Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 55 (2) 74-81, 2013

A NEW APPROACH FOR PRODUCTION OF COFFEE OIL FROM WASTE COFFEE RESIDUE AS A FEEDSTOCK FOR BIODIESEL

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Received December 12, 2012, Accepted March 30, 2013

Abstract

The coffee oil is liquid and contains glycerides of palmitic, stearic, and linoleic acids, and small amounts of coffee sterol. The lipid substances are contained entirely within residue and almost are not extracted during the extraction in the coffee drink. In this study we were performed the microwave irradiation processing and drying at 120-150°C for 4 hours of the coffee residue from the vending machine. The products obtained were used as raw materials for the extraction of lipids by n-hexane. The lipid extract derived from the processing of coffee residue with microwave radiation power of 600W, contains the greatest amount of lipids (8.07%). This is probably due to the flow of high-energy cracking under the influence of powerful microwave radiation to the molecules in the coffee residue, resulting in increased total lipid content.

***Keywords**:* coffee oil; waste coffee residue; microwave irradiation; biodiesel feedstock; lipid extraction.

1. Introduction

The world is currently facing the worst energy crisis in history. Many countries worldwide are still heavily dependent on petroleum as their main source of electricity and transportation fuel, and its price has been setting record highs in recent days. Thus, the only possible solution to this crisis is to find a sustainable (renewable) and economically feasible source of alternative energy. There are many alternative energy sources such as wind, solar, geothermal and biomass that fulfill the first criterion (sustainability). However, few of these can fulfill the second criterion (economic feasibility). The best option, fulfilling both criteria, is biofuel, particularly that made from readily available biomass feedstock [1–3].

Biomass refers to all the vegetable matter that can be obtained from photosynthesis. The great versatility of biomass as a feedstock is evident from the range of materials that can be converted into various solid, liquid and gaseous fuels using biological and thermo-chemical conversion processes. Biomass energy is by far the largest renewable energy source, representing 10.4% of the world's total primary energy supply or 77.4% of global renewable energy supply [4, 5].

Vegetable oils include edible and non-edible oils. More than 95% of biodiesel production feedstocks come from edible oils since they are mainly produced in many regions and the properties of biodiesel produced from these oils are much suitable to be used as diesel fuel substitute [2]. However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel [6].

Moreover, it will cause deforestation in some countries because more and more forests have been felled for plantation purposes. In order to overcome these disadvantages, many researchers are interested in non-edible oils which are not suitable for human consumption because of the presence of some toxic components in the oils. Furthermore, non-edible oil crops can be grown in waste lands that are not suitable for food crops and the cost of cultivation is much lower because these crops can still sustain reasonably high yield without intensive care [2, 7].

However, most non-edible oils contain high free fatty acids. Thus they may require multiple chemical steps or alternate approaches to produce biodiesel, which will increase the production cost, and may lower the ester yield of biodiesel below the standards [8, 9, 10]. Animal fats contain higher saturated fatty acids and normally exist in solid form at room temperature that may cause problems in the production process. Its cost is also higher than vegetable

oils [11]. UFO is not suitable for human consumption but is a feedstock for biodiesel production. Its usage significantly reduces the cost of biodiesel production. However, the quality of UFO may cause concern because its physical and chemical properties depend on the contents of fresh cooking oil and UFO may contain lots of undesired impurity, such as water, free fatty acids [2,11- 13]. Since the cost of raw materials accounts about 60–80% of the total cost of biodiesel production, choosing a right feedstock is very important [2,11]. Also, the yield and properties of biodiesel products produced from different feedstocks would be quite different from each other.

Coffee, together with tea, is one of the most popular drinks across the world. Its commercial and social importance is obvious. Coffee production is located mainly in South America, Brazil being the first producing country (42%). Africa accounts for 20.4% of the total production and Asia produces 18.5%. Nevertheless, Europe is the main coffee consumer [14]. There are two varieties of the coffee plant with economic importance: Coffea arabica and Coffea canephora, known in the trade as arabica and robusta, respectively. Coffee beverages are made from roasted beans belonging to one of these two varieties or blends of them. The better quality coffees, and thus the most expensive ones, are considered to be the arabicas [15]. Frequently, green coffee beans of the arabica and robusta varieties can be distinguished by their size but the roasting process eliminates this macroscopic criterion. Therefore, reliable methods are required to differentiate these varieties [16].

Clearly, the procedures used in fat extractions are not standardized. In this study, we attempted to quantify the variation resulting from using different methods of waste coffee residue preparation and then lipid extraction by n-hexane, when it is used in Soxhlet extractor.

2. Experimental

2.1. Materials

The coffee residue "Bianchi" from vending-machine was used for the experiments. An organic solvent n-hexane with analytical grade was obtained from Sigma-Aldrich Ltd. (Germany).

3. Methods

3.1. Microwave assisted thermal treatment of the coffee residue

The experiment was conducted inside a fume hood in the laboratory using a Samsung MW 82N. The procedure used as the initial guideline for our experiment was as follows:

A) We were prepared 20g sample of coffee residue in 800cm^3 flask, cover with upside-down 750cm^3 flask.

B) Then we were placed in microwave cavity, microwave for 20 minutes at (300W, 450W and 600W).

C) Finally we were removed the product from microwave using tongs, allowed cooling, and weighting the solid pyrolyzate.

3.2. N-hexane oil extraction via Soxhlet apparatus

Oil extraction was performed using a Chemglass 300cm^3 Soxhlet apparatus with n-hexane as solvent. The Soxhlet apparatus allowed the extraction of oil from the coffee residue using a distillation extraction method. Twenty grams of coffee residue were placed into a porous cellulose thimble inside the extraction chamber. The extraction chamber was placed into the Soxhlet apparatus above a flask containing 300cm^3 of n-hexane and under an overhead condenser. The flask was submerged in a water bath and heated to approximately 90°C using a hotplate, evaporating the solvent into the condenser which trickled back down into the extraction chamber soaking the coffee residue. Eventually the oil was concentrated in the bottom flask, and the n-hexane was evaporated and reclaimed into another flask using an overhead condenser leaving only the lipids behind.

3.3. Analytical methods

3.3.1. Gas chromatography with mass spectrometry

To determine the fatty acid composition of the total lipid extracts, aliquots were subjected to acid-catalysed transesterification [17] and the resulting fatty acid methyl esters purified by thin layer chromatography on silica-coated glass plates using hexane:acetone (100:8 v/v) as developing solvent. After that, the purified fatty acid methyl esters were analysed by capillary gas chromatography as follows: Apparatus TRACE GC ULTRA (Thermo Fisher

Scientific, Bremen, Germany), equipped with a column 60m x 0.25mm x 0.25μm DB-225 (Agilent Technologies, Santa Clara CA, USA), and autosempler flame ionization detector, helium carrier gas a flow rate 1cm^3/min. Temperature gradient was used from 120°C to 240°C with step of 5°C/min and hold at final temperature 25 min. The temperature of injector and detector was 260°C. Identification of fatty acids was made from a standard mixture and confirmed by gas chromatography with mass spectrometry.

First of all, a class of neutral lipids were identified by analytical thin-layer chromatography (TLC) on laboratory prepared glass plates with 4x19cm layer of silica gel with a mobile phase hexane-acetone (100:8, v/v) versus standard mixture containing sterol ester, methyl ester, triacylglycerol, diacylglycerol, sterol monoacylglycerol and free fatty acid. The separated zones were visualized by spraying the layer with 50% sulfuric acid in ethanol and charring on a plate heated to 200°C.

The amount of individual lipid classes was determined by preparative TLC gravimetry, using laboratory-prepared glass plates with 20x20cm layer of silica gel. To do this on the plate are mapped (exactly weighed) 100 mg sample as a solution in hexane, poster is shown with a mobile phase of hexane-acetone (100:8, v/v) was sprayed with 0.1% solution in ethanol solution of 2', 7'-dihlorfluorestcein, areas outlined under UV light (366 nm), were scraped, and were transferred into glass columns and eluted with diethyl ether in pre-weighed containers. After evaporation of the eluent under a stream of nitrogen was determined the weight of each zone and restated its percentage in the sample.

3.3.2. FT-IR spectrometry

The FT-IR spectra were recorded using KBr pellets. The samples were prepared as follows: 2 mg of the studied samples were grounded together with 200 mg KBr (Merck) into the fine powder with the particles size below 5 μm and compressed to form of clear disk. The FT-IR spectra were recorded using Brücker Tensor-27 spectrometer at ambient temperature in the wave number 4000-400cm^{-1}.

4. Results and discussion

The chemical composition of coffee is complex, and it was largely solved by various chemical and instrumental methods. There are significant changes in the composition of raw and roasted coffee. Of importance is also its origin, and in roasted coffee and technology (level and duration) of roasting.

The raw coffee contains: water - 8.15%, lipids - 10.95%, protein - 11.29%, mineral salts - 4.14%, insoluble in water, alcohol and benzene substances - 47.6%.

The coffee oil is liquid and contains glycerides of palmitic, stearic, and linoleic acids, and small amounts of coffee sterol. The lipid substances are contained entirely within residue and almost are not extracted during the extraction in the coffee drink.

Microwaves are electromagnetic waves with wavelengths longer than infrared light, but shorter than that of radio waves. The microwaves, known as radio waves with ultra high frequency, have wavelengths approximately in the range of 30 cm (frequency = 1GHz) to 1 mm (300GHz). However, the boundaries between the lower limit of the infrared light, microwaves and radio waves are contingent and accepted differently in different areas.

The first step of our study was the treatment with microwave irradiation /according to the procedure described above in the experimental part/ and drying at 120-150°C for 4 hours of raw material /coffee from the vending machine/. The products obtained after processing were used as raw materials for the extraction by n-hexane. The quantities of the original material before and after treatment are presented in Table 1 and 2.

The second step of our study was the extraction of lipids from coffee, dried at 150°C for 4 hours and treated coffee residue under different conditions with microwave irradiation by the methodology described above in the experimental section.

To characterize the composition of the extracts we used the methods of IR spectroscopy and gas chromatography with mass spectrometry. The resulting IR spectra of the extracts are similar /Fig. 1/ and the data from them can be interpreted as follows:

There is a fundamental characteristic brand for triglycerides at 1745 cm^{-1}, which falls in the range of 1763 to 1730 cm^{-1}. The other bands are in the spectral range of (cm^{-1}): 1491 to 1448, 1429 to 1400, and 1390 to 1367. An indication for unsaturated compounds is the characteristic oscillation at 3009 cm^{-1} and deformation vibrations for δ=CH_2- at 1418 cm^{-1}. The brands at 2924 cm^{-1} and 2853 cm^{-1} belong to the valence vibrations of CH_2-group (asymmetrical and symmetrical). The brand at 722 cm^{-1} is typical for more than

four CH_2-groups present in the spectra of compounds containing CH_2- long-chain higher fatty acids.

Table 1. Lipid content after extraction of the material irradiated by microwave.

№	Coffee residue, g.	Microwave irradiation, W	Time of irradiation, min.	Raw material for extraction, g	Time of extraction, h	Product, g.
1.	20	600	20	13.7527	2	1.5092
2.	20	450	20	16.4640	2	1.4276
3.	20	300	20	17.7204	2	1.5105

Table 2. Lipid content after extraction of the dried material.

№	Coffee residue, g.	Temperature of drying, °C	Time of drying, h.	Raw material for extraction, g	Time of extraction, h	Product, g.
1.	20	150	4	20	2	0.8577
2.	20	20	24	20	2	1.6805

The results of gas chromatographic analysis of the lipid extracts are shown in Fig. 2-6. Based on the chromatograms above we were quantified the fatty acid composition of the methyl esters of fatty acids and neutral lipid classes. The data are presented in Table 3 and 4.

Table 3. A fatty acid composition of the total lipids.

Name of fatty acid	Lipid extract from coffee residue (%)				
	irradiated by 450W microwave for 20 min.	irradiated by 300W microwave for 20 min.	dried at 20°C for 24 hours.	dried at 120-150°C for 4 hours.	600W microwave for 20 min.
C14:0 (Myristic)	0.1	0.1	0.1	0.2	0.1
C16:0 (Palmitic)	33.2	34.0	32.3	39.9	37.1
C18:0 (Stearic)	7.6	7.9	6.9	9.9	8.5
C9-18:1 (Oleic)	12.3	11.8	12.1	14.0	12.6
C11-18:1 (Ricinoleic)	0.4	0.4	0.4	0.5	0.4
C18:2 (Linoleic)	40.4	39.5	43.1	27.9	35.0
C18:3(Linolenic)	0.7	0.7	0.8	0.1	0.4
C20:0(Arachidic)	3.6	3.7	3.0	4.9	4.0
C20:1 (Gadoleic)	0.4	0.5	0.4	0.5	0.4
C21:0(Heneicosanoic)	0.1	0.1	0.1	0.2	0.1
C22:0 (Beheric)	0.7	0.9	0.5	1.1	0.8
C23:0 (Tricosanoic)	0.1	0.1	0.1	0.2	0.2
C24:0 (Lignoceric)	0.4	0.3	0.2	0.6	0.4

Table 4. The neutral lipid classes of the lipid extracts.

Lipid class	Lipid extract from coffee residue (%)				
	irradiated by 450W microwave for 20 min.	irradiated by 300W microwave for 20 min.	dried at 20°C for 24 hours.	dried at 120-150°C for 4 hours.	irradiated by 600W microwave for 20 min.
sterol esters	5.2	5.8	5.2	5.6	4.9
triacylglycerols	65.7	65.4	67.1	46.8	56.0
non identified lipid zone	5.0	3.8	7.5	8.4	4.2
Sterols + diacylglycerols + free fatty acids	16.8	18.2	15.7	24.3	23.7
monoacylglycerols + Polar lipids	7.3	6.8	4.5	14.9	11.2

The data for the quantitative interpretation of the fatty acid composition classes and neutral lipids are presented at the figures 7-8.

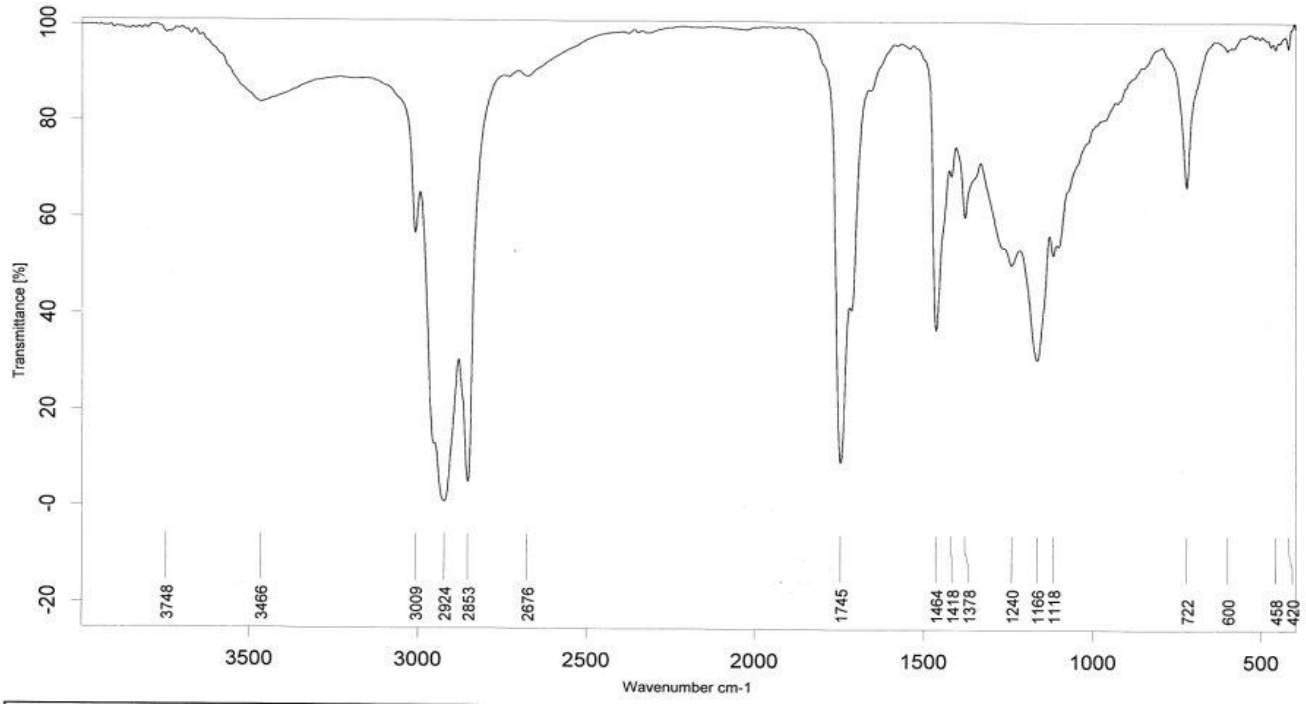

Fig. 1. IR spectra of lipid extract, obtained by n-hexane extraction of the coffee residue from vending-automat.

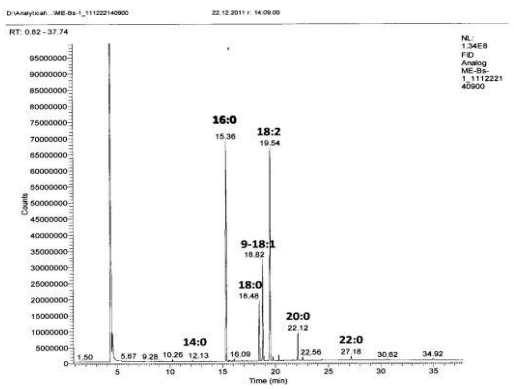

Fig. 2. GC chromatogram of the lipid extract from coffee residue irradiated by 450W microwave for 20 minutes

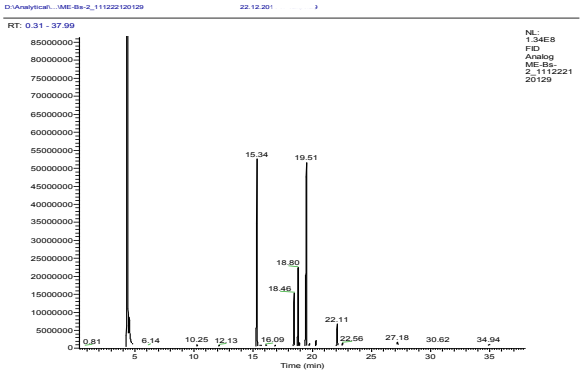

Fig. 3. GC chromatogram of the lipid extract from coffee residue irradiated by 300W microwave for 20 minutes

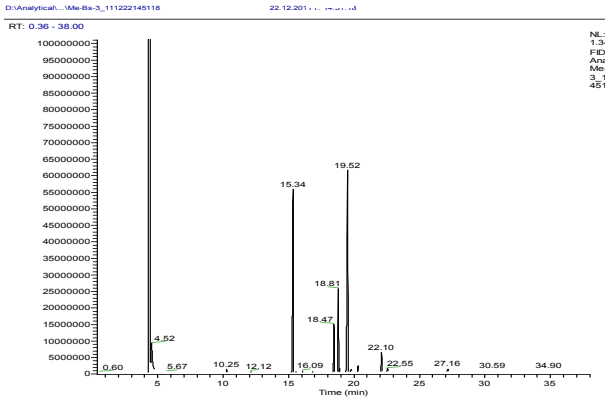

Fig. 4. GC chromatogram of the lipid extract from coffee residue dried at 20°C for 24 hours

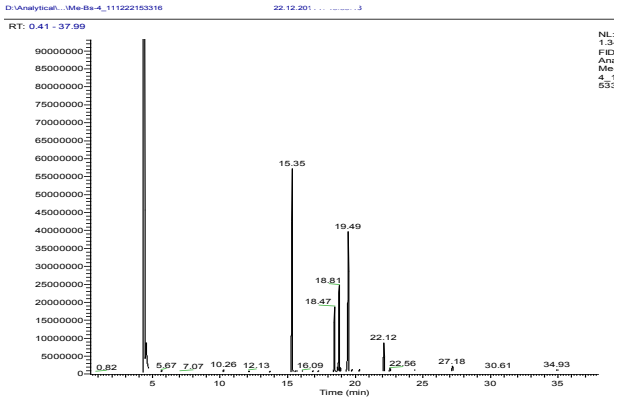

Fig. 5. GC chromatogram of the lipid extract from coffee residue dried at 120-150°C for 4 hours

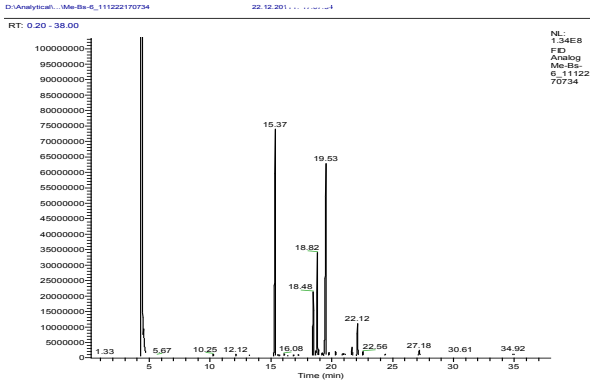

Fig. 6. GC chromatogram of the lipid extract from coffee residue irradiated by 600W microwave for 20 minutes

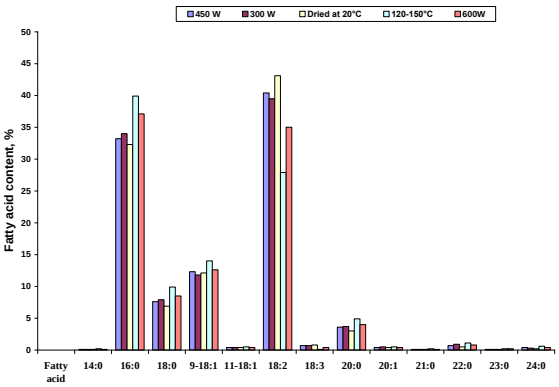

Fig. 7. Fatty acid content based on the results from Table 3.

From our study and the data shown in Figure 7, we observe that any type of pretreatment (microwave irradiation or heat treatment only) of coffee residue from vending automat increases the amount of saturated fatty acids.

The palmitic and linoleic acids have the highest percentage in the analyzed extracts. The amount of stearic, oleic and arachidic acids are significant. The percentage of all other fatty acids is less than one.

If the coffee residue is not processed in any way, the greatest is the amount of unsaturated fatty acids with more than one double bond. The residue treated at 120-150°C have a significant content of saturated fatty acids and those containing one double bond, and therefore the least amount of fatty acids with two or more double bonds.

The coffee residue that was treated at 600W microwave has the fatty acid composition similar to those of residue processed at 120-150°C. The residue processed at 450W microwave irradiation has the fatty acid composition similar to those of residue dried at 20°C. The sample treated at 300W microwave irradiation has a similar composition as those processed at 450W microwave irradiation.

The triacylglycerols have the higher content in the neutral lipids (over 45%). This rate is the lowest in the sample that was treated at 120-150°C (46.8%). The residue dried at 20°C has the highest percentage of triacylglycerols (67.1%). The residues dried at 120-150°C and irradiated at 600W microwave have the higher percent of sterols, diacylglycerols, and free fatty acids in sum.

The percentage of lipids is calculated from the original sample by the extraction that was made. In our case, when we were added the amounts of lipid classes and adjustment to lipid extract were obtained the percentages of dyes, etc. accompanying substances that differ in polarity of the lipid classes. Based on the data from Figure 9 and Tables 5 and 6, we can say that the lipid extract derived from the processing of coffee residue with microwave radiation power of 600W, contains the greatest amount of lipids (8.07%). This is probably due to the flow of high-energy cracking under the influence of powerful microwave radiation to the molecules in the coffee residue, resulting in increased total lipid content.

Due to the higher melting point of saturated fatty acids and correspondingly lower oxidative stability of the unsaturated fatty acids containing one or more double bonds have to find their balanced composition in the production of biofuels. The sample obtained at 600W microwave has the balanced composition of saturated and unsaturated fatty acids of approximately 50%. This allows us to offer exactly this way of handling the raw material to obtain the biodiesel.

Table 5. Lipid content of the extracts from sources irradiated by microwave.

Coffee residue, g.	Microwave irradiation, W	Time of irradiation, min.	Raw material for extraction, g	Time of extraction, h	Product, g.	Total lipid content, %
20	600	20	13.7527	2	1.5092	8.07
20	450	20	16.4640	2	1.4276	5.94
20	300	20	17.7204	2	1.5105	5.63

Table 6. Lipid content of the extracts from dried sources.

Coffee residue, g.	Temperature of drying, °C	Time of drying, h.	Raw material for extraction, g	Time of extraction, h	Product, g.	Total lipid content, %
20	150	4	20	2	0.8577	2.29
20	20	24	20	2	1.6805	5.63

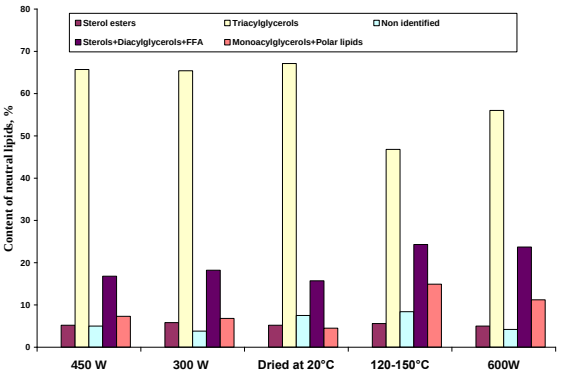

Fig. 8. Data for the content of neutral lipids from extracts based on the results for Table 4

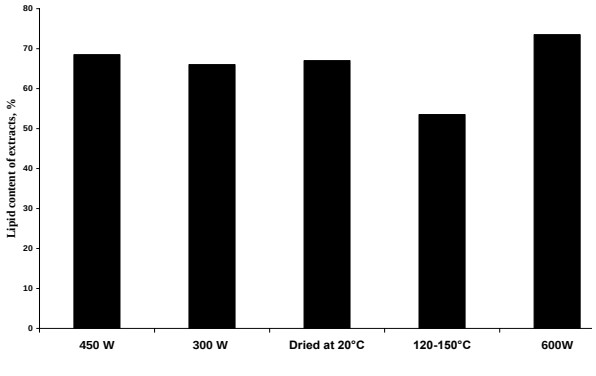

Fig. 9. Lipid content of the extracts.

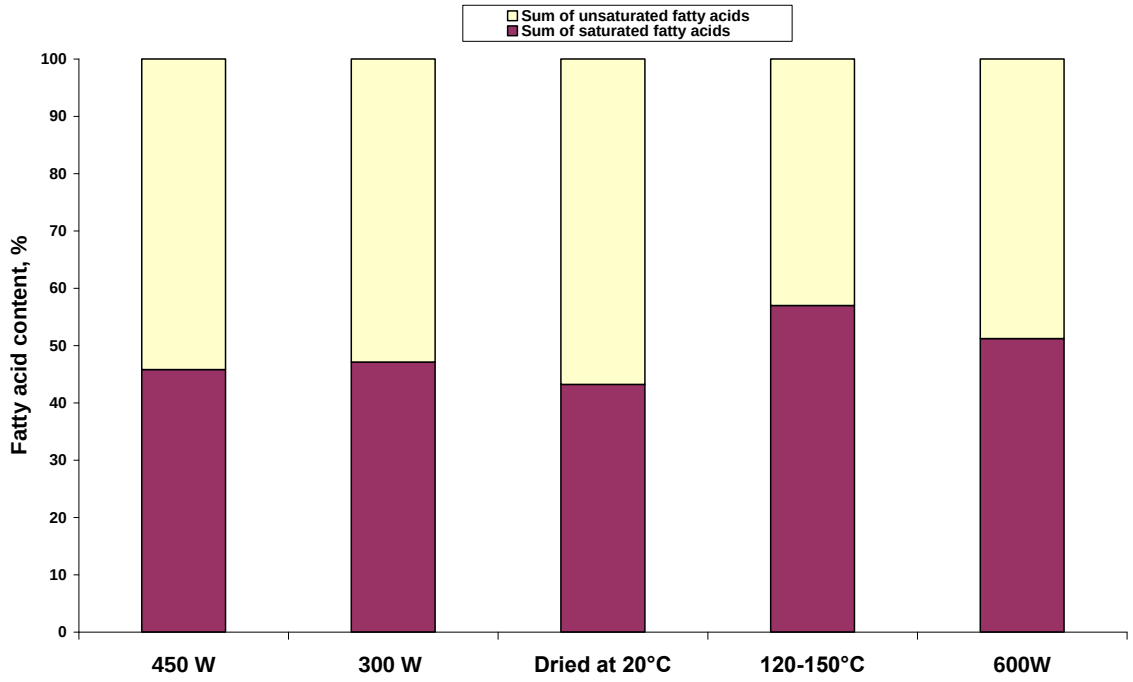

Fig. 10. Content of the unsaturated and saturated fatty acids in the extracts.

5. Conclusions

1. We were performed the microwave irradiation processing and drying at 120-150°C for 4 hours of the coffee residue from the vending machine. The products obtained were used as raw materials for the extraction of lipids by n-hexane.
2. From our study we may conclude that microwave irradiation and heat treatment of the coffee residue increase the amount of saturated fatty acids of the coffee oil.
3. The lipid extract derived from the processing of coffee residue with microwave radiation power of 600W, contains the greatest amount of lipids (8.07%). This is probably due to the flow of high-energy cracking under the influence of powerful microwave radiation to the molecules in the coffee residue, resulting in increased total lipid content.
4. The sample obtained at 600W microwave has the balanced composition of saturated and unsaturated fatty acids of approximately 50%. This allows us to offer exactly this way of handling the raw material to obtain the biodiesel.

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