



Original Research Paper

Integrated volarization of spent coffee grounds to biofuels

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HIGHLIGHTS

- Oil extraction was studied for different Solvents
- Two-step biodiesel production method due to high FFA
- Pelletized fuel of the over left solid and glycerin
- Biofuel without growing plants and/or converting food to fuel.

GRAPHICAL ABSTRACT



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ABSTRACT

Biodiesel is a renewable energy source produced from natural oils and fats, and is being used as a substitute for petroleum diesel. The aim of this study was to investigate the potential of using spent coffee grounds for biodiesel production and its by-products to produce pelletized fuel, which is expected to help the biodiesel production process achieve zero waste. For this experiment, spent coffee grounds sample was collected from Kaldis coffee, Addis Ababa, Ethiopia. Extraction of the spent coffee grounds oil was then conducted using n-hexane, ether and mixture of isopropanol to hexane ratio (50:50 %vol), and resulted in oil yield of 15.6, 17.5 and 21.5 %w/w respectively. A two-step process was used in biodiesel production with conversion of about 82 %w/w. The biodiesel quality parameters were evaluated using the American Standard for Testing Material (ASTM D 6751). The major fatty acid compositions found by Gas chromatography were linoleic acid (37.6%), palmitic acid (39.8%), oleic (11.7%), and stearic acid (8.6%). In addition, solid waste remaining after oil extraction and glycerin ratio (glycerin content from 20-40%) was evaluated for fuel pellet (19.3-21.6 MJ/Kg) applications. Therefore, the results of this work could offer a new perspective to the production of biofuel from waste materials without growing plants and/or converting food to fuel.

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1. Introduction

Biodiesel, a mixture of long-chain fatty acid alkyl esters obtained from renewable feedstock, such as vegetable oil or animal fats, for use in compression ignition engines (Murugesu et al., 2009). Recently, biodiesel has become more attractive because it is biodegradable and non-toxic in nature, environmentally friendly and derived from renewable resources. It can also be

produced from any material that contains fatty acids, either linked to other molecules or present as free fatty acids (Balat and Balat, 2009).

However, a global debate has now emerged because this fuel is derived primarily from soybean oil or other cereals and using food to produce fuel is not reasonable considering the increase in world population. In order to overcome this problem, industries use waste vegetable oil and grease and animal fats from poultry to produce biodiesel (Nebel and Mittelbach, 2006).

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Therefore, it would be very useful to look for new raw sustainable materials for biodiesel production that do not involve the use of cereals and land to grow. In this work, production of biodiesel from spent coffee grounds as well as fuel pellets from its by-products has been carried out.

Coffee is one of the world's most widely consumed beverages. It is the most important cash or export crop in Ethiopia, providing approximately 30.6% of Ethiopia's foreign exchange earnings in 2010-2011 (Bureau of African Affairs, 2012). According to the report in (Mebratu et al., 2013) Ethiopia is producing an estimated 9.804 million 60-kg bags of coffee and half of it is consumed domestically.

Spent coffee grounds are the main coffee industry residues with a worldwide annual generation of 6 million tons and 235,296 tons in Ethiopia, obtained from the treatment of coffee powder with hot water to prepare instant coffee (Mebratu et al., 2013; Tokimoto et al., 2005). Considering this huge amount of coffee residue produced all over the world, the reutilization of this material is a relevant subject. Some attempts for reutilization of SCG have been made. However, none of these attempts have yet been routinely implemented, and most of these residues remain unutilized, being discharged to the environment where they cause severe contamination and environmental pollution problems due to the toxic nature (presence of caffeine, tannins, and polyphenols) (Leifa et al., 2000).

The biodiesel from spent coffee grounds possesses better stability than biodiesel from other sources, due to its high antioxidant content (Campo et al., 2007; Yanagimoto et al., 2004). SCG is also considered as easily available and an inexpensive adsorbent for the removal of cationic dyes in wastewater treatments (Franca et al., 2009).

2. Materials and methods

2.1. Materials and chemicals

This work used spent coffee grounds (coffee Arabica) collected from Kaldis coffee shop (Addis Ababa, Ethiopia). All analytical grade chemicals and solvents were obtained from the department of chemical engineering (Addis Ababa University, Ethiopia). Experimental and laboratory work was undertaken in the department of chemical engineering (Addis Ababa University), Ethiopian Petroleum Supply Enterprise (EPSE), Ethiopian Health and Nutrition Research Institute and Geological Survey of Ethiopia Central Laboratory.

2.2. Experimental

2.2.1. Moisture content Determination

The spent coffee grounds (SCGs) were allowed to air dry for several days and then characterized to evaluate its moisture content by repeated cycles of oven drying at 105 °C followed by cooling in a desiccator over silica gel (0% relative humidity) and weighing until a constant weight. The moisture content was determined as in Equation 1;

$$M = \left(\frac{W_1 - W_2}{W_1} \right) \times 100 \% \quad (1)$$

Where M, W_1 , W_2 are moisture content, initial mass and final mass

2.2.2. Spent coffee grounds (SCGs) oil extraction

Different solvents were tested to evaluate their suitability for oil extraction from oven dried SCG (at 105 °C). 300 g of the dried SCG sample was placed in a 2 L round bottom flask of the soxhlet apparatus and extracted for 4-8 h using n-hexane, ether and mixture of isopropanol to hexane ratio (50:50) as a solvent. 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 was separated from the solvents using a rotary evaporator (Buchi RE111 Rotavapor, BUCHI, Flawil, Switzerland). The solvents were reused in the next batch of extraction. The oil yield was determined as in equation 2;

$$\text{SCG oil content} = \frac{W_o}{W_s} \times 100 \% \quad (2)$$

Where: W_o = weight (g) of oil extracted and

W_s = weight (g) of sample (dry base)

2.2.3. Physicochemical characterization of SCGs oil

Prior to transesterification, oil quality properties of the SCG oil were determined. These properties included saponification value, peroxide value (ASTM D3703), water and sediment (ASTM D2709), iodine value (EN14111), acid value (ASTM D974) density (ASTM D1298), kinematic viscosity (ASTM D445), flash point (ASTM D93), cloud point (ASTM D97) and higher heating value (HHV) (ASTM D240). The oil properties were analyzed in accordance with ASTM D 6751 and EN 14214. All experiments were run in triplicate and mean values were reported.

2.2.4. Two-step Biodiesel Production Process

2.2.4.1. Acid-catalyzed esterification

The SCG oil was heated to 54 °C to homogenize the oil. The reaction was conducted in a 1 L round-bottomed flask attached with a reflux condenser and a thermometer placed in an oil bath. The oil is mixed with methanol (a molar ratio of alcohol to free fatty acids of 20:1) and significant quantities of HCl (10 wt% of total fatty acid content). The reactor was stirred at about 600 RPM, at a temperature of 54 °C for 90 minutes (Santori et al., 2012). Then the reaction product mixture was poured into a separating funnel and allowed to settle for 24 h. The top layer, which is comprised of unreacted methanol and water, was removed.

2.2.4.2. Base-catalyzed transesterification

The transesterification of the oil was carried out under ambient pressure in a 1 L two-necked round bottom reactor equipped with a thermometer, a hot plate with magnetic stirrer, and a reflux condenser. The reaction was carried out at 54 °C for 90 minutes with 1 wt% of KOH and methanol-to-oil molar ratio of 9:1 (Kondamudi et al., 2008). The resulting product was cooled to room temperature without any agitation and transferred to a separatory funnel for glycerol and methyl ester separation. It was left overnight to allow separation by gravity. After the two phases have separated, the upper phase was collected and the excess alcohol in it removed using a vacuum evaporator operated at 80 °C.

2.2.5. Purification

The resulting methyl ester obtained was purified by successive washing with warm (55 °C) deionized water to remove residual catalyst, glycerol, methanol and soap. A small quantity of sulfuric acid was used in the second washing to neutralize the remaining soap and catalyst. Finally, the SCG oil methyl ester was dried over anhydrous sodium sulfate (Na_2SO_4) to remove residual water. A filtration process followed to remove solid traces. The dried methyl ester was then bottled and kept for characterization studies.

2.2.6. Characterization of SCG Biodiesel

Physical and chemical properties of SCG biodiesel esters were characterized using internationally accepted standards. Density (15 °C) (ASTM D1298), Kinematic viscosity (40 °C) (ASTM D445), Gross calorific value (ASTM D240), Cloud point (ASTM D97), Iodine number (EN14111), water and sediment (ASTM D2709), Ash content (ASTM D874), acid value (ASTM D974), Carbon residue (ASTM D189), flash point (ASTM D93), Distillation, 90% recovery (ASTM D86) and Copper corrosion (ASTM D130) were used.

2.2.7. Fatty acid composition of SCG methyl ester

Fatty acid composition of the synthesized alkyl ester was determined by gas chromatography. Gas chromatography (DANI GC 1000) equipped with flame ionization detector (FID) was employed during fatty acid determination. The GC was calibrated by injecting standards at varying concentrations. The samples were injected (1 μ L) one by one in a DANI GC 1000, equipped with a capillary column of EC TM-5 (25 m x 0.53 mm x 1 μ m). The GC oven was primarily kept at 50 °C for 2 min, and then heated at 4 °C/min up to 250 °C, where it was kept for 15 min, and a pressure of 1.25 Bar was applied. The carrier gas used was nitrogen at (1 ml/min).

2.2.8. Glycerin and solid waste remaining after biodiesel production for Pellets

The by-products of spent coffee ground biodiesel were analyzed as pellets. The solid waste remaining after oil extraction were mixed with glycerin content (20-40%) by weight ratio and blended by hand in a large mixing bowl. The glycerin and solid waste ratio were then mixed to produce a crude unfinished material. The pellet mixture (approximately 12g) is placed inside a rolled piece of newspaper wrapping, and the ends are folded down so that both ends of the cylinder are covered. No adhesive is used, and until the pellet is compressed this will remain prone to unwrap. The major quality properties of the pellet like heating value (Bomb calorimeter), specific density (Gravimetric method and water replacement), moisture content (Oven-drying of 1 g of pellet sample at 104-110°C for 1 hour), combustion ash, volatile matter, and fixed carbon were analyzed following the ASTM methods.

3. Results and discussions

3.1. Oil content of spent coffee ground (SCG)

Extraction of oil from spent coffee grounds was carried out using solvents such as n-hexane, ether and mixture of isopropanol to hexane ratio (50:50) under reflux conditions. 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 was recovered after solvent rotavapor. The solvent extracted crude oil yields are (15.6% w/w hexane, 17.5% w/w ether and 20.6 %w/w mixture of isopropanol to hexane ratio (50:50). The solvent that allowed for the higher oil recovery was a mixture of isopropanol to hexane ratio (50:50) but with a lower solvent recovery. On the other hand, hexane was the solvent that allowed for lower oil recovery, with a longer extraction time. Also hexane was one of the solvents with higher recovery rate while ether showed the opposite result. But ether was also the solvent that took the longest time to finish the extraction and one of the solvents with a lower recovery rate. 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.

The obtained oil content is relatively higher than that reported in the SCG oil (10-15%) depending on the coffee species as in (Kondamudi et al., 2008, Deligiannis et al., 2011). The oil content of this study is higher than previous studies (19.73 %w/w) using hexane. Higher value (28.3 %w/w) as in (Caetano et al., 2012) for SCG oil was extracted with a mixture of isopropanol and hexane. The variation in the oil yield could be attributed to differences in varieties of coffee, solvent type and cultivation climate. Compared to some other oilseeds such as olive, soybeans and cotton seeds, which have average

oil contents of only 17%, 20% and 14%, respectively, this may result in lower operating costs as in (Rossel, 1987).

3.2. Properties of the extracted coffee oil

SCG oil was characterized to determine its physiochemical properties to utilize as a feedstock in the production of biodiesel. The obtained results were compared with that of American Standard for Testing Materials (ASTM D 6751). The standard values and the results obtained are summarized in Table 1.

Table 1
Characterization of the oil extracted from waste coffee ground.

| Property | Units | Test Methods | Limits | Results |
|-----------------------------|-----------------------|--------------|-----------|---------|
| Density (15 °C) | g /cm ³ | D1298 | 0.86–0.90 | 0.917 |
| Kinematic Viscosity (40 °C) | mm ² /s | D 445 | 1.9– 6.0 | 42.65 |
| Gross calorific value | MJ/kg | D 240 | Report | 38.22 |
| Cloud point | °C | D 97 | Report | 11 |
| Iodine Value | gI ₂ /100g | EN14111 | 120 max | 79 |
| Water and sediment | %volume | D2709 | 0.050 max | 0.03 |
| Acid value | Mg | D974 | 0.8 max | 9.85 |
| Flash point | °C | D93 | 130 min | >200 |
| Saponification value | mgKOH/g | AOCSCd 3-25 | ----- | 167.28 |

The viscosity of the oil is too high to be used in direct combustion engines. The oil was found to be very acidic and the saponification value was also high as in “Table 1” to be directly converted into biodiesel without pretreatment, which may indicate a higher degree of oxidation and occurrence of hydrolysis reactions (Knothe, 2007). In order to overcome this problem the oil was first esterified using hydrochloric acid as a catalyst prior to transesterification. The relatively high HHV suggests that this oil can be used for direct combustion. The SCG oil has high density, so cannot be used directly as fuel; since this high density would polymerize and leads to the formation of deposits in the car engine. The high cloud point of SCG oil indicates its unsuitability as biodiesel feedstock. The peroxide value is low, means its rancidity is low and can store for a long time. The flash point is very high, making it better suited for biodiesel production with respect to safety during storage and transportation.

3.3. Biodiesel yield of SCG oil

Biodiesel yield estimation was done after the separation and purification of the transesterified product. The 82 %w/w yield of SCG oil synthesized was calculated. The %FFA of the SCG oil was decreased from 4.9% to 0.5% after three consecutive esterification steps. After esterification, the oil pretreatment loss was found to be 6.8 %w/w based on the initial sample of SCG oil.

3.4. Spent Coffee Ground biodiesel Fuel properties

Transesterification of the oil to biodiesel was carried out using methanol and KOH. The properties of biodiesel fuel prepared from spent coffee grounds are analyzed by ASTM analysis (Table 2). The analysis of the results shows that biodiesel obtained from spent coffee grounds is a strong candidate as an alternative to diesel (Barnwal and Sharma, 2005).

Table 2
Characterization of the oil extracted from spent coffee ground.

| Property | Units | Test Methods | Limits | | SCG oil methyl ester |
|----------------------------|-----------------------|--------------|------------|------------|----------------------|
| | | | ASTM 14214 | D6751 EN | |
| Density (15°C) | g /cm ³ | D1298 | ----- | 0.86 – 0.9 | 0.88 |
| Kinematic viscosity (40°C) | mm ² /s | D445 | 1.9 -6.0 | 3.5-5 | 5.4 |
| Gross calorific value | MJ/kg | D240 | ----- | ----- | 39.6 |
| Cloud point | °C | D97 | Report | ----- | 13 |
| Iodine value | gI ₂ /100g | EN14111 | ----- | 120 max | 74 |
| Water and sediment | %volume | D2709 | 0.05 max | 500 mg/kg | 0.01 |
| Ash content | W% | D874 | 0.02 max | 0.02 max | 0.01 |
| Acid value | mg KOH/g | D664 | 0.5 max | 0.50 max | 0.7 |
| Carbon residue | % mass | D189 | 0.05 max | 0.3max | 0.033 |
| Flash point | °C | D93 | 93.0 min | 120 min | 220 |

3.5. Fatty acid composition of spent coffee ground oil methyl ester

Investigation of the fatty acid components of SCG biodiesel was carried out using GC. The fatty acid profile of the methyl ester was identified and quantified as shown in figure 1. GC analysis showed the presence of C16-C20 methyl esters of fatty acids. SCG biodiesel consists of both saturated and unsaturated esters (Figure 1), where more than 98.3% of the total composition were methyl esters of linoleic acid (37.3%), palmitic acid (35.8%), oleic acid (13.9%), stearic acid (8.1%), arachidic acid (3.2%) and arachidic acid (3.2%) and other (1.7%).

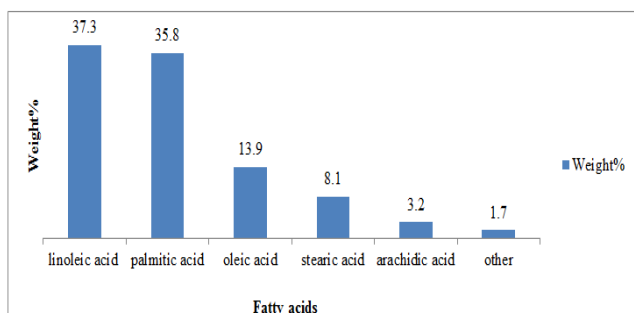


Fig.1. SCG methyl ester fatty acid composition.

3.6. Pelletized fuel quality

SCGs are composed of 13.8% of cellulose, 36.7% of hemicelluloses, 13.6% of proteins and 33.6% of lignin (Caetano et al., 2012; Mussatto et al., 2011). Cellulose is considered as a major source of volatile content in the biomass, while lignin serves as a natural binder in the biomass (Biswas et al., 2011; Wahyudiono and Goto, 2013). Although the SCG contain relatively high lignin content, the addition of a binder, like glycerin, is expected to enhance combination of biomass particles well. Table 3 presents the bulk density, the proximate analysis results, the heating value and pellet quality demands suggested by EUBIA (EUBIA, 2007).

Table 3
Properties of pelletized fuel prepared from SCG after oil extraction and glycerin.

| Glycerin content (%) | Bulk density (kg/m ³) | Proximate Analysis (% wt) | | | | Heating value (MJkg ⁻¹) |
|----------------------|-----------------------------------|---------------------------|-----------------|------|--------------|-------------------------------------|
| | | Moisture content | Volatile matter | Ash | Fixed carbon | |
| 20 | 996.6 | 5.12 | 73.4 | 5.08 | 16.4 | 19.3 |
| 25 | 995.7 | 4.99 | 76.8 | 4.4 | 13.81 | 19.7 |
| 30 | 996.0 | 4.33 | 78.0 | 3.7 | 13.97 | 19.8 |
| 35 | 997.8 | 3.12 | 79.1 | 3.2 | 14.58 | 20.2 |
| 40 | 995.5 | 5.03 | 77.8 | 2.8 | 14.37 | 21.6 |
| EUBIA [21] | >650 | <10 | - | <0.5 | - | >17 |

All the tested properties of the studied fuel sample pellets were found to comply with the suggested EUBIA values, except for the ash content. An increase of glycerin in the solid waste remaining after oil extraction appears to benefit the reduction of the ash content of the fuel. However, the maximum glycerin of 40% still produced an amount of ash greater than the criterion value of 0.5%. The test results show that the fuel sample can satisfy the fuel pellet quality demands for domestic use as suggested by the European Biomass Industry Association (EUBIA) for pellet characteristics of the bulk density and moisture content (EUBIA, 2007). Since the finished fuel pellet was oven-dried at 105°C for 24 h, it contained relatively low moisture content of 3.12- 5.12 %wt. The heat of combustion of the fuel sample indicates that the pelletized fuel provided a better fuel quality. The pelletized fuel had the heating value greater than the suggested EUBIA value of 17 MJ/kg. An increase of the glycerin content from 20% to 40% can increase the combustion heating value from 19.3 to 21.6 MJ/kg. The use of glycerin as a binder helps to improve the biomass pelletized fuel for its calorific property.

This fuel pellet has high calorific value compared to the biomass energy obtained from groundnut (12.60 MJ/Kg) (Musa, 2007), cowpea (14.37 MJ/Kg) and soybeans (12.94 MJ/Kg) reported by (Enweremadu et al., 2004). The energy values and combustion qualities of the fuel produced in this study is sufficient enough to produce the required heat for domestic cooking and also for industrial application especially the energy requirement of the small-scale industries.

4. Conclusion

The aim of this study was to evaluate spent coffee grounds as a potential source to produce biodiesel and its by-products as fuel pellets. Oil extraction with a mixture of hexane/isopropanol (50:50 vol/vol) that allowed for the higher oil recovery (21.5 %) at a relatively lower cost was converted to biodiesel with 82% yield. GC analyses indicated that the spent coffee ground biodiesel consisted of both saturated (47.1%) and unsaturated (51.2%) esters. The quality of the obtained biodiesel was evaluated according the ASTM standard, showing that the biodiesel obtained is within the standard limits for all the evaluated parameters except for carbon residue.

The solid waste remaining after oil extraction and glycerin, which are by-products from the biodiesel production, are experimentally proven to be promising raw materials for producing fuel pellets (21.6 MJ/kg). The production of the solid waste after oil extraction and glycerin pellets can also promote a zero waste approach for the biodiesel production process and can eliminate disposal cost of the crude glycerin. This work will give new insight to producing biofuels without growing plants and/or converting food to fuel.

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