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Spent Coffee Grounds as a Versatile Source of Green Energy

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The production of energy from renewable and waste materials is an attractive alternative to the conventional agricultural feed stocks such as corn and soybean. This paper describes an approach to extract oil from spent coffee grounds and to further transesterify the processed oil to convert it into biodiesel. This process yields 10−15% oil depending on the coffee species (*Arabica* or *Robusta*). The biodiesel derived from the coffee grounds (100% conversion of oil to biodiesel) was found to be stable for more than 1 month under ambient conditions. It is projected that 340 million gallons of biodiesel can be produced from the waste coffee grounds around the world. The coffee grounds after oil extraction are ideal materials for garden fertilizer, feedstock for ethanol, and as fuel pellets.

KEYWORDS: Coffee grounds; green energy; biofuel; biodiesel

INTRODUCTION

Biodiesel is a good alternative for fossil fuel. In recent years, biodiesel production from vegetable oils and animal fats (*1*) has gained attention because of its ecofriendly nature, liquid nature, and easy portability (*2, 3*). However, biodiesel is more expensive than fossil fuels, which limits its applications. The major production cost of biodiesel is from its feedstock (*4*). The foremost problem that the biodiesel industry faces nowadays is the availability of low-cost and good quality feedstock. To meet this problem, industries use waste vegetable oil and grease and animal fats from poultry to produce low-cost biodiesel (*5, 6*). In addition, researchers are developing certain crops with high oil content just for the production of biodiesel (*7*−*10*). In this work, we have demonstrated that spent coffee grounds can be a potential source for the production of biodiesel as well as fuel pellets (**Figure 1**).

Coffee is one of the largest agricultural products that are mainly used for beverages. According to the U.S. Department of Agriculture, the world's coffee production is 16.34 billion pounds per year (*11*). The amount of oil in the coffee source varies from 11 to 20 wt % depending its types (*12, 13*). On average, the spent coffee grounds contain ∼15% oil, which can be converted to a similar amount of biodiesel using transesterification methods. This is quite significant as compared to other major biodiesel feedstocks such as rapeseed oil (37−50%), palm oil (20%), and soybean oil (20%) (*14*). This can add approximately 340 million gallons of biodiesel to the world's fuel supply. The biodiesel from coffee possesses better stability than biodiesel from other sources due to its high antioxidant content (which hinders the rancimat process) (*15, 16*). The remaining solid waste can be utilized as compost as a feedstock to produce ethanol (*17*) and as fuel pellets. A brief description on the extraction, transesterification, and purification process to produce biodiesel from spent coffee grounds is reported here. The composition of the biodiesel and preliminary cost estimation are also discussed.

MATERIALS AND METHODS

Materials. Starbucks's (Reno, Nevada) "grounds for your garden" spent coffee grounds were used throughout unless otherwise stated. Fatty acid methyl esters (99% assay), anhydrous methanol [high-performance liquid chromatography (HPLC) grade], tannic acid (ACS

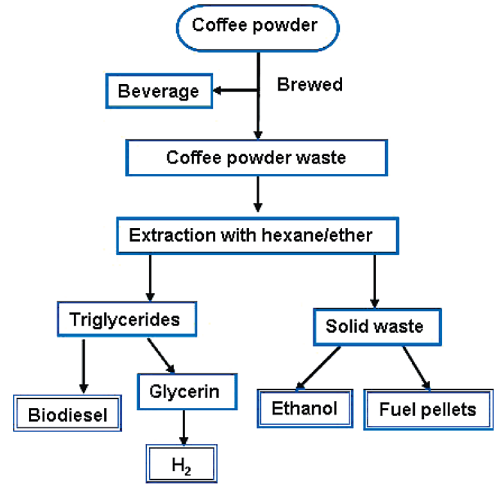

Figure 1. Schematic representation of the biodiesel production process from spent coffee grounds. The other value-added products such as H_2, ethanol, and fuel pellets can also be achieved from this waste feedstock.

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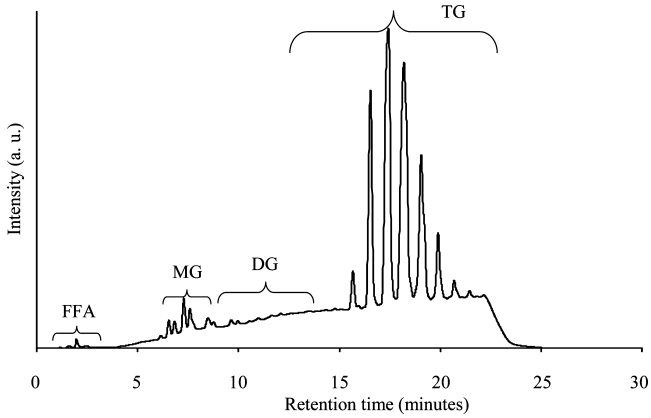

Figure 2. HPLC chromatogram of the oil extracted from spent coffee grounds indicating the presence of TG, a small amount of DG, MG, and FFA.

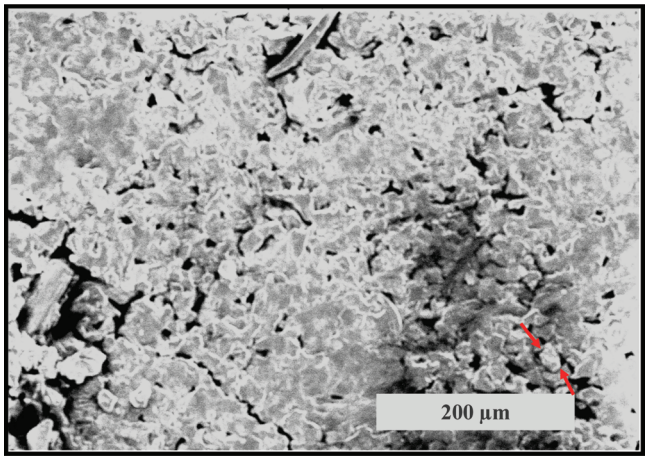

Figure 3. SEM image that shows the particle size of dried spent coffee grounds as 20−30 μm. The grounds were pressed into pellets, and SEM (Hitachi S-4700 at 20V) was taken.

grade), potassium hydroxide (KOH, 86%), hexane (ACS grade), diethyl ether (ACS grade), and dichloromethane (HPLC grade) were purchased from Sigma Aldrich (United States) and used as received.

Oil Extraction. Spent coffee grounds were dried overnight in an oven (Isotemp 655G) at 50 °C to remove moisture (mostly 50−60 wt %) and then refluxed for 1 h with low-boiling organic solvents such as *n*-hexane, ether, and dichloromethane to extract the oil from the coffee particles. Three hundred mL of solvent was used for 100 g of dried spent coffee grounds (adjusted to 95% dry matter basic) for the extraction of oil. All of the experiments were carried out using a 1 L round-bottomed glass flask. The resultant solution containing 15 g of oil was separated from the spent coffee grounds by filtration using a Buckner funnel under vacuum. The oil was separated from the solvents using a rotary evaporator. The solvents were reused in the next batch of extraction. The collected crude oil was characterized and quantified using HPLC. The free fatty acids (FFAs) present in the crude oil were separated by converting them into soap by mixing a basic solution with the extracted oil. Soap was removed from the pure oil by centrifuging the mixture for 30 min (5000 rpm; Beckman centrifuge model J2-21).

Transesterification Process. In a typical transesterification process, first the coffee oil was heated to 100 °C to remove the traces of water present, and the oil was mixed with 40 v % methanol and 1.5 wt % catalyst (KOH). The reaction mixture was refluxed at ~70 °C for the biodiesel production. Optimization of the reaction was carried out by varying the amounts of methanol, KOH, and reaction time (through HPLC analysis) to get maximum yield. The reaction time for a complete transesterification process was monitored through HPLC using methanol, hexane, and isopropanol as solvents (see the Supporting Information for details) (*18*). The reaction was stopped when the oil (mostly triglycerides, TG) peaks in the HPLC analysis disappeared, and the peaks corresponding to biodiesel were saturated. The reaction mixture, after the reaction, was cooled to room temperature and allowed to stand overnight. The bottom layer of glycerin was separated from the biodiesel layer (top layer). The produced crude biodiesel was then washed twice with warm water (40−50 °C) and acidified water (0.5 wt % tannic acid) to remove the excess methanol and the traces of catalyst (*19, 20*).

Characterization. The yield and composition of the biodiesel were investigated using HPLC (Shimadzu LC solution). This was carried out by diluting 5 μL of the biodiesel (diluted to 1 mL by adding 995 μL of hexane), and 10 μL of this solution was injected through the column. The percentage compositions of each fatty acid were analyzed by injecting standard solutions under similar conditions. Further investigation of the composition of the biodiesel was carried out using gas chromatography coupled with mass spectrometry (GC-MS; Thermo Finnegan PolarisQ). A Perkin-Elmer Series II, CHNS/O analyzer model 2400, was used to estimate the C/N ratio of the used coffee grounds before and after the oil extraction process.

RESULTS AND DISCUSSION

Extraction of oil from spent coffee grounds was carried out using solvents such as hexane, ether, and dichloromethane under reflux conditions. A 10 μL amount of the reaction mixture was taken out in each 5 min interval and was analyzed by HPLC. There was an increase in peak intensity for TG observed with an increase in reflux time. The saturation point was observed at 45 min for hexane extraction. A small amount of FFA, monoglycerides (MG), and diglycerides (DG) was also observed in the oil (**Figure 2**). Because the particle size of the grains was around 20 μm [obtained from scanning electrom microscopy (SEM) micrograph, **Figure 3**], a countercurrent extraction would be more economical for industrial purposes (*21*). The pH of the oil extracted from different solvents was observed to be different due to the variation in the FFA amounts. More polar

Table 1. Comparison of Coffee Oil with Other Waste Feedstock for Biodiesel Production

source	amount (million gallons/year)	advantage	disadvantage
		animal fat	
tallow, brown grease, pork fat (white grease), lard, fish oil, poultry fat	5.5[a]	oxidative stability, less expensive	high sulfur content, high FFA (50−90%), bad odor, bad cold flow properties, high cloud point, high pour point, transportation costs, purification required
		vegetable oil	
used vegetable oil	2.8[a]	less expensive, readily available	bad odor, high FFA
coffee oil	2.92	less expensive, higher stability, well-established transportation, pleasant smell	extraction of oil from spent coffee grounds required

[a] Alleman, T. L.; McCormick, R. L. Results of the 2007 B100 Quality Survey; NREL/TP-540-42787, March, 2008.

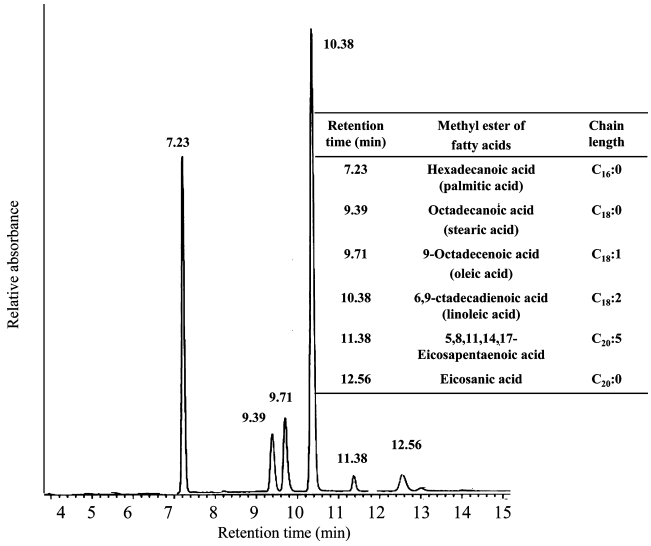

Figure 4. GC analysis of the biodiesel shows the different methyl esters of fatty acids present in the biodiesel produced from the used coffee grounds. The presence of various methyl esters in coffee biodiesel obtained by MS is shown in the inset table (spectra not shown).

solvents extracted greater amounts of FFA and, in turn, more crude oil yields (13.4% hexane, 14.6% diethyl ether, and 15.2% dichloromethane), which caused a decrease in pH. Hexane extraction resulted in a more neutral pH (6.8) of the extracted crude oil, when compared to the other solvents such as diethyl ether (4.7) and dichloromethane (4.5). Hence, hexane was selected as a suitable solvent for the oil extraction process. The quality of the coffee oil as feedstock for biodiesel production was also found to be a better quality and cost-effective as compared to other waste sources available to date (**Table 1**) (*22, 23*).

Transesterification of the oil to biodiesel was carried out using methanol and KOH. The highly intense TG peak (retention time at 17.5 min) in the HPLC was monitored to estimate the progress of the reaction. The maximum yield of biodiesel was obtained when 40 v % methanol and 1.5 wt % catalyst were used, where 100% oil-to-biodiesel transformation took place (details are available in the Supporting Information). It was also observed that coffee biodiesel consists of esters of palmitic acid, linoleic acid, and stearic acid.

Further investigation of the composition was carried out using GC-MS (**Figure 4**). GC-MS analysis showed the presence of $C_{18}-C_{16}$ methyl esters of fatty acids (MS spectra are not shown). Coffee biodiesel consists of both saturated and unsaturated methyl esters, where more than 99% of the total composition was methyl esters of palmitic acid (51.4%), linoleic acid (40.3%), and stearic acid (8.3%). This is in line with HPLC analysis. Oliveira et al. (*24*) also reported a similar composition of coffee oil prepared from defective coffee beans. The oil and biodiesel formed in this process were found to be stable over 1 month without any observable physical changes. 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 (*25*).

Currently, the use of spent coffee grounds is limited to gardens as compost for the plants. Ideal coffee grounds for the soil need a C/N ratio (wt) of 20:1 (*26*). The C/N ratio after the oil extraction process showed that there was no significant change in the C/N ratio before (19.8:1) and after (15.7:1) the extraction process. This indicated that the processed coffee

Table 2. ASTM Results for the Coffee Biodiesel

test name	test method	limit	results
free glycerin (mass %)	ASTM D 6584	max 0.020	0.006
MG (mass %)	ASTM D 6584	N/A	0.076
DG (mass %)	ASTM D 6584	N/A	0.027
TG (mass %)	ASTM D 6584	N/A	0.000
total glycerin (mass %)	ASTM D 93	max 0.240	0.109
phosphorus (ppm)	ASTM D 4951	max 10	2.0
Ca + Mg (ppm)	EN 14538	max 5	2.0
Na + K (ppm)	EN 15438	max 5	2.0
viscosity at 40 °C	ASTM D 445	1.9−6.0	5.84
TAN (mg KOH/g)	ASTM D 664	max 0.50	0.35
oxidation stability by rancimat (h)	EN 14112	min 3.00	3.05
cloud point (°C)	ASTM D 2500	N/A	11.0
pour point (°C)	ASTM D 97	N/A	2.0
sulfur, by UV (ppm)	ASTM D 5453	15	8.0

grounds could still be used as compost for the garden and/or as fuel pellets (1 lb pellet ≡ 8691 BTUs of energy). After the oil is extracted from the grounds, the grounds can immediately be pelletized into fuel pellets. Our preliminary calculations indicate that in the United States only (considering the waste generated by Starbucks stores), this process can run with a profit of more than $8 million/year, if both biodiesel and pellets can be marketed (see the Supporting Information, Table S1).

In conclusion, we have demonstrated that spent coffee grounds can be used as a potential source to produce quality biodiesel and fuel pellets. Around 15% of the oil obtained from spent coffee grounds was converted to biodiesel with 100% yield. GC-MS and HPLC analyses indicated that the coffee biodiesel consisted of both saturated (51.4%) and unsaturated (48.6%) esters. ASTM analysis confirmed that this biodiesel can be used industrially as an alternative to diesel. This can add approximately 340 million gallons of biodiesel to the world's fuel supply. This work will give new insight to producing biofuels without growing plants and/or converting food to fuel.

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Supporting Information Available: Optimization conditions for the extraction and transesterification of coffee oil and HPLC column conditions (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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