Spent Coffee Ground Oil as a Potential Alternative for Vegetable Oil Production: Evidence from Oil Content, Lipid Profiling, and Physicochemical Characterization

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Abstract: In this work, routinely measured physicochemical indices and lipid profiling of oil extracted from spent coffee grounds (SCG) were evaluated to assess the suitability of SCG as a new candidate for oil production. The obtained results reveal that the oil yield was 18.55±1.5 g/100g. Physicochemical indices were comparable to those of widely consumed vegetable oils in the range set in several studies. The main fatty acids of SCG oil were linoleic acid 43.20±2.19 g/100g, palmitic acid 31.78±2.02 g/100g, and oleic acid 12.68±1.15 g/100g dry basis. For sterol composition, β-sitosterol was the most abundant sterol (44.70±0.01%), followed by stigmasterol (27.57±0.01%) and campesterol (12.16±0.01%). In conclusion, this composition is typical for many other vegetable oils. Therefore, this oil may be considered a good alternative for vegetable oil production for new multi-purpose products such as cosmetic and industrial pharmaceutical uses.

Keywords: spent coffee ground oil; fatty acids; sterols; vegetable oil; environment.

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1. Introduction

With coffee on every street in the world, it is no surprise that it is one of the most consumed beverages in the world [1]. Furthermore, it is the third most consumed beverage around the globe. Recent estimates from the International Coffee Organization show that the global consumption of coffee exceeded 10.16 billion kilograms in 2019-2020. Europe ranked first in terms of consumption (32.71%), followed by Asia and Oceania (21.9%), North America (22.15%), South America (16.02%), Africa (7.07%), and both Central America and Mexico (3.23%). In Morocco, coffee consumption exceeds 35 million kilograms in the same period [2]. Unfortunately, coffee consumption leads to the generation of millions of tons of wastes, such as; aluminum capsules, plastic cups, and spent coffee grounds (SCG).

Previous studies showed that one ton of raw green coffee produces almost 650 kg of SCG through the process of soluble coffee preparation [3]. SCGs are reported to be involved in serious environmental issues. For instance, phytotoxic substances and organic acids in these
by-products affect soil, water quality and restrict crop growth [4]. When SCGs are sent to landfill, they can produce greenhouse gases like methane and carbon dioxide that contribute to global warming [5]. Furthermore, SCGs discarded in the environment may pose a risk to human and environmental health [6]. However, SCG chemical composition reveals a rich product in sugars, proteins, antioxidants, polyphenols components, and oil [7-9].

In this context, SCGs may present promising valorization opportunities to reduce their environmental impacts on one hand and obtain added-value products on the other hand. In fact, several works were devoted to SCGs valorization globally. For instance, several options can be considered to manage this waste material, for example; antioxidants [10], anti-inflammatory additives [11], metal scavengers [12], production of biofuels [13,14], cosmetics, soap [15], and other food and health applications [16].

This work had as goals to (i) assess the potentiality of using SCGs as a raw material to produce vegetable oil, (ii) evaluate the quality of obtained oil, and (iii) compare SCGs oil quality attributes to commonly consumed vegetable oils (soybean, sunflower, rapeseed, and coconut oils).

2. Materials and Methods

2.1. Plant material and chemicals reagents.

All samples were a concoction of Robusta beans (Coffea canephora) and Arabica beans (Coffea arabica). Indeed, samples are collected by taking an average of 4 kg for each brand of coffee. After collection, the samples were dried in ambient air (until 2.5% of moisture). Then, they were grounded in order to obtain a homogeneous structure. Afterward, the SCG oil (SCGO) was extracted using a Soxhlet extractor with n-hexane as a solvent. Later, various analyses were carried out, namely, oil yield, physicochemical indices, fatty acids, and sterols.

All the chemical reagents were analytical or HPLC grade and purchased from Professional Labo (Casablanca, Morocco).

2.2. Oil yield.

A Soxhlet system was used to extract the oil from the crushed SCGs (dry matter, DM). n-Hexane was used as extraction solvent with a solvent ratio of 20 g of weight for 200 mL of solvent, with a solid to solvent ratio of 1:10 [17]. The extraction was carried out for 8 hours. The hexane was evaporated in a rotavapor under reduced pressure. The yield of oil (%) was then calculated as follows:

\[ \text{Oil Yield (\%, DM)} = \frac{\text{extracted oil (g)}}{\text{SCGs sample (g)}} \times 100 \]

2.3. Physicochemical indices.

Routinely measured physicochemical indices in oil consist mainly of free fatty acids (FFA), acidity or acid value, peroxide value, iodine, saponified values, refractive index, and density.

Acidity (a measure of the amount of free fatty acids in oil) was determined using the official analytical method [18]. Acidity was expressed as the oleic acid (C18:1) in the mass percentage of oil by titration of a solution of oil in ethanol with NaOH (0.1N). Peroxide value, expressed as milliequivalents of active oxygen per kilogram of oil (meq O₂/kg oil), was
determined by iodine titration of a solution of oil in iso-octane/acetic acid (3:2) [19]. Iodine value (a measure of the relative degree of unsaturation in oil) was calculated from the relative percentage of fatty acids using the formula [20]:

\[ IV = (0.998 \times \text{C16:1}) + (0.899 \times \text{C18:1}) + (1.811 \times \text{C18:2}) + (2.736 \times \text{C18:3}) + (0.818 \times \text{C20:1}) \]

The saponification value was determined according to the ISO 3657 standard method, and the iodine value (a measure of the relative degree of unsaturation in Argan oil) was determined using the ISO 3961, 2018 method [20]. The extinction coefficient was determined according to the ISO 3656, 2011 standard method [21].

The density and the refractive index were measured at 20 °C ± 0.2 °C [22]. The saponified value (a measure of the content of ester linkages) was determined following the official analytical method ISO 3657, 2020 [23]. In a 250 mL round-bottomed flask, 1g of fatty substance is placed with 3 mL of solvent (ethanol-ether (v: v)) and 25 mL of alcoholic potassium hydroxide with a concentration of 0.5 N. the flask is then placed in a water bath for 60 minutes. After cooling the flask to room temperature, 2 to 3 drops of phenolphthalein are added. The excess of potassium hydroxide was determined with hydrochloric acid at a concentration of 0.5 N up to the endpoint (discoloration of the solution). Under the same conditions, a blank test was carried out.

For the identification of \( p \)-anisidine value, the absorbance of the oil samples was determined at 350 nm with a spectrophotometer (CARY 100 Varian UV). The value of \( p \)-anisidine was determined following the official analytical method ISO 6885, 2006 [24].

2.4. Fatty acid determination.

The composition of fatty acids was determined following the official analytical method ISO 12966-2, 2011 [25]. Prior to analysis, fatty acids (FAs) were converted to fatty acid methyl esters by shaking a solution of 60 mg oil and 3 mL of hexane with 0.3 mL of 2N methanolic potassium hydroxide for 25 min. The fatty acid composition was measured as their corresponding methyl esters by gas chromatography on a CPWax 52CB column (60 m x 0.25 mm i.d., 0.25 µm film thickness), Helium (with a flow rate of 1 mL/min) was used as a carrier gas. Oven, injector, and detector temperatures were set at 185, 200, and 230 °C, respectively. The injection volume of the samples was 1 µL in a split mode (split ratio 1:50). Results were expressed as the relative percentage of the area of each individual fatty acid peak [26].

2.5. Sterols determination.

Sterols composition was determined following the official analytical method ISO 12228-1, 2014 [27]. After trimethylsilylation of the crude sterol fraction, we used an Agilent 6890 GC-System equipped with a VF-1 column (30 m x 320 µm i.d., 0.25 µm film thickness) and applied Helium (flow rate 1.6 mL/min) as a carrier gas. The program of column temperature was prepared as follows: from 200 to 280 °C (5 °C/min). Injector and detector temperature were set at 300 °C. The injection volume was 1 µL in a split mode (split ratio 1:50). Peaks were determined either by standard compounds (\( \beta \)-sitosterol, campesterol, stigmasterol) by a mixture of sterols isolated from sunflower oil (\( \Delta^7 \)-stigmasterol, \( \Delta^7 \)-campesterol, and \( \Delta^7 \)-avenasterol) or by a mixture of sterols isolated from rapeseed oil (brassicasterol). The results
were expressed as the relative percentage of the area of each individual sterol peak and individual sterol [19].

2.6. Statistical analysis.

All determinations and measurements were performed in triplicate. Values were represented as means ± SD (standard deviations). Differences were considered significant at 5% as a probability level. In addition, principal component analysis (PCA) was carried out on fatty acids mean values of studied SCGO and various plant oils (soybean, sunflower, rapeseed, and coconut oils) from published literature. All statistical analyses were carried out using version XVII of STATGRAPHICS package (Statpoint Technologies, Inc., Virginia, USA).

3. Results and Discussion

3.1. Oil yield.

The economic value of vegetable oil is dependent on yield oil [28]. Oil extracted from SCGs has a significant potential for cosmetics, food soap production, and other industrial uses [15]. Moreover, it may be utilized as a substrate for producing poly 3-hydroxybutyrate), which is a whole biodegradable alternative to synthetic polymers [29]. Furthermore, other studies reported that SCGO could be a good source of essential fatty acids needed in the human body [30].

The oil yield of SCG extracted by the Soxhlet method is presented in Table 1. The SCGO yield was 18.5 ± 1.5 g/100g. However, such yield is much lower than that reported for sunflower oil (44 g/100g), coconut oil (38.1 g/100g), and rapeseed oil (28.27 g/100g), but similar to that of soybean seed oil (19g/100g) (Table 1). This result is similar to the SCGO yield reported in other studies [31, 32].

3.2. SCGO physicochemical indices.

Parameters used systematically to measure physicochemical properties of oils are the density, the refractive index, the iodine value, the saponification value, the free fatty acids (acidity), and the peroxide value. The density and the refraction index depend on the temperature and the fatty acid composition of the oil [33]. The refraction index rises as the oil's unsaturation level rises [34]. Table 1 summarizes the ranges of the main physicochemical parameters of SCGO and as well as other vegetable oils reported in the literature. Density and refractive index were similar to that of other vegetable oils (Table 1). The iodine value is a measure of the total number of double bonds present in fats and oils. SCGO showed a low iodine value (92.275 g (I₂)/100 g), likely due to its important content of saturated fatty acids (SFA) (Table 2). This value is lower than that of rapeseed oil (94-120 g (I₂)/100 g), sunflower oil (130 g (I₂)/100 g), and soybean seed oil (134.5 g (I₂)/100 g) but higher than that of coconut oil (6.3-10.6 g (I₂)/100 g) [35]. In addition, a high iodine value indicates that SCGO contains a greater number of double bonds than low iodine-value oil and usually has reduced oxidative stability [36]. These results suggest that SCGOs have a very good oxidative stability, and its significant content of SFA is likely responsible for this higher stability.

The saponification value is a measure of the average chain length of fatty acids. In fact, the shorter fatty acid has a higher saponification value. The saponification value of SCGO
analyzed is 187.5 ± 1.5 mg KOH/g, and it is lower than that of soybean, sunflower, and coconut oil (Table 1).

It is noteworthy that a high saponification value indicates that oil has a high triglyceride content and hence is very appreciated in cosmetology [22]. The oxidative state of oil can be examined from peroxide value which indicates the presence of primary oxidation products [37]. The peroxide value of SCG oil was determined as 5.5 Meq O₂/kg. Another parameter index used to evaluate the secondary oxidation products is the p-anisidine value [38].

This parameter has registered a value of 9.5, suggesting that over-oxidation was currently occurring at the time of extraction. On top of that, this value is close to that reported in the literature [39] and higher than that found in all studied oils; sunflower oil, rapeseed oil, coconut oil and, soybean oil. After extraction, free-fatty acids (FFA) quantity was found to be 7.5% (Table 1). Furthermore, high FFA contents have already been announced in other scientific researches [40]. This important value is generally an indication for strong enzymatic hydrolysis of SCGO during handling, harvesting, and oil processing [41].

A high level of free fatty acids, peroxide value, and p-anisidine value in SCGO indicate that this oil ought to be refined before its use [17]. Thus, the oil obtained using solvent extraction is frequently refined before consumption to remove impurities such as free fatty acids and oxidation products [42].

3.3. Fatty acids.

Fatty acids are the main important abundant components present in vegetable oils [19], [22]. They are closely related to stability, nutritional, and cosmetic quality [50, 51]. Table 2 shows the fatty acid profile of SGCO. Our results showed that SCGO contained three types of fatty acids. Indeed, the polyunsaturated fatty acids were the most abundant, accounting for 44.98 ± 2.5g/100g followed by saturated fatty acids (42.29 ± 2.3g/100g), and monounsaturated fatty acids (12.68 ± 1.15g/100g). The main unsaturated fatty acid in SCGO was linoleic acid (43.20 ± 2.19%). This value is similar to that reported by [39, 52]. Linoleic acid is considered the main essential fatty acid, also often referred as omega-6 fatty acid [53]. The linoleic acid content of SCGO is higher than that observed in rapeseed oil (16.22 ± 0.41%) and coconut oil (1.91 ± 0.04%) and similar to that of soybean oil but is much lower than that of sunflower oil (73.24 ± 0.35%). Linolenic acid is only a minor polyunsaturated in SGCO with a concentration less than 1 g/100 g. This value is lower than that reported by other authors [39, 52].

Unsaturated fatty acids are the major component of SCGO (54.59%). Both oleic and linoleic acids constitute 53.3% of total SCGO fatty acids.

The main saturated fatty acids of the SCGO in ascending order were arachidic acid (3.03 ± 0.99), stearic acid (7.25 ± 0.78 mg/100g), and palmitic acid (31.78 ± 2.02mg/100g). It is noteworthy that palmitic acid is an important element for cosmetic uses [54]. This result is similar to those reported in other works [39, 52]. However, the SFA composition observed in SCGO was higher than that of other vegetable oils (Table 2).

Additionally, palmitic acid is an important component of the saturated fatty acids fraction in SGGO.
Table 1. Mean values of physical and chemical parameters of SCGO and other vegetable oils found in the literature. Results are presented as means ± SD.

|                      | SCGO          | Sunflower oil | Rapeseed oil | Coconut oil | Soybean oil |
|----------------------|---------------|---------------|--------------|-------------|-------------|
| Oil yield [g/100g]   | 18.5 ± 1.5    | 10–20         | 44           | 28.27       | 19          |
| Density [20 °C]      | 0.909 ± 0.01  | 0.917         | 0.919–0.92   | 0.908–0.921 | 0.91        |
| Refraction index [20 °C] | 1.469 ± 0.01 | --            | 1.463        | 1.464       | 1.4543      |
| Saponification value [mg KOH/g] | 187.5 ± 1.5 | 167.28        | 191          | 168–181     | 248–265     |
| Iodine value [g (I2/100 g)] | 92.22        | 79            | 130          | 94–120      | 6.3–10.6    |
| Peroxide value [meq O2/kg] | 5.21 ± 0.1 | 3.77          | 0.7          | 3.62        | 2.2         |
| Para anisidine value | 9.5 ± 0.5     | 8             | 1.08         | 0.14        | 0.16–0.19   |
| FFA [g/100g]         | 7.5 ± 0.5     | 6.14          | 0.05         | 0.08        | 0.13–0.27   |

Table 2. Mean values of fatty acids of SCGO and other vegetable oils. Results are presented as means ± SD.

| Fatty acids | SCG oil | Sunflower oil | Rapeseed oil | Coconut oil | Soybean oil |
|-------------|---------|---------------|--------------|-------------|-------------|
| Source      | Our study | [39]         | [52]         | [58]        | [59]        | [58]        | [60]        |
| C14: 0      | 0.09 ± 0.02 | 0.05         | 0.1          | 0.87 ± 0.00 | --          | 11.39       |
| C16: 0      | 31.78 ± 2.02 | 32.45        | 32.80        | 5.29 ± 0.02 | 2.69 ± 0.01 | 7.76 ± 0.02 | 14.04 ± 0.62 |
| C18: 0      | 0.08 ± 0.00 | 0.03         | --           | --          | --          | --          |
| C18: 1      | 0.39 ± 0.1   | 0.39         | --           | --          | --          | --          |
| USFA        | 57.84 ± 3.3  | 59           | 56           | 88.39       | 92.46       | 8.8         | 81.14       |

This fatty acid is the principal constituent of refined palm oil [55] and, the biological and nutritional properties of palmitic acid have been extensively studied [55-57]. Indeed, similar to palm oil, the saturated fatty acid of SGGO is mostly palmitic acid, this last considered to be important and valuable by the industry, notably for cosmetics uses. With such an approach, the commercial success of palm oil has been global. Therefore, this SGGO is perfectly suitable for large-scale use and could follow the path of cosmetic palm oil.

3.4. Principal component analysis of fatty acids.

Principal component analysis was carried to visualize similarities among various plant oils, including SCGO and those from literature based on fatty acids as the major fraction. As summarized in Figure 1, the points plotted on the surface were delimited by the first two components, which accounted for more than 80% of the total variability. The second component (PC2, 35.74%) seemed to separate between plant oils. On its negative side, sunflower oil and SCGO interacted with higher values of C16: 0, C18: 0, C20: 0, and C18:2. In contrast, coconut oil was associated mainly with the best score of C14: 0, while both rapeseed and soybean oils were linked to the greatest content of C18:1 and C18:3. PCA was successfully used as a discriminative approach as well as the reduction and explanation of data variability [38, 61–64].
The two segments are representing C16:0 and C20:0 (Figure 1) are pointing almost in the same direction indicating thus a positive association between these fatty acids. However, C18:2 and C14:0 are pointing in opposite directions, so they are negatively correlated. Nevertheless, C18:2 and C18:3 are unrelated (they are orthogonal).

The dendrogram of the hierarchical classification shows that the five studied oils are divided into two main classes which are found on the factorial plane of axes 1 and 2 of the PCA (Figure 2 and 3). The first class has two subclasses, one containing rapeseed oil and the other containing sunflower oil and soybean oil. The second class also has two underclasses, one containing coconut oil and the other one containing SCGO. Therefore, the results of the hierarchical classification categorized our samples into four groups according to their fatty acids content. The first one represents rapeseed oil, the second encompasses both soybean and sunflower oil, the third is related to coconut oil, and the fourth is linked to SCGO.

Figure 1. Principal component projections on PC1 and PC2 for the studied spent coffee grounds along with other vegetable oils (coconut, soybean, rapeseed, and sunflower oils). Points plotted are related to vegetable oils, and blue segments represent various fatty acids.

Figure 2. 3D Hierarchical classification.

Figure 3. 2D Hierarchical classification.
3.5. Phytosterols.

Phytosterols are a minor component of oils [65]. Analysis of these compounds is a useful parameter for detecting alterations or verifying authenticity, as they can be considered an oil impression [56]. Furthermore, these important molecules are endowed with potent biological properties [66–68].

The total content of phytosterols in the unsaponifiable fraction of SCGO is about 1138 ± 0.01 mg/100g. Generally, SCGO phytosterols composition was found to be satisfactory and within the range of published values by [69]. This value is higher than that reported for all other oils (sunflower, soybean, rapeseed, and coconut oil) (Table 3).

A higher level of phytosterols in SGG oil than other vegetable oils could be explained by dehydration of some β-sitosterol during refining, especially in the bleaching step [70].

Δ-5-Avenasterol, Campesterol, Stigmasterol and β -Sitosterol were found to be the major sterols of SGG oil. The β-Sitosterol is significantly the sterol present in high amount. It represents 44.70 ± 0.01% of the total sterol fraction, which is similar to coconut oil (32.6-50.7%). Nevertheless, β-sitosterol detected in SCGO is lower than that observed in sunflower oil (58-64%). This sterol is also found in coconut oil but with contents lower than that found in SCGO (Table 3).

Table 3. Sterols profile of SCGO and other vegetable oils (g/100g). Results are presented as means ± SD.

| Vegetable oil | SCG oil | Sunflower oil | Rapeseed oil | Soybean oil | Coconut oil |
|---------------|---------|---------------|--------------|-------------|-------------|
| Sterols/Reference | Our study | [69] | [22] | [35] | [22] | [35] |
| Cholesterol | 0.41±0.01 | -- | < 0.4 | < 0.05 | < 1 | < 0.05 |
| Campesterol | 15.87±0.01 | 18.36 | 8-11 | 24.7-38.6 | 19-23 | 6.0-11.2 |
| Stigmasterol | 21.57±0.01 | 22.48 | 7-10 | 0.2-1.0 | 17-19 | 11.4-15.6 |
| β-Sitosterol | 44.70±0.01 | 48.00 | 58-64 | 45.1-57.9 | 47-59 | 32.6-50.7 |
| Δ-5-Avenasterol | 12.16±0.01 | 9.07 | 2-7 | 2.5-6.6 | 2-4 | 20.0-40.7 |
| Δ-7-Stigmasterol | 0.25±0.01 | 0.62 | 9-14 | < 0.05 | 1-3 | < 0.05 |
| Δ-5-Avenasterol | 0.51±0.01 | 0.80 | 4-6 | < 0.05 | 1-2 | < 0.05 |
| Total mg/100g | 1382±0.01 | 1900 | 325-515 | 450-1130 | 250-418 | 40-120 |

Figure 4. Principal component projections on PC1 and PC2 for sterols in spent coffee grounds oil along with other plant oils (coconut, soybean, rapeseed, and sunflower oils). Points plotted are related to vegetable oils, and blue segments represent various sterols. SCG oil L = spent coffee grounds oil reported in the literature.

β-sitosterol has beneficial and physiological effects on human health. It reduces cholesterol levels [41], inhibits breast cancer development [71], enhances the efficacy of
vitamin D [72], and has anti-carcinogenic, antipyretic, and anti-inflammatory effects. Generally, all phytosterols composition in SCGO analyzed were found to be satisfactory and within the range of published values [69].

The second major phytosterol detected in SCGO is stigmasterol with 21.57±0.01%. This amount is higher than that found in sunflower oil, rapeseed oil, and coconut oil. Finally, Δ-7- stigmasterol, Δ-7-avenasterol, and cholesterol are detected but with a minor component (less than 0.5%).

3.6. Principal component analysis of sterols.

Principal component analysis for sterols (Figure 4) shows that most data variability can be explained by the first two components (PC 1 + PC 2 = 99.84%). Both SCG oil investigated in our study and that from the literature [69] presented high similarity with vegetable oils and were rich in total sterols compared to coconut oil.

4. Conclusions

Recycling is reprocessing and recovery of waste materials for another use in new products. The present study demonstrated that SCG could offer potential and cheap alternative raw material for vegetable oil production, oil yield was encouraging since it reached (18.55 g/100g). Likewise, fatty acids composition showed an interesting fatty acid profile (linoleic and palmitic) and are a very good source of phytosterols (β-sitosterol, stigmasterol, and campesterol). Its high amounts of phytosterols, linoleic acid, and palmitic acid could open important applications for SCGO, and it can be a new source of palmitic acid. Such compositional attributes found in this oil are even more important than some plant oils, which could open important applications of SCGO, such as in the food industry, pharmaceutical applications, and cosmetics uses.

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Conflicts of Interest

The authors declare no conflict of interest.

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