

Valorization of Coffee Grounds for Biodiesel Production

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This work evaluates the use of spent coffee grounds (SCG) for biodiesel production. The SCG were characterized for their moisture content (12.1 wt%), total carbon (TC) and total nitrogen (TN) (52.2 and 2.1 wt% respectively), cellulose and total lignin contents (33.6 wt% and 13.8 wt% respectively), carbon/nitrogen mass ratio (C/N = 24.8) and higher heating value (HHV, of 19.3 MJ/kg). For extracting the oil from the SCG, several solvents were tested at different contact times: hexane, ethanol, isopropanol, heptane and a mixture of hexane/isopropanol in the proportions of 50:50; 60:40; 70:30 and 80:20 (vol/vol). Results revealed an oil content ranging from 6.3 to 28.3 wt%, depending on the extraction conditions. For example, using hexane/isopropanol (50:50, vol/vol) a 21.5 wt% of oil recovery was obtained after 3 h of contact time, while using isopropanol a 21.0 wt% of oil recovery was obtained in 6.8 h, but at higher operating cost, considering the energy and solvent consumption. Regarding the oil characterization the following parameters can be highlighted: HHV of 36.4 MJ/kg, iodine value of 54.4 (g I₂)/(100 g oil), water content of 2004 ppm and acid value of 118.4 (mg KOH)/(g oil). Finally, the possibility of using the recovered coffee oil for biodiesel production was evaluated. In this regard it was performed the oil esterification in three consecutive steps (using 1% of H₂SO₄ and 40 % of methanol for 2 h of reaction time at 60 °C and 500 rpm) followed by one transesterification step (1 % of NaOH and 40 % of methanol during a 2 h reaction time at 60 °C and 500 rpm). The resulting biodiesel was characterized for its acid value, density, viscosity at 40 °C, iodine value and esters content (65.7 to 72.9 %), of which only the iodine value of 26 and 58.4 (g I₂)/(100 g biodiesel) was within the NP EN14214:2009 standard limits. The reaction yield varied between 58.8 and 62.2 wt%. Results suggest the need for a further process optimization in order to obtain a biodiesel complying with this standard quality requirements.

1. Introduction

Recent decades have seen a significant rise in coffee production and consumption, and consequently an increase in the coffee waste generation. Thus, alternative routes are needed for this waste management, developing new treatment or valorization strategies that should be viable both technically and economically. The composition of SCG is very complex as a wide variety of chemical compounds are present, suggesting that this residue can be used for various applications. The presence of nitrogen allows it to be directly used as fertilizer or as soil improver (or compost) (Kondamudi et al., 2008). Due to its high lignocellulosic content, another possible valorization route is the production of

sugars to be fermented for bioethanol that can be used as fuel or for any other purpose. On the other hand, SCG still have oil content in the order of 10-20 wt% which can be recovered and used for biodiesel. Bioethanol can be used in conjunction with the lipid fraction extracted from coffee to produce biodiesel via a transesterification reaction (Caetano, 2011).

Biodiesel is a biodegradable fuel that can be used instead or added to diesel fuel in internal combustion engines with little or none modifications. The most common process to produce biodiesel is through transesterification, a reaction between triglycerides and an alcohol with a low molecular weight (ethanol or methanol) in the presence of a basic catalyst (NaOH or KOH), to obtain esters and glycerol (Mata et al., 2010, 2011; Morais et al., 2010a). The efficiency of biodiesel production is also dependent on factors such as the catalyst, type of alcohol and oil, the alcohol: oil molar ratio, reaction time and temperature, and stirring during reaction (Moser, 2009). The reaction is very sensitive to feedstocks purity, especially to water and free fatty acids (FFA) contents, as more than 0.5 wt% and 1 wt%, respectively, will reduce the yield and quality of biodiesel, usually requiring a pre-treatment in order to avoid soap formation in the presence of alkaline catalysts (Morais et al., 2010b).

This work aims to identify the most adequate operating conditions to perform the oil extraction from SCG and the oil transesterification to biodiesel, assessing the resulting biodiesel quality.

2. Materials and methods

2.1 Spent coffee grounds characterization

This work used a mixture of SCG (in residual coffee capsules and of spent coffee grounds) collected from a local coffee shop. It was allowed to air dry for several days and then characterized to evaluate its moisture content by repeated cycles of oven (WTB Binder) drying at 105 ± 5 °C followed by cooling in a desiccator and weighing until a constant weight. Then the TC was determined (using a SHIMADZU, TOC-VCSN Analyser) and the TN was determined using a conventional Kjeldahl procedure (sample digestion with H₂SO₄ in a Raypa digester, and distillation using a Raypa DNP1500 distiller). The protein content was estimated according to the procedure suggested by Alves et al. (2007), the ash content was determined according to the procedure of Standard Methods 2540 E (APHA, 1999), using a furnace (Vulcan A-550) at 550 ± 5 °C. The cellulose content was determined according to the procedures of the Portuguese standard NP-1005:1974, using a heating plate (SELECTA, Agimatic-E), a vacuum filtration apparatus and a vacuum pump (Neuberger), an analytical balance (Kern ALJ 220-4), a furnace (Vulcan A-550) and an oven (WTB Binder). The insoluble (or Klason) and soluble lignin content were determined according to the procedure of the standard TAPPI T222om-02, using a heating plate (SELECTA, Agimatic-E) and a UV-Vis spectrophotometer (Shimadzu, UV-1700 pharmaspec) to measure the absorbance of the filtered solution resulting from the previous procedure at a 205 nm wavelength.

2.2 Oil extraction and characterization

Different solvents were tested to evaluate their suitability for oil extraction from about 10 g of oven dried SCG (at 105 °C). Therefore, 200 mL of solvent was used in a Soxhlet extractor during 2.5 to 9.5 h of contact time, depending on the type of solvent used. The extraction procedure was stopped when three consecutive measurements of the solvent refraction index were constant and close to the pure solvents' value. The oil extraction rate and the solvent recoverability were determined for hexane (Pure, Valente e Ribeiro, Lda.), isopropanol (Pure, Sigma-Aldrich) and mixtures of both in various volume ratios (50:50, 60:40, 70:30 and 80:20), and also for heptane (Pure, Sigma-Aldrich), octane (95 %, Carlo Erba) and ethanol (99.8 %, AGA). Then, a vacuum distillation system at constant temperature was used to recover the oil from the extracting solvent using a rotary evaporator (Rotavapor, Heidolph) and a vacuum pump (Neuberger).

The recovered oil and solvent were then quantified and the oil was characterized to assess its quality. Thus iodine number was determined by the titrimetric method using Wijs reactant (EN 14111), acid value was determined by volumetric titration according to (EN 14104), water content was determined by Karl Fischer coulometric titration (EN ISO 12937), kinematic viscosity was determined at 40 °C using a Cannon Fenske viscometer and a thermostatic water bath (Thermomix BM) (according to EN ISO 3104), density was determined at 15 °C using a hydrometer method (NP EN 14214:2009) and the

higher heating value (HHV) was determined using an oxygen bomb calorimeter (Parr 6722, ASTM D5865-10).

2.3 Biodiesel production

When the acid value of oil is higher than 3 % (Van Gerpen, 2005) acidity must be lowered in order to increase the reaction yield, which can be done by neutralization with an alkaline compound or by esterification with methanol as reagent in the presence of an acid catalyst. Thus, several esterification steps were performed successively at 60 °C and 500 rpm in an orbital acclimatized shaker (Ivymen, 200D N/S), controlling the esterification process every two hours by determining the acid value. At the end of each step the phases of methanol/H₂O were allowed to separate, and about 1 % (wt/vol) of H₂SO₄ (96 %, Panreac) and 40 % (wt/wt) of methanol (Analytical Reagent Grade, Fisher Scientific) were added to the reaction flask to perform another esterification step. When the acid value of the resulting product was lower than 3 (mg KOH)/(g oil), the transesterification reaction was performed by adding 40 % (w/w) of methanol (Analytical Reagent Grade, Fisher Scientific) with previously dissolved 1 % (w/w) of NaOH catalyst (José M. Vaz Pereira), for 2 h at 60 °C and 500 rpm. Then, biodiesel was separated from the glycerol phase in a separatory funnel, washed with acidified hot water, followed by washing with distilled water until neutral pH. A further step of drying was carried out over the neutralized biodiesel by adding magnesium oxide (MgO) and stirring the suspension for 15 min, followed by vacuum filtration in cellulose membranes (Whatman, 4-7µm) to remove the particles of Mg(OH)₂ and MgO.

2.4 Biodiesel characterization

The analysis of biodiesel specifications has great importance in assessing the quality of fuel, either environmentally or in terms of preservation of the motorized equipment. Thus, for the biodiesel characterization some of the most important parameters were considered whose compliance is essential for its usage in vehicles engines. These include the density at 15 °C (according to the NP EN 14214:2009 standard), the kinematic viscosity at 40 °C (according to the EN ISO 3104 standard), the acid value (according to the EN 14104 standard), the iodine value (according to the EN 14111 standard) and the methyl esters content (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 °C, while the flame ionization detector (FID) temperature was set to 250 °C and the oven temperature to 195 °C. The carrier gas used was He at 1 mL/min flow. Injection was made in a split mode, using a split ratio of 1:80, and the volume injected was 0.1 µL).

3. Results and discussion

3.1 Spent coffee grounds

The composition of the SCG is shown in Table 1.

Table 1. Composition of spent coffee grounds

Parameter	This work	Reference value
Moisture (%)	12.2	1.18-5.54 ^(a)
Total carbon (%)	52.2	47.8-58.9 ^(b,c)
Total nitrogen (%)	2.1	1.9-2.3 ^(b,d)
Protein (g _{protein} /100 g)	13.3	6.7-13.6 ^(a,e)
Ash (%)	1.43	0.43-1.6 ^(a,e)
Cellulose (%)	13.8	8.6 ^(f)
Klason lignin (%)	31.9	-
Soluble lignin (%)	1.7	-
Total lignin (%)	33.6	-
Higher heating value (MJ/kg)	4619.2	21.8-26.9 ^(g)

All the % values are on a dry weight basis, except the moisture content. (a) Lago et al. (2001); (b) Melo et al. (2007); (c) Bizzo (2003); (d) Nogueira and Costa (1999); (e) Mussatto et al. (2011a); (f) Mussatto et al. (2011b); (g) Bizzo. (2003).

Comparing the results obtained in this work with those from the literature, three major differences can be found. First, the moisture content in our samples is substantially higher (Lago et al., 2001). This may be due to different coffee extraction procedures (pressures) that soak SCG differently with water or to different storage conditions of the SCG. The second difference lies on the cellulose content (Mussatto et al., 2011b). This may be due to different kinds of coffee used in the tests, since it is known that *arabica* and *robusta* have different properties. Finally, the HHV determined in this work is lower than the value referenced in the literature (Bizzo, 2003). This may be due to either the much higher water content of our SCG as well as to the different nature of the coffee samples in both studies.

3.2 Oil extracted by different solvents

To extract and recover oil from SCG, the same SCG/solvent ratio (5:100, wt/vol) was used. The extraction was processed at each solvent boiling temperature during 2.5 to 9.5 h being the shortest and the longest extraction time corresponding to hexane/isopropanol mixture (80:20, vol/vol) and n-octane, respectively.

At least three extraction tests were run for each solvent and the mean ratio of oil extracted from SCG to dry weight of SCG used that was recovered after solvent distillation is shown in Figure 1 and the percentage of solvent recovered is shown in Figure 2.

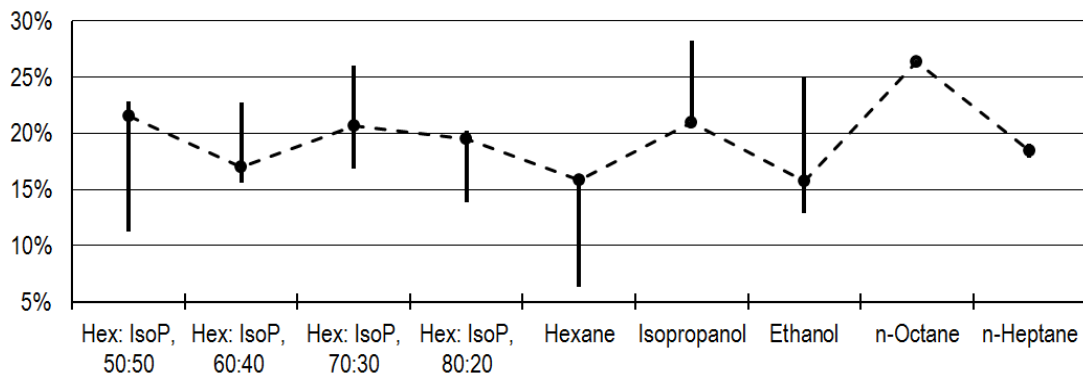


Figure 1. Oil extraction with different solvents.

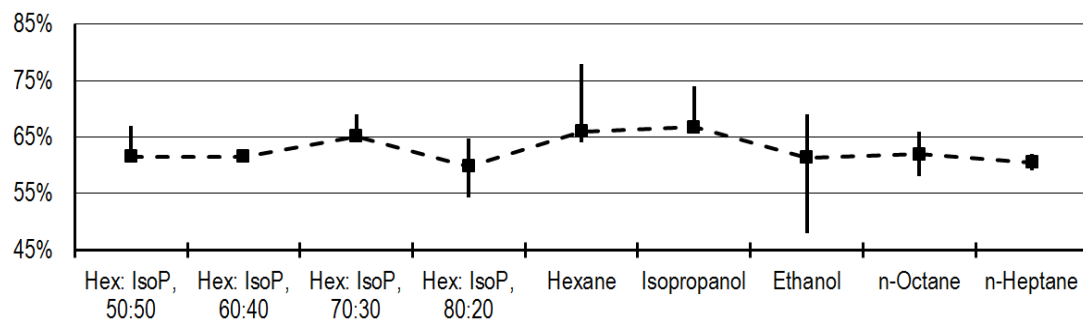


Figure 2. Solvent recovery for different pure solvents and mixtures of solvents.

The solvent that allowed for the higher oil recovery was octane. But this was also the solvent that took the longer time to finish the extraction and one of the solvents with a lower recovery rate. On the other hand, ethanol and hexane were the solvents that allowed for lower oil recovery, with respectively the shortest and the second longer extraction time. Also hexane was one of the solvents with higher recovery rate while ethanol showed the opposite result. Isopropanol showed a very good compromise between the capacity of oil extraction (but with higher variability) and the solvent recovery, followed by the mixture of hexane and isopropanol at a 50:50 (vol/vol) ratio that allowed for high oil extraction but

with a lower solvent recovery.

Considering the cost of the solvents and the energy consumption needed to perform the oil extraction and the solvent recovery by distillation, the mixture 50:50 (vol/vol) of hexane and isopropanol was chosen to perform further extractions.

It must be stated that part of the solvent loss was due to the solvent that was soaking the dried SCG what could be reduced if the extraction were performed over the wet instead of the dry SCG.

3.3 Properties of the extracted coffee oil

The results of oil characterization are shown in Table 2. The iodine value is very low, meaning that the coffee oil is very saturated (its molecules have few double bonds). The viscosity of the oil is too high to be used in direct combustion engines. The oil is also too acid to be directly converted into biodiesel without any pre-treatment, which may indicate a higher degree of oxidation and occurrence of hydrolysis reactions (Knothe, 2007). The relatively high HHV suggests that this oil can be used for direct combustion.

Table 2. Characterization of the oil extracted from coffee grounds

Parameter	Oil of Coffee Grounds
Acid Value [(mg KOH)/(g oil)]	118.4
Iodine Value [(g I ₂)/(100 g oil)]	54.3
Kinematic Viscosity at 40 °C (mm ² /s)	22.23
Density at 15 °C (kg/m ³)	917.0
Water content (ppm)	2004
Higher Heating Value (MJ/kg)	36.4

3.4 Biodiesel properties and composition

The biodiesel was produced using the oil recovered from SCG was analyzed and the results are shown in Table 3.

Table 3. Characterization of the biodiesel

Parameter	Coffee Oil Biodiesel	NP EN 14214:2009 limits
Reaction yield (%)	60.5	-
Acid value [(mg KOH)/(g fuel)]	2.14	<0.5
Iodine value [(g I ₂)/(100 g fuel)]	46.5	120
Kinematic viscosity at 40°C (mm ² /s)	12.88	3.50-5.00
Density at 15 °C (kg/m ³)	911	860-900
Methyl esters content (wt%)	69.3	>96.5
myristate (C14:0)	33.24	-
palmitate (C16:0)	9.19	-
stearate (C18:0)	6.27	-
oleate (C18:1)	19.51	-
linoleate (C18:2)	0.42	-
linolenate (C18:3)	33.24	-

Although the acid value and viscosity have been drastically reduced, the obtained biodiesel does not comply with the NP EN 14214:2009 standard specifications. Also the reaction yield and the methyl ester content were very low, meaning that the reaction was still incomplete. This may be due to the high water content in the oil and to the still high acid value after 3 esterification's steps that caused soap formation consuming catalyst and hindering the reaction. The relatively high density is a consequence of the incomplete reaction.

4. Conclusions

This work studied the viability of producing biodiesel from oil extracted from SCG. Oil extraction with isopropanol and a mixture of hexane/isopropanol (50:50, vol/vol) allowed for the higher oil recovery (21 and 21.5 % respectively) at a relatively lower cost. Due to the high FFA content, the oil had to be esterified prior to transesterification. The quality of the obtained biodiesel was evaluated according the NP EN 14214:2009 standard, showing that the biodiesel obtained is out of this standard limits for all the evaluated parameters. Nevertheless, there are still many improvements that must be done in the process in order to achieve either higher reaction yields but above all a higher methyl ester content such as: drying the oil, water removal between esterifications, neutralization of the excess acid before transesterification, use of different methanol:oil molar ratios, etc. This would certainly contribute to improve the quality of biodiesel.

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