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Waste coffee oil: A promising source for biodiesel production

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Abstract

The oil from waste coffee possesses the potential as a feedstock for biodiesel production. In this study, waste coffee grounds were collected from Turkey. Then the oil was extracted from waste coffee grounds using N-hexane. The two-step acid-base catalyst transesterification process was used to produce biodiesel as the acid value of the crude oil was found higher (15.4 mgKOH/g). This was followed by an investigation of some physical and chemical properties. It was found that the properties of waste coffee biodiesel fell within the limit of ASTM standards. So the studied physicochemical properties of the waste coffee biodiesel suggest that this fuel can be used as a fuel in diesel engines.

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1. Introduction

Recently, the dramatic increase in fossil fuel consumption in the industrial sector, transportation sector and technology developments has been leading to the depletion of the fossil fuel reserves worldwide [1-3]. Because of this, researchers have been putting more attention to finding the alternative energy such as biodiesel which is believed can lower the dependency on fossil fuel and support the environmental sustainability [4-8]. Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from a renewable feedstock such as vegetable oils, animal fats, and alcohols [2, 9]. However, the feedstock types, availability and material cost are the obstacles to the commercialization of biodiesel production.

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To overcome the obstacles, industries use waste vegetableoil, grease and animal fats from poultry to produce low-cost biodiesel [10, 11]. Also, researchers are putting much effort to develop the certain crops with high oil content for the production of biodiesel. The coffee bean is one of the largest agricultural products in the world[12]. About 7.2 billion tonnes of coffee has been produced around the world every year. Greece is the 12th largest consumer of coffee in the world, with 5.5 kg/ person per year. Depending on the type of coffee beans, 11 to 20 wt. % of the oil can be extracted. On an average, 15% oil can be extracted from spent coffee grounds. This oil can be converted into biodiesel easily and efficiently with transesterification methods[13].

In this work we have carried out studies on the waste coffee oil obtained from the coffee grounds, evaluating the characteristics and chemical composition of the biodiesel, besides any potential application in biodiesel production.

2. Materials and Method

2.1 Materials

Waste coffee grounds were collected from Turkey. All reagents used are methanol, H₂SO₄, CH₄, NaOH, CaCl₂ anhydrous, Na₂SO₄ anhydrous and Whatman filter paper size 150 mm (filter Fiorina, France) were purchased from local market.

2.2 Waste coffee oil extraction

The collected grounds were dried in an oven at 105° C to remove moisture (mostly 18-45 wt. %) and then the oil was extracted by applying a Soxhlet process. A low-boiling organic solvent such as n-hexane was used. The Soxhlet device temperature was kept at 65–70 °C. At the end of the process, the oil was separated from the organic solvent using rotary vacuum evaporator, dried at 60 °C and weighed. The yieldwas calculated on dry weight basis. The experimental results showed that the oil content of coffee grounds is between 10-15 % w/w (on a dry weight basis). The oil extraction process from waste coffee grounds is shown in **Fig. 1**.

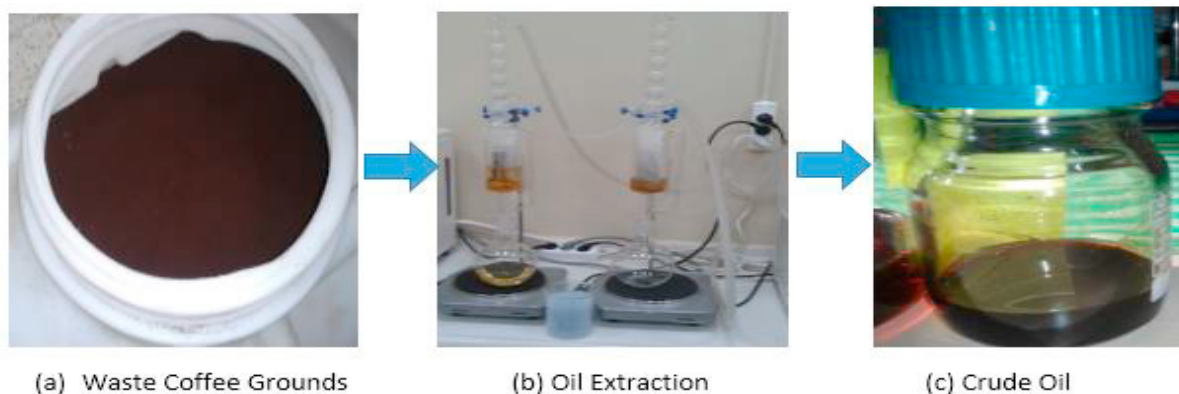


Fig. 1: Oil extraction process from waste coffee grounds.

The oil yield of waste coffee oil was calculated by the following equation:

$$\text{Oil yield} = \left(\frac{O_{so}}{W_{so}} \right) \times 100\%$$

Where O_{so} = the weight of extracted oil (g), W_{so} = the weight of waste coffee grounds (g).

2.2. Production of Waste Coffee Biodiesel

In this study, a small-scale laboratory reactor consisting of 1 L double-jacketed condenser, thermometer and motor stirrer was used to produce biodiesel from waste coffee oil. Fig. 2 shows the flow chart of biodiesel production process.

In the pre-treatment process, crude waste coffee oil was entered into a rotary evaporator and heated to remove moisture for 1 hour at 95°C under vacuum. In the esterification process, the molar ratio of methanol to refined oil was maintained at 12:1 (50% v/v). 1% (v/v) of sulphuric acid (H_2SO_4) was added to the pre-heated oils at 60°C for 3 hours under 600 rpm stirring speed in a glass reactor. On completion of this reaction, the products were poured into a separating funnel to separate the excess alcohol, sulphuric acid and impurities presented in the upper layer. The lower layer was separated and entered into a rotary evaporator and heated at 95°C under vacuum conditions for 1 hour to remove methanol and water from the esterified oil. In the transesterification process, crude waste coffee oil was reacted with 25% (v/v) of methanol and 1% (m/m) of potassium hydroxide (KOH) and maintained at 60°C for 2 hours and 600 rpm stirring speed. After completion of the reaction, the produced biodiesel was deposited in a separation funnel for 15 hours to separate glycerol from biodiesel. The lower layer which contained impurities and glycerol was drawn off.

Then the unrefined biodiesel was washed to remove the entrained impurities and glycerol. In this process, 50% (v/v oil) of distilled water at 60°C was sprayed over the surface of the ester and stirred gently. This process was repeated several times until the pH of the distilled water became neutral. The lower layer was discarded, and the upper layer was entered into a flask and dried using Na_2SO_4 and then further dried using a rotary evaporator to make sure that biodiesel is free from methanol and water.

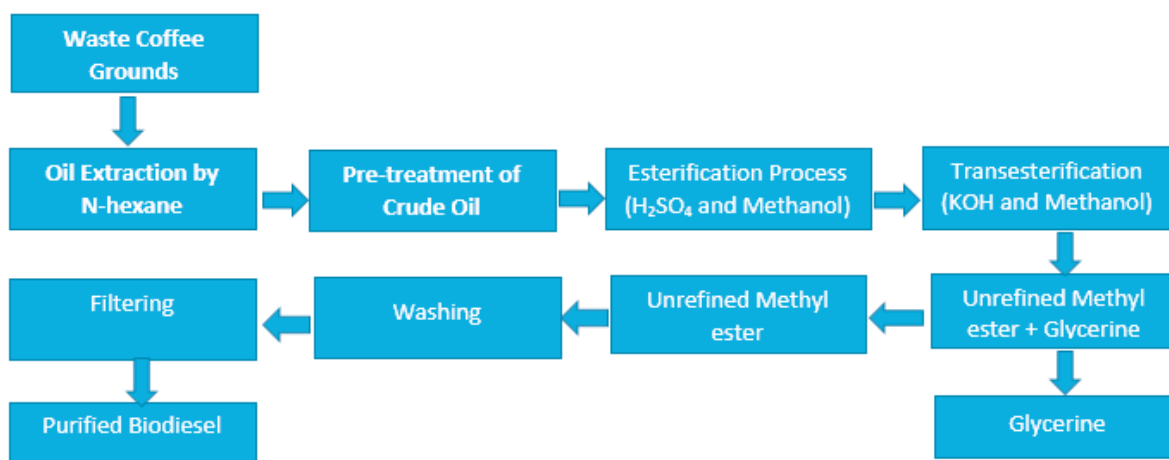


Fig. 2: Flow chart of oil extraction and biodiesel production process

2.3. Characterization of Crude Waste Coffee Oil and Biodiesel

The physical and chemical properties of the crude oil and biodiesel produced in this study were tested according to ASTM 6751 and EN 14214 standard. Table 1 shows a summary of the equipment and method used to analyze the properties.

Table 1: Summary of the equipment and method used to analyze the properties

Property	Equipment	Standard method	Accuracy
Kinematic viscosity	NVB classic (Norma lab, France)	ASTM D445	± 0.01 mm ² /s
Density	DM40 LiquiPhysics™ density meter (Mettler Toledo, Switzerland)	ASTM D127	± 0.1 kg/m ³
Flash point	NPM 440 Pensky-martens flash point tester (Norma Lab, France)	ASTM D93	± 0.1 °C
Cloud and pour point	NTE 450 Cloud and pour point tester (Norma lab, France)	ASTM D2500	± 0.1 °C
Acid number	Automation titration rondo 20 (Mettler Toledo, Switzerland)	ASTMD664	0.001 mg KOH/g
CFPP	NTE 450 CFPP tester (Norma lab, France)	ASTM D6371	± 0.1 °C

Cetane number (CN), Higher heating value (HHV), iodine value (IV), saponification value (SV), the degree of unsaturation (DU) and long chain saturated factor (LCSF) were calculated from the fatty acid profile of all biodiesel using following equations described by Mofijur et. al [2].

$$\text{CN} = 46.3 + (5458/\text{SV}) - (0.225 \cdot \text{IV}) \quad (1)$$

$$\text{SV} = \sum(560 \cdot A_i) / M_{wi} \quad (2)$$

$$\text{IV} = \sum(254 \cdot A_i \cdot D) / M_{wi} \quad (3)$$

$$\text{LCSF} = 0.1 \cdot (\text{C16:0, wt.}\%) + 0.5 \cdot (\text{C18:0 wt.}\%) + 1 \cdot (\text{C20:0 wt.}\%) + 1.5 \cdot (\text{C22:0 wt.}\%) + 2.0 \cdot (\text{C24:0 wt.}\%) \quad (4)$$

$$\text{DU} = \sum(\text{MUFA} + 2 \cdot \text{PUFA}) \quad (5)$$

Where A_i is the percentage of each component, D is the number of double bond and M_w is the molecular mass of each component.

2.4. Determination of Fatty Acid Composition

In this test 0.25g of waste coffee oil, biodiesel was diluted with 5ml n-heptane. The solution was then entered into GC (GC 7890A, Agilent Technologies). Table 2 shows the operating condition used to perform this analysis.

Table 2: Operating condition maintained for GC analysis

Property	Specification
Carrier gas	He at 23.878Psi
Linear velocity	44.124 cm/s at 100°C
Flow rate	Air = 450mL/min H ₂ = 40mL/min He = 20mL/min
Detector temperature	250°C
Column head pressure	23.878Psi
Column dimensions	30m x 0.25mm x 0.25µm
Injector	Type = split and splitless Split ratio 50:1 Injection volume.0.3µL
Temperature Ramp 1	100°C hold for 0 min
Temperature Ramp 2	10°C/min to 250°C hold for 5 min

3. Results and Discussion

3.1. Properties of Crude Waste Coffee Oil

The physicochemical properties of the waste coffee oil are presented in Table 3. The viscosity and acid values measured were high which are of 26.74 mm²/s and 15.42 mgKOH/g, respectively.

Table 3: The physical properties of crude waste coffee oil

Properties	Crude Waste Coffee oil
Density at 15 °C (kg/m ³)	934.40
Kinematic viscosity at 40 °C (mm ² /s)	26.74
Acid value (mg KOH/g)	15.42
Cloud point (°C)	10
Pour point (°C)	9

3.2. Physical Properties of Waste Coffee Oil Biodiesel

The fuel properties of waste coffee oil biodiesel were analyzed and compared with diesel, ASTM D6751 and EN 14214 standards[14]. Table 4 shows the fuel properties of waste coffee oil biodiesel. It was found that the kinematic viscosity of waste coffee oil biodiesel is 5.16 mm²/s, oxidation stability is 4 h, higher heating value is 39.67 MJ/kg and the acid value lowered to 0.5 mgKOH/g. Also, the cetane number was found 53 which is higher than diesel fuel. However, all these results are within the specified limit either ASTM D6751 or EN14214 standards (1.9–6 mm²/s). The flash point (FP) was found 192 °C, which is much higher than diesel fuel (68.5 °C) that indicates waste coffee oil biodiesel fuel is safer to handle and storage. The OS and HHV of waste coffee biodiesel were found 4 h and 39.67 MJ/kg, respectively.

Table 4: The physical properties of waste coffee oil biodiesel

Properties	Unit	Waste Coffee OilBiodiesel	Diesel	ASTM D6751	EN14214
Kinematic Viscosity at 40 °C	mm ² /s	5.16	3.23	1.9-6	3.5-5
Density at 15 °C	kg/m ³	895.0	827.2	-	860-900
Heating Value	MJ/kg	39.67	45.30	-	-
Oxidation Stability	h	4	-	3	6
Acid Value	mgKOH/g	0.5	-	0.05 max	0.5 max
Flash Point	°C	192.0	68.5	130 min	101 min
Pour Point	°C	14	0	-	-
Cloud Point	°C	13	8	report	-
CFPP	°C	7	5	-	-
Cetane Number	-	53	48	47 min	51 min
Iodine Number	-	85.89	-	-	120 max
Saponification Value	-	209.54	-	-	-

3.3. Chemical Properties of Waste Coffee Oil Biodiesel

Table 5 shows the fatty acid composition of waste coffee oil biodiesel. It can be seen that waste coffee oil biodiesel has 37.61% saturated and 62.27% unsaturated fatty acids. Linoleic acid (18:2) was the predominant fatty acid (28.71%) in biodiesel sample. The degree of unsaturation and long chain saturated factor was found 90.98 and 8.22, respectively.

Table 5: The chemical properties of waste coffee oil biodiesel

Fatty Acids	Molecular Weight	Structure	Formula	Waste Coffee OilBiodiesel (wt. %)
Myristic acid	228	14:0	C ₁₄ H ₂₈ O ₂	3.82
Myristoleic	226	14:1	C ₁₄ H ₂₆ O ₂	20
Palmitic	256	16:0	C ₁₆ H ₃₂ O ₂	19
Stearic	284	18:0	C ₁₈ H ₃₆ O ₂	6.73
Oleic	282	18:1	C ₁₈ H ₃₄ O ₂	9.27
Linoleic	280	18:2	C ₁₈ H ₃₂ O ₂	28.71
Arachidic	312	20:0	C ₂₀ H ₄₀ O ₂	2.96
Tricosanoic	338	23:0	C ₂₃ H ₄₆ O ₂	5.11
Lignoceric	368	24:1	C ₂₄ H ₄₆ O ₂	4.29
Total saturated fatty acid				37.61
Total monounsaturated fatty acid (MUFA)				33.56
Total polyunsaturated fatty acid (PUFA)				28.71
DU				90.98
LCSF				8.22

4. Conclusions

Coffee oil was extracted and chemically converted via an alkaline transesterification reaction to fatty acid methyl ester. Based on the preliminary results obtained it can be concluded that waste coffee oil biodiesel has good physical and chemical fuel properties especially higher heating value, flash point, cetane number and acid value. Only the

pour point and cloud point is not good enough, but that could be improved using different additives. Finally, it could be used a potential alternative, sustainable and environment-friendly fuel in diesel engines. A further study of blending of biodiesel with petrol diesel is suggested since it would be able to improve the waste coffee oil biodiesel properties in a diesel engine.

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