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Integrated Approach to Spent Coffee Grounds Valorization in Biodiesel Biorefinery

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Abstract: With the increasing consumption of coffee beverages, an increased amount of food waste—spent coffee grounds (SCG)—is generated and disposed into landfills or combusted in incinerators. SCG are characterized as a highly polluting substance with partial toxicity due to the presence of caffeine, tannins, and polyphenols. It also contains 15% of oil on average, and its potential for biodiesel production is thus considerable. The aim of the presented work is to evaluate the possibility and technical potential of biodiesel production from the SCG oil (SCGO) by esterification and transesterification reaction. According to the characterization of the studied SCGO, this stream must be adjusted and purified to be utilized in the existing biodiesel production plant. Fatty acids (FA) represent 85.85% of the SCGO, with two dominant FAs—linoleic and palmitic acids. The necessity of removal and disposal of unsaponifiable matter, which accounts for 15% of the SCGO content, must be highlighted when producing biodiesel from the SCG. The objective of this research was the comparison of different biodiesel production processes, where a two-step transesterification process has been identified as the most successful method for biodiesel production from the SCGO with the highest ester content of 89.62% and the lowest content of unsaponifiable and unidentified matter in the final product. The novelty of the analyses is a characterization of the d unsaponifiable matter present in the SCGO, and the article highlights the importance of progression to be considered when evaluating the technical potential of the SCG biodiesel production integrated into a biorefinery. Nevertheless, the SCG biodiesel can contribute to fulfilling the mandatory share of advanced biofuel in the fuel energy mix given by national legislation and contribution to the circular economy approach of biorefineries.

Keywords: spent coffee grounds; coffee waste; advanced biodiesel; transesterification; coffee oil; waste valorization

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1. Introduction

Coffee is one of the most traded commodities globally and one of the most consumed beverages worldwide [1]. According to the International Coffee Organization, annual global coffee production is still expected to increase, with the highest production of over 10 million tons (Mt) recorded in the last coffee year (October 2021–September 2022) [2]. Increased consumption of coffee beverages leads to the increased generation of spent coffee grounds (SCG). Spent coffee grounds are generated after coffee brewing or instant soluble

coffee production [3]. Every kilogram of ground coffee used for coffee beverage preparation produces almost 2 kg of wet spent coffee grounds (WSCG), while 1 kg of roasted coffee beans produce 0.91 kg of the dried SCG (DSCG), which results in 20 Mt of WSCG (the equivalent of 9 Mt of DSCG) as a by-product [4,5]. Almost half of this amount is produced by coffee shops and industrial plants, while the remaining amount is produced domestically [6]. Currently, SCG are treated together with food or municipal waste; however, there are initiatives of cities or coffee shops for collecting the SCG separately for fuel pellets production (Bio-bean, London, UK) [7]. Moreover, a few emerging companies producing coffee cups from coffee waste, e.g., Kaffeeform [8], Beanused® [9], or Rekava [10], can be found operating in Europe. After coffee brewing, the SCG contain a significant number of compounds potentially suitable for value-added compound production [4,11]. Three main groups of compounds can be found in the SCG—saccharides, oil fraction, and other components (lignin, alkaloids, proteins, polyphenols, phytosterols and others) [3]. Figure 1 summarizes the basic compounds' content in the SCG as reported in the literature.

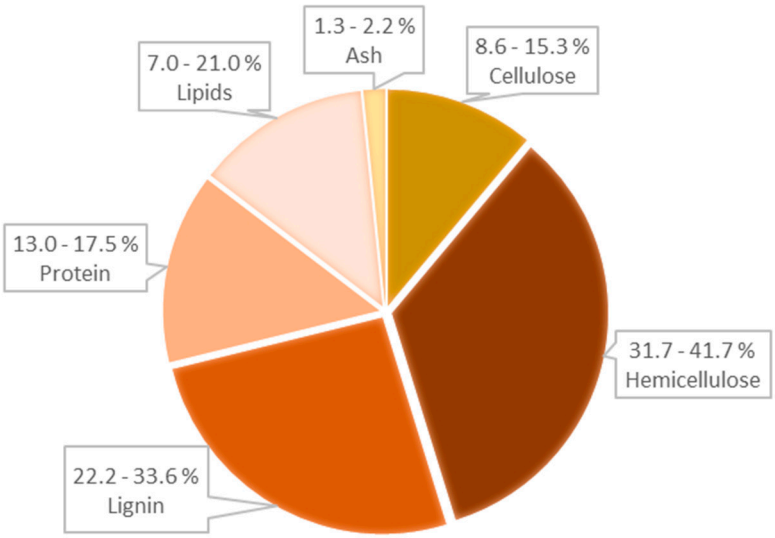

Figure 1. Basic compounds analyses of SCG (% wt. dry matter). Source: Own elaboration based on data published in [11].

SCG are considered to be an abundant and low-cost resource for biodiesel production as it might contain a high oil content (7–21%) [7,12]). The amount and composition of oil in the SCG depend on various parameters, such as coffee species/coffee blend, growing conditions, transportation and storage conditions, and roasting and brewing process [11,13]. However, for the evaluated biodiesel production, qualitative parameters of oil need to be defined precisely as oil comprises compounds that could deteriorate biodiesel quality and may also have a negative impact on biodiesel storage (e.g., phytosterols and steryl glycosides) [14], and biodiesel production technology itself (e.g., free fatty acids content) [11].

The overall biodiesel production chain from oil extracted from the SCG (SCGO) includes the SCG collection and transport, drying, oil extraction process, and subsequent biodiesel production [13]. As the water content of the WSCG is in the range of 55 to 80%, depending on the prepared coffee beverage [15], the drying process is necessary to prolong the storage time, achieve the SCG weight reduction, and, most importantly, to prevent the growth of molds in the SCG [16]. Another reason for the SCG drying in biodiesel production is the lower yield of oil during the extraction process as well as biodiesel yield during the transesterification (TE) reaction (due to soap formation) in the presence of moisture [11,13]. Caetano et al. (2014) showed that the lipid content is higher (doubled) after oil extraction from the DSCG compared to extraction from the WSCG with a moisture content of approx. 66%, vol./wt. [17]. Therefore, the moisture content of the DSCG below 10% is recommended [16].

The SCGO extracted with hexane has a chocolate brown color and a characteristic coffee aroma. According to Campos-Vega et al. (2015), extracted oil mainly consists of glycerides (generally up to 80–90%) with the following oil composition (% of total lipids)—84.4% of triacylglycerols, 12.3% of diterpene alcohol esters, 1.9% of sterols, 1.3% of polar compounds, and 0.1% of sterol esters [18]. Among fatty acids, the SCGO predominantly contains linoleic (C18:2) and palmitic (C16:0) acids, followed by stearic and oleic acids [19]. The obtained oil yield and composition depend on many variables, such as different brewing methods, fresh coffee type, the moisture content in the SCG, particle size, amount and polarity of the used solvent, the extraction process, and extraction time [20]. Oil extraction from spent coffee grounds can be performed by three different processes: conventional, Soxhlet, and supercritical CO_2 extraction. As Soxhlet extraction is found to be more effective than any conventional process, it is the most used method for coffee oil extraction [21]. Among solvents, a high coffee oil recovery rate is reached by long extraction with hexane. In general, non-polar solvents are more suitable for oil extraction than polar ones since the almost neutral nature of non-polar solvents facilitates their penetration in the low-polarity SCG structure [11]. The highest recorded oil recovery reported in the literature was for isopropanol solvent and hexane/isopropanol mixture (1:1, vol.), providing 21% and 21.5% oil recovery, respectively [22].

Based on the studies, the SCGO can be characterized by high stability due to its high antioxidant content and represents a cost-effective feedstock for biodiesel production compared to other waste sources [23,24]. Another advantage of the SCG compared to the other wastes is the lack of seasonal behavior. However, due to a large number of widely dispersed collection points, the logistics from households and coffee shops represent a huge challenge [25]. Biodiesel production from the SCGO feedstock has been carried out at the laboratory scale using mainly esterification and transesterification reactions (Figure 2). If the free fatty acid (FFA) content of extracted coffee oil is below 1% FFA (corresponds to an acid value of 2 mg KOH/g), a one-step alkali-catalyzed transesterification can be carried out [20]. As the extracted coffee oil ordinarily contains more than 1% FFA, the most suitable process for biodiesel production is represented by the two-step catalytic process (acid-catalyzed esterification to decrease the acid value of oil followed by base-catalyzed transesterification step) [21]. The two-step transesterification process effectively provides biodiesel yields up to 99% [24]. Although this process has a high conversion yield, it is energy- and time-intensive. Therefore, a direct transesterification process (in situ transesterification) has been attempted. In this type of process, transesterification and oil extraction are conducted simultaneously in one step [26]. The process is simple; however, very low overall biodiesel yield has been achieved due to soap formation and higher refining loss [20,27]. Therefore, in situ transesterification is suitable only for feedstocks with an initial oil acid value below 1 mg KOH/g [27]. In this research, one-step alkali-catalyzed TE and two-step TE were realized and investigated.

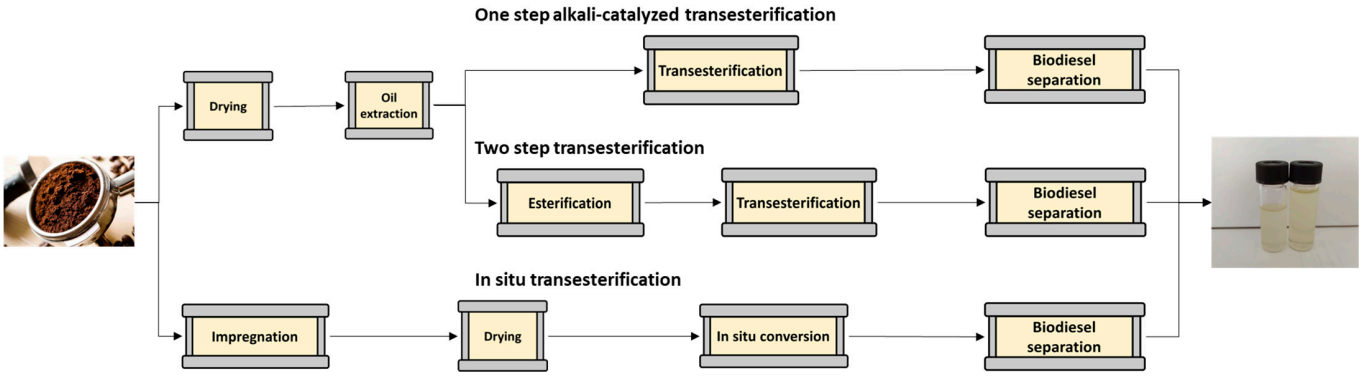

Figure 2. Scheme of biodiesel production from spent coffee grounds. Source: Own elaboration based on data published in [20].

Biomass waste utilization in biorefinery has emerged as a sustainable approach toward circular bioeconomy [28]. As the SCG comprise a range of organic compounds, the idea of the SCG valorization has received growing attention [29]. Different approaches to the SCG valorization in biorefineries have been evaluated. Most of them have been targeted for biofuel production, such as biodiesel utilizing coffee oil extracted from spent coffee grounds, while delipidized spent coffee grounds were evaluated for bioethanol production or fuel pellets manufacturing [30,31]. Despite the extensive research in valorization options, the potential of spent coffee grounds integrated into biodiesel refinery and deeper analysis of coffee oil extracted from spent coffee grounds have not been presented to fulfill complex valorization of spent coffee grounds commercially. Most of the published articles analyze only the physicochemical parameters and fatty acid profile of extracted coffee oil as the most important parameters for biodiesel production [32,33]. A deeper analysis of extracted coffee oil is requisite for applying the appropriate SCGO refining process as extracted coffee oil contains a higher amount of unsaponifiable matter and compounds deteriorating biodiesel quality [34]. Nowadays, biodiesel is mainly produced as first-generation biofuel using oil from edible seed crops (rapeseed, palm, soybean, or sunflower) as feedstock. The investigation of alternative feedstocks suitable for biodiesel production, such as energy or non-edible crops and wastes, has received increasing attention ensuring food and energy self-sufficiency [13,35], as well as meeting the set mandates and national legislation for advanced biofuel content in the fuel energy mix. Furthermore, utilizing wastes as feedstock can reduce material costs, generally accounting for up to >70% of the total production cost [35]. Therefore, the main characteristics of the SCG (low costs, non-edible crop, large annual generation) make it a promising biorefinery feedstock [25].

This is a first-of-its-kind report where authors present the technical potential of spent coffee grounds for biodiesel production integrated into the existing biorefinery based on the analyses of the SCGO and unsaponifiable matter present in the SCGO, considering related obstacles within the SCG biodiesel production. The overall intention and the future perspective on the SCG valorization lie in the application of the circular economy approach proposed in Figure 3. The concept for the complex SCG valorization is based on the SCG collection from coffee shops or instant coffee producers, with the integration of the delipidized SCG processing for coffee-to-go cups (e.g., cups produced by the company, Kaffeeform) and the SCGO valorization for biodiesel production. The produced the SCG biodiesel will be blended with fossil diesel and, subsequently, used for refueling transport vehicles, which may deliver fresh coffee beans to coffee shops or instant coffee producers.

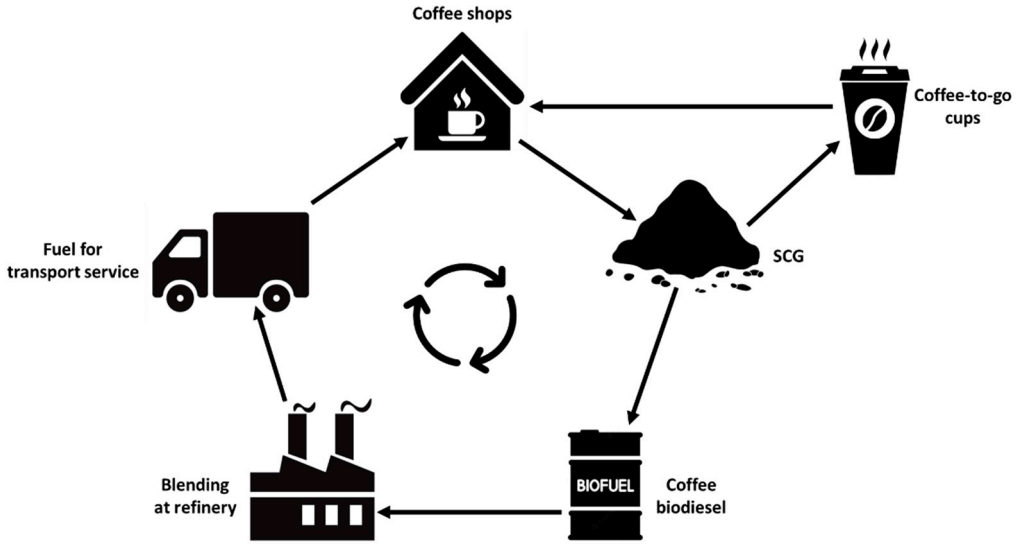

Figure 3. Circular economy approach for spent coffee grounds—the concept of project by Envien Group.

2. Materials and Methods

Single-type Arabica coffee from Brazil (medium roasted coffee—City Plus Roast), produced by a local coffee roastery, was used for tests. WSCG from espresso preparation were collected and dried, applying a process based on the study by Tun et al. [16] on drying process evaluation. Oven UF55 (Memmert GmbH, 2021) with forced air circulation was used at 80 °C, 6 h, for the SCG layer thickness approx. 2–2.5 cm.

2.1. Dry Matter and Oil Content Analysis

Before SCG drying, the dry matter content of SCG was determined using a moisture analyzer MB90 (OHAUS Europe GmbH, Nänikon, Switzerland, 2021). Approximately 1 g of a sample was spread on the surface of the dish and dried at 105 °C to a constant weight. The dry matter content was read from the measuring device after the measurement.

Determination of oil content in SCG was carried out by extraction. A sample of approximately 1–2 g of dry/wet SCG was weighed, mixed with 70 mL of hexane, and put in an extraction thimble. Oil was extracted from the test sample using solvent extractor VELP SCIENTIFICA SER 148 (VELP Scientifuca Srl, Usmate, Italy) using a three-step procedure. In the first step, the extraction thimble with the sample was immersed in a boiling extraction agent in an extraction flask for 60 min. Then, the extraction thimble was lifted from the extraction agent and placed under the cooler, where the condensed solvent dripped and was extracted from the sample for 60 min at 180 °C. The third step was solvent removal by evaporation in the extractor. Finally, the extract was dried for 30 min at 105 °C and weighed. For the initial oil content analysis in SCG and roasted coffee beans, the extraction method was repeated three times, and the yields were summed up. The result was calculated as an average of three values.

2.2. Extraction of Coffee Oil from SCG

Subsequently, the prepared dried spent coffee grounds (DSCG) were used for coffee oil extraction in an extraction system similar to Soxhlet extraction, with the difference of using room temperature and the pressure of 500 mbar. N-hexane (for analysis EMSURE, Merck, Darmstadt, Germany) was used as the solvent. SCG in a 5 cm extraction thimble was slowly washed with n-hexane until the triglyceride (TAG) content in the extract was below 1% of the initial TAG content at the beginning of the extraction. More prolonged extraction is not desirable as a larger quantity of polar substances could be extracted into the lipid fraction of coffee oil. The prepared oil was further analyzed and used for the preparation of biodiesel by esterification and transesterification reactions. The solvent was evaporated using a rotary evaporator, and the recovered oil was dried by air aeration at 60 °C for 2 h at 20 mbar to remove the residual solvent and moisture.

The yield of SCGO (1) and extraction efficiency (2) were calculated using the equations:

$$Y_{SCGO} = m_{SCGO}/m_{SCG} * 100\%, \quad (1)$$

$$EE = Y_{SCGO}/OC * 100\%, \quad (2)$$

where Y_{SCGO} is the yield of SCGO in %, m_{SCGO} is the weight of SCGO after extraction in g, m_{SCG} is the weight of SCG used for extraction in g, EE is extraction efficiency in %, and OC is extractable oil content in SCG in % determined using solvent extractor VELP SCIENTIFICA SER 148.

2.3. Analysis of Basic Parameters of Coffee Oil after Extraction

Acid value (AV) was determined by titration. The weighed sample (approximately 10 g) was dissolved in a mixed solvent (diethyl ether and ethanol in the ratio of 1:1) and titrated with 0.1 M ethanolic KOH solution to the equivalent titration point using phenolphthalein as an indicator. The acid value was then calculated using Equation (3):

$$AV = (sp * f * c * 56.1)/n, \quad (3)$$

where AV is the acid value in mg KOH/g of oil, sp is the consumption of 0.1 M ethanolic KOH solution in mL, f is the correction factor of prepared 0.1 M ethanolic KOH solution determined by titration, c is the concentration of the ethanolic KOH solution, n is the weight of the sample in g, and 56.1 is the molecular weight of KOH in g/mol. The result was calculated as an average of three values.

The amount of elements P, Ca, Mg, Na, K, and S were determined by inductively coupled plasma emission spectroscopy. The sample was diluted with kerosene (for lighters, ŠK Spektrum, s.r.o.) in the ratio of 1:1 (wt.), as were the standards (Oil analysis standards S-21 + K, 500 ppm, Conostan and Sulfur, 0.01%, Conostan). The prepared sample was analyzed on a SPECTRO Genesis FES device (Spectro APS, Martin, Slovakia, 2017). The content of individual elements was determined by comparing the spectra of the sample and standards at the wavelength of 177 and 495 nm, respectively. The result was calculated as an average of three values.

Water content in the oil was determined using the coulometric titration method, according to Karl Fisher. A sample of 0.2 g was injected into the titration vessel with a syringe with a needle. In the titration vessel of the Karl Fisher coulometric titrator (Coulometer 831 KF, Metrohm AG, Bratislava, Slovakia), iodine is generated coulometrically at the anode. An electrometric detector detected excess iodine by titrating the entire amount of water into the sample. After the titration, the water content in the sample was read from the titrator in wt.%. The result was calculated as an average of three values.

2.4. Analysis of Fatty Acids (Esters) Profile

The fatty acid (esters) profile was determined using two different methods in order to compare the differences between individual analyses. The first method used base transesterification with sodium methanolate for sample treatment. This method enables the analysis of fatty acids present in the form of triglycerides, diacylglycerides, monoacylglycerides, phospholipids, waxes, and sterol esters with fatty acids. However, free fatty acids cannot be analyzed by this procedure. A Network GC System 6890 N device (Agilent Technologies, Santa Clara, CA, USA) was used for analysis. A column with a polar stationary phase DB-23 was used for the separation of individual methyl esters, and an FID detector was used for detection (sample marked as "SCGO analysis 1"). The second applied method for the fatty acids (esters) analysis narrowed the determination of lipid composition in the sample. A sample of coffee oil was saponified and esterified according to ISO 12966-2 [36] and then analyzed according to EN 14103 (sample marked as "SCGO analysis 2") [37].

2.5. Major Compounds Analyses and Identification of Unsaponifiable Matter

For the analysis of major compounds in SCGO, the sample silylation technique with the derivatizing agent 1,1,1,3,3,3-hexamethyldisilazane (HMDS) was chosen to derivatize acidic hydrogens found in the carboxyl, hydroxy, or amino group. Silylated compounds were subsequently analyzed using a Network GC System 6890 N (Agilent Technologies) using high-temperature gas chromatography with an FID detector, which allowed the measuring of compounds up to the size of C80. Capillary column DB-1 was used for the compounds' separation. Here, silylated free fatty acids, sterols, mono-, di-, and triacylglycerides, waxes, phospholipids or other non-polar substances were separated.

GC/MS technique was used for the analysis of unsaponifiable matter. The sample was diluted in acetone (14 mg/mL) without any significant visible residue. Before injection prepared sample in acetone was filtrated with a PTFE syringe filter, pore size 0.45 µm and 13mm diameter. As gas chromatograph GC 7890A (Agilent Technologies) was used. The separation was made on a 30 m × 250 µm × 0.25 µm (length × inner diameter × film thickness) i.d. fused silica capillary column HP-5MS. The injection volume was 1 µL, and the injector temperature was 300 °C set in splitless mode. The oven temperature was held at 100 °C for 2 min, secondly heated to 200 °C at a rate of 8 °C/min and then heated to 300 °C at a rate of 10 °C/min. The final temperature was kept for 6 min, and the whole method lasted 30.5 min. Helium was used as the carrier gas with a flow of 2 mL/min. The end of

the column was introduced into the ion source of the Agilent Technologies model 5975C series mass selective detector operated in electron impact ionization mode (70 eV). The data acquisition system used the ChemStation E 02.01.1177 software, and all compounds were identified with NIST and Wiley electronic libraries while excluding methyl esters, unreacted fatty acids and compounds with a quality lower than 90.

2.6. Biodiesel Production

Three different sets of biodiesel production experiments were realized to produce biodiesel with the highest fatty acid methyl esters content.

The first experimental biodiesel production was based on a set of base-catalyzed transesterification (TE) reactions—2 TE were realized with the purification of the resulting biodiesel with active silica gel. TE run based on the optimal condition from the study [38] with the exception of using potassium hydroxide under the following conditions: MeOH:SCGO = 6:1 (mol), KOH:MeOH = 1:23 (mol), 60 °C, 1 h, 1000 rpm [38]. After the first TE reaction, the phase interface between the biodiesel and glycerol phase was absent, so the whole intermediate product was washed with hot water to remove methanol, and the process was repeated. After the second TE, the separation of biodiesel and G-phase was observed, so the purification process was subsequently applied. The biodiesel phase was washed with hot water (methanol removal), centrifuged (313 g, 20 min., room temperature), and separated. Further purification process included activated silica gel column chromatography to remove unsaponifiable matter. Biodiesel was eluted with n-hexane, while the unsaponifiable matter was eluted with acetone. The unsaponifiable matter was analyzed according to the method described in subchapter 2.5.

The second biodiesel production method is based on a two-step biodiesel production process consisting of acid esterification (AE) with sulfuric acid (96%, p.a.) and base-catalyzed transesterification. First, AE was applied under the following conditions based on the study [39]: SCGO: H_2SO_4 ratio = 50:1 (vol.), MeOH:SCGO ratio = 6:1 (mol), 75 °C, 3 h, 1000 rpm. The intermediate product was centrifuged (313 g, 20 min, room temperature) to separate the solid precipitate and washed (methanol removal). Subsequently, TE occurred at the same conditions as in the first experiment, followed by a purification process similar to the process above (hot water washing, centrifugation, purification with activated silica gel).

The third biodiesel production method is also based on a two-step biodiesel production process consisting of ion-exchange esterification with Amberlyst^{TM} 16wet as a catalyst and base-catalyzed transesterification. Ion-exchange esterification with Amberlyst is similar to acid esterification [40]. Therefore, ion-exchange esterification ran under similar conditions as acid esterification with an excess of the catalyst and MeOH: 10 wt.% Amberlyst, 1000 rpm, 75 °C, 3 h, MeOH:SCGO ratio = 8:1 (mol). The intermediate product was filtered to separate the solid precipitate. The following TE ran under the same reaction conditions as in the previous experiment. Subsequently, washing with NaCl solution and centrifugation steps were applied for purification.

The fatty acid methyl esters profile was analyzed using the method described in Section 2.4.

3. Results and Discussion

3.1. SCG Drying and Oil Content Analysis

This work measured the amount, and dry matter of the SCG after espresso preparation, and the oil content of the WSCG and DSCG was determined. Several references stated that 2 kg of the WSCG and 0.91 kg of the DSCG is generated by coffee beverages or soluble coffee preparation from 1 kg of roasted coffee beans [5,41]. Our results show that from the 1 kg sample, 1.79 kg of the WSCG with 50.9% dry matter content was generated after espresso preparation on an automatic espresso machine, which results in the mass ratio of the DSCG to roasted coffee beans of 0.96. Differences between these values can be affected by many factors, type of espresso machine, size of particles—coffee grind size, type of coffee, and roasting process. The results are shown in Table 1.

Table 1. WSCG and DSCG amount after espresso preparation from roasted coffee beans and oil content of WSCG and DSCG.

	Roasted Coffee Beans	WSCG	DSCG
Sample weight (g)	50.45	90.50	48.43
Conversion to kg	1	1.79	0.96
Dry matter (wt.%)	98.5	50.9	95.1
Dry matter (kg)	0.985	0.913	0.913
Oil content (wt.%)	12.78	5.98–6.26	8.12–9.55

For the integration of biodiesel production from the SCG into an existing biorefinery, initial oil extraction from the SCG are necessary. As the SCG are a wet material after coffee beverage preparation, the influence of water content on oil extraction was evaluated by measuring and comparing the oil content in the WSCG and DSCG. Results confirmed lower extraction yield due to the higher water content in the SCG as expected according to [17]; thus, the drying process was implemented before the oil extraction step. As a result, the yield of oil extraction from the DSCG was 23–37% higher compared to that from the WSCG, similarly to [11,17]. The same trend is reported in the literature for canola/rapeseed seeds commonly used for first-generation biodiesel production, where it is recommended to keep the moisture content of canola seeds below 8.4% [42]. The oil content of the WSCG and DSCG is shown in Table 1.

The literature states that the average oil content in the SCG ranges from 10–15% [24]. The SCG used within this work had an overall oil content of 12.09%, indicating a much lower yield compared to oilseeds oil content (rapeseed, sunflower, and others); however, the SCGO has a significant potential given the character of the waste material and its broad possible application [32]. The SCGO for further analyses and biodiesel production was prepared by extraction with the yield of 2.2 kg of oil per 20 kg of the SCG, which equals to oil yield of 11% resulting in an extraction efficiency of 91%. Compared to the literature, the presented extraction efficiency is in the range of reported extraction efficiency of 90–97% when n-hexane is used as an extraction agent [43,44].

3.2. Analysis of Basic Parameters of Coffee Oil after Extraction

Basic parameters of the SCGO were measured, and some characteristics, such as aroma and color, were observed. The main characteristics of the SCGO extracted by hexane were dark brown color and the characteristic aroma of roasted coffee. The density of the extracted SCGO was 0.89 kg/dm^3, which is within the range of reported values of 0.88–0.917 kg/dm^3 [32,45,46].

The basic parameters of the SCGO were compared with commercially-used crude rapeseed and corn oil (Table 2), the most important of these parameters being the acid value which indirectly determines the amount of free fatty acids [3]. Generally, the SCGO exhibits a relatively high acid value (6.5–16.6 mg KOH/g), negatively influencing the biodiesel production process [47]. Free fatty acids tend to form soap byproducts during the alkali-catalyzed transesterification process, which promotes the formation of stable emulsions unwanted in commercial biodiesel production. In addition, the presence of free fatty acids during biodiesel separation from glycerol after the transesterification reaction leads to lower biodiesel production yield [48]. Considering these facts, biodiesel production from the SCGO could be effectively carried out when adjusting the acid value by mixing the SCGO into oils with a lower amount of FFA or by a two-step transesterification process.

Table 2. Basic parameters of studied SCGO and commercially used rapeseed and corn oil.

Sample	SCGO	Rapeseed Oil *	Corn Oil *
AV (mg KOH/g)	9.5	1.6	22.3
P (mg/kg)	24.5	406.1	12.7
Ca (mg/kg)	5.1	73.1	0.2
Mg (mg/kg)	7.3	28.9	1.3
Na (mg/kg)	1.4	0.7	2.9
K (mg/kg)	4.9	111.7	9.3
S (mg/kg)	35.6	20.7	14.9
Water content (wt.%)	0.01	0.06	0.4

* Average values of vegetable oil parameters used for commercial biofuel production in Slovakia.

The presence of microelements can lead to operational problems or a biodiesel quality decrease. The presence of phosphorus in biodiesel may decrease the ability of after-treatment systems to reduce exhaust emissions. Sodium, potassium, magnesium, and calcium can form deposits in fuel injection system components and poison emission control after-treatment systems. The sulfur content is necessary to keep below standardized value to meet emission standards of biodiesel fuel [49]. Microelements content analyses did not reveal any increased metal content in the SCGO, which would negatively affect biodiesel production or its quality. The only slightly increased parameter in the SCGO compared to oils used in industrial biodiesel production was sulfur and phosphorus content. In a study by He et al. (2009), the sulfur content was significantly reduced in the process of oil refining and biodiesel production to below 10 mg/kg in biodiesel in most cases [50]. Generally, phosphorus in oil is bound to phospholipids, and their removal is part of oil refining (a process called degumming) at a commercial scale [51]. The analysis of microelements content in the SCGO has not been conducted yet in the published articles; only data on microelements content in the SCG can be found [13].

3.3. Analysis of Fatty Acids (Esters) Profile

Generally, the SCGO contains up to 80–90% of the total fatty acid content. The composition of the extracted oil is dependent on the coffee bean variety as well as on the processing and coffee brewing methods [52]. The fatty acid profiles also vary based on the extraction methods and reaction conditions [53]. Fatty acids in the studied SCGO accounted for 85.85%. As reported in many studies, the SCGO contains mostly linoleic (C18:2) and palmitic (C16:0) acids, which account for almost 75% of total fatty acid content or more than 60% of the SCGO content. Linoleic acid is also present in higher amounts in corn (CO), soybean (SBO), and sunflower (SFO) oil. Palmitic acid is the most abundant in palm oil (PO) (see Table 3).

Table 3. Fatty acids (FA) profile in SCGO, comparison with FA of oils for commercial biodiesel production, and FA profile of SCGO reported in the literature (RSO—rapeseed oil, CO—corn oil, SFO—sunflower oil, SBO—soybean oil, PO—palm oil).

FA (% hm.)	SCGO Analysis 1	SCGO Analysis 2	SCGO (lit.) [18,32]	RSO *	CO *	SFO	SBO	PO
C16:0	32.97	33.14	27.5–43.6	4.6	12.8	4.7–8.0	9.7–13.3	39.1–45.5
C18:0	7.16	7.34	5.3–19.6	1.7	2.1	2.8–4.1	3.3–4.9	3.3–5.2
C18:1	9.36	9.22	5.5–24.0	64.5	28.4	15.3–28.0	21.5–25.5	38.2–43.6
C18:2	45.45	41.94	25.8–49.9	18.7	53.9	61.2–73.9	50.8–55.9	8.3–11.9
C18:3	1.44	1.26	0.8–4.1	7.7	1.3	0.0–0.4	4.7–8.9	0.1–0.5
C20:0	2.51	2.68	0.0–6.9	0.6	0.4	0.1–0.4	0.1–0.6	0.2–0.5
C20:1	0.34	0.39	0.3–3.2	12.0	0.3	0.0–0.2	0.0–0.4	0.1–0.2
C22:0	0.53	0.62	0.4–1.2	0.3	0.2	0.4–0.9	0.1–0.5	0.0–0.1
C24:0	0.24	0.25	0.1–0.3	0.1	0.2	0.2–0.4	0.0–0.3	0.0–0.1

* Average values of vegetable oil parameters used for commercial biofuel production in Slovakia.

The content of the fatty acids in the oily feedstock is an important parameter for biodiesel quality evaluation [54]. Fatty acids and their esters profile determine final biodiesel properties. Specifically, the cetane number (CN), cold flow properties (CFP), and oxidative stability (OS) of biodiesel are influenced by the number of carbon-carbon double bonds [41].

According to EN 14214 [55], the minimal cetane number must be 51. The study [56] confirmed that the CN decreased with higher content of unsaturated fatty acid in vegetable oil. Based on the study [56], the prediction of the studied SCG biodiesel CN is expected to be in the range of 58–60. For low-temperature applications, it is necessary to determine the CFPP (cold filter plugging point) as the most critical parameter from the CFP. It has been proven that the CFPP depends on saturated fatty acid content (the higher the saturated fatty acid content, the higher the CFPP) [57]. The prediction of the SCG biodiesel CFPP was calculated according to a study [57], resulting in a CFPP value equal to −0.6 °C. The CFPP limitations are not listed in EU standard specifications; each country can specify certain temperature limits for a different season of the year and the local climate conditions [57]. Calculated CFPP of the studied SCG biodiesel based on the fatty acid profile is not recommended to be applied in winter season, or it can be applied in biodiesel blend with lower CFPP biodiesel. The degree of unsaturated fatty acid also affects the oxidation stability of biodiesel. According to the study [57], the oxidation stability must be more than 6 h to meet the EU standard EN 14214. The calculated OS for the studied SCG biodiesel is in the range of 5.7–6.1 h, which means that only a small adjustment of OS should be performed by blending with biodiesel with higher OS or by adding a small volume of additives to improve OS.

3.4. Major Compounds Analysis and Identification of Unsaponifiable Matter

The lipidic fraction of coffee oil is composed of a saponifiable part (glycerides, FFA) and a minor fraction known as unsaponifiable matter (fat-soluble vitamins, carotenoids, sterols, polyphenols) [32]. As mentioned, a saponifiable part of studied the SCGO is equal to 85.85%, which means that almost 15% of oil extracted from the SCG were unsaponifiable matter (UM) unsuitable for biodiesel production. Such a high UM content in the SCGO (i.e., lower fatty acids content) indicates the necessity of oil refining or impurities removal. Unsaponifiable matter in the SCGO may consist of organics, such as diterpenes and their esters, phytosterols, tocopherols, and other polar substances, which decrease the biodiesel stability or deteriorate the quality of produced biodiesel [3,54].

The number of major compounds found in the studied SCGO are shown in Table 4, showing lower content of triglycerides and higher content of diglycerides, as expected. According to the literature, more than 80% of the total lipids content in the SCGO are represented by triglycerides. The results of diglycerides content can interfere with diterpene esters content as they elute simultaneously.

Table 4. Major compounds analysis of SCGO.

Compound	Area (%)
Free fatty acid	22.49
Monoglycerides	1.14
Sterols	1.89
Diglycerides	9.06
Triglycerides	65.42

From the compounds characterized as unsaponifiable matter, the results showed several unknown compounds found in the SCGO after hexane extraction (Table 5). The most represented compound was caffeine, whose presence in the SCGO have not been mentioned yet in the published articles. On the contrary, an article [58] published that using hexane as an extraction agent, less caffeine was extracted compared to 2-methyloxane (or

most of the caffeine amount remained in the delipidized SCG), despite the lower oil yield when extracted with hexane [58].

Table 5. The composition of the extract of the unsaponifiable part dissolved in acetone (excluding unpurified methyl esters, unreacted fatty acids, and compounds with quality lower than 90).

RT (min)	Area (Ab ∗ s)	Compound	Quality	Mol Weight (amu)	CAS Number
15.237	355,763,565	Caffeine	97	194.08	000058-08-2
20.197	121,181,206	(Z)-9-Octadecenamide	99	281.272	000301-02-0
27.303	24,486,743	Stigmasterol	99	412.371	000083-48-7
27.929	21,656,564	γ-Sitosterol	99	414.386	000083-47-6
25.202	20,499,232	β-Tocopherol	99	416.365	000148-03-8
18.452	15,666,889	n-Hexadecanoic acid	93	256.24	000057-10-3
25.971	7,061,250	Vitamin E	99	430.381	000059-02-9
28.123	6,068,755	(3-β,24Z)-Stigmasta-5,24(28)-dien-3-ol	95	412.371	000481-14-1
23.65	2,930,511	Squalene	99	410.391	000111-02-4

The presence of phytosterols and tocopherol were identified in the study SCGO (Tables 4 and 5). Massaya et al. (2019) summarized that the total phytosterols content in the extracted SCGO is 7.57–15.60 wt.% with the highest content of sitosterol (3.5–7.1 wt.%), followed by stigmasterol (2.9–6.0 wt.%) and campesterol (1.2–2.4 wt.%) [59]. It has been proven in the studied SCGO that stigmasterol and sitosterol are the most abundant sterols in the SCGO. In the case of tocopherols, β-tocopherol was indicated as a part of UM. According to the literature, α-tocopherol and β-tocopherol in the SCGO are in the range of 0.06–0.28 wt.% and 0.84–2.37 wt.%, respectively, with the absence of γ- and δ-tocopherols, which is attributed to losses during roasting, brewing, or storage [52,60]. The presence of vitamin E and squalene could also be attractive when valorizing them from another waste stream—UM. The content of individual unsaponifiable compounds depends on the roasting process of coffee and extraction process of oil from the SCG, mainly solvent polarity and extraction temperature, as some of these compounds, such as tocopherols, cafestol, and kahweol, are thermolabile [11,19]. Despite the negative impact of UM compounds on biodiesel quality or stability, they positively affect human health, such as lowering the serum cholesterol and antioxidant activity of sterols and tocopherols [11,59], so they might be further valorized.

3.5. Biodiesel Production

Based on the studied SCGO acid value, two-step transesterification appears to be the best option for biodiesel production from the SCGO, but also base catalyzed TE was chosen to compare these two methods. After the first TE reaction, the product was practically unchanged compared to the input oil sample. The refractive index at 20 °C (RI) and density of the SCGO were 1.4725 and 0.917 kg/dm^3, respectively, while the intermediate product had a refractive index (20 °C) and density of 1.4710 and 0.913 kg/dm^3, respectively. The sample subjected to the second TE reaction acted like a common feedstock for biodiesel production with a clearly visible interface between the biodiesel and glycerol phases. Purifying the product on activated silica gel after TE separated unsaponifiable matter from the final biodiesel. The separated matter had an orange-red color, high viscosity, RI of 1.4809, and partial solubility in KOH solution. The resulting biodiesel product was light yellow in color with an RI of 1.4545. The prepared biodiesel samples are shown in Figure 4.

Figure 4. Biodiesel samples prepared by TE (**left**), AE + TE (**middle**), IEE + TE (**right**).

Two-step TE run under similar conditions, with the main difference in the first step where acid esterification reaction (AE) or ion-exchange esterification (IEE) took place. When H_2SO_4 was applied as the acid catalyst, the brown color of the SCGO changed to dark blue, and the formation of a blue-green-colored solid precipitate with a particle size of up to 0.1 mm was observed. Similar observations were published by Jenkins et al. (2014)—the formation of blue-green unsaponifiable precipitates during an esterification reaction using an acid catalyst. These precipitates originate from various compounds, such as sterols, terpenes, and organic acids [54]. These experimental findings can be considered valuable evidence of the presence of UM. Therefore, it is obvious that successful biodiesel production from the SCGO requires excluding the unsaponifiable matter from the SCGO or final product. The final biodiesel product had a bright yellow color and an RI of 1.4550. The lower precipitate formation was observed when Amberlyst was applied as the catalyst for ion-exchange esterification. The final biodiesel had dark yellow color and RI of 1.4490, different from the other studied final biodiesel samples.

Ester content was also analyzed as an important quality parameter of biodiesel (Table 6). The highest ester content, or biodiesel yield, was measured in the case of AE + TE (89.62 wt.%). A similar biodiesel yield was determined in the study [30], which reported a biodiesel yield of 89.2 wt.% from spent and fresh coffee grounds oil, and the biodiesel properties of the biodiesel indicated it is a good alternative to diesel. Based on previous studies, biodiesel yield in wt.% of fatty acid esters does not change significantly, and it ranges between 60 and 100%, while the recovery of 100% of biodiesel is possible under reflux conditions [11,61]. The lowest ester content after IEE + TE could be influenced by the different molar ratio of MeOH/SCGO (8:1). Bui et al. (2021) reported that the increase in the MeOH/SCGO ratio from 4:1 to 6:1 resulted in an increase transesterification yield, which was, however, reduced with further increase of the MeOH/SCGO ratio [62]. Additionally, the lower unidentified matter was observed in the sample of final biodiesel after AE + TE. Thus, the two-step transesterification process with acid-catalyzed esterification and base-catalyzed transesterification was confirmed as the most suitable method for biodiesel production if the acid value was above 2 mg KOH/g. However, more than 10% of unsaponifiable matter and/or residual oil remains in the biodiesel sample, so an additional purification step is necessary to reach commercial biodiesel quality. According to the study by Battista (2020), the efficiency of the two-step TE is influenced by the presence of unsaponifiable substances in the SCGO, which affects the interactions among reactants during TE [11].

Table 6. Comparison of final biodiesel produced by different process methods.

FFA (wt.%)	SCGO	TE	AE + TE	IEE + TE
Refractive index (20 °C)	1.4725	1.4545	1.4550	1.4490
Ester content (wt.%)	-	84.98	89.62	65.44
C16:0	33.14	28.15	31.29	19.12
C18:0	7.34	6.26	7.09	4.14
C18:1	9.22	8.15	9.47	6.94
C18:2	41.94	37.36	36.04	31.82
C18:3	1.26	1.20	1.01	0.98
C20:0	2.68	2.25	2.63	1.35
Unidentified matter (wt.%)	-	1.26	0.18	1.65

3.6. Coffee Biodiesel Potential Determination

The existing biodiesel plant comprises oil purification, esterification and transesterification reaction, and biodiesel purification. In this study, we evaluate the potential of the SCG for biodiesel production based on the characterization of extracted SCGO without previous purification.

Microelements content in the SCGO determine the unpurified SCGO suitability for biodiesel production. Considering the low microelements content in the SCGO compared to other crude vegetable oils for biodiesel production, specific pretreatment for microelements decrease is not necessary. By predicting CN number (58–60), CFPP (−0.6 °C) and OS (5.7–6.1 h) values according to fatty acid content and composition, we found out that application of the SCGO to existing biodiesel biorefinery is possible only if blending a small portion of the SCGO with other oils improving the final biodiesel quality parameters and biodiesel stability. CN number, CFPP, and OS are parameters influenced by the unsaturated/saturated fatty acids ratio and determine biodiesel quality and stability. The fatty acid composition represented by ~75% of fatty acid content (more than 60% of the SCGO content) with C18:2 (linoleic) and C16:0 (palmitic) appears to be appropriate only if adjusted by oil with improved parameters addition or biodiesel additives addition. Moreover, the unexpectedly lower content of fatty acids in the SCGO (85.85%) and the higher content of unsaponifiable matter (almost 15%) require further purification before the SCGO implementation as a feedstock for commercial biodiesel production. A higher amount of unsaponifiable matter in the SCGO could decrease both the yield of the transesterification reaction and the biodiesel quality if retained in the final biodiesel or increase biodiesel production costs (because of the necessary additional purification of produced biodiesel). This study shows that unsaponifiable matter in the studied SCGO contains mainly caffeine, phytosterols, and tocopherols, compounds potentially valuable in the food, pharmaceutical, or cosmetic industry.

Categorized as an advanced fuel component, the SCG are a viable solution for biodiesel production to fulfill the mandatory advanced biofuel energy share in fuels in the upcoming years given by legislation. Considering the higher acid value of the studied SCGO compared to other raw oils, the two-step transesterification process (acid-catalyzed esterification and base-catalyzed transesterification) appears to be the most suitable process for biodiesel production compared to other tested methods, as confirmed by the results—the highest ester content (89.62%), or biodiesel yield, was measured in case of two-step transesterification biodiesel production under the following conditions of acid esterification: SCGO:H_2SO_4 ratio = 50:1 (vol.), MeOH:SCGO ratio = 6:1 (mol), 75 °C, 3 h, 1000 rpm; and transesterification: MeOH:SCGO = 6:1 (mol), KOH:MeOH = 1:23 (mol), 60 °C, 1 h, 1000 rpm.

The presented research results enable the determining of the potential of biodiesel production from the SCGO. As a case study, we calculated the potential of the SCG biodiesel for Slovakia. The five-year average of roasted coffee beans consumption in Slovakia is 15,129 tons (Table 7) [63].

Table 7. Roasted coffee beans consumption in Slovakia in recent five years.

Year	2021	2020	2019	2018	2017
Consumption (tons)	15,450	13,900	15,609	17,010	13,680

Considering the conversion factor of coffee beans to the SCG of 0.96 and oil extraction efficiency of 91% (11 wt.% of extracted the SCGO) with an experimentally stated fatty acid content of 85.85%, the potential of suitable purified feedstock for biodiesel production is 1371 tons. Utilizing this feedstock results in 1,228 tons (1.06 ktoe) of advanced biodiesel produced in Slovakia. In Slovakia, MEROCO, a.s. is the largest biodiesel producer with an annual production capacity of 120,000 tons of FAME, meaning that the SCG biodiesel can potentially increase overall biodiesel production in Slovakia by 1%. Furthermore, considering the current legislative and fuel consumption estimation in 2030, biodiesel from the SCG would constitute a 2.6% share of mandatory energy share for advanced biofuel in Slovakia in 2030.

4. Conclusions

The SCG are considered a great source of a significant number of compounds potentially suitable for value-added compound production. The presented study evaluates the possibility and potential of integrating the SCG into biodiesel production biorefinery based on the SCGO characterization and the SCG biodiesel preparation. Overall biodiesel production from the SCGO includes their extraction from the SCG, the SCGO purification, biodiesel production and biodiesel purification. As existing commercial oil processing plant uses hexane as a solvent, the direct implementation of the SCGO extraction from the SCG appear as not suitable for direct integration into such biorefinery due to the high extractability of unsaponifiable matter (nearly 15% of the SCGO content) in hexane, which can influence biodiesel production process, deteriorate biodiesel quality or decrease biodiesel stability. Therefore, unsaponifiable matter content needs to be decreased or removed from the SCGO to be applied for biodiesel production. The results showed the fatty acid content in the SCGO equals 85.85%, with linoleic and palmitic acids as the most abundant fatty acids (represented by ~75% of fatty acid content). The quality parameters (cetane number and CFPP) and oxidation stability of SCG biodiesel based on the fatty acid composition and content are predicted to be worse compared to biodiesel standards, therefore, SCG biodiesel could be used only in blend with biodiesel, improving the overall biodiesel blend quality and stability, or additives would be necessary to apply to final biodiesel.

Despite the disadvantages of biodiesel production from the SCG identified in the presented paper, the SCGO appears to be a valuable feedstock that can contribute to the fulfillment of mandates for the use of advanced biofuels in transport. Based on laboratory experiments, yields of individual processes in biodiesel production from the SCG and statistical data on coffee consumption in Slovakia, the annual potential of advanced biodiesel production of as much as 1228 tons can be predicted. The future plans will be focused on the SCGO purification evaluating technologies applicable to the existing biorefinery. The production of such a quantity of biodiesel from the SCG will also require focus on the implementation of: 1. effective SCG collection; 2. increase of the SCG collection attractivity not only for households but also for the cafés where the waste is concentrated; 3. efficient WSCG drying using low-cost or waste heat sources; 4. disposal of the waste after oil extraction according to the circular economy approach.

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Abbreviations

AE	acid esterification
AV	acid value
CFP	cold flow properties
CFPP	cold filter plugging point
CN	cetane number
CO	corn oil
DSCG	dried spent coffee grounds
FA	fatty acid
FFA	free fatty acid
IEE	ion-exchange esterification
OS	oxidative stability
PO	palm oil
RI	refractive index
RSO	rapeseed oil
SBO	soybean oil
SCG	spent coffee grounds
SCGO	oil extracted from spent coffee grounds
SFO	sunflower oil
TAG	triacylglyceride/triglyceride
TE	transesterification
UM	unsaponifiable matter
WSCG	wet spent coffee grounds

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