

Review

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*Review*

# Coffee Oil Extraction Methods: A Review

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**Abstract:** Green and Roasted coffee oils are products rich in bioactive compounds, such as linoleic acid and diterpenes cafestol and kahweol, being a potential ingredient for food and cosmetic industries. An overview of oil extraction techniques most applied for coffee and their influence on the oil composition is presented. Both green and roasted coffee oil extractions are highlighted. Pressing, Soxhlet, microwave, and supercritical fluid extraction were the most used techniques used for coffee oil extraction. Conventional Soxhlet is most used on lab-scale, while pressing is by industry. Supercritical fluid extraction has also been evaluated due to the goal of increasing the coffee oil diterpenes content. One of the highlighted activities in Brazilian agribusiness is the industrialization of oils due to their increasing use in the formulation of cosmetics, pharmaceuticals, and foods. Green coffee oil (raw bean) has desirable bioactive compounds, increasing the interest of private companies and research institutions in its extraction process to preserve the properties contained in the oils.

**Keywords:** Arabica coffee; Canephora coffee; green coffee oil; roasted coffee oil; Soxhlet; press; supercritical fluid

## 1. Introduction

Coffee is one of the most popular beverages and most traded commodities worldwide. It is cultivated in about 80 countries and, according to USDA [1], the global production for 2024/25 is estimated in 176.2 million bags of coffee (60 kg/bag), mainly due to the recovery of Brazil and Indonesia productions. Brazil has been the leading producer and exporter of coffee, accounting for approximately 39% of world coffee production and one of the most representative consumers. World coffee production is mainly focused on selling beans for hot beverages for domestic use across the countries, as well as in bars, restaurants and hotels. The unique flavor and aroma of roasted coffee make possible to obtain a very pleasant oil to the food industry, used in candies, chocolates, ready-to-eat drinks, for gourmet applications and for instant coffee aromatization.

Coffee is also recognized to produce an oil rich in unsaponifiable matter, obtained from both green (or raw) and roasted beans, with quite distinct sensorial and physico-chemical aspects. Green coffee oil is greenish yellow with a slight odor usually obtained by pressing. Its main application is in cosmetics and skin care products due to its antioxidant and moisturizing properties as also for the

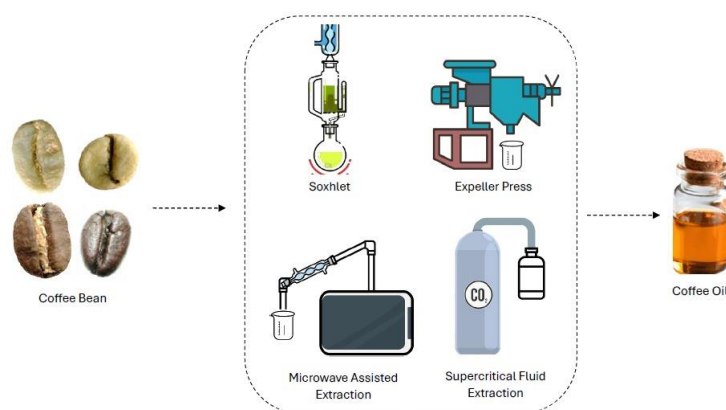
growing demand towards natural products. Roasted coffee oil is a brown viscous liquid usually obtained by pressing or CO<sub>2</sub> supercritical extraction, which color and aroma are mainly related to Maillard reaction that occur during the roasting process. Chemically, aldehydes, ketones, furans, pyrazines and other *N*-heterocycles, besides phenolic compounds, are the most representative volatiles [2].

Although there are 124 species of coffee (*Coffea* sp.) [3], only two are commercially important: *Coffea canephora* P. (about 25% of world production) and *C. arabica* L. (75%), with their diversity of botanical varieties. Among the coffee compounds, up to 17% correspond to a complex lipid fraction that gives rise to coffee oil from Arabica beans and up to 10% are observed in Canephora, all them serving as an important sources of bioactive components [4–6]. The major class of compounds in coffee oil are triacyl glycerides (up to 75%). As reported by Folstar (1985) [7], the fatty acids of the coffee oil are present predominantly in two triacyl glycerides, the PLP (about 28.1%) and PLL (about 27.5%), with significant quantities of SLP (about 8.6%), LLL (about 6.7%), POP (5.9%) and SLL (4.2%), where the letters correspond to the fatty acids palmitic (P), linoleic (L), stearic (S), and oleic (O).

In Arabica beans there is also a representative amount of diterpene esters (around 17%) besides free and esterified sterols, serotonin amides, phosphatides and tocopherols, as will be discussed later. An important difference in the constitution of coffee oil from other beans is the presence of the esterified diterpenes cafestol and kahweol, which are not found in any other matrix [6]. Related to the green beans, the levels of total phenolic compounds vary between 4% and 8.4% for *C. arabica*, while for *C. canephora* it is between 7% and 14.4% [8]. Differences in alkaloid concentrations between *C. arabica* and *C. canephora* are significant, with the latter generally having higher levels of caffeine (around 1% for Arabica and up to 2.7% for Canephora) and lower amounts of trigonelline [9–11].

One of the highlighted activities in Brazilian agribusiness is the industrialization of oils due to their increasing use in the formulation of cosmetics, pharmaceuticals, and foods [12]. Green coffee oil (raw bean) has desirable bioactive compounds that increase the interest of private companies and research institutions in its extraction process to preserve the properties contained in the oils. Several methods of coffee oil extraction are proposed to increase their lipid content. In the literature, physical and chemical treatments are applied to the beans, and their parameters are usually discussed in terms of efficiency, applicability, cost, and environmental risks [13].

Some advanced extraction technologies have emerged since conventional Soxhlet and pressing extraction techniques, such as microwave-assisted enzymatic extraction, ultrasound-assisted extraction, supercritical fluid technology, high pressure-assisted extraction, and pulse electric field-assisted extraction (Figure 1), ranging from the yield of oil to aspects that impact sustainability of the process [14,15]. Brazil also has the world's largest coffee research program through the Brazilian Coffee Research and Development Consortium - CBP&D/Café, coordinated by the Brazilian Agricultural Research Corporation - Embrapa, with research investments in genetic improvement, pest management, irrigation, production quality and biotechnology, with concern for economic sustainability and environmental preservation [16].



**Figure 1.** Most used processes and techniques for coffee oil production.

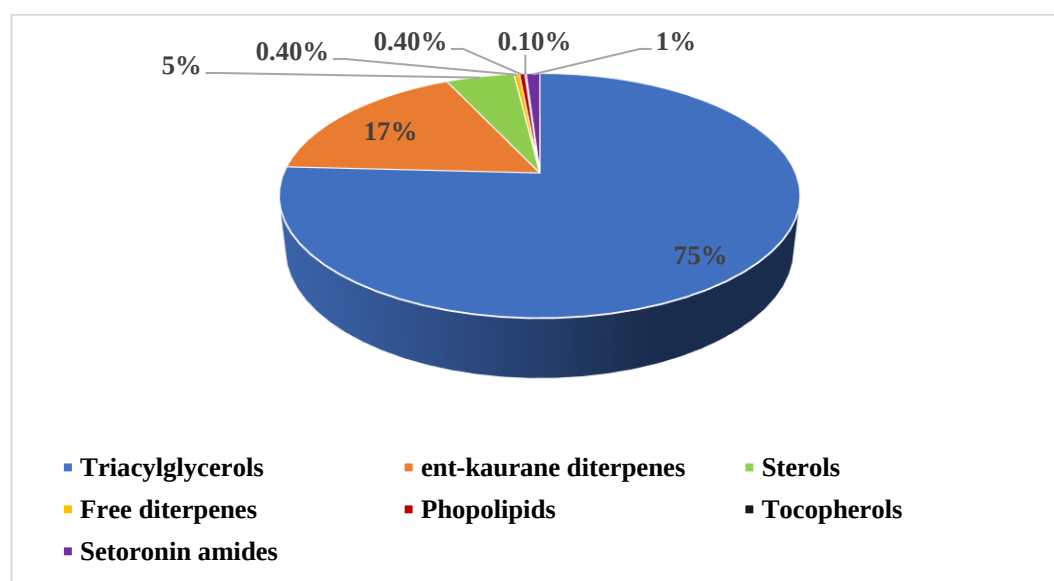
Considering this context, alongside the Brazilian significant role in the agricultural coffee sector, this article aims to discuss aspects related to the most used processes and techniques for coffee oil production, as also the chemical composition of green and roasted coffee oils. Soxhlet, pressing, microwave-assisted extraction, supercritical fluid extraction and more recently, extrusion associated to Soxhlet were the techniques covered in this text.

## 2. Green and Roasted Coffee Oils

### 2.1. Chemical Composition of Green Coffee Oil

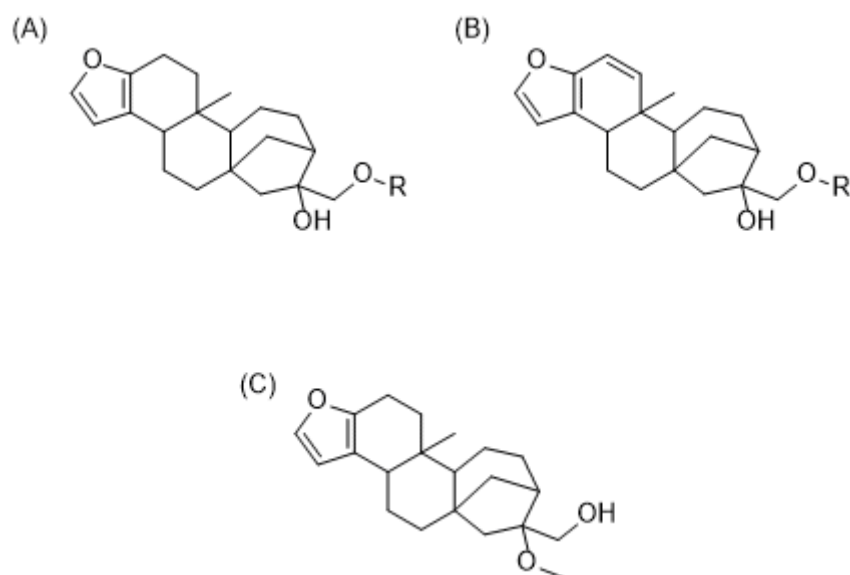
Lipids of green coffee beans are located in the endosperm and in a lower extent as a wax on the outside of the bean<sup>17</sup>. The lipid fraction in Arabica coffees is around 17%, while *Canephora* coffee content is usually lower, up to 10% [6].

Arabica oil is composed of triacylglycerols - TAG (around 75%), esterified *ent*-kaurane diterpenes (up to 17%), free diterpenes (up to 0.4%), sterols (up to 5%), tocopherols (0.1%), phospholipids (0.4%) and serotonin amides (1.0%) [17–20] (Figure 2). Lipids *C. canephora* var. *robusta* coffee was recently detailed and quantified by lipidomics through LC-ESI-MS/MS [21]. Speer and Kolling-Speer (2006) detailed some differences between Arabica and Robusta coffee oils and verified stearic acid content (in esterified form) is much lower than that of oleic acid for Robusta samples, while in Arabica both are present in equivalent quantities. Also, the total amount of diterpenes in green Arabica coffee varies from 1.3% to 1.9% (w/w), while in Robusta beans it ranges from 0.2% to 1.5% (w/w) [22].



**Figure 2.** Chemical composition of Arabica coffee lipid fraction.

Arabica coffees diterpenes are mainly composed of cafestol (2.99 - 5.84 g/kg) and kahweol (4.15 - 6.73 g/kg) and small amounts of 16-*O*-methylcafestol (0.01 - 0.14 g/kg), represented in Figure 3, while Robusta coffees have 16-*O*-methylcafestol (0.45 - 1.39 g/kg), cafestol (0.76 - 1.91 g/kg) and small amounts of kahweol (0.04 - 0.12 g/kg)[23]. 16-OMC is one of the major markers for detecting the presence of Robusta coffee in blends [7] (Figure 3). Cafestol and kahweol are vastly explored in scientific literature [6,24–26] and have been correlated to antitumor, antioxidant, and anti-inflammatory properties. Cafestol is known to present a hypercholesterolemic effect, and many studies have already associated this biological activity to the ingestion of non-filtered hot beverages as in Turkish and French Press brews [27–29].

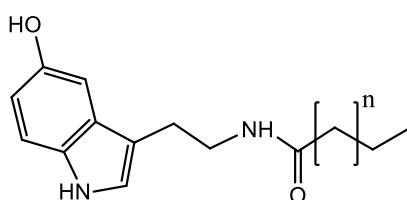


**Figure 3.** Chemical structures of: (A) cafestol, (B) kahweol and (C) 16-O-methylcafestol.

The main fatty acids present in green coffee beans are linoleic (C18:2) and palmitic (16:0) acids, ranging from 42.5-50.2% for C16:0, 8.9-17.5% for C18:0, 7.2-11.0% for C18:1, 20.5-25.8 for C18:2, 4.5-6.0% for C20:0, and 1.1-2.5% for C22:0<sup>4,6</sup>. Besides acylating of mono, di, and triacylglycerides in coffee beans, these acyl moieties also appear esterifying diterpenes, sterols, serotonin and minor lipids [6,30–32].

The sterol content in coffee lipid fraction is very similar to other bean vegetable matrices.  $\beta$ -Sitosterol (52%), stigmasterol (22%), and campesterol (16%) represent nearly 90% of this class, while 5-avenasterol, campestanol, 24-methylenecholesterol, sitostanol, 7-stigmastenol, 7-avenasterol, 7-campesterol, and clerosterol represents the remainder 10% [6,33,34].

Coffee oil lipid unsaponifiable fraction also contains  $\beta$ N-alkanoyl-5-hydroxytryptamines (Cn-5HTs), in Figure 4, which consist of a serotonin unit conjugated to acyl moieties through an amide link, mostly represented by C-20 and C-22 units [32]. Cn-5HTs, typically found in the wax bean, have interesting biological properties, such as anti-inflammatory, antinociceptive, anxiolytic, and others [32,35–37], but also are correlated to stomach irritation [38,39]. Due to this property, associated to the hypercholesterolemic effect of cafestol, A fermentative wet post-harvest process with commercial yeasts with *Saccharomyces cerevisiae* was developed in which substantial reductions for C-5HTs (up to 38% for C20-5HT and 26% for C22-5HT) as well as for diterpenes (54% for cafestol and 53% for kahweol) [40].



**Figure 4.** Chemical structure of  $\beta$ N-alkanoyl-5-hydroxytryptamines.

The cosmetic industry is interested in moisture retention in the skin and green coffee oil is also a potential ingredient to prevent photoaging [41,42]. Coffee oil provides properties against UV-B absorption without cytotoxic effects, being useful in sunscreen factor formulations and improving its stability, as well as for other cosmetic products [43–47]. Some of these properties may also be present in roasted coffee oil, as few components are altered by roasting profiles [12,48].



## 2.2. Chemical Composition of Roasted Coffee Oil

The roasting process consists of heating the green coffee beans to high temperatures (often exceeding 200 °C) to develop aroma and flavor components of interest, typically appreciated on roasted coffees. The time and temperature of the roasting depend on the desired characteristics of the final products [49–51]. In the roasting process, the coffee beans lose water, some volatile compounds are formed and some are lost. Moreover, the degradation of carbohydrates, amino acids, and chlorogenic acids give aroma compounds, mainly by Maillard and Strecker reactions, as also melanoidins, brown nitrogen-containing polymers that accounts for up to 25% in the roasted coffee beans [49–52]. The oil content extracted from roasted Arabica coffee reaches 15.4%, and its chemical composition contains a high amount of fatty acids, the main ones being linoleic acid (40.3%) and palmitic acid (34.5%) [12].

The lipid content in roasted coffee beans increases when compared to green beans since bean cell walls are partially degraded and allow the release of oil, which favors aroma retention. In general, the roasted Arabica coffee beans present about 4.1-16.8% of lipids, whereas the Canephora has 3.2-11.5% [53–56].

Coffee diterpenes can suffer intramolecular water eliminations and oxidation reactions during the roasting and their concentration depends on the intensity of the roasting process, as reviewed recently [57].

Serotonin amides suffer an intense degradation during roasting and an  $\alpha$ -cleavage to serotonin was described, following the production of 5-hydroxyindole, 3-methyl-5-hydroxyindole, 3-ethyl-5-hydroxyindole, free fatty acids, amides, and nitrile compounds [58].

A small amount of *trans*-fatty acids and peroxides are formed during coffee roasting [59,60]. The presence of *trans*-fatty acids is undesirable for food formulation due to its intake association with an increased risk of cardiovascular disease [60,61].

Roasted coffee oil is rich in diterpenes (3.72%), with a content of kahweol and cafestol of about 1.98 and 1.74%, respectively. It also presents a high content of tocopherols (0.91%), being  $\beta$ -tocopherol (0.88%) the main component, followed by  $\alpha$  (0.03%) and  $\delta$  isomers (0.002%). Moreover, this oil may also have chlorogenic acid (0.010%) and caffeine (0.35%), depending on the polarity of the solvent used in the extraction process [53].

The roasted coffee oil contains most of the compounds responsible for the pleasant roasted coffee aroma, therefore, it is used to flavor products such as instant (soluble) coffee, cakes, and candies. This oil is also suitable for food formulation as a source of bioactive compounds (such as linoleic acid, tocopherols, and diterpenes) and for cosmetics applications due to its sun protection factor [53,56].

## 3. Coffee Oil Extraction Methods

The botanical species, bean quality, particle size, extraction time, and solvent, if present, are important parameters in coffee oil extraction [6,62]. Several techniques have been used to obtain coffee oil, mainly pressing, Soxhlet extraction, microwave, and supercritical fluid. Despite this, there are important aspects related to the production processes that will be discussed below.

### 3.1. Mechanical Extraction

Extraction conditions generally impact the chemical composition and biological properties of the extracted oil. The fact that extraction by mechanical pressing is a method that does not use organic solvents and, therefore, does not produce potentially toxic residues, reduces environmental and human health concerns, which is attractive for the food and cosmetics industries.

Pressing is one of the oldest processes for extracting oils. Studies indicate that it was used in the ancient times, employing stone mills powered by animal traction. It is a physical process in which oils are obtained from a range of matrices, especially oilseeds, and is usually used when there is interest in keeping original organoleptic properties. Production costs are reduced since no organic solvent is used. The total yield obtained through this process is usually inferior to solvent extraction (usually 60-80%), but in the case of coffee lower yields are usually obtained. Temperature is often

used to increase pressing yield when there are no thermolabile substances. Other parameters such as seeds moisture content, screw speed, press exit size, and particle size can also impact the total yield [63,64].

There are two main types of presses used nowadays: hydraulic and screw press. The oil extraction process currently uses continuous presses (expeller), where the beans (for example, coffee) are moved forward and compressed by a worm screw. At the exit, an adjustable cone allows the pressure inside the press to be increased or decreased, resulting in crude vegetable oil and a cake, the solid part resulting from pressing. The oil must pass through a filter press to remove suspended solid parts, and the cake can be toasted, ground, and sold for consumption in beverage preparation [65]. In 2020, Hussein briefly reviewed some researches on cold pressed green coffee oil focusing its different applications including cosmetic products [66].

### 3.1.1. Hydraulic Press

The hydraulic press is a tool for producing compressive force by means of a fluid. Its foundation is based on Pascal's principle, according to which the pressure in a closed entity is constant [67]. Therefore, for the force to occur, two hydraulic servomechanisms are required: the first, which supports the punching tool and the second, which is used in the loading and unloading operations of the block holder [68].

A mechanical hydraulic press was used to investigate the effect of pressure applied through a flat piston on wet and dry roasted defective coffee beans (RDCB). The RDCBs were pressed at room temperature for 60 min, with the pressure applied increasing from 350 to 550 bar at 20 min intervals. As a result, lipid amount corresponded to a yield of 2.47% w/w, or a recovery of crude lipids of 21.6% w/w in relation to the average yield in lipids extracted by Soxhlet with hexane (11.41%) [69].

Due to the low oil recovery through the hydraulic press, this method is not very popular in coffee oil extraction. Although its use is declining, hydraulic pressing is still used to this day on processes such as cocoa butter extraction, virgin olive oil production and oil production from some other matrices [70,71].

### 3.1.2. Expeller Press

An expeller press is composed of a barrel shaped outer casing with perforated walls and a metal screw that feeds oil bearing products. The material is continuously grinded and crushed, rupturing the oil cells which turns possible oil collection through the perforations in the casing. The material from which oil is extracted is known as cake. Capacities may vary but most expeller are able to process between 8 and 45 kg per hour [70].

Aiming to determine green and roasted defective coffee beans proximate composition and fatty acid profile, the beans were subjected to two subsequent pressing cycles in a Mazziere Press. Healthy coffee beans had a similar but higher oil content ( $10.8 \pm 0.3\%$ ) compared to defective coffee beans ( $9.9 \pm 0.1\%$ ). The fatty acid composition showed no significant difference between healthy and defective coffee beans. Screw-pressed unsaponifiable matter (12.8 g/100 g oil) and solvent-extracted PVA (9.2 g/100 g oil) oils showed significant differences, reinforcing that screw pressing is not a selective process to lipids [72].

The production of bioactive carboxymethylcellulose films enriched with green coffee oil and its residues was investigated by using a continuous expeller press at 25 °C. The temperature of the oil at the outlet of the expeller, measured by a thermocouple varied between 40 and 45 °C. After the crude oil (oil with sludge) was centrifuged for 20 min at 3100 g and 25 °C, the oil content was  $4.56 \pm 0.74\%$ . The phenolic compounds extracted from the pressing residues were incorporated into a bioactive carboxymethyl cellulose films, managing to produce films with UV-is radiation blocking properties and high antioxidant capacity [73].

Silva et al. [63] studied how some pressing parameters affect the yield and lipid composition of green Arabica coffee oil, focusing on fatty acids, diterpenes and serotonin amides content, the last for the first time described in a coffee oil. A design of experiments was made to evaluate particle size ( $< 0.850$  mm;  $> 0.850$  mm and  $< 2.00$  mm), screw speed (18 and 30 rpm), press exit nozzle size (4 and

5 mm) and preheating (on and off). Oil yield varied between 2.65 and 6.27% and all the parameters had significant impact on oil yield. Diterpenes kahweol and cafestol content ranged from 13.33 to 16.72 mg/g and 37.11 to 47.14 mg/g of oil, respectively. Serotonin amides content ranged from 114.42 to 577.37 µg/g for C20-5HT and 193.50 to 1068.08 µg/g for C22-5HT. Difference on fatty acids composition related to press conditions was not significant.

### 3.2. Soxhlet Extraction and Its Comparison to Supercritical Fluid and Microwave Extraction Techniques

In this topic, articles that deal with coffee beans extraction by Soxhlet alone or combined will be reviewed. Supercritical fluid will be briefly compared here and discussed in detail in item 3.4, as more detailed studies for coffee were performed with this technique.

Soxhlet extraction is one of official standard methods to determinate oil content [74]. In summary, the sample is placed on a cellulose filter (thimble) that is gradually filled with solvent (also called fresh condensed extract) from a distillation flask. When the liquid reaches the overflow level, a siphon sucks it from the thimble and discharges it back into the distillation flask, thus transporting the extracted analytes into the bulk liquid. This operation can be repeated until complete extraction is achieved.

Speer and Kolling-Speer [6] cited two official methods for oil extraction by Soxhlet, the German Foundation for Scientific Research (Deutsch Forschungsgemeinschaft, DFG, 1952) [75] and the AOAC (2005) [76]. Both use petroleum ether for 4 and 16 h, respectively. They also cite the study by Picard et al. [77], who emphasized that different solvents, such as diethyl ether, petroleum ether, hexane and their mixtures make results comparison difficult, a problem that still remains.

Green Canephora coffee oil extraction equilibrium yields (Soxhlet with hexane, 16 h) and chlorogenic acid was studied. The coffee oil average yield was 8.3%, and green coffee oil/ chlorogenic acid equilibrium extraction showed an increasing function of temperature and a decreasing function of the mass ratio of ground coffee to solvent. According to the authors, the equations derived by this study could be used within the boundaries studied, which were 30-50°C for temperature and 0.1-1.0 for mass ratio [78].

Soxhlet extraction from Arabica and Canephora gave coffee oils analyzed their sterols. For lipid extraction, about 50 g of ground sample were extracted with hexane in a Soxhlet for 8 h, syphoning six times per hour. As a result, the average lipid content of the Canephora coffees was 12% to 17%, and for Arabica 15% to 20%. Using sterols as chemical descriptors,  $\Delta^5$ avenasterol and sitostanol were considered the most differentiating variables. Thus, based on these descriptors, any new sample could be easily classified. The data from this article shows a significantly higher oil content when compared to other articles reported in the literature [79]. Carrera's study touches on an important point in Soxhlet extraction studies, which is the number of siphonages. Most articles that use this technique report extraction time but do not reference the number of siphons used, this being the moment where the extraction occurs, so an important parameter to be measured.

Twenty grams of green coffee and commercial roasted Arabica coffee were ground, with particle size between 0.297 and 0.35 mm, 0.35 and 0.42 mm, and 0.42 and 0.50 mm. Soxhlet extraction was performed using hexane (10 mL/g sample) for 16 h. The authors also performed supercritical fluid extractions, investigating temperature (35 to 55 °C), type of material (coffee beans and cake) and type of solvent (ethanol, acetone and ethyl acetate), in a fixed ratio of solvent to solid mass (5:1), and the diterpenes were determined by HPLC. As a result of Soxhlet extraction, the green coffee oil content was of 11.37% for green beans and 15.49% for roasted beans, while for diterpenes it was observed 3.84 g/kg of cafestol and 4.76 g/kg of kahweol for the green beans and 3.28 g/kg and 3.98 g/kg for the roasted beans, respectively [80]. Supercritical data will be discussed below.

The removal of oil from healthy and defective Arabica coffee beans using an industrial Soxhlet device, with a capacity of 25 kg and using hexane as a solvent for 16 h, was investigated. Solvent was removed in a rotary evaporator and a transesterification step was carried out to produce biodiesel. Soxhlet's oil yield varied from 10 to 12% and the highest ester yield (70.1% for healthy beans and 73.8% for deficient beans) was obtained with MeOH at 25 °C for 1 h [81]. Regardless the ester yields, coffee oil showed potential as a candidate raw material in biodiesel production.



The roasting conditions was studied focusing the influence on coffee oil properties. Robusta coffee beans were roasted by varying roasting temperature (190 to 216°C), air speed (0.5 and 1 m/s) and air humidity (0.07 to 1%). Oil removal took place in an automatic Soxhlet apparatus for 1 h using petroleum ether at 40 to 60°C and the solvent was recovered in the apparatus itself. Oil removal best conditions were a roasting temperature of 216 °C, air flow speed of 0.5 m/s and dry air, with an oil content of 11.31%, 210°C, 1.0 m/s and humid air, with an oil content of 11.20%. At 216°C, 1.0 m/s and dry air, the oil content was 11.07%. The first two conditions resulted in enriched aroma [60].

Diterpenes from roasted Arabica coffees extracted with the Bligh Dyer method, cold and hot saponification and compared with Soxhlet for 6 h with *t*-butyl methyl ether was investigated. Saponification with KOH was done to obtain unesterified diterpenes. An apparent overestimation of oil extracted by the Soxhlet method was observed (18.6% yield) compared to Bligh Dyer (13.5%). For the diterpenes, the extraction by Bligh Dyer proved to be less efficient than the Soxhlet method, whose contents of cafestol and kahweol corresponded to 170.2 and 318.7 mg/100 g, respectively [82].

Green coffee oils extraction by microwave-assisted extraction (MAE) and Soxhlet using petroleum ether were also compared. Coffee oil content varied from 7.5 to 9.5% by the Soxhlet method, while by MAE there was a variation from 5.8 to 7.6%. Quantification of cafestol and kahweol diterpenes was monitored by HPLC/UV. A full factorial design was applied for the MAE to evaluate time (2, 6, and 10 min) and temperature (30, 37.5, and 45 °C) parameters. MAE best condition was achieved at 45 °C and 10 min, much faster when compared to a 4 h Soxhlet extraction. Regarding the cafestol and kahweol content, green coffee oil obtained by MAE could lead to a space–time diterpenes yield six times higher when compared to the Soxhlet method. Another advantage of MAE is the reduced amount of solvent needed when compared to the traditional Soxhlet extraction method [83].

Microwave-assisted extraction (MAE) applies microwave energy to heat the solvent in contact with a sample matrix to extract target compounds. Under conventional heating, the sample in contact with the equipment wall is first heated, thus heating occurs from external to internal environment with heat transfer by conduction, followed by radiation and convection transfer. Heating by microwave irradiation will depend on solvent's dielectric properties, usually takes about 15-30 min and uses a solvent volume of around 10-30 mL, which represents a considerable extraction time and solvent volume reduction compared to the Soxhlet extraction method [84].

Green Arabica coffee oil was obtained by supercritical extraction and Soxhlet, which showed similar chemical compositions by ATR-FTIR infrared spectra. Soxhlet was performed for 7 h using hexane and supercritical CO<sub>2</sub> extraction yield was higher and required less extraction time than Soxhlet [85].

Oliveira et al. [86] evaluated the role of different solvents (acetone, ethanol, ethyl acetate, hexane, isopropanol, and petroleum ether) in Soxhlet extraction related to total soluble solids and some bioactive compounds from green coffee beans. The soluble solids/oil extraction was performed by Soxhlet for 3 and 5 h and the temperature were used according to the boiling point of each solvent. As a result of soluble solids/oil content it was found 8.31% using acetone, 11.78% using ethanol, 6.44% using ethyl acetate, 8.85% using hexane, 10.23% using isopropanol and 7.67% using petroleum ether. Ethanol was found to be the ideal solvent for extractable phenolic and antioxidant compounds. Only for  $\beta$ -carotene bleaching assay (BCBA) analysis, ethyl acetate yielded the best results for antioxidant activity.

Recently, Ribeiro et al. [87] used extrusion pretreatment to extract coffee oil from healthy and defective beans followed by Soxhlet. The study varied the temperature parameters (40 to 80 °C) and screw rotation speed (60 to 100 RPM) for extrusion, and Soxhlet extraction consisted of using 20 grams of material and 150 mL of hexane for 4 h. The optimized extrusion condition (68°C and 60 rpm) with subsequent Soxhlet extraction resulted in oil contents of 16.42% and 15.29% for healthy and defective grains, respectively. Extrusion pre-treatment oil levels were significantly higher than those found only by Soxhlet, being 9.05 and 9.47%, for healthy and defective grains, respectively. The extruder's ability to deconstruct raw coffee bean recalcitrant structure and consequently the lipid pockets was the main cause associated with this excellent performance.

Soxhlet comparison to other conventional extraction techniques has disadvantages such as the long extraction time (4-16 h) and the large amount of solvent used, producing more waste. Another disadvantage is the exposure of the extracted solute to the solvent boiling point for a long period and the possibility of heating thermolabile compounds, bringing undesirable results [88–90].

There are still few studies that explore the scale-up of Soxhlet for industrial applications. Soxhlet transition to large-scale extraction processes faces significant challenges, such as the need for larger volumes of solvents, temperature and pressure control, as well as energy efficiency and safety issues. Therefore, while Soxhlet continues to be the method of choice for detailed and accurate analyzes in the laboratory, application on an industrial scale still requires further research and development to overcome these obstacles and enable its use in larger extraction processes [91,92].

### 3.4. Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction (SFE) is used to extract components from different matrices using a fluid in temperature and pressure conditions above its critical point. Supercritical fluid forms a homogeneous phase that presents both liquid-like and gas-like properties. Physicochemical properties such as viscosity, diffusivity, and dielectric constant can be controlled by varying supercritical fluid temperature and pressure, without phase changes to occur [93,94]. These properties provide supercritical fluids with solvation power similar to liquids, acting as solvents. High diffusivity and low viscosity allow them to have properties like gases, with high penetration power in solid matrices, favoring extraction process mass transfer [95,96].

SFE is considered a selective extraction that presents low environmental impact when compared to solvent extraction, as SFE allows high extraction yields with no or small amount of organic solvent. Moreover, SFE requires low extraction time and is inexpensive to operate. However, the high setup cost is a disadvantage when compared to other extraction techniques [97,98].

There are different substances that could be applied for supercritical extraction, such as carbon dioxide, ethanol, propane, and water, for example. Among these, carbon dioxide is the most used due to its availability at high purity, non-toxicity, non-flammability, low cost, and relatively low critical temperature (31.1 °C) and pressure (72.8 bar) in comparison to other supercritical fluids [97,98]. However, CO<sub>2</sub> is a nonpolar solvent and, therefore, its affinity is limited. To overcome this disadvantage, a co-solvent may be applied to increase supercritical CO<sub>2</sub> solvation power and, consequently, more-polar analytes solubility. Ethanol and methanol are the most common co-solvents applied [98].

The CO<sub>2</sub> supercritical fluid extraction with and without the addition of co-solvents has been extensively applied for green, roasted, and spent coffee oil extraction for food, pharmaceutical, and cosmetic applications, as can be seen in the next paragraphs. Supercritical fluid extraction presents itself as an attractive technique to obtain raw and roasted coffee oils due to the ease of recovering the solute (coffee oil) and recycling the solvent (CO<sub>2</sub>), by simple thermodynamic control of pressure and temperature [94].

Commercial green and roasted coffees extraction was studied with CO<sub>2</sub> SFE by optimizing temperature (60–90 °C) and pressure (235–380 bar) conditions. The oil yield and diterpene levels were compared with the Soxhlet extraction with hexane, as previously discussed. In general, the correlation between extracted oil yield and diterpene content was inverse. CO<sub>2</sub> supercritical green coffee oil most efficient condition was achieved at a temperature of 90 °C, pressure of 373 bar and CO<sub>2</sub> density of 0.77 g/ml. However, this condition presented the lowest diterpenes concentration (4.14 g/kg). The CO<sub>2</sub> supercritical extraction that presented the highest concentration of diterpenes (0.45 g/kg) was at 70 °C, 327 bar and CO<sub>2</sub> at 0.81 g/ml, a content 43% lower when compared to oil obtained with Soxhlet extraction. Regarding the roasted coffee, this oil presented a significantly lower content of diterpenes when compared to green coffee oil, showing a reduction of 14.4% and 16.5% for cafestol and kahweol, respectively. The best oil extraction condition was at 70 °C, 371 bar, and CO<sub>2</sub> at 0.84 g/ml, a condition that presented the lowest diterpenes concentration (0.21 g/kg) [80].

Green coffee oil, caffeine and chlorogenic acids extraction was investigated using CO<sub>2</sub> SFE and CO<sub>2</sub> SFE with the addition of ethanol (5% w/w) and isopropyl alcohol (5% w/w) at 50 and 60 °C and

152 and 352 bar. The Soxhlet extraction using benzene, a very toxic solvent, was carried out to estimate the total oil content. An increase in the pressure resulted in higher oil extraction yield with all the solvents tested (pure CO<sub>2</sub>, CO<sub>2</sub>-ethanol, and CO<sub>2</sub>-isopropyl alcohol). The increase in extraction temperature decreased the oil yield when using only CO<sub>2</sub> as a solvent. However, with the use of a co-solvent, a different behavior was observed and the increase in temperature resulted in a higher oil extraction. Under the same process conditions, the oil extraction was higher when using CO<sub>2</sub>-ethanol mixed solvents, followed by the CO<sub>2</sub>- isopropyl alcohol. The CO<sub>2</sub> conditions at 70 °C and 352 bar provided an extraction of 17.65 g of the oil mass fed. Regarding caffeine and chlorogenic acid extraction, these compounds showed less affinity when compared with the coffee oil, and low yields were achieved [99].

The CO<sub>2</sub> SFE was also optimized to obtain a green coffee oil enriched in diterpenes, cafestol and kahweol. The oil extracted at 200 bar and 70 °C presented a cafestol content of 50.2 and kahweol at 63.8 mg/kg green coffee oil. This value was higher than the achieved by conventional pressing methods that presented 7.5 and 12.8 mg/kg green coffee oil for cafestol and kahweol, respectively. Regarding the fatty acids composition, the values obtained with the supercritical fluid were in agreement with the literature, presenting the linoleic acid (38.3%) and palmitic acid (32.4%) as the major fatty acids [100].

The roasted coffee oil CO<sub>2</sub> SFE was also evaluated. A central composite experimental design was performed to establish the effect of the pressure (150–300 bar) and temperature (40–60 °C) on the oil yield and fatty acids composition. Response surface analysis indicated that pressure had a greater influence on oil extraction yield than temperature, and the optimum yield (8.9%) was obtained at 331 bar and 35.9 °C. Regarding the fatty acids profile, all extraction conditions showed palmitic and linoleic acid as the major fatty acids. The optimum linoleic acid extraction (37.8%) was obtained at the same condition as the optimum yield. However, the optimum palmitic acid extraction (50.3%) was obtained by increasing the temperature to 64.1 °C [101].

CO<sub>2</sub> SFE green coffee oil solubility was studied by a static method under temperatures and pressures ranging from 40 to 80 °C and 300 and 350 bar, respectively. At 300 bar, green coffee oil solubility increased with temperature, between the range 40–60 °C. However, at 70 °C and 80 °C the solubility decreased. Similar results were observed at 350 bar, with an increasing in solubility with the increase of temperature to 70 °C, but a decreasing at 80 °C. Regarding the yields, the highest ones were achieved at 70 °C and 300 bar (7.58%) and 80 °C and 350 bar (7.60%), while the content obtained by Soxhlet was 7.57%. There was no significant difference between the fatty acid profile obtained by Soxhlet extraction and the different experimental conditions with the supercritical CO<sub>2</sub> extraction [102].

CO<sub>2</sub> SFE green coffee oil solubility at different temperatures (40–60 °C), pressures (200–400 bar) and supercritical CO<sub>2</sub>/ethanol ratios (0–5.7% w/w of ethanol) was also investigated. The green coffee oil solubility values increased at higher pressures. By using 2.9% of ethanol, the solubility was 63% higher than the one in pure supercritical CO<sub>2</sub> and the crossover pressure point was about 20 bar higher. The extract phase obtained with supercritical CO<sub>2</sub> and supercritical CO<sub>2</sub> + ethanol presents fatty acids, kahweol, and cafestol contents up to 3.4, 4.4, and 4.0 times greater than the green coffee oil extracted by pressing. Regarding the fatty acids content, the mass percentage of each was similar between the green coffee oil extract by pressing, supercritical CO<sub>2</sub> and supercritical CO<sub>2</sub> + ethanol [103].

The green coffee oil CO<sub>2</sub> SFE using ethanol as co-solvent was also evaluated. The effect of the temperature (50 – 70 °C), pressure (15.0 – 30.0), and ethanol content (5 – 20%) on the extraction of green coffee oil yield and total phenolic compound content was evaluated using a face-centered central composite design. The pressure and co-solvent content showed a positive impact in the extraction yield. Regarding the total phenolic content, the co-solvent presented a positive impact, while the temperature presented a maximum peak at 62°C. The experimental data were fitted to a second-order polynomial model and the desirability suggested that the optimal conditions were at 300 bar, 62 °C and 20% of co-solvent, predicting an extraction yield of 7.7% and a total phenol content of 5.4 mg gallic acid equivalent per g of green coffee supercritical extract (GCSE). Moreover, the effect

of the temperature on the caffeine and 5-caffeoylquinic acid content was also evaluated by comparing the GCSE extracted in the optimal condition with the one extracted at 20% co-solvent, 300 bar, and 50 °C. The GCSE obtained at the optimal condition showed higher content of caffeine and 5-caffeoylquinic acid, according to the authors this behavior is related to a decrease in the density of the solvents in higher temperature [104].

Supercritical fluid extraction is a green technique for extracting target compounds due to the non-use of toxic solvents that can pollute the environment. The properties of supercritical fluids allow it to be carried out at relatively low temperatures in the oxygen and light absence, avoiding thermo- and photodegradation of sensitive compounds, as well as oxidation reactions that degrade the sample [15,88].

### 3.5. Other Techniques

Dong et al. [105] compared the ultrasonic/microwave-assisted extraction (UMAE), microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), and pressurized liquid extraction (PLE) in the green coffee oil yield and composition. Among the four techniques evaluated, the ultrasonic/microwave-assisted extraction presented the highest yield (10.58%), while pressurized liquid extraction (6.34%) was the lowest.

The green coffee oil extract by pressurized liquid extraction showed the highest tocopherol, total phenols and phytosterol content, while the oil extracted by the ultrasonic/microwave-assisted extraction showed the highest diterpenes content. Regarding the fatty acid content in the four green coffee oils evaluated, the different techniques did not show an overall effect, but the ultrasonic/microwave-assisted extraction showed a subtle decrease in the linoleic acid content and an increase in palmitic acid.

## 4. Conclusions

Coffee is one of the most traded commodities in the world and its composition presents a considerable amount of lipids. Coffee oil is an important source of bioactive compounds, including diterpenes and tocopherols, and presents linoleic acid as a major fatty acid. Both green and roasted coffee oils have potential use in the cosmetic industry in sunscreen formulations. In addition, roasted coffee oil is widely used in the food industry due to its characteristic and pleasant flavor. Oil yield is influenced by extraction methods, chemical composition, and applicability. The most used methods to extract coffee oil are pressing, Soxhlet and supercritical fluid extraction. Conventional Soxhlet has the appeal for analytical use while pressing and supercritical fluid extraction can be scaled and has been quite evaluated to increase the coffee oil diterpenes content.

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