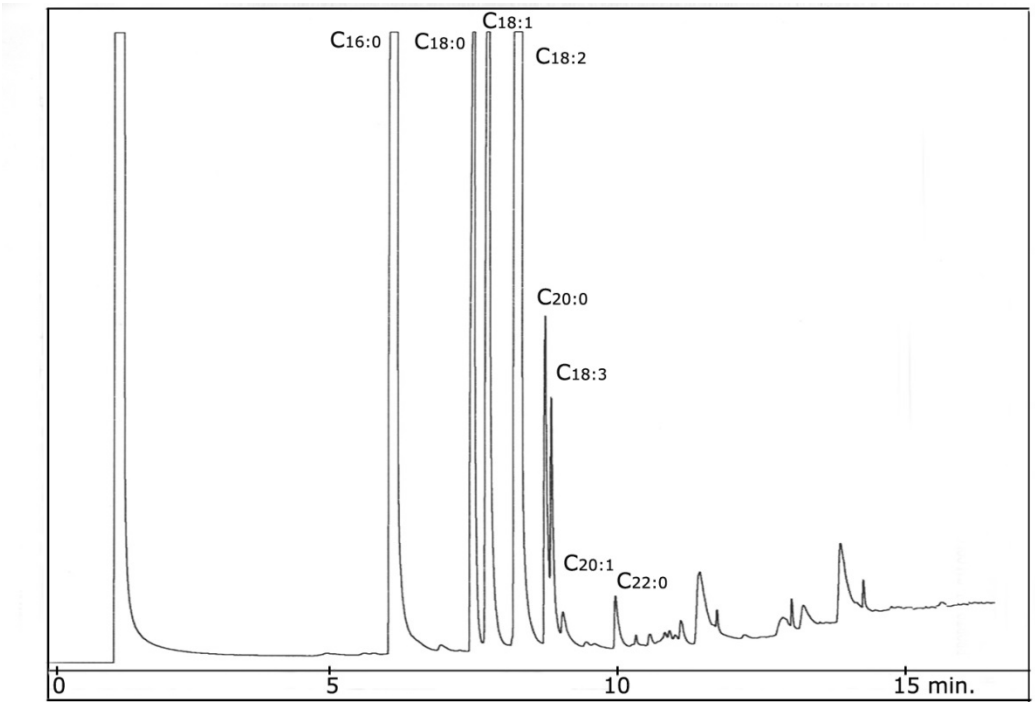

Figure 3: GC chromatograph of coffee ground coffee obtained at 250 bar and 40 °C

The spectra highlights the fatty acid (FA) composition of the oil extracts obtained by SC-CO2. The main fatty acids are linoleic (C18:2) and palmitic acid (C16:0), followed by oleic (C18:1) and stearic acid (C18:0). Other minor acids present in the extracts are linolenic (C18:3), arachidic (C20:0), behenic (C22:0) and gadoleic (C20:1) confirming the literature data [8].
At the same experimental conditions of 40°C and 250 bar, the extraction time effect (ET) on the mass yield and on the FA composition was considered. The data reported in Table 2 show an increase of Y % with ET, while no substantial effect were observed in the oil composition.

ET (min)	**Y (%)**	**FA**	**30**	**60**	**90**	**120**	**150**	**180**	**360**
30	2.93	C18:1	8.55±0.01	8.91±0.02	8.76±0.03	8.72±0.01	8.71±0.03	9.28±0.04	9.13±0.01
60	4.31	C18:0	5.9±0.01	6.13±0.02	6.22±0.02	6.23±0.01	6.08±0.01	6.29±0.01	7.23±0.02
90	5.84	C18:2	43.45±0.08	43.1±0.11	43.81±0.08	43.80±0.02	43.83±0.03	44.01±0.06	43.62±0.02
120	6.84	C18:3	1.59±0.02	1.62±0.02	1.57±0.01	1.61±0.01	1.64±0.01	1.70±0.01	1.61±0.02
150	7.66	C20:0	1.44±0.04	1.44±0.01	1.59±0.03	1.55±0.02	1.51±0.01	1.58±0.02	2.18±0.04
180	10.20	C16:0	38.47±0.11	38.32±0.21	37.5±0.21	37.43±0.04	37.6±0.01	36.40±0.10	35.3±0.06
360	12.45	C20:1	0.32±0.01	0.31±0.02	0.29±0.04	0.36±0.01	0.33±0.01	0.37±0.01	0.43±0.01
		C22:0	0.29±0.01	0.30±0.01	0.33±0.01	0.32±0.02	0.30±0.01	0.32±0.01	0.51±0.02

Table 2: spent coffee ground oil composition.

CONCLUSIONS

Supercritical fluid extraction of lipids from spent coffee grounds is more influenced by pressure and experimental time. After 6 hours, at 40°C and 250 bar, a maximum yield of 12% of oil extracted was obtained. The main fatty acids present in the oil extracts were linoleic and palmitic acid, with an average percentage of 43.7 and 37.3 wt%, respectively.

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