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Biodiesel production from fats extracted from coffee husks: esterification with H_2SO_4 and transesterification with KOH

Aiello-Mazzarri Cateryna*; Salazar Yenmilet; Urribarrí Aidin; Arenas-Dávila Elsy; Sánchez-Fuentes John; Ysambertt Fredy

University of Zulia, Maracaibo 4001, Venezuela. E-mail: caiello@fing.luz.edu.ve

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ABSTRACT: The search for non-food feedstocks is one of the main challenges in the production of biofuels. For biodiesel, research is oriented towards the use of non-conventional crops, as well as towards residues or wastes with a high content of fats and oils. Coffee grounds contain a good proportion of fats and are a commercial and domestic waste. In this work, the production of biodiesel using fats extracted from coffee grounds was evaluated in a two-step process. The fats extracted from coffee grounds with boiling to refiujo with hexane as solvent presented high acidity, 32.07 ± 0.01% (70.24 ± 0.03 mg KOH/ g fat), indicating a high content of free fatty acids (FFA). First, the fats were esterified at 60°C and 100 rpm, varying the reaction conditions. At the best conditions, 0.7% H_2SO_4 concentration, 1:6 GMR:MeOH for 120 min, the acidity decreased below 1%, with 94.92% FFA conversion to methyl esters. They were subjected to a transesterification process with KOH (1.5% m/v) in the presence of methanol (RMG:MeOH of 1:15) at 60°C and 100 rpm for 30 min. The biodiesel was separated by decantation and purified by successive washes with acidified water, which resulted in a mixture of methyl esters of linoleic (48.40%), palmitic (36.21%), stearic (8.69%) and oleic (6.69%) acids, whose properties conform to the requirements of ASTM D 6751 and EN 14214.

KEYWORDS: Coffee grounds; Biodiesel; Esterification; Transesterification

Introduction

The high global energy demand, as well as the uneven distribution of the world's oil reserves, makes many regions dependent on others to meet their fuel needs. This, coupled with the pollution problems caused by the widespread use of fossil fuels and their effect on the climate and the environment, makes it necessary to develop clean and renewable energy sources[1-4].

Biodiesel is a renewable fuel whose use has increased in recent years, either as an alternative or as a blend to fossil diesel. It consists of a blend of long-chain fatty acid methyl esters (FAME) derived from renewable sources, such as vegetable oils or animal fats[57]. Transesterification is the key to the whole process that aims to produce a cleaner and environmentally safer biodiesel from vegetable oils[1].

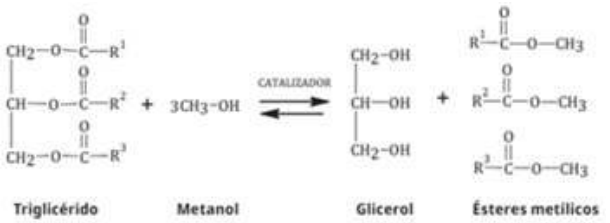
Transesterification or alcoholysis is a reaction of three successive steps between a fat and oil and an alcohol, whose overall reaction is shown in equation (1), which generates the fatty acid methyl esters that make up biodiesel and glycerol as a by-product. Since the reaction is reversible, the addition of excess alcohol is required to shift the equilibrium towards product formation, which ensures the conversion of triglycerides[8].

In general, methanol is used given its low cost and its fisicochemical properties[9-10] that dissolves the catalyst faster than other alcohols. Another alternative would be ethanol because of its solubility in fats and low toxicity compared to methanol[11]. Catalysts can be homogeneous, such as potassium hydroxide (KOH), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4), or heterogeneous catalysts, such as metal oxides or carbonates. Bases catalyze the reaction by removing a proton from the alcohol, whereas acids catalyze the reaction by donating a proton to the carbonyl group[9-10].

The acidity of fats or oils affects the transesterification reaction, causes the formation of soap and water, and dificult the separation of the product from the glycerol[1]. If the acidity is higher than 5%, a previous acid ste-rification step is necessary to reduce the levels of free fatty acids (FFA) [9]. The esterification reaction, in equation (2), requires an excess of methanol to ensure the conversion of FFA.

$$R\text{-}COOH + CH_3OHR - COO - CH_3 + H_2O \xrightarrow{H+} \quad (1)$$

For the production of first-generation biodiesel, edible oils such as soybean, corn, palm, sunflower, rapeseed, coconut and peanut oils have been used as feedstock[11-13]. However, great controversy has been generated by the use of these raw materials for human and animal food. This has encouraged research into the production of second-generation biodiesel, which uses non-edible oils from seeds and plants, animal fats, as well as residues or wastes such as coffee grounds as feedstock[11-12,14]. However, fats from this type of feedstock usually contain a high content of impurities, such as free fatty acids (FFA), water, gums, among others, which make it necessary to include additional steps prior to the catalytic process[11,13,15].



(2)

Coffee grounds are an economical and attractive alternative, easy to obtain and common in many countries, since coffee is one of the most consumed beverages in the world[16-17]. It is one of the most important crops in the world and is second only to oil in terms of value and commercial activity[18-21]. Annually, more than 140 million bags of coffee are produced in the world, which is equivalent to more than 7 million tons of roasted coffee[22-24]. In Venezuela, coffee production has decreased by almost 50% since 2009, standing at about 33 000 t of roasted coffee per year by 2014[22]; however, consumption of ground coffee has remained at 60 000 t per year[25].

Coffee grounds are the main residue obtained from the production of soluble coffee or from the processing of coffee as a beverage. It has been reported that about 0.91 kg are generated for each kilogram of coffee processed[26], so that in Venezuela, according to its annual consumption, an estimated generation of 54,600 t is estimated. Coffee grounds have no commercial value, so they are commonly disposed of with municipal solid waste or incinerated[27]. Due to its high organic matter content, high biochemical oxygen demand (BOD), the presence of compounds such as caffeine, tannins and polyphenols, it can cause a negative effect on the environment, and incineration can result in the release of greenhouse gases[28]. In some cases, it has been used as a fertilizer in vegetable production, as a supplement in animal feed, and as a bio-cleaning agent in oxidation ponds[29].

Coffee grounds have a fat content ranging from 11 to 16%[17,30-32] and a natural antioxidant content between 17 and 24mg GAE/g BC[33-34], which confirm a high stability to the extracted fats. Previous studies have demonstrated the potential of the extracted fats for biodiesel production[21,25,33,33,35-38]. In this work, fats extracted from coffee grounds were subjected to an esterification process with H_3PO_4 as a catalyst in the presence of methanol, and the effect of operating conditions on fat acidity and the conversion of free fatty acids to methyl esters was studied. Then, the esterified fats were subjected to an alkaline transesterification process to obtain biodiesel.

Materials and methods

Coffee grounds

The coffee grounds resulting from processing to obtain coffee as a beverage, which were obtained from several coffee shops in the city of Maracaibo, Zulia State, Venezuela, were used. Once collected, it was dried in an oven at (60 ± 2°C) for 12 h, to eliminate humidity and avoid microbial growth. It was then stored in hermetically sealed plastic containers until use.

Extraction and characterization of fats

The extraction of the fats was carried out by boiling at refiujo, in a water bath with a constant temperature of 80°C for 3 h, and hexane was used as the extracting solvent. The coffee grounds were placed in a cotton cloth filter, ensuring that it did not pass into the extracted phase during the process,inside glass tubes with hexane[32]. To separate the fats, the mixture was heated at 70°C for 3 h in a water bath, in which the hexane was recovered and evaporated. The extracted fats were characterized following the procedures established in ASTM D-445 for kinematic and dynamic viscosity[39], ASTM D1298 for density and specific gravity[40], ASTM D664 for acid number[41], ASTM D1796 for moisture[42] and ASTM D482 for ash[43].

Acid esterification of the extracted fats

The fats extracted from coffee grounds were subjected to an esterification process to reduce the content of free fatty acids and to favor the transesterification reaction[44]. The esterification reaction was performed at 60°C with 100 rpm agitation, H_2SO_4 (Merck)was used as catalyst in the presence of methanol (Fisher, 98% purity) and the alcohol/oil molar ratio was varied (1:3, 1:4, 1:5, 1:6, 1:7 and 1:8), catalyst concentration (0.6, 0.7, 0.8, 0.9 and 1% v/fat) and reaction time (0, 30, 60, 90, 120, 120, 150 and 180 min). The selection of the best conditions was made on the basis of the lowest acidity[32] and the highest conversion of free fatty acids to methyl esters. The conversion was calculated by equation 3, where, A GE is the acidity of the esterified product and A G is the initial acidity of the extracted fats.

$$\text{Conversión (\%)} = \left(1 - \frac{A_{GE}}{A_{GE}} \times 100\right) \quad (3)$$

After the reaction was completed, it was left to stand for 12 h at 40°C and the phases formed were separated by decantation. The lower phase formed (methyl esters and unreacted fats) was passed to the transesterification process, while the upper phase (water obtained in the esterification process, regenerated catalyst and excess methanol) was heated at 65°C in a rotary evaporator to recover the methanol.

Transesterification of esterified fats.

Transesterification of the fats previously was performed using potassium hydroxide (2 mg KOH/g fat) as catalyst in the presence of methanol, with a fats/methanol molar ratio (RMG:MeOH) of 1:6. The reaction was carried out in files of 250 mL, for 1 h in an orbital incubator (New Brunswick Scientific) at 60°C and 100 rpm agitation. The mixture obtained was allowed to stand for 24 h at 40°C and the two phases formed were separated by decantation. The crude biodiesel (upper phase) was washed with slightly acidified distilled water(10% v/v) at 70°C to remove the traces of catalyst present[45], and repeated as many times as necessary for the biodiesel to present a pH similar to that of distilled water[46]. It was then placed in an oven at 110 ± 2°C for 4 h and stored in amber glass containers until characterization. The lower phase with impurities and the glycerin formed as a by-product of the reaction were separated and stored for further study.

Characterization of biodiesel

The composition of methyl esters was determined by gas chromatography, using an Agilent 6890N, equipped with an automatic sample injection system and flame ionization detector (FID) and an HP-5 capillary column (30 m x 0.320 mm x 0.25 um). Helium was used as carrier gas and a mixture of 37 methyl esters (FAME-37 MIX SUPELCO) as standard standard. The initial oven

temperature was 150°C which increased to 260°C at a rate of 4 °C min^{-1}. The injector and detector temperatures were fixed at 220°C and 250°C, respectively. Infrared spectra were collected with 10 scans from 400 to 4000 cm^{-1}, an FTIR spectrometer(Shimadzu Prestige-21) was used as KCl windows impregnated with the liquid and the data were analyzed using soware IR solution, version 2.0. The kinematic viscosity, density, acid number and infiamation point of biodiesel were determined by ASTM D-445[39], D-1298[40], D-664[41] and D-93[47], respectively.

Statistical analysis

For statistical analysis of the data, analysis of variance and Tukey's HDS mean tests were performed, with a significance level a = 0.05, and SPSS Statistics17.0 software was used.

Results and discussion

Characterization of extracted fats

The fats at the time of extraction are liquid, but when they reach room temperature they become solid, with a brown color in both physical states. Hexane was used as the extracting agent because, being a volatile solvent, it produces less volatilization losses, which translates into a good recovery percentage[30,32,36]. In addition, because it is non-polar, the extracting solvent does not interact with polar components present in the flock, thus avoiding solubilization phenomena of undesired compounds[48].

Table 1 shows the results of the characterization of the fats extracted from the coffee grounds. It is observed that they have a low ash content, which indicates that there are no impurities or contaminants that could affect the biodiesel produced. The fats present a high acid value of 32.07 ± 0.01% (70.24 ± 0.03 mg KOH/g fat), similar to those obtained by[49] of 32.0% and[32] of 31.02%. However, it is much higher than the value reported by[44] of 10.04% for fats extracted from defective coffee beans and[30] of 3.65%.

The acidity of fats is directly proportional to the free fatty acid content. Acidity values above 1% (2 mg KOH/g fat) have a negative effect on the production of methyl esters (FAME) during the transesterification process, since the presence of free fatty acids causes catalyst losses during the neutralization reaction, leading to an increase in triglyceride levels in the esterified phase and resulting in a lower FAME content in the biodiesel and thus lower yield[50]. This could be solved by adding a higher amount of catalyst; however, both too much and too little catalyst can lead to soap formation and prevent completion of the transesterification reaction[51]. Because of this, a prior esterification step is necessary to reduce acidity levels. The values of melting point (29.2°C), density (896 kg/m^3), kinematic viscosity(31.50 mm^2/s) and dynamic viscosity (0.028 kg/m.s) are similar to the values reported by[49] and[32] of 29.0°C, 896.0 kg/m^3, 31.25 mm^2/s and 0.028 kg/m,s, but lower than those reported by[30] of 919.2 kg/m^3, 55.473 mm^2/s and 0.051 kg/m,s, respectively.

Table 1 Physical and chemical characteristics of the fats extracted from coffee grounds

Parameter	Value 1
Ashes (4)	0.06±0.01*
Acidity (5)	32.07 ±0.01*
Acid value (mg KOH/g fat)	70.24±0.03*
Melting point (°C)	29.2±0.5*
Density 40°C(kg/m^2)	896.00
Dynamic viscosity 40°C (kg/m-s)	0.028
Kinematic viscosity (mm^2/s)	31.50

Esterification of the extracted fats.

The fats extracted from coffee grounds were subjected to an acid esterification process in which H_2SO_4 was used as catalyst in the presence of methanol, in order to decrease the acid value, convert the free fatty acids into methyl esters and evaluate the effect of the reaction conditions. **Table 2**

Table 2 Effect of catalyst concentration on acidity and free fatty acid conversion during esterification of fats extracted from coffee grounds

Catalyst concentration (v/vfat)	Acidity(%)	acid number (mg KOH/g fat)	Conversion(%)
Control	32,073±0,015a	70,241±0,033a	–
0,6	2,781±0,034b	5,532±0,068b	82,752±0,212b
0,7	2,678±0,066b	5,328±0,131b	83,388±0,407b
0,3	2,768±0,015b	5,507±0,029b	82,831±0,091b
0,9	2,754±0,041b	5,478±0,080b	82,921±0,254b
1	2,747±0,092b	5,464±0,182b	82,962±0,568b

shows the effect of catalyst concentration (0.6, 0.7, 0.8, 0.9 and 1% v/fat) on fat acidity and conversion during esterification at 60°C with RMG:MeOH molar ratio of 1:5 for 2 h at 100 rpm.

The initial acidity of the fats (32%) decreased drastically in all tests, which obtained the lowest acidity value, 2.678 ± 0.066% (5.532± 0.068 mg KOH/g fat, when the 0.7% concentration was used; no statistically significant differences ($p>0.05$) were found between this value and those achieved at the other catalyst concentrations tested. This value represents a conversion of free fatty acids to methyl esters of 83.38%. The acidity value obtained is lower than that reported by[38] of 3.76% in the esterification of fats extracted from coffee grounds, which employed an H_3PO_4 catalyst concentration of 2.5% v/fat, with a maximum conversion of 87.77%.

Table 3 shows the effect of the fat-alcohol molar ratio (RMG:MeOH) on the acidity and conversion during the esterification of fats extracted from coffee grounds at 60°C, which used the catalyst concentration selected in the previous experiment of 0.7 v/v H_2SO_4 for 2 h at 100 rpm. In general, the acidity of the fats decreases as a result of the acid esterification reaction and reaches values below 1% as the GMR:MeOH increases above 1:4.

Table 3 Effect of fat-alcohol molar ratio (RMG: MeOH) on acidity and conversion during esterification of fats extracted from coffee grounds

Molar ratio fats/alcohol (G/AOH)	Acidity(%)	Acid value (mg KOH/g fat)	Conversion(%)
Control	32,073±0,015a	70,241±0,033a	–
1:3	1,2181±0,034b	2,423±0,082b	92,445±0,256b
1:4	0,890±0,069c	1,771±0,137c	94,477±0,427c
1:5	0,533±0,020d	1,060±0,039d	96,695±0,121d
1:6	0,722±0,033e	1,287±0,047e	95,989±0,145e
1:8	0,778±0,030f	1,547±0,060f	95,176±0,187'f

The lowest acidity value was 0.533 ± 0.020% (1.060 ± 0.039 mg KOH/g fat) obtained for the GMR:MeOH of 1:5, representing a conversion of 96.69%, in which statistically significant differences ($p<0.05$) are found in relation to the values found for the other molar ratios studied.

At the RMG: MeOH of 1:6, the acidity obtained is also below 1%, which also allows maintaining an excess of methanol in the reaction. At this molar ratio, a conversion of 95.01% was achieved, higher than the values reported by[49] in the esterification of fats extracted from coffee grounds of 91.1 and 55.87% that used HCl and H3PO4 as catalyst, respectively, at the same GMR: MeOH. It has been reported that, to ensure the formation of methyl esters, it is necessary to use an excess of methanol for the esterification reaction of free fatty acids to occur. If the amount of alcohol is not sufficient, the product will contain monoglycerides and diglycerides as interme-

diate products of the transesterification, which crystallize very easily in the biodiesel and can cause filter plugging and other engine problems[52].

In **figure 1**, the variation of acidity as a function of reaction time during the esterification of coffee grounds fats at 60°C with 100 rpm agitation, which used the catalyst concentration (H_2SO_4) of 0.7% v/v and GMR: MeOH of 1:5 and 1:6, is shown in **figure 1**. In general, it is observed that the acidity of the extracted fats (32.073%) decreases as the esterification reaction proceeds, after which at 120 min minimum values of 0.539 and 0.727% are reached for the 1:5 and 1:6 GMR: MeOH, respectively, which remains practically constant until 180 min ($p>0.05$). In both cases, a high conversion was reached during the first half hour of reaction, 88.51 and 86.95% for RMG: MeOH of 1:5 and 1:6, which progressively decreased until reaching maximum values at 120 min of 96.66% for 1:5 and 95.49% for 1:6. This behavior is similar to that reported by[52] of 85%, when the same reaction time elapsed and H_2SO_4 was used as catalyst in the esterification of used vegetable oils, which further indicates that, despite the decrease in the reaction rate between 30 and 120 min, the conversion percentage increased above 95%.

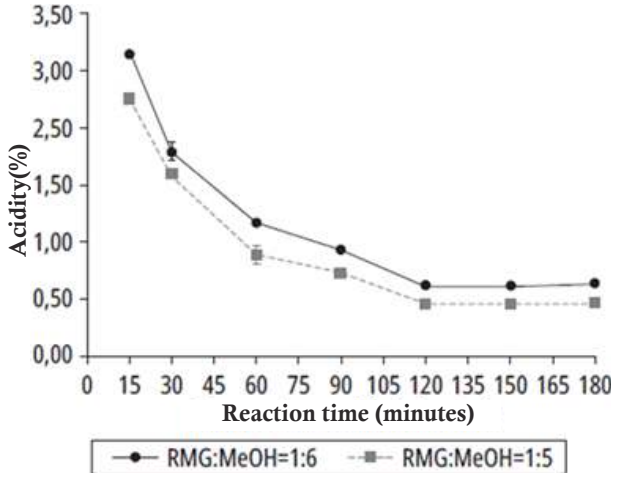


Figure 1 Effect of reaction time on acidity during esterification of fats extracted from coffee grounds at 60°C) with 100 rpm agitation and 0.7% catalyst concentration (H_2SO_4)

Source: Own elaboration.

Transesterification of esterified fats.

The fats esterified at the previously selected conditions were subjected to the alkaline transesterification process at 60 °C that used a catalyst concentration of 2 mg KOH/g fat, RMG:MeOH of 1:15 and agitation of 100 rpm for 1 h[49]. The product obtained, a mixture of crude biodiesel, water, glycerol, methanol and unreacted catalyst, was left at rest to separate by decantation the two phases formed. The biodiesel obtained, the upper phase, was subjected to a purification process by successive washes in order to eliminate the traces of catalyst present and then characterized.

The biodiesel samples were analyzed by gas chromatography, in which the peaks were identified by comparison with the chromatogram obtained for the standard pattern, and it was found to be a mixture of methyl esters of palmitic, linoleic, oleic and stearic acids, whose percentage composition is shown in **figure 2**. Similar composition has been reported by other researchers[32,36,38,49,53], which indicates that the biodiesel obtained from coffee husk fats is composed of saturated and unsaturated methyl esters, in which more than 97% corresponds to methyl esters of palmitic, linoleic, oleic and stearic acids.

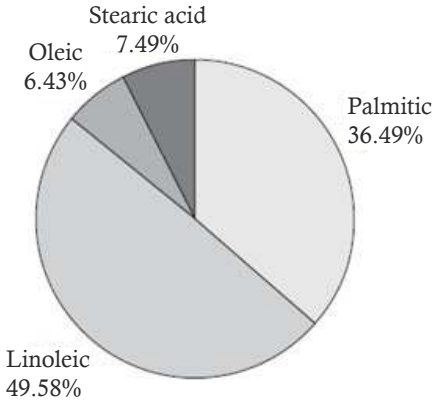


Figure 2 Percentage composition of methyl esters in the biodiesel produced.

Source: Own elaboration.

The total concentration of methyl esters was calculated as the sum of the individual concentrations of the fatty acid methyl esters, in which a value of 145.91 ± 4.43 g/L was found on average. This value is higher than that obtained by[38] of 112.924 ± 7.768 g/L for biodiesel obtained by transesterification at the same conditions of fats extracted from coffee grounds previously esterified

with 2.5% H_3PO_4 as catalyst, with an acidity of 1.99%.

In **figure 3**, the FTIR spectra used to identify the functional groups and bands corresponding to various stretching and fiexion vibrations in the fats and biodiesel samples are presented.

The band between 3150 and 3600 cm^{-1} corresponds to the stretching of the O-H group. In the spectrum of fats, it is attributed to the presence of free fatty acids (carboxylic acids) and mono- and diglycerides in the sample. In the biodiesel spectrum, this band decreases but does not disappear, indicating low methanol residue or moisture content[54]. In both spectra, the bands between 2800 and 3000 cm^{-1} indicate the presence of symmetric and asymmetric C-H bonds. The peaks at 2916 cm^{-1} in the fats and at 2922 cm^{-1} in the biodiesel correspond to stretching vibrations of the methyl groups, while the peak at 3007 cm^{-1} is attributed to -HC=CH stretching of the methyl ester, characteristic of unsaturated compounds[55-59]. The peaks between 1462 and 1400 cm^{-1} in the spectrum of fats and at 1458 and 1435 cm^{-1} in that of biodiesel are attributed to asymmetric stretching of the -C-H bond and asymmetric fiexions of the functional group. Both spectra show a peak at 721 cm^{-1} indicating the presence of -CH_2 groups, due to the fact that fats contain long-chain higher fatty acids; whereas in biodiesel, methyl esters corresponding to[55-56].

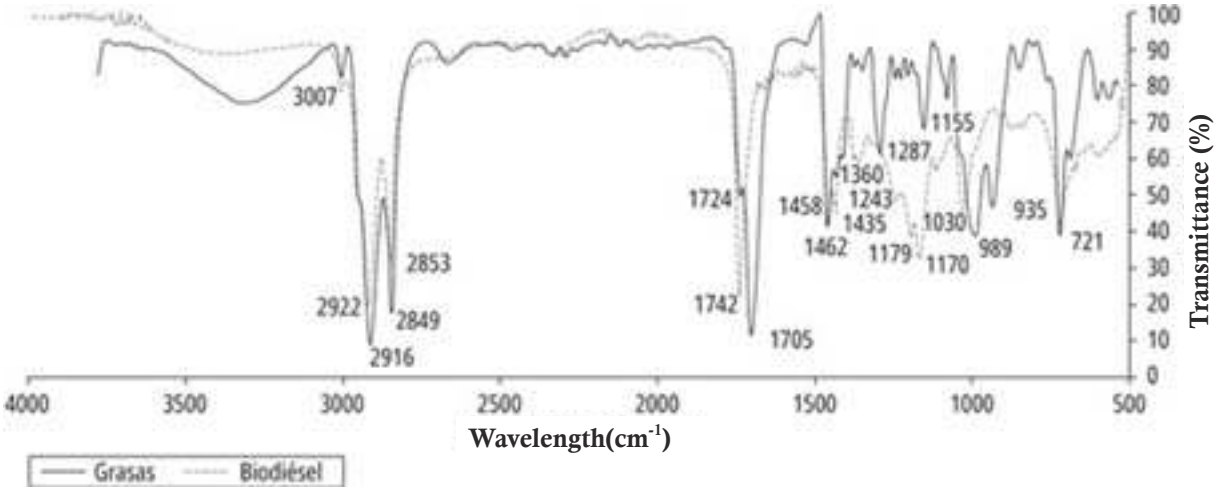


Figure 3 FTIR spectra of fats extracted from coffee grounds and biodiesel produced.
Source: Own elaboration.

In the spectrum of fats, the peaks at 1705 and 1724 cm^{-1} correspond to the stretching of the C=O group in carboxylic acids, due to the presence of free fatty acids and triglycerides. In the spectrum of biodiesel, the peak at 1724 cm^{-1} (carboxylic acids) present in fats disappears, after which the appearance of a peak at 1742 cm^{-1} corresponding to the carbonyl group (C=O) that identifies esters is observed[55,59-61]. In the spectrum of fats, the signals between 1300 and 930 cm^{-1} are attributed to coupled asymmetric vibrations, C-C(=O)-O and O-C-C, of the ester group present in the triglyceride molecule, while the strong absorption signals at 1242 and 1179 cm^{-1} in the biodiesel spectrum correspond to axial deformation of C-C(=O)-O attributed to ester bonds and the peak at 1170 cm^{-1} to asymmetric deformation of O-C-C bonds. These three bands are characteristic of long-chain methyl esters[57], which, together with the disappearance of the peak at 1724 cm^{-1}, indicate the conversion of fats to biodiesel.

Properties of biodiesel

Table 4 presents the fisicochemical properties of the biodiesel produced from the fats extracted from coffee grounds. It is observed that the density of the biodiesel obtained (863 kg/ m^3) is very close to the minimum limit of the range established by both ASTM D6751 and the European standard EN 14214 of 860-900 kg/m^3. This value

Table 4 Properties of biodiesel obtained from fats extracted from coffee husks

Property	Coffee grounds	Biodiesel ASTM D6751	EN 14214	Petrodiesel ASTM D975
Density at 25°C (kg/mJ)	663	860-900	860-900	850
Flash point (°C)	177	>130	>120	68
acid number (mg KOH/q biodiesel)*	0,41±0,16	<0,8	<0,5	0,35
Kinematic viscosity at 40°C (mm2/s)*	5,35±0,06	1,9-6,5	3,5-5,0	2,6

is close to that reported by[49] of 870 kg/m^3 in biodiesel from coffee husk fats obtained by transesterification with HCl as catalyst.

The infiamation point of the obtained biodiesel of 177°C meets the requirements of ASTM D-6751 and EN 14214, which establish minimum values of 130 and 120°C, respectively. This parameter is related to the purity of the biodiesel produced and is indicative of the eficiency in methanol removal[62]. The acid number was 0.41 mg KOH/g, which is within the limit established by both ASTM D6751 (<0.80 mg KOH/g) and EN 14214 (<0.50 mg KOH/g), and is higher than the value of 0.35 mg KOH/g for petroleum diesel. Acidity values in biodiesel above 0.80 mg KOH/g can cause corrosion in engines[60].

The kinematic viscosity of biodiesel was 5.35 mm^2/s, which is within the range required by ASTM D6751 (1.96.5 mm^2/s), but slightly higher than the maximum limit established by EN 14214 (3.5-5.0 mm^2/s). It is also 2.1 times higher than the viscosity of mineral diesel (2.6 mm^2/s). Viscosity infiuences on the good performance of the engine using this fuel,whereby high viscosities lead to poor fuel atomization and affect injection behavior, which is accentuated at low temperatures or cold start[62 64]. The viscosity of biodiesel is generally higher than that of petroleum diesel, in many cases up to twice its value[61]. In general, the properties determined in the biodiesel produced meet the standards established by international norms. However, it is advisable to carry out a more extensive study of its fisicochemical properties.

Conclusions

The fats extracted from coffee grounds have an acid value higher than 1%, so they contain a high amount of free fatty acids. The esterification of the fats extracted from coffee grounds at 60°C with 100 rpm agitation were catalyst concentration (H_2SO_4) of 0.7%, RM-G:MeOH of 1:5 and reaction time of 2 h, which reduced the initial acidity (32.073%) below 1% (0.539%) with a conversion of free fatty acids to methyl esters of 96.66%.

FTIR spectra confirmed the conversion of the fatty acids to methyl ethers. The biodiesel obtained by alkaline transesterification of the previously esterified fats is a mixture of methyl esters of palmitic (36.46%), linoleic (49.58%), oleic (6.43%) and stearic (7.49%) acids.

The properties determined for the biodiesel produced are in accordance with the requirements established by ASTM D-675, as well as with those of EN 14214, with the exception of kinematic viscosity, whose value is slightly higher than the established limit.

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