

High Quality Biodiesel from Spent Coffee Grounds

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ABSTRACT

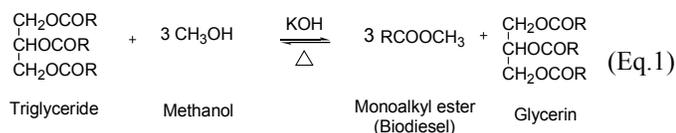
The production of energy from renewable and waste materials is an attractive alternative to conventional agricultural feed stocks such as corn and soybean. According to the United States Department of Agriculture, the world's coffee production is 16.34 billion pounds/yr, which produces approximately the same amount of spent coffee grounds. The spent coffee grounds contain approximately 15% oil, which introduces approximately 281,000 tons/yr of CO₂ into the environment. Laboratory tests conducted at the University of Nevada, Reno with spent coffee grounds show that not only we can eliminate this environmental pollution, but we can also produce biodiesel from it. It is estimated that 3 million gallons/yr of biodiesel can be extracted in the U.S.A. from the Starbucks' coffee operation, which can eliminate 40,000 tons/yr of CO₂ from the environment. The total biodiesel production from spent coffee grounds would be approximately 621 million gallon/yr world wide. Although small as compared to the gasoline demand, nevertheless, it has a strong potential to help energy demand. Moreover, the coffee grounds after oil extraction are ideal materials for garden fertilizer due to good carbon-to-nitrogen ratio and improved biological oxygen supply.

This paper will give an overview of the cost-effective production process of biodiesel from spent coffee grounds. The biodiesel derived from coffee grounds is stable at room temperature for a long period of time (due to its high antioxidant contents). A detailed kinetics study, purification, antioxidant amount and analysis by HPLC and GC-MS will also be discussed.

Keywords: Spent coffee grounds, transesterification, biodiesel

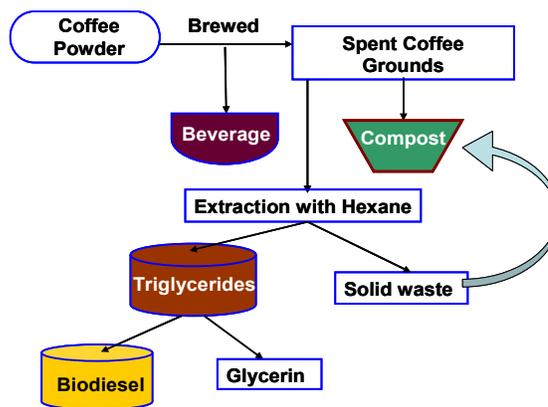
1. INTRODUCTION

Biodiesel is defined as a fuel comprised of mono alkyl esters of long chain fatty acids that are derived from vegetable oils or animal fats by a process called transesterification [1].



In recent years, biodiesel production has gained attention because of its liquid nature, portability, ready availability, higher heat content, lower sulfur content, lower aromatic content and biodegradability. It emits lesser amounts of green house gases [2–3]. However, the economics of biodiesel production are not on a par with fossil fuels, which are available at lower prices. The major production cost (75-80% of the total production) of biodiesel is from its feed stock [4]. The price and quality of the biodiesel depends on the type of the feed stock employed in its production. The foremost problem that the biodiesel industry faces nowadays is the availability of cheap and good quality feed stock. Hence, the use of spent coffee grounds for the production of biodiesel can potentially contribute to the issue of usable feedstock.

Coffee is one of the largest agricultural products that is mainly used for beverages. According to the United States Department of Agriculture, the world's coffee production is 16.34 billion pounds per year [5]. The raw seeds of coffee contain 20% triglycerides (TG) [6]. The spent coffee grounds contain 15% TG, which can be converted to biodiesel using various transesterification methods. For an average of 15% TG production from the spent coffee grounds, approximately 340 million gallons of biodiesel can be produced per year. A simple biodiesel generating process from spent coffee grounds is shown in Scheme 1.



Scheme 1. Schematic representation of the biodiesel production process from used coffee grounds

The additional advantages of spent coffee grounds in the production of biodiesel are their low caffeine content and high antioxidant activity compared to the raw coffee beans (roasting enhances Maillard reaction, which produces 20% more antioxidants in coffee) [7].

2. EXPERIMENTAL

2.1 Oil extraction

Used coffee grounds were dried overnight in an oven (*Isotemp Oven Model 655G*) at 50°C to remove moisture and then refluxed for one hour with n-hexane to extract the oil from the coffee particles. 300 mL of solvent was used for 100 g of dried spent coffee grounds for extraction of oil. The resultant solution containing oil was separated from the spent coffee grounds by filtration. 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 (FFA) present in the crude oil were converted into soap by mixing caustic water with the extracted oil. Soap was removed by centrifuging the crude oil for 30 minutes @5000 rpm (*Beckman centrifuge Model J2-21*). Thus, purified coffee oil was used for biodiesel production via transesterification (Eq. 1).

2.2 Biodiesel production

Varying amounts of methanol and potassium hydroxide were used for the optimization of the transesterification reaction. In this process, first the coffee oil was heated to 100 °C to remove the traces of water present, and a solution of methanol and potassium hydroxide were added to the TG. The reaction mixture was refluxed for 2 hours each time.

The transesterification kinetics were monitored through HPLC every 5 minutes up to the first 15 minutes, and after that every 30 minutes up to the next 2 hours. A glass column was used with 150 X 3.2 mm packed with C18 particles with a diameter of 7 μm. Gradient elution was set by mobile phases A (methanol) and B (Isopropanol : hexane = 4:5 by volume). The course of the gradient was: 0 to 20 minutes reached to 50% B, 20 to 21st minute changes to 100% A, then it continued at this condition for another 4 minutes. The dosing volume was 10μL, and the dilution of the sample was done 1: 20 in phase B. Spectrophotometric detection in the UV region at 205 nm was used [8]. The reaction was stopped when the TG peaks in the HPLC analysis disappeared, and the peaks corresponding to biodiesel were saturated. Different amounts of methanol and catalyst were tested to optimize the reaction conditions.

After the transesterification step, the reaction mixture was cooled to room temperature overnight. The bottom layer (glycerin) was separated. The top layer, biodiesel, was then washed twice with hot water (50 °C) and acidified water (0.5 wt% tannic acid) to take off the excess methanol and the traces of catalyst [9]. Characterization was done using HPLC and with a *Thermo Finnegan PolarisQ* GC-MS.

A qualitative study was done with GC-MS. 1μ liter of the biodiesel dissolved in hexane was introduced in the column. A quantitative study of the coffee biodiesel was done with HPLC. Different standards of fatty acid methyl esters from C₁₆ to C₁₈ were purchased from Sigma-Aldrich and used without any modification. 5μ liters of each pure sample was diluted to 1mL and injected through the column; the area under the curve was noted. For each and every fatty acid methyl ester, calibration plots were made with concentration vs area under the curve. Finally, 5μ of the biodiesel diluted to 1mL and the percentage compositions of each fatty acid were measured. 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.

3. RESULTS AND DISCUSSION

3.1 Oil extraction and biodiesel production

Extraction of oil from spent coffee grounds was carried out using hexane under reflux conditions. A 10μL of the solution was taken out in each 5 min of the reflux and was analyzed by HPLC (Figure 1). There was an increase in peak intensity for the TG observed with an increase in the reflux time. The saturation point was observed at 45 min for hexane

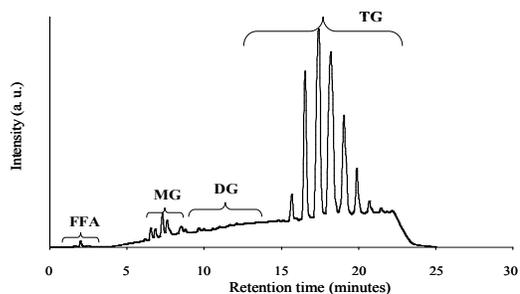


Figure 1. HPLC chromatogram of the oil extracted from spent coffee grounds indicating the presence of triglycerides (TG), diglycerides (DG) and monoglycerides (MG).

extraction. Since the particle size of the grains was around 20 microns (Fig 2) counter current extraction would be suitable for industrial purposes. The FFAs were converted into soap

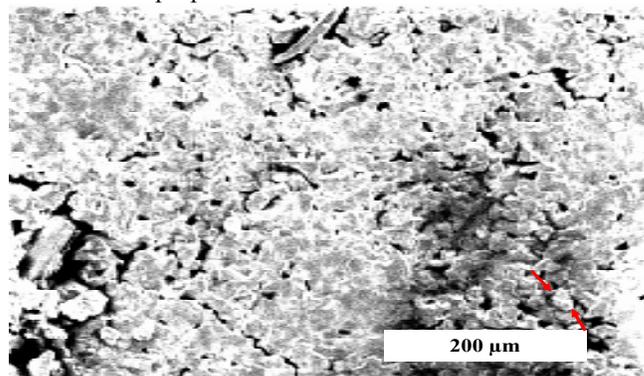


Figure 2. Scanning Electron Microscope (SEM) image shows the particle size of dried spent coffee grounds as 20–30 μm.

by mixing caustic water with the extracted oil. Soap was removed by centrifugation.

3.2 Optimization of the reaction conditions

When 1 wt% catalyst and 20 vol% methanol were used in the initial reaction, only a small amount of the biodiesel was yielded; instead formation of diglycerides (DG) and

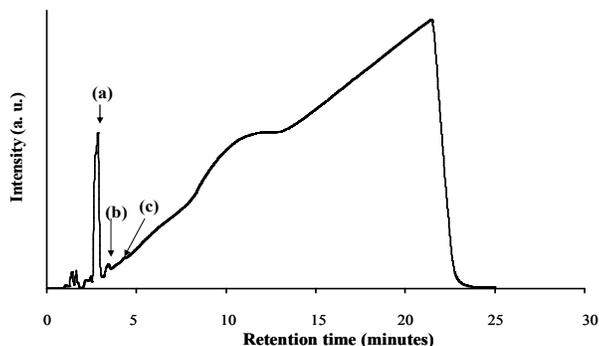


Figure 3. Complete conversion of oil to biodiesel was observed when 1.5 wt% catalyst and 40 vol% methanol were used. The presence of Linoic (a), Palmitic (b) and Oleic (c) acid methyl esters can be observed.

monoglycerides (MG) were observed. By increasing the volume % of methanol to 40% and keeping the catalyst amount the same, an increase in the yield was observed. After 2 hours of the reaction with the initial catalyst amount (1% by

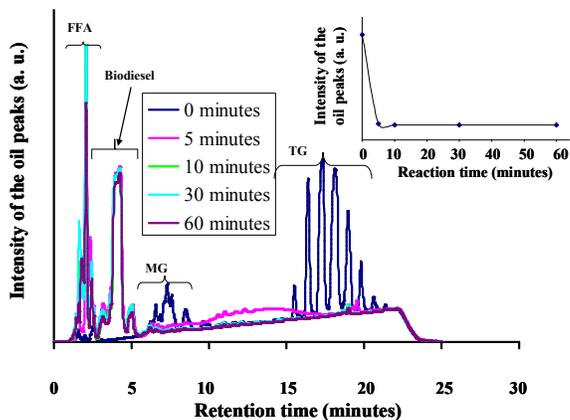


Figure 4. The intensity of highly intense oil peak was monitored with time during transesterification. The reaction was completed within the first 10 minutes of reflux. 40 vol% methanol and 1.5 wt% catalyst were used as the optimum conditions for the kinetic study of the coffee oil transesterification.

wt) the presence of TG was still in the reaction mixture. The highly intense TG peak was approximately 40% to the initial TG peaks. An additional amount of 0.5 wt% was added to the reaction mixture, and the reaction was again monitored by HPLC. After one hour the TG peaks were completely diminished. Thus the reaction conditions at 40 vol%

methanol and 1.5 wt% catalyst were set as optimum conditions for transesterification of the coffee oil since the reaction went to 100% and no TG peaks were observed in the reaction mixture (Figure 3).

3.3 Kinetics of transesterification

Once the optimized conditions were found, the transesterification reaction was carried out and a decrease in the intensity of the oil was observed (Figure 4) as stated in the experimental part. The reaction was completed within 10 minutes. Reaction kinetics were observed to be faster by prior heating of the oil.

3.4 Purification and characterization of biodiesel

The reaction mixture contained excess methanol, biodiesel, catalyst, and glycerin. An overnight waiting period formed two layers; biodiesel formed the top layer and glycerin formed the bottom layer. The initial pH of biodiesel was observed to be 11.9. After each wash with water the pH of the biodiesel was observed to go down. The final pH of the biodiesel was observed as 6.8, indicating complete removal of the catalyst. A final wash was given with 0.5% tannic acid to further remove the traces of the catalyst. The solubility of trace amounts of tannic acid gave a weak acidic nature to the biodiesel. However, the presence of the phenolic groups (tannic acid) imports antioxidant properties to the biodiesel [10]. A water wash also diminished the intense color of the biodiesel, indicating the removal of any water soluble pigments. GC measurements showed various types of methyl esters formed from coffee oil (Figure 5).

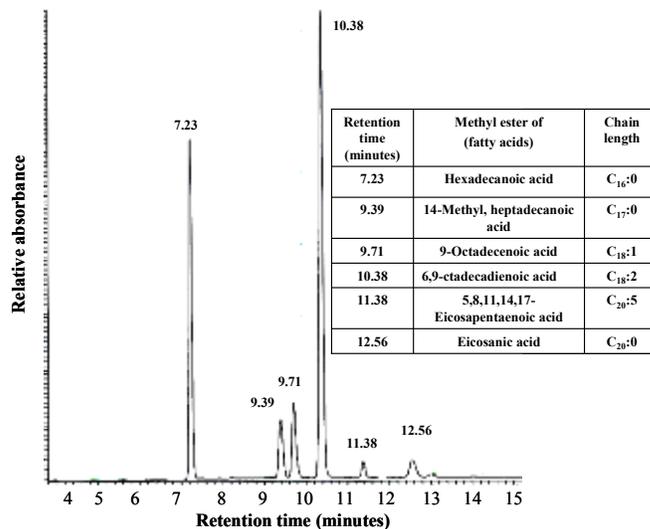


Figure 5. Gas Chromatogram (GC) of the biodiesel shows the different methyl esters of fatty acids present in the biodiesel produced from the used coffee grounds. Presence of various methyl esters in coffee biodiesel obtained by Mass Spectroscopy were shown in the inset (Spectra not shown).

In addition GC-MS analysis showed the presence of C₁₈-C₁₆ methyl esters of fatty acids (MS spectra were not shown). The coffee biodiesel consisted of both saturated and unsaturated methyl esters. 90% of the total composition was methyl esters of palmitic acid (51.4%), linoleic acid (40.3%), and stearic acid (8.3%).

3.5 C/N ratio

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 of 20:1 [11].

Table 1. C/N ratio of the used coffee grounds before and after oil extraction process

Spent coffee	%C	%N	C/N
Before processing	48.76	2.45	19.86:1
After processing	41.16	2.62	15.7:1

However, the C/N ratio after the oil extraction process showed that there was no significant change in the C/N ratio. Table 1 shows the C/N ratio of the coffee grounds before and after the oil extraction process, indicating the processed coffee grounds can still be used as compost for garden. It was shown that the C/N ratio before and after the TG extraction process was 20:1 and 16:1, respectively.

3.6 CO₂ emission

The amount of oil present in the spent coffee grounds has adverse physical effects on the biotic life in the soil, if thrown in unprocessed. The stoichiometric equations of the CO₂ production are shown in Table 2. From Table 2 and Section 3.4, each gram of the oil can produce 2.75g of CO₂ into the

Table 2. The stoichiometric equations of the CO₂ production per gram of each fatty acid

Fatty acid	Chemical reaction with environmental oxygen	CO ₂ produced g/g)
Palmitic acid	$C_{16}H_{32}O_2 + 23 O_2 \rightarrow 16 CO_2 + 16 H_2O$ 256.4g 704g	2.7
Linolenic acid	$C_{18}H_{32}O_2 + 25 O_2 \rightarrow 18 CO_2 + 16 H_2O$ 280.4g 792g	2.8
Stearic acid	$C_{18}H_{36}O_2 + 26 O_2 \rightarrow 18 CO_2 + 18 H_2O$ 284.4g 792g	2.8

environment (Eq.2). Because of unprocessed coffee grounds, approximately 281,000 tons of CO₂ are produced every year which is proportional to the total world coffee production.

$$\{0.514*(2.7) + 0.403*(2.8) + 0.083*(2.8)\} * 1g \text{ oil} = 2.75g \text{ CO}_2. \quad (\text{Eq. 2})$$

4. CONCLUSION

In conclusion, we have shown that spent coffee grounds can be used as a renewable energy source to produce biodiesel. The extraction process was optimized to get 15% triglycerides from the coffee powder. Transesterification reaction conditions were optimized with 1.5 wt% KOH and 40 vol% methanol with a reflux time of 15 minutes at 75 °C. A yield of 10% can be achieved by a controlled transesterification process. It was also shown that the major compositions of methyl esters in coffee biodiesel are from palmitic and oleic acid.

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