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Potential of Spent Coffee Grounds for Biodiesel Production and Other Applications

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This work studied the extraction of lipids from spent coffee grounds (SCG) and the possibility of using the extracted lipids for biodiesel production. Thus, the SCG were first characterized, in particular for their carbon/nitrogen ratio (C/N ≈ 8) and higher heating value (HHV = 19.0 MJ/kg). These results show that besides its common use as fertilizer rich in nitrogen, SCG can be used as solid fuel. Concerning the lipids extraction, the best results were obtained using pure hexane and a 50:50 (vol/vol) mixture of hexane and isopropanol and yielded about 6 % (vol/dwt), being higher (about the double) when dry SCG was used instead of wet SCG (with a moisture content of about 66 %, vol/wt). The use of ultrasounds had no significant effect on the extracted lipids. Regarding the lipids characterization, results have shown an acid value in the range of 3.9-12.5 mg KOH/g, a density at 15 ºC in the range of 912-934 kg/m^3, a viscosity at 40 ºC in the range of 14.9-44.0 mm^2/s, an iodine number in the range of 47.6-70.5 g iodine/100 g, and a HHV in the range of 35.4-39.9 MJ/kg, which are negatively influenced by the lipids water content and by the solvents used for the extraction. Due to the relatively high free fatty acid content of the extracted lipids, their conversion into biodiesel was done in a two steps process: an esterification of the free fatty acid followed by a transesterification of triglycerides. The characterization of biodiesel revealed an iodine number of about 70.0 g iodine/100 g lipids, an acid value of about 1.8 mg KOH/g lipid and an ester content of about 86 % (determined by GC analysis). Although these values are not within the NP EN 14214:2009 standard of biodiesel quality, there is the potential for using lipids from SCG for biodiesel production if they are blended with lipids from other sources in order to meet the standard requirements.

1. Introduction

Biodiesel is a renewable fuel that is being increasingly used in Europe alternatively or in addition to fossil diesel. But as the demand for biodiesel increases, the conventional oleaginous crops used for its production are being increasingly questioned, as they present some sustainability issues: diversion of arable land from food to biofuel, deforestation to gain more arable land, as well as some societal constraints (Mata et al., 2011, 2013). Therefore, there is a growing search for non conventional or residual materials that can be used for biodiesel, including waste cooking oil (Mata et al., 2012a), animal fats or grease (Mata et al., 2010) or even other oil rich crops (Mata et al., 2012b, 2013b,c) and wastes such as spent coffee grounds (SCG) (Caetano et al., 2012a). In fact, coffee is currently known as one of the most widespread types of beverage consumed around the world, as drinking coffee everyday is a habit of many people, whether it is espresso, freshly ground, latte, cappuccino or even instant coffee. As a consequence its residues, the SCG, increasingly need alternatives to be adequately managed. Some possibilities include its use as adsorbent to remove heavy metals (Lavecchia et al., 2010) extracting high-value phenolics (Zuorro and Lavecchia, 2011), lipids for biodiesel production and use of the final residue as fertilizer, soil improver (or compost) or even as solid fuel (Kondamudi et al., 2008). Therefore, through several laboratorial experiments this work aims to explore biodiesel production from SCG's lipids and, after the lipids extraction, the use of SCG's residues as solid fuel.

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2. Materials and methods

2.1 SCG characterization

SCG collected from a coffee shop were characterized for their humidity, carbon, nitrogen, protein, ash, cellulose and lignin content, according to the methods described by Caetano et al. (2012a). SCG energy content (higher heating value, HHV) was determined using a Parr 6722 calorimeter, according to ASTM D5865-10 standard.

2.2 Oil extraction and recovery

SCG were extracted using a pilot scale Soxhlet extractor and different solvents: a mixture of commercial hexane (Labsolve) and isopropanol (50:50 vol/vol), pure hexane (pa, 96 %, Carlo Erba) and isopropanol (pa, Carlo Erba) (50:50 vol/vol), the recovered solvents, and pure hexane. Therefore, about 2.4 kg of SCG were extracted with about 10 L of the selected solvent (or mixture of solvents), for several extraction cycles, until constant refraction index of the solvent measured in three consecutive samples.

To recover the extracted oil and the solvents, a rotary evaporator (Rotavapor, Heidolph) and a vacuum pump (Neuberger) were used.

2.3 Oil characterization

The recovered oil was then characterized for some important parameters to evaluate its quality. Thus, acid value was determined by volumetric titration, iodine number was determined by the titrimetric method using Wijs reactant, kinematic viscosity was determined at 40 ºC using a Cannon Fenske viscometer and a thermostatic water bath (Thermomix BM), density was determined at 15 ºC using a hydrometer method and water content was determined by Karl Fischer coulometric titration (according to the standards specified in EN 14214:2009. Also, the higher heating value (HHV) was determined using an oxygen bomb calorimeter (Parr 6722), according to the procedure in the ASTM D5865-10 standard.

2.4 Biodiesel production

Biodiesel was produced using three different procedures. Therefore, **1)** for the oil resulting from the extraction with pure hexane and isopropanol (50:50 vol/vol) biodiesel was produced by direct transesterification of the oil with 40 wt% methanol (Analytical Reagent Grade, Fisher Scientific) with previously dissolved 1.4 wt% NaOH. The reaction took place at 60 ºC, under constant stirring at 80 rpm for a 3 h reaction time; **2)** for the oil extracted from dried SCG with pure hexane, esterification with H_2SO_4 and methanol (Analytical Reagent Grade, Fisher Scientific) was first applied and then, followed by transesterification using 1 wt% NaOH and different amounts (40, 60 and 80 %) of methanol (Analytical Reagent Grade, Fisher Scientific) at 60 ºC, under constant stirring at 80 rpm for 2 h of reaction time. Finally, **3)** the oil extracted using the different extraction procedures tested was converted to biodiesel and then recovered following the method described by Abou-Shanab et al. (2011). After production of biodiesel under procedures **1)** and **2)**, glycerol was allowed to separate from biodiesel in a separatory funnel. Then, biodiesel was washed with hot water acidified with a few drops of concentrated H_3PO_4, to neutralize the excess NaOH, followed by washing with distilled water until neutral pH. Magnesium oxide (MgO) was used to dry the neutralized biodiesel, stirring the suspension for 15 min, followed by vacuum filtration using cellulose membranes (Whatman, 4-7 µm) to remove the particles of $Mg(OH)_2$ and MgO.

2.5 Biodiesel characterization

The European standard EN14214 specifies a large amount of parameters and the corresponding procedures to characterize biodiesel, including the kinematic viscosity at 40 ºC, the density at 15 ºC, the acid value, the iodine value and the methyl ester content, among other important parameters. In this work only the methyl ester content was evaluated (according to the procedures described in EN 14103 standard) for all the biodiesel samples produced (determined by gas chromatography using a Dani GC 1000 DPC gas chromatograph (DANI Instruments S.P.A.) equipped with an AT-WAX (Heliflex capillary, Alltech) column (30 m, 0.32 mm internal diameter and 0.25 µm film thickness); the injector temperature was set to 250 ºC, while the flame ionization detector (FID) temperature was set to 250 ºC and the oven temperature to 195 ºC; He at 1 mL/min was used as the carrier gas; 0.1 µL sample was injected and the injection was made in a split mode, using a split ratio of 1:80). Also visual appearance of biodiesel (color and physical state), the acid value and the iodine value, the water content and the yield of the process were evaluated.

3. Results and discussion

3.1 SCG composition

SCG were characterized before and after oil extraction. The results, as well as some reference values from literature, are shown in Table 1.

Table 1: Characterization of SCG

Parameter	Before extraction	After extraction	Reference value
Higher heating value, HHV (MJ/kg)	19.3	19.0	21.8-26.9[(a)]
Moisture (%)	65.7	9.4	1.18-5.54[(b)]
Total carbon (%, dwt)	67.3	69.5	47.8-58.9[(a, c)]
Total nitrogen (%, dwt)	2.2	2.0	1.9-2.3[(c, d)]
Protein ($g_{protein}$/100 g)	13.7	12.3	6.7-13.6[(b, e)]
Ash (%, dwt)	2.2	1.65	0.43-1.6[(b, e)]
Cellulose (%, dwt)	13.8	15.31	8.6[(f)]
Klason lignin (%, dwt)	31.9	31.19	-
Soluble lignin (%, dwt)	1.7	40.13	-
Total lignin (%, dwt)	33.6	71.32	-

[(a)] Bizzo (2003), [(b)] Lago et al. (2001), [(c)] Melo et al. (2007), [(d)] Nogueira and Costa (1999), [(e)] Mussatto et al. (2011a), [(f)] Mussatto et al. (2011b)

Extraction of oil from SCG contributes also to its water removal as demonstrated by the huge drop in moisture content (before and after extraction values of Table 1). The HHV of the extracted SCG is slightly lower than that of the raw SCG. The amounts of water and oil in the SCG are lower what has opposite effect on the energy content of the spent coffee grounds, and similar to other agriculture residues such as straw (18.5 MJ/kg) and to some types of wood residues, such as eucalyptus (19.2-19.4 MJ/kg) (Sousa, 2009), allowing it to be used as solid fuel.

Upon extraction, the C/N ratio increased from 30 to 35, but if only cellulose and not lignin is considered, the C/N ratio is about 8, meaning that SCG can be used as N source.

Also the extraction procedure contributes to lignin solubilization, possibly due to the effect of the solvent that causes extreme swelling of the lignin molecules and finally breaks down the polymer chains. Despite this, the main differences from the experimental results to those found in the literature lie in the total carbon and cellulose content (respectively higher and lower in this work) and consequently, on the energy content of the SCG (that is lower in this work). This may be due to differences in the original composition of the SCG used in this study and in the other works.

The high cellulose content of the extracted SCG means that it could also be used for bioethanol production.

3.2 Effect of the solvent on the oil extraction and quality

In order to identify the influence of ultrasounds and of the presence of water on the oil extraction from the SCG, some preliminary experiments were run using only hexane, either with dry or wet SCG and with or without sonication, being the total extraction time 25 h. The corresponding results are shown in Table 2.

Table 2: Effect of sonication and water content of SCG in oil yield

Parameter	Sonication	Contact	Oil yield (wt %)
Dry SCG	Yes	1 min manual + 10 min ultrasounds	5.3
Wet SCG (65.7 % moisture)	No	1 min manual	6.0
	Yes	1 min manual + 10 min ultrasounds	1.8
	No	1 min manual	2.9

The use of ultrasounds did not improve oil extraction but the presence of water significantly hindered the oil extraction. Therefore, this work proceeded with the extraction of oil from dried SCG.

As mentioned above, the oil extraction was performed using a pilot scale Soxhlet, and a constant ratio of 2.4 kg SCG/ 10 L solvent, by using different solvents and their mixtures: A) Pure Hexane:Isopropanol (50:50); B) Commercial Hexane:Isopropanol (50:50); C) Recovered Hexane:Isopropanol; D) Pure

Hexane_Dry SCG; E) Pure Hexane_Wet SCG; F) Commercial Hexane_Wet SCG. Thus, the results of the extraction obtained under these conditions are shown in Table 3.

Table 3: Characterization of the oil extracted from SCG

Parameter	Solvent Mixture Used for Extraction					
	A	B	C	D	E	F
Color	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown
Moisture (%)	0.092	0.118	0.853	0.114	0.119	0.132
HHV (MJ/kg)	39.4	35.4	18.4	40.8	38.9	36.1
Density at 15 °C (kg/m^3)	927	934	na	912	929	942
Viscosity 40 °C(mm^2/s)	33.0	43.9	na	14.9	39.8	40.6
Acid value (mg KOH/g SCG)	3.9	5.6	21.8	9.9	9.4	12.5
Iodine value (g I_2/100g SCG)	61.5	70.5	49.0	47.6	67.9	51.4

In which concerns the water content, it is significantly higher in the oil extracted with the recovered Hexane:Isopropanol mixture, whereas it is lower in the oil extracted with the mixture of pure solvents. The same trend was observed when commercial vs pure hexane was used. This may be due to the presence of larger amounts of water in the lower purity solvents. Regarding the HHV, it was higher for the oil extracted from dry SCG with pure hexane and the lower value was obtained for the oil extracted with the recovered mixture of solvents. This may also be due to the higher water content of the later oil (Ferreira et al., 2007). The density and the viscosity of the oil extracted from dry SCG with hexane was the lowest but for the same solvent when wet SCG was used, the highest values were observed. The acid value of the oil extracted with the lowest purity solvents was significantly higher than the one of the oil extracted with the most pure solvents or from wet SCG. This may be due to the presence of impurities in the solvents that are of acid nature. The extracted oil is too acid to be directly transesterified (especially the samples obtained from extraction with recovered mixture of solvents and using hexane). Regarding the iodine value, the highest value was the one obtained for the oil extracted with the mixture of commercial solvents being the lowest value obtained with the recovered mixture of solvents, so it seems that the quality of the extracted oil is significantly affected by the quality of the solvents and by the presence of water in the SCG. Also iodine value is very low, meaning that the coffee oil is very saturated (few double bond fatty acids)

3.3 Biodiesel production and properties

As stated before, biodiesel was produced using the extracted oil under 3 different experimental procedures. The experimental procedure and the corresponding results are shown in Table 4.

Table 4: Biodiesel from SCG: methyl ester content

Extraction method	Production method	Experimental conditions	Ester content (%)
A	3		62.2
B	3	10 mg oil; 2 mL chloroform/methanol (2:1 vol/vol); 1 mL	70.9
C	3	chloroform nonadecanoic acid standard; 1 mL methanol; 300	61.5
D	3	µL H_2SO_4; mixing 5 min; 100 °C for 10 min	47.4
E	3		63.4
B	1	40 % Methanol; 1.4 % NaOH; 60 °C; 3 h; 80 rpm	86.0
D	2	40 % Methanol; 1 % NaOH; 60 °C; 2 h; 80 rpm	63.0
D	2	60 % Methanol; 1 % NaOH; 60 °C; 2 h; 80 rpm	65.0
D	2	80 % Methanol; 1 % NaOH; 60 °C; 2 h; 80 rpm	54.2

According to these results, the oil resulting from the dry SCG extraction with pure hexane was the one that yielded the lowest methyl ester (ME) content, when the acid esterification was performed over the oil, whereas the highest ME content was obtained for the oil extracted with the mixture of commercial solvents. This may be due to the removal of the glycerol formed during the reaction, due to the simultaneous presence of isopropanol. Nevertheless, the biodiesel produced from the oil extracted with the mixture of commercial solvents under the conventional alkaline transesterification procedure was the one with the highest ME content of 86%, still substantially below the limiting value of 96.5 % imposed by the EN 14214 standard. This may be caused by the relatively high content of FFA (free fatty acids) of the oil that may have been saponified and thus, reducing the yield in ME. This problem could have been at least partially reduced if an esterification of the oil was performed previously to the transesterification reaction,

as it was the case of the samples of oil extracted from dry SCG with pure hexane. In fact, this procedure allowed for a much higher ME content (65 %) when compared to the direct transesterification procedure (47.3 %), although it is not possible to extrapolate the results, but is in good agreement to the results by Al-Hamamre et al. (2012).
But biodiesel quality cannot be evaluated only by the ME content. Therefore, for the biodiesel with the highest ME content (the one that was produced with the oil extracted with the pure mixture of solvents) a more complete characterization was done. The results are shown in Table 5.

Table 5: Biodiesel characterization

Parameter	Biodiesel	EN 14214:2008 limits
Color	Dark brown	-
Appearance	Liquid	-
Reaction yield (%)	37.3	-
Water content (ppm)	2708	< 500
Iodine value (g I_2/100 g sample)	70	< 120
Acid value (mg KOH/g sample)	1.85	< 0.5
Methyl ester content (wt%)	86.0	> 96.5

In spite of the reduction of the acid value, the biodiesel still does not comply with the specifications in EN 14214 standard. The water content may be substantially reduced by improving the drying procedure and the acid value may also be reduced either by increasing the oil conversion, or by improving the neutralization procedure.
The low reaction yield may be caused by the high water content in the oil and by the relatively high FFA contents of the oil that react with the catalyst and forms soap what hinders the reaction.

4. Conclusions

Results have shown a carbon/nitrogen ratio of about 8 in the SCG residue allowing it to be used as fertilizer rich in nitrogen, and a HHV (19.0 MJ/kg) similar to other agriculture residues such as straw (18.5 MJ/kg) and to some types of wood residues, such as eucalyptus (19.2-19.4 MJ/kg) (Sousa 2009), allowing it to be used as solid fuel.
Concerning the oil extraction, the best results were obtained using pure hexane and the mixture of pure hexane and isopropanol in the ratio of 50:50 (vol/vol). The maximum oil content obtained for SCG was about 6 % (vol/wt), being higher in dry SCG (about the double) than in wet SCG (with a moisture content of about 66 %, vol/wt). In respect to the influence of ultrasounds, there are no significant differences in the extracted oil. Regarding the oil characterization results have shown an acid value in the range of 3.9-12.5 mg KOH/g, a density at 15 ºC in the range of 912-934 kg/m^3, a viscosity at 40 ºC in the range of 14.9-44.0 mm^2/s, an iodine number in the range of 47.6-70.5 g I_2/100 g oil, and a HHV in the range of 35.4-39.9 MJ/kg, which are negatively influenced by the oil water content and by the solvents used in the extraction process.
Due to the relatively high free fatty acid content of the extracted oil, their conversion to biodiesel was tested in different processes. A two steps process including an esterification of the free fatty acids followed by a transesterification of triglycerides was used when the acid value was high and showed better ME results than a direct transesterification with H_2SO_4. Nevertheless, in spite of the relatively high FFA content of the oil, the conventional transesterification method yielded higher ME content than the direct transesterification method. Therefore, the results suggest that the best procedure for oil with high FFA conversion into biodiesel would be the two step process of acid esterification followed by alkaline transesterification.
The characterization of biodiesel revealed an iodine value of 70.0 g I_2/100 g, an acid value of 1.8 mg KOH/g and the GC analysis revealed an ester content of 86 %. Although these values are not within the specifications of EN 14214:2008 standard of biodiesel quality, there is the potential of using oil from SCG for biodiesel production if it is blended with oil from other sources this way meeting the standard requirements.

References

Abou-Shanab R.A.I., Hwang J., Cho J., Min B. and Jeon B., 2011, Characterization of microalgal species isolated from fresh water bodies as a potential source for biodiesel production, Applied Energy, 88, 3300-3306.

Al-Hamamre Z., Foerster S., Hartmann F., Kroger M., Kaltschmitt M., 2012, Oil extracted from spent coffee grounds as a renewable source for fatty acid methyl ester manufacturing, Fuel, 96, 70–76.
Bizzo W., 2003, Generation, distribution and use of steam, Apostila de Curso, UNICAMP, Brasil. (in Portuguese),
Caetano N.S., Silva V.F.M., Mata T.M., 2012a, Valorization of coffee grounds for biodiesel production, Chemical Engineering Transactions 26, 267-272.
Caetano N.S., Teixeira J.I.M., Mata T.M., 2012b, Enzymatic catalysis of vegetable oil with ethanol in the presence of co-solvents. Chemical Engineering Transactions, 26, 81-86.
EN 14214, 2009, Automotive fuels - fatty acid methyl esters (FAME) for diesel engines - requirements and test methods. European Committee for Standardization.
Ferreira J., Furtado T., Neves M. and Brandi M., 2007. Influence of moisture content on the calorific components of different ages and from Pinus Taede In: 1º Congresso Brasileiro sobre Florestas Energéticas. 2-5 Jun. Belo Horizonte. Minas Gerais. Brasil. 4pp (in Portuguese).
Kondamudi N., Mohapatra S.K., Misra M., 2008, Spent coffee grounds as a versatile source of green energy, Journal of Agricultural and Food Chemistry, 56, 11757-11760.
Lago R., Antoniassi R., Freitas S., 2001, Proximate composition and of amino acids in green coffee, roasted coffee and soluble coffee grounds . Embrapa – Agroindústria de Alimentos II, Simpósio de pesquisa dos Cafés do Brasil, 1473-1478 (in Portuguese),
Lavecchia R., Pugliese A., Zuorro A., 2010, Removal of lead from aqueous solutions by spent tea leaves. Chemical Engineering Transactions, 19, 73-78.
Mata T.M., Cardoso N., Ornelas M., Neves S., Caetano N.S., 2010. Sustainable production of biodiesel from tallow, lard and poultry and its quality evaluation, Chemical Engineering Transactions, 19, 13-18.
Mata T.M., Martins A.A., Sikdar S., Costa C.A.V., 2011. Sustainability considerations of biodiesel based on supply chain analysis, Clean Technol. Envir. Policy, 13, 655-671.
Mata T.M., Sousa I., Caetano N.S., 2012a, Transgenic corn oil for biodiesel production via enzymatic catalysis with ethanol, Chemical Engineering Transactions, 27, 19-24.
Mata T.M., Melo A.C. Simões M., Caetano N.S., 2012b. Parametric study of a brewery effluent treatment by microalgae *Scenedesmus obliquus*, Bioresource Technology, 107, 151-158.
Mata T.M., Martins A.A., Sikdar S., Costa C.A.V., Caetano N.S., 2013a, Sustainability considerations about microalgae for biodiesel production, Ch.31: Advanced Biofuels & Bioproducts, Ed. Lee J.W., Springer, New York.
Mata T.M., Almeida R., Caetano N.S., 2013b, Effect of the Culture Nutrients on the Biomass and Lipid Productivities of Microalgae *Dunaliella tertiolecta*, Chemical Engineering Transactions, 32, 973-978.
Mata T.M., Melo A.C., Meireles S., Mendes A.M., Martins, A.A., Caetano, N.S., 2013c, Potential of Microalgae *Scenedesmus obliquus* Grown in Brewery Wastewater for Biodiesel Production, Chemical Engineering Transactions, 32, 901-906.
Melo G., Melo V., Melo W., 2007, Composting, Faculdade de Ciências Agrárias e Veterinárias, Jaboticabal, Brasil, 10p (in Portuguese).
Mussatto S., Carneiro L., Silva J., Roberto I., Teixeira J., 2011a, A study on chemical constituents and sugars extraction from spent coffee grounds, Carbohydrate Polymers, 83, 368-374.
Mussatto S., Machado E., Martins S., Teixeira J., 2011b, Production, composition and application of coffee and its industrial residues, Food and Bioprocess Technol., 4(5), 661-672.
Nogueira A., Costa D., 1999, Temperature range for composting solid organic waste, Universidade Federal do Espírito Santo, Brasil, 8p (in Portuguese).
Sousa C., 2009, Energy recovery from industrial textiles and polymeric wastes. MSc thesis, Universidade do Minho, 130pp (in Portuguese).
Zuorro A., Lavecchia R., 2011, Polyphenols and energy recovery from spent coffee grounds, Chemical Engineering Transactions, 25, 285-290.