## Extraction of Value-added Compounds from Spent Coffee Grounds using Supercritical Fluid

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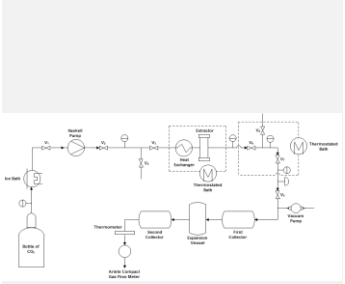
*Ercília M. S. Machado[1,*], Maria Gabriela Bernardo-Gil[2], José A. Teixeira[1], Solange I. Mussatto[1]. (1) CEB – Centre of Biological Engineering, University of Minho, Braga, Portugal; (2) Centre for Biological and Chemical Engineering, Instituto Superior Técnico, Lisboa, Portugal; *lyamachado86@gmail.com.*



In this work, supercritical fluid extraction (SFE) using carbon dioxide ($CO_2$) as solvent was used for the recovery of antioxidant phenolic compounds and proteins from spent coffee grounds (SCG). Extraction assays were carried out under different conditions of temperature and pressure. The highest contents of flavonoids (164.57 mg QE/g extract), protein (160.97 mg BSA/g extract), and antioxidant activity (FRAP = 0.5843 mM Fe (II)/g extract; and total antioxidant capacity = 272.26 mg α-tocopherol/g extract) were obtained when using 250 bar and 333.15k. On the other hand, SFE at 200 bar and 313.15k was the best condition to recover phenolic compounds from SCG (33.63 mg GAE/g extract).

### Introduction

Coffee is the most consumed beverage in the world being served more than 400 billion cups per year. As a consequence, large amount of wastes are generated in the coffee industry every year. Among these wastes, the spent coffee grounds (SCG) are one of the most important in terms of amount generated [1]. This waste is a rich source of volatile compounds with industrial interest. Therefore, the extraction of volatile compounds from SCG could be an interesting alternative for the valorisation of this agro-industrial waste [2].

Supercritical fluid extraction (SFE) is a technology that presents many advantages over conventional methods of extraction, especially because it uses as solvents harmless substances to the environment and human health. This technology has been used industrially for the extraction of valuable compounds from plants, such as oils, fragrances, and active components (flavours), as well as to remove impurities and other food products for human consumption, as is the case of removing caffeine from coffee [3].

This study aimed to evaluate the extraction of antioxidant phenolic compounds from SCG by SFE and determine the operating conditions that maximize the release of such compounds.

### Material and methods

Spent coffee grounds (SCG) was supplied by NovaDelta - Comércio e Indústria de Cafés, Lda (Campo Maior, Portugal). This material was dried in an oven at 60 °C until 10% moisture content and stored for use in the following steps.

The extraction experiments were carried out in a semi-batch flow extraction apparatus and supercritical carbon dioxide was the solvent used in this process. Table 1 shows the conditions used for the different extraction assays.

**Table 1.** Conditions of pressure (bar) and temperature (K) used in the extractions assays, and $CO_2$ density at the respective conditions.

| Assay | Pressure (bar) | Temperature (K) | $CO_2$ density ($Kg/m^3$) |
|---|---|---|---|
| 1 | 150 | 313.15 | 780.3 |
| 2 | 150 | 323.18 | 699.8 |
| 3 | 150 | 333.17 | 603.9 |
| 4 | 200 | 313.18 | 839.9 |
| 5 | 200 | 323.19 | 784.4 |
| 6 | 200 | 333.20 | 723.8 |
| 7 | 250 | 313.21 | 879.6 |
| 8 | 250 | 323.22 | 834.4 |
| 9 | 250 | 333.23 | 786.8 |

Phenolic compounds in SCG extracts were determined by the Folin-Ciocalteau method [4]. Flavonoids were quantified by colorimetric assay [5] and proteins by the Bradford method [6]. The antioxidant activity of the produced extracts was determined using two different methods: FRAP [7] and total antioxidant capacity [8].

### Results and discussion

Tables 2 and 3 summarize the composition and antioxidant potential of the extracts produced from SCG under different SFE condition.

The highest value of total phenolic compounds (33.63 mg GAE/ g extract) was obtained at 200 bar and 313.15 K. When compared to the results reported by Andrade et al. [9], who obtained 24.1 mg GAE/ g extract during the SFE of SCG at 200

bar and 323.15 K, the result obtained in the present study under the same extraction conditions is close similar (26.43 mg GAE/ g extract). However, when compared to the results reported for other extraction techniques, the utilization of SFE provided lower values of phenolic compounds extraction. For example, a phenolic compounds content of 587 mg GAE/ g extract was obtained when SCG was submitted to ultrasound-assisted extraction with ethanol as solvent [9].

The highest contents of proteins (160.97 mg BSA/ g extract) and flavonoids (164.57 mg QE/ g extract) in the extract were obtained when the SFE was performed at 250 bar and 333.15 K (Table 2). Such conditions are different of those that maximized the extraction of total phenolic compounds (200 bar and 313.15 K). The best results of antioxidant activity were also found in the extracts produced at 250 bar and 333.15 K (Table 3).

**Conclusion**

Antioxidant phenolic compounds, proteins and flavonoids were extracted from SCG by supercritical fluid extraction using $CO_2$ as solvent. The highest amount of phenolic compounds (33.63 mg GAE/ g extract) was extracted when the process was carried out at 200 bar and 313.15 K; while the maximum values of proteins, flavonoids and antioxidant activity were obtained in the extracts produced at 250 bar and 333.15 K. These results suggest that other substances than phenolic compounds may be contributing to the antioxidant potential of the extracts.

The results obtained in the present study for the extraction of antioxidant phenolic compounds from SCG are lower when compared to others already published in the literature using different extraction techniques. Additionally, higher costs are also reported for implementation of SFE on industrial scale. However, SFE is a more environmental friendly technique of extraction when compared to other methods that use of organic solvents, for example. Further studies using different supercritical solvents are needed to improve the extraction results obtained by SFE in order to become this technique more competitive to the technologies current used for extraction of antioxidant phenolic compounds from natural resources.

**Table 2.** Total phenolic compounds, proteins and flavonoids contents in the different extracts obtained by SFE of SCG.

| Extraction condition | Solvent flow rates $CO_2$ (g/min) | Total Phenolic (mg GAE/ g extract) | Proteins (mg BSA/ g extract) | Flavonoids (mg QE/ g extract) |
|---|---|---|---|---|
| 150 bar/ 313.15 K | 10.28 | 32.00 ± 1.84 | 120.13 ± 4.05 | 56.30 ± 2.15 |
| 150 bar/ 323.15 K | 9.61 | 17.93 ± 0.82 | 80.26 ± 7.52 | 45.00 ± 1.43 |
| 150 bar/ 333.15 K | 8.58 | 26.43 ± 1.90 | 114.87 ± 2.78 | 44.37 ± 1.36 |
| 200 bar/ 313.15 K | 9.70 | 33.63 ± 2.03 | 130.70 ± 4.13 | 86.76 ± 1.29 |
| 200 bar/ 323.15 K | 9.89 | 21.84 ± 2.49 | 114.64 ± 4.96 | 73.82 ± 3.94 |
| 200 bar/ 323.15 K | 10.26 | 26.43 ± 3.10 | 93.20 ± 4.18 | 77.56 ± 3.91 |
| 200 bar/ 323.15 K | 10.04 | 24.34 ± 0.69 | 97.87 ± 2.66 | 62.70 ± 6.59 |
| 200 bar/ 333.15 K | 9.38 | 29.34 ± 3.43 | 116.64 ± 4.81 | 44.88 ± 4.98 |
| 250 bar/ 313.15 K | 10.40 | 24.01 ± 0.80 | 136.53 ± 3.10 | 118.54 ± 4.43 |
| 250 bar/ 323.15 K | 9.95 | 25.99 ± 0.68 | 99.25 ± 2.24 | 89.38 ± 1.74 |
| 250 bar/ 333.15 K | 9.84 | 27.05 ± 0.80 | 160.97 ± 4.07 | 164.57 ± 5.41 |

**Table 3.** Antioxidant activity of the different extracts obtained by SFE of SCG.

| Extraction condition | Solvent flow rates (g/min) | FRAP [a] (mM Fe (II)/ g extract) | Total Antioxidant Capacity (mg α-Tocoferol/ g extract) |
|---|---|---|---|
| 150 bar/ 313.15 K | 10.28 | 0.2911 ± 0.0167 | 252.88 ± 18.03 |
| 150 bar/ 323.15 K | 9.61 | 0.2844 ± 0.0108 | 182.31 ± 6.02 |
| 150 bar/ 333.15 K | 8.58 | 0.3154 ± 0.0102 | 229.25 ± 4.48 |
| 200 bar/ 313.15 K | 9.70 | 0.3072 ± 0.0084 | 252.12 ± 7.33 |
| 200 bar/ 323.15 K | 9.89 | 0.2985 ± 0.0167 | 237.12 ± 10.49 |
| 200 bar/ 323.15 K | 10.26 | 0.2806 ± 0.0098 | 238.59 ± 9.37 |
| 200 bar/ 323.15 K | 10.04 | 0.2795 ± 0.0048 | 207.87 ± 12.72 |
| 200 bar/ 333.15 K | 9.38 | 0.3604 ± 0.0110 | 218.79 ± 7.36 |
| 250 bar/ 313.15 K | 10.40 | 0.2471 ± 0.0055 | 212.57 ± 8.23 |
| 250 bar/ 323.15 K | 9.95 | 0.2378 ± 0.0089 | 201.90 ± 5.13 |
| 250 bar/ 333.15 K | 9.84 | 0.5843 ± 0.0120 | 272.26 ± 17.14 |

[a] FRAP: antioxidant activity by the ferric reducing antioxidant power assay.

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