

Production and Investigation of Biodiesel Fuels from Spent Coffee Grounds

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Abstract: The oil fractions, extracted under different conditions from spent coffee grounds, were used to produce biodiesel fuels and investigate their FAME profiles. For producing of fuels, esterification and transesterification of oils with homogeneous catalysts were applied. Investigation of the esters composition (FAME) in biodiesel is carried out by modified gas chromatographic method EN 14103. The content of each individual ester was calculated using the method of internal standard. The results of total and individual FAME content in all studied objects are shown. The results show the feedstocks and extraction conditions (catalysts, temperatures) for obtaining the biodiesel with high yield and balanced composition.

Keywords: Coffee oil, spent coffee grounds, microwave irradiation, biodiesel feedstock, fatty acid methyl esters, gas chromatography.

1. INTRODUCTION

Biodiesel is defined as a fuel comprised of monoalkyl esters of long – chain fatty acids derived from vegetable oils, (sunflower, rapeseed, soy, palm), animal fats, waste cooking oil, algae and waste organic materials [1,2]. The resulting esters represent an excellent fuel for existing diesel engines. The benefits of biodiesel as fuel have been extensively studied and described in a large number of scientific papers.

Atadashi [3], Gerpen [4], and others authors [5] point out that using the biodiesel reduces greenhouse gas emissions in the atmosphere. Biodiesel is biodegradable, ready availability, non-toxic, non-flammable, environmentally friendly, contains no sulfur and aromatic compounds, so the exhaust emissions do not contain sulfur oxides and the total hydrocarbon content in them is 93% lower than in emissions of petroleum diesel [6]. Biodiesel has a higher cetane number (about 60 to 65) than diesel oil (53) and contains 10 - 11% oxygen, which contributes to its better burning [7]. It has good lubricating properties, it reduces corrosion and wear and increases overall engine efficiency [8]. Biodiesel can be successfully used in blends with petroleum diesel up to 20% (B20) without engine modifications. There is a higher ignition temperature, making it safe to transport and store [9, 10]. One of the main advantages of the biodiesel is that it reduces dependence on imported oil as local inputs

used for its production. The production of the biodiesel supports rural development because it has a good potential for employment.

The feedstocks for biodiesel production determine its properties. The two main biodiesel quality standards are ASTM D6751 [11] in the US and Canada and EN 14214 in Europe, developed by the European Committee for Standardization [12].

In the search for cheaper feedstocks in recent years, research on the use of waste from industry, agriculture and forestry and households has become more and more important: industrial wastes, mostly obtaining from waste water treatment [13], active sludge [14], waste fish oil [15,16], tall oil from the paper pulping process [17-19], spent coffee grounds [20-22], citrus seeds from orange juice production [23] and other wastes. Thus, the cost of these feedstocks is at present significantly lower than that of the edible and non-edible oils.

Coffee is one of the world's most widely consumed beverages. Spent coffee grounds (SCGs) are the main coffee industry residues. The biodiesel from spent coffee grounds possesses better stability than biodiesel from other sources due to its high antioxidant content [21, 24]. Statistical average annual consumption in Bulgaria is about 17-18 million kilograms of coffee. This would generate almost the same amount of SCG as a valuable cheap resource for extracted oil components to be processed into biodiesel fuel.

The scientific literature provides data on the compositional profile of biodiesel obtained from oil

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fractions extracted from SCGs. It can be seen that esters of palmitic (C16: 0), stearic (18: 0), oleic (C18: 1), linoleic (C18: 2), linolenic (C18:3) acids are predominant [25-30]. The amount of saturated and unsaturated acids is almost the same, with a slight excess of saturated acids.

Biodiesel properties with a similar FAME profile meet the standard specifications [25,30].

The aim of this study is to produce and investigate FAME profiles of biodiesel fuels from spent coffee grounds. In the course of the study, the conditions for obtaining high yield oil and biodiesel with balanced composition have been established.

2. EXPERIMENTAL PROCEDURES

2.1. Materials and Standards

The organic solvents n-hexane and methanol with analytical grade were obtained from Sigma-Aldrich (Switzerland). The reagents employed were anhydrous sodium sulfate (Na_2SO_4) and homogeneous catalysts H_2SO_4 (sulfuric acid) and NaOH (sodium hydroxide).

FAME Mix C14 – C22, Fatty acid methyl esters (C14:0; C16:0; C16:1; C18:0; C18:1; C18:2; C18:3; C20:0; C20:1; C22:0; C22:1; C24:0; C24:1) and methyl heptadecanoate (C17:0) were purchased from Sigma – Aldrich (Switzerland) and Supelco.

2.2. Samples

Residue of coffee “Bianchi” collected by vending-machines was used for the experiments. Eleven oil fractions extracted from spent coffee grounds were used to produce biodiesel fuels applying acid-catalysed esterification and alkali-catalysed transesterification.

2.3. Methods

2.3.1. Oil Extraction from Residue

We have previously developed a method for oil extraction from spent coffee grounds [31] and applied this method in the study.

2.3.2. Two Step Transesterification

Acid-Catalysed Esterification

The oil fraction (up to 500 mg) is dissolved in hexane (2 ml) in a test tube and 1% sulphuric acid in methanol is added. The mixture is left overnight in a stoppered tube at 50°C (or is refluxed for 2 h), then

water (10 ml) is added and the required esters are extracted with hexane (2×5 ml), using Pasteur pipettes to separate the layers. The hexane layer is dried over anhydrous sodium sulphate. The solution is filtered and the solvent removed.

Alkali-Catalysed Transesterification

The obtained ester extract from the first step is dissolved in hexane (1 ml) in a test-tube, 0.5 M sodium methoxide in anhydrous methanol (2 ml) is added, and the solution is maintained at 50°C for 10 min, then water (10 ml) is added and the required esters are extracted with hexane (2×5 ml), using Pasteur pipettes to separate the layers. The hexane layer is dried over anhydrous sodium sulfate. The solution is filtered and the solvent removed [32].

2.4. Biodiesel Sample Preparation for GC Analysis

Accurately weighed approximately 250 mg of sample is placed in 10 ml vial and 5 ml solution of internal standard (IS) is added. The solution of IS is 10 mg/ml methyl heptadecanoate in heptane [33]. The samples are then analyzed under the chromatographic conditions (2.5).

2.5. GC Analysis

GC analysis were carried out on a GC system Agilent Technologies 7890A equipped with FID, split/splitless injector and Agilent 7693 A automated liquid sampler. Column: HP INNOWAX, 30m x 0.32 mm ID, 0.25µm film thickness. Temperature program of the oven: initial temperature 210°C for 9 minutes, rate 20°C/min to 230°C, 10 minutes. Detector temperature: 300°C, injector temperature: 250°C. Carrier gas: He, column flow 1.5 ml/min, split ratio 1:80. Hydrogen flow 40 ml/min, air flow 400 ml/min, make-up gas (nitrogen) 40 ml/min. Injection volume 1µl. ChemStation for GC was used for instrument control, data acquisition and data analysis. The identification of fatty acids methyl esters was made using the standard mixture (2.1).

3. RESULTS AND DISCUSSION

Eleven oil extracts from spent coffee grounds (objects) were formed by a combination of factors - temperature, contact time, microwave irradiation of raw material and different solvent system (Table 1). The yield and fatty acid composition of the oil fractions were investigated. The optimum conditions of the process were established by applying multi-criteria optimization techniques [31].

Table 1: The Experimental Design - the Eleven Objects of Optimization

Objects	Dried at ambient conditions and microwave assisted pretreatment of SCG	
A	15-20°C	24 h
B	120-150°C	4h
C	450 W	20 min
D	600 W	20 min
E	300 W	20 min
F	300 W	30 min
G	450 W	30 min
H	600 W	30 min
I	600 W	10 min
J	450 W	10 min
K	300 W	10 min

The oil fractions, extracted under different conditions from spent coffee grounds, were used to produce biodiesel fuels. For producing of fuels,

esterification and transesterification with homogeneous catalysts were applied. Investigation of the esters composition (FAME) in biodiesel is carried out by applying a modified gas chromatographic method EN 14103 [33, 34].

Tables 2 and 3 show the contents of total and individual methyl esters in biodiesel obtained from feedstocks - oils from spent coffee grounds using *n*-hexane and *n*-hexane: methanol (1:1) as solvents. Feedstocks are marked with the same letters as objects in optimization (Table 1).

It can be seen (Table 2) that for feedstocks B, D and E the total amount of esters is very low. By this indicator, the feedstock A is the most suitable, since the biodiesel has the highest FAME content (76.1%). With lower FAME content (73.6% and 68.7%), but still high are characterized the feedstocks F and I. It is also seen that the individual compositions of the feedstocks A, F and I are almost the same except for C18: 2, which is likely to result in close properties of the biodiesels obtained. The total content of esters of

Table 2: FAME Content (%) Using *n*-Hexane as Solvent

F A M E	FEEDSTOCKS										
	A	B	C	D	E	F	G	H	I	J	K
C14:0	0.08	0.05	0.08	0.05	0.05	0.09	0.09	0.08	0.08	0.08	0.08
C16:0	29.8	19.46	22.30	16.08	15.98	28.50	25.50	20.80	28.10	26.10	21.40
C16:1	0.17	0.08	0.08	0.07	0.14	0.10	0.08	0.09	0.22	0.08	0.18
C18:0	7.00	4.55	5.24	3.71	3.87	6.77	5.80	4.94	6.59	6.10	5.70
C18:1	8.90	5.89	7.60	5.06	5.42	9.24	7.80	7.39	7.95	8.30	9.40
C18:2	23.90	14.66	13.60	11.07	13.79	21.90	16.10	13.80	18.82	21.30	25.10
C18:3	0.36	0.22	0.19	0.13	0.20	0.29	0.20	0.17	0.27	0.30	0.41
C20:0	3.01	1.96	2.54	1.70	1.67	3.02	2.66	2.37	3.06	2.66	2.49
C20:1	0.36	0.24	1.00	0.45	0.25	0.54	0.70	0.89	0.62	0.46	0.43
C22:0	0.53	0.34	0.57	0.35	0.33	0.63	0.58	0.52	0.62	0.60	0.51
C22:1	0.06	0.03	0.08	-	-	0.07	0.11	0.09	0.07	0.05	0.04
C24:0	0.26	0.18	0.20	0.14	0.12	0.25	0.22	0.21	0.27	0.23	0.22
C24:1	-	-	0.08	-	-	0.06	0.08	0.07	0.05	-	-
\sum_s	40.69	26.54	30.90	22.03	22.02	39.27	34.85	28.88	38.68	35.76	30.43
\sum_{unsat}	33.79	21.12	22.63	16.78	19.80	32.18	25.07	22.50	28.00	30.44	35.54
$-\sum_{\text{mus}}$	9.49	6.24	8.84	5.58	5.81	10.01	8.77	8.53	8.91	8.89	10.05
$-\sum_{\text{pus}}$	24.30	14.88	13.79	11.20	13.99	22.17	16.30	13.97	19.09	21.55	25.49
\sum_{FAME}	76.10	49.03	56.28	40.00	42.69	73.59	61.87	53.58	68.71	67.86	67.60

\sum_s - sum of esters of saturated fatty acids; \sum_{unsat} - sum of esters of unsaturated fatty acids; \sum_{mus} - sum of esters of mono unsaturated fatty acids; \sum_{pus} - sum of esters of poly unsaturated fatty acids; \sum_{FAME} - sum of FAME calculated by applying the gas chromatographic method EN 14103.

Table 3: FAME Content (%) Using *n*-Hexane: Methanol (1:1) as Solvent

F A M E	FEEDSTOCKS										
	A	B	C	D	E	F	G	H	I	J	K
C14:0	0.09	0.07	0.07	0.07	0.08	0.09	0.08	0.06	0.08	0.07	0.08
C16:0	28.50	25.10	21.90	23.60	25.90	27.80	25.90	19.29	28.90	27.40	28.70
C16:1	0.19	0.20	0.20	0.21	0.20	0.22	0.20	0.19	0.22	0.22	0.20
C18:0	6.67	6.27	5.51	5.73	6.17	6.57	6.28	4.64	6.82	6.47	6.57
C18:1	8.71	7.69	7.38	7.38	8.01	8.33	8.01	6.16	8.64	8.51	8.60
C18:2	21.80	16.75	15.76	15.48	18.18	17.51	15.94	9.30	18.67	18.46	20.60
C18:3	0.32	0.21	0.22	0.20	0.24	0.21	0.18	0.07	0.24	0.29	0.29
C20:0	2.88	2.77	2.53	2.76	3.12	2.94	2.92	2.21	3.13	2.87	2.79
C20:1	0.34	0.31	0.70	0.57	0.47	0.52	0.55	0.71	0.67	0.48	0.40
C22:0	0.52	0.51	0.60	0.61	0.58	0.58	0.62	0.47	0.65	0.59	0.53
C22:1	0.06	0.05	0.05	0.09	0.06	0.07	0.09	0.06	0.03	0.10	0.08
C24:0	0.22	0.22	0.23	0.25	0.24	0.23	0.25	0.17	0.26	0.24	0.21
C24:1	-	-	0.04	0.08	0.05	-	0.05	-	-	-	-
Σ_s	38.89	34.93	30.84	32.98	36.11	38.18	36.01	26.84	39.80	37.64	38.88
Σ_{unsat}	31.46	25.21	24.35	24.01	27.21	26.86	24.99	16.49	28.47	28.06	30.17
$-\Sigma_{\text{mus}}$	9.30	8.25	8.37	8.33	8.79	9.14	8.90	7.12	9.56	9.31	9.28
$-\Sigma_{\text{pus}}$	22.16	16.96	15.98	15.68	18.42	17.72	16.09	9.37	18.91	18.75	20.89
Σ_{FAME}	72.00	62.00	58.00	59.00	65.00	67.00	63.00	45.00	70.50	68.28	71.00

saturated and unsaturated acids in these objects is in the required balance.

The results in Table 3 show that feedstocks C, D and H are not appropriate since their biodiesel has a very low total FAME content. Again the content of esters from feedstock A (72.0%) is the highest. A little lower is the total content of esters from feedstocks I (70.5%). The content of individual esters and the total content of esters of saturated and unsaturated acids shows the same trends as in the previous table.

4. CONCLUSIONS

Spent coffee grounds were used as raw material for biodiesel production. It has been shown that coffee waste is an inexpensive and efficient biodiesel feedstock.

High yield biodiesel with balanced composition can be obtained by using oil extracted from the spent coffee grounds under the following conditions: drying at room temperature for 24 h and microwave radiation power of 600W for 10 min.

Highest total FAME content is obtained by transesterification of oil from SCG, when the residue was dried at room temperature for 24 h and the

extraction is carried out with *n*-hexane. A little lower, but also high is the ester content of this feedstock by using *n*-hexane: methanol (1:1) as solvent.

When SCG is microwave treated, highest total FAME content is obtained at microwave radiation power of 600W for 10 min using *n*-hexane: methanol (1:1) as solvent. A little lower, but also high is the ester content of this feedstock by using *n*-hexane.

The lower content of esters in the biodiesel from microwave treated SCG is successfully compensated by a much shorter pretreatment time - 24 h versus 10 min.

The total content of esters of saturated and unsaturated acids and distribution of individual esters in the biodiesel from both types of feedstocks is similar and it can be expected that the resulting biodiesel will have similar properties.

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