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Optimization of the Oil Extraction, Study the Chemical and Physical Properties of Arabica Spent Coffee Grounds

Sasikarn Panpraneecharoen*, Saowapa Chumanee

Division of Chemistry, Faculty of Science and Technology, Phetchabun Rajabhat University, Phetchabun 67000, Thailand

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ABSTRACT

This research is to study the extraction of oil from Arabica spent coffee grounds with hexane solvent. The extraction time was 1, 2, 4, 6 and 8 hours by using the soxhlet method. The result found that the 2 hours of 100% n-hexane was the highest yield of 14.42±0.43 g/100g of dry basis. Linoleic acid and palmitic acid were the major fatty acids found in coffee oil. The physical and chemical properties of coffee extracted oil was investigated. The result showed that the FFA was 7.52±1.23%, the peroxide value was 23.96±2.09 mgEqv/kg oil, the density was 1.38±0.04 g/cm^3, the viscosity was 34.66±0.41 cSt, the iodine value was 97.25 g I_2/100g and the saponification number was 204.12 mgKOH/g. The main functional groups of coffee oil were characterized by using the FTIR spectroscopy.

Keywords: Oil extraction; Spent coffee grounds; Arabica coffee; Physical property; Chemical property

1. Introduction

Coffee is one of the most favorite and popular beverages around the world, being consumed for its stimulating and refreshing properties, which are defined by the green beans composition and changes occurring during the roasting process [1]. Two species of coffee with significant economic importance are coffee Arabica providing 75% and coffee Robusta providing 25% of the world production [2]. Nowadays, the coffee business is expanding rapidly. Coffee shops, as well as the coffee industry, are responsible for generating large quantities of residues. Spent coffee grounds are the residual material obtained during the treatment of roasted coffee powder with hot water or steam for the instant coffee preparation. Almost 50% of the worldwide coffee production is processed for soluble

***Corresponding author:** preaw_parn@hotmail.com **doi:** 10.14456/scitechasia.2020.45

coffee preparation, which generates around 6 million tons of spent coffee grounds per year [3]. Spent coffee grounds are solid residues from natural materials, the composition of which depends on the species of coffee beans, cultivation area, roasting conditions and extraction process. The composition of spent coffee grounds includes 1) an oil fraction (7.9-26.4%), 2) crude fiber (19.7-22.1%), and 3) different components such as alkaloids, proteins, etc. [4].

In recent years, research has been developed for the spent coffee grounds and their application. Sumnuk et al. optimized the four solvents extraction, hexane, anhydrous ethanol, hydrous ethanol and methanol from spent coffee grounds. The 14.7% wt of oil was obtained as the highest efficiency and stability of coffee oil yield from the hexane solvent extraction [5]. Haile investigated the waste coffee ground for biodiesel production. They found that the major fatty acids were found to be linoleic acid (39.8%), palmitic acid (37.6%), oleic acid (12.7%), and stearic acid (7.6%). The 73.4%w/w biodiesel conversion was obtained by a two-step process, i.e. acid catalyzed esterification followed by base catalyzed transesterification using catalysts sulphuric acid and sodium hydroxide, respectively [6]. Moreover, spent coffee grounds could be used as a feed utilization. Rahimnejad et al. reported on the use of spent coffee grounds as an ingredient for fish feed. They studied the terms of growth performance, feed utilization, body composition, and antioxidant enzyme activity [7]. In addition, Scully et al. investigated the espresso spent coffee grounds as a renewable source of bioactive compounds and industrially important sugars. They found that spent espresso coffee grounds could be systematically exploited as biomass for the production of fermentable sugars glucose, mannose, galactose and arabinose, in addition to extractable lipids, polyphenols and caffeine [8]. Phung et al. evaluated the content of lipid hydroperoxide, total phenolic content, flavonoid content and antioxidant in spent coffee ground extracts. They showed that the oil recovery yield was in the range from 9.42% to 17.96%. The phenolic recovery yield was between 5.76% and 12.3%. The results indicated the high antioxidant capacity of the extract [9].

Khao Kho District, Phetchabun Province had been named “Switzerland of Thailand” because there is beautiful scenery and cold climate. As a result, there are many coffee shops appearing nowadays. In addition, many tourists in Khao Kho like to drink coffee and that causes a lot of coffee grounds after consumption. In this research, the aim of the present study consisted in evaluating the oil extraction, chemical and physical properties of extracted coffee oil from Arabica spent coffee grounds in Khao Kho District, Phetchabun Province, as a low-cost and versatile resource material. The extracted coffee oil could be used in multiple applications in the biomass field and developed for the renewable energy industrial areas.

2. Materials and Methods

2.1 Materials

Arabica spent coffee grounds, provided by a local rice mill from Narin Coffee Plantation, Khao Kho District, Phetchabun Province, Thailand were used as a raw material for the oil extraction. All chemicals were purchased from Labscan (Thailand).

2.2 Oil extraction

The extracted oil was determined by gravimetric analysis using 100% n-hexane as a solvent. The 10 g of dry spent coffee grounds were settled in a cellulose thimble. The extraction was performed for 1, 2, 4, 6 and 8 h in a soxhlet apparatus with 200 ml of solvent. After extraction, the solvent was evaporated under vacuum and the oil

fraction was dried until a constant weight in an oven at 60°C. Then, the yield of extracted oil was calculated by using equation (1). The dried material was sampled in triplicate.

$$\%\text{Yield} = \frac{a}{b} \times 100, \quad (1)$$

when a is weight of extracted oil (g) and b is weight of dry spent coffee ground (g).

2.3 Characterization of extracted coffee oil

2.3.1 Free fatty acid content and peroxide value

The free fatty acid (FFA) content and peroxide value (PV) were determined following AOCS official methods [10]. For the FFA content analysis, the 0.5 g sample of extracted oil was mixed with 50 ml of ethanol and phenolphthalein indicator was added. Then, the sample was titrated with 0.1 M NaOH standard solution by vigorously shaking until the appearance of the first faded pink color. The percentage of FFA was calculated following the AOCS Official Method Ca 5a-40. For the PV analysis, the 0.5 g sample of extracted oil was mixed with 30 ml of 3:2 %v/v of acetic acid to chloroform and 0.5 ml of saturated solution potassium iodide and 30 ml of distilled water. Then, the sample was titrated with 0.01 M sodium thiosulfate by vigorously shaking until the appearance of the light-yellow color. After that, starch indicator was added and the sample solution turned blue color. Then the sample was titrated with 0.01 M sodium thiosulfate by vigorously shaking until the blue color faded. The percentage of PV was calculated following the AOCS Official Method Cd 8b-90.

2.3.2 Fatty acid composition using gas chromatography

The extracted oil from spent coffee grounds was examined for fatty acid composition of the oil using gas chromatography (GC). Briefly, seed oils were methylated with boron trifluoride in methanol followed with NaOH/methanol treatment to form methyl esters as described by the AOAC 969.3 official method [11]. The fatty acid methyl esters were identified using GC equipment with a chromatography analysis section using the capillary column SP-2560 100m x 0.25mm x 0.2um Supelco, USA. The oven temperature was set from 70 to 240 °C. The injector temperature was maintained at 240°C split 10: 1 and the detector temperature was set at 250 °C throughout the experiment. A flame ionization detector (FID) was used for the analysis. The carrier gas flow was helium. The fatty acid methyl esters (FAME) were analyzed by using an internal standard solution and by comparing the retention time and quantification performed by the area normalization method.

2.3.3 Iodine value and saponification number

The iodine value (IV) and saponification number (SN) were determined following equations (2) and (3), respectively [12].

$$IV = \frac{\sum(254 \times D \times A_i)}{MW_i}, \quad (2)$$

$$SV = \frac{\sum(560 \times A_i)}{MW_i}, \quad (3)$$

where

A_i is the percentage of each fatty acid component,

D is the number of double bonds of each fatty acid, and
MW_i is the average molecular weight of each fatty acid.

The parameters attesting for the quality of the oil were estimated in relation to the molecular structures, which may vary according to carbon chain sizes and the amount and/or position of double bonds. These molecular characteristics greatly influence the main parameters of oil quality.

2.3.4 Fourier transform infrared spectroscopy (FT-IR) analysis

The IR spectrum of extracted oil was recorded with an FT-IR instrument (PerkinElmer, USA). The dark brown oil was placed on diamond crystals for attenuated total reflectance spectroscopy. A background spectrum was taken before the run sample spectrum. The spectrum was collected in the range of 4,000-400 cm^{-1}.

2.3.5 Density and viscosity analysis

The density and viscosity were determined following ASTM D1298 and ASTM 445, respectively [13]. The density was explained by containing the extracted oil into a pycnometer at 15°C and weighing it. The relative density was calculated from this weight and the previously determined weight of water that was required to fill the pycnometer at the same temperature. The viscosity was explained by containing the extracted oil into a viscometer, allowing approximately 10 minutes for the sample to come to the bath temperature at 40°C, and measuring the efflux time. The kinematic viscosity in mm^2/s (cSt) of the sample was calculated by multiplying the efflux time in seconds by the viscometer constants.

3. Results and Discussion

3.1 Oil content

After extraction of spent coffee ground oil using soxhlet apparatus with hexane solvent, the freshly extracted oil was dark brown in color having a mild coffee odor. In the previous research, the oil content in the coffee source varies from 11 to 20 wt.% depending on its type and the extraction process [14]. Table 1 shows the %yield of extracted oil by using 100% hexane as a solvent and different extraction times. The yield of coffee oil ranges from 13.59±0.22 wt.% to 14.42±0.43 wt.% on a dry weight basis. In many research studies, the coffee oil from spent coffee grounds contains 10–15 wt.% with the various extraction methods such as the solvent extraction or supercritical fluid extraction [5, 15].

Table 1. Oil content of the spent coffee grounds.

Extraction time (h)	% Yield of extracted oil (wt.%)
1	$13.59±0.22^b$
2	$14.42±0.43^a$
4	$14.22±0.08^a$
6	$14.40±0.14^a$
8	$14.41±0.29^a$

Values are means±standard deviation (n=3). Values in the same column with the same superscript letter are not significantly different (Duncan, $p > 0.05$).

In this study, the highest yields of oil were extracted with 100% hexane (non-polar solvent) 14.42±0.43% in 2 hours of extraction time from soxhlet extraction, similar to that reported by Somnuk et al. The soxhlet extraction was a very uncomplicated and low-cost technique. Moreover, this method could extract more sample yield than other methods because it constantly keeps the system from equilibrium by extracting the sample from solid matrix to solvent. In the other extraction techniques, such as microwave, ultrasound assisted extraction or supercritical fluid extraction was needed to improve the design and scale of these new extraction methods to enhance their lab scale to industrial applications, but those

have a high cost of investment and technical complexity [16].

Additionally, the hexane solvent used for extraction was observed to have extracted the least amount of crude extracts and is not significantly influenced ($p > 0.05$) by extraction time beyond 2 h. This might be due to the fact that the main chemical structures of lipid, fat or oil are non-polar and the hexane solvent carried no or only low charges. The extraction process was based on like-dissolve-like principle that affects the extraction efficiency. The non-polar solvents were better suited to oil extraction than polar ones. Thus, they were able to penetrate into the low polar matrix of spent coffee grounds.

3.2 Fatty acid composition

The fatty acid profile of oil is the most important factor which affects the overall commercial success of coffee cultivation and its use as an industrial crop. The linoleic acid (C18:2) and palmitic acid (16:1) are the major fatty acid composition in coffee oil. Fig. 1 and Table 2 explain fatty acid composition of coffee oil by GC analysis.

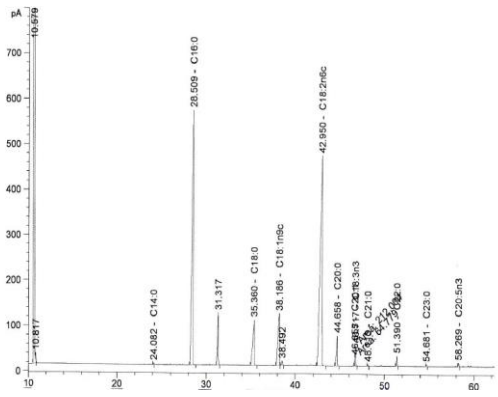

Fig. 1. GC chromatogram of coffee oil.

Table 2. Fatty acid composition of coffee oil.

Common name	Fatty acid	Content (wt.%)
Myristic acid	C14 : 0	0.07±0.01
Palmitic acid	C16 : 0	33.75±0.15
Stearic acid	C18 : 0	7.26±0.32
Oleic acid	C18 : 1	7.72±0.13
Linoleic acid	C18 : 2	44.64±0.37
Linolenic acid	C18 : 3	2.16±0.01
Arachidic acid	C20 : 0	3.04±0.08
Eicosenoic acid	C20 : 1	0.26±0.00
Eicosapentaenoic acid	C20 : 5	0.26±0.00
Heneicosanoic acid	C21 : 0	0.08±0.01
Docosanoic acid	C22 : 0	0.66±0.03
Hexacosanoic acid	C23 : 0	0.09±0.01

Table 2 shows the amount of each fatty acid. The results show that the main fatty acids are linoleic acid (44.64±0.37 wt.%), followed by palmitic acid (33.75±0.15 wt.%), oleic acid (7.72±0.13 wt.%), stearic acid (7.26±0.32 wt.%), arachidic acid (3.04±0.08 wt.%) and linolenic acid (2.16±0.01 wt.%), respectively. The summation of saturated fatty acid was 44.95 wt% and the summation of unsaturated fatty acid was 55.04 wt.%.

The average molecular weight (g/mol) of coffee oil was determined by a weight average method utilizing the fatty acid compositions. Specifically, the molecular weight of each fatty acid found in acid oil was multiplied by its corresponding weight percentage as determined by GC. The sum of these values was divided by one hundred, resulting in an average molecular weight of both acid oils. The results showed the average molecular weight of fatty acid and molecular weights of triglyceride obtained from of coffee oil were 274.34 and 861.05 g/mol, respectively.

A comparison of the fatty acid composition in our work with that of Somnuk et al., who also studied the variability of extracted oil from spent coffee ground in Thailand, showed similarities as the fatty acid composition of coffee oil had a high in linoleic acid (43.12%) and palmitic acid (34.44%) [5].

3.3 Chemical and physical properties

After extraction of coffee oil using the soxhlet apparatus with hexane solvent, the freshly extracted coffee oil was dark brown in color. The data collected from the study of physical and chemical properties of coffee oil are shown in Table 3.

Table 3. The chemical and physical properties of coffee oil.

Chemical and physical properties	Extracted coffee oil
FFA (%)	7.52±1.23
Peroxide value (mg Eqv/kg oil)	23.96±2.09
Density (g/cm^3)	1.38±0.04
Viscosity (cSt)	34.66±0.41
Iodine value (g I_2/100 g)	97.25
Saponification number (mgKOH/g)	204.12

Values are means±standard deviation (n=3).

Free fatty acid (FFA) and peroxide value (PV) were the important parameters used for determination of the chemical quality of the extracted coffee oil. The high FFA and peroxide value content in these oils will increase the oxidation reaction, reduce oil stability and degradation. The results found that the coffee oil contained the highest 7.52±1.23% of FFA and 23.96±2.09 mgEqv/kg oil of peroxide value. Al-Hamamre et al. reported the FFA in coffee oil from spent coffee ground extraction. They found that the high FFA content was in the range 3.25-6.40% [14]. The high FFA content also affects the physical properties in oil because the density and viscosity of oil increase. The density and viscosity in this study were 1.38±0.04 g/cm^3 and 34.66±0.41 cSt, respectively.

The iodine value provides information about the coffee oil samples unsaturation. The recorded values were situated in the range 76-101 g I_2/100 g, available in the literature for coffee oil. In addition, the European organization standard mentioned earlier set the iodine value at below 120. The IV of coffee oil is 97.25 g I_2/100 g sample and thus also met the standard's specifications for the iodine value. The coffee oil in this study exhibited a low iodine value, indicating higher stability and longer shelf life.

The saponification number (SN) is an indicator of the molecular weight of the fatty acid or the chain length of the fatty acid in the oil. The coffee oil in this study had a high SN value (204.12 mg KOH/g sample), similar to that determined by Al-Hamamre et al (173.90-222.60 mg KOH/g sample) [14]. This result indicates that the coffee oil consisted of long chain fatty acids such as linolenic acid (C18:2) and arachidic acid (C20:0) acids as mentioned earlier in the fatty acid composition analysis.

However, the chemical and physical properties of extracted coffee oil could be different values that depend on the different extraction solvents [14]. In this study, the results showed that the coffee oil extracted by hexane extraction appeared to have the appropriate values.

3.4 Fourier transform infrared spectroscopy (FT-IR) analysis

FTIR spectroscopy is a rapid and non-destructive technique that has been used for investigating covalent bond vibration in coffee. The FTIR spectrum of coffee oil is shown in Fig. 2.

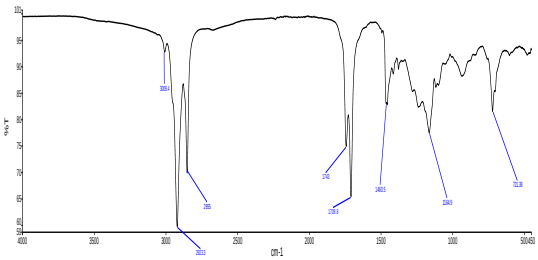

Fig. 2. FTIR spectrum of coffee oil.

The 3009.4 to 2852.7 cm^{-1} region in the majority of spectra were typical for the fatty acid moiety of lipids due to C–H stretching symmetric vibration of the cis double bonds (3009.4 cm^{-1}), asymmetric and symmetric stretching vibration of C–H bonds (2923.3 and 2852.7 cm^{-1}).

The 1740.7 to 1709.8 cm^{-1} region contained stretching vibration of ester carbonyl functional groups of triglycerides (O-C=O) and stretching vibration of free fatty acid carbonyl group (C=O), respectively. The 1462.7 cm^{-1} showed the bending vibration of C–H of CH_2 and CH_3 aliphatic group and the 1173.7 cm^{-1} exhibited stretching and rocking vibration of C–O ester group. The overlapping of aliphatic CH_2 rocking vibration and the out of plane vibration of cis-disubstituted olefins were showed in 719.17 cm^{-1} region. Similarly, FTIR spectra in all of the region was present in the FTIR spectra of coffee oil in accordance with the previous literature [17].

4. Conclusion

The optimum condition for the coffee oil extraction was 2 h and used hexane as a solvent that obtained the highest of the oil content 14.42±0.43 g/100g of dry basis. The physical and chemical properties of coffee extracted oil were investigated. The result showed that the linoleic acid and palmitic acid were the major fatty acid compositions in coffee oil. The FFA, the peroxide value, the density, the viscosity, the iodine value and the saponification number that could be indicative of the coffee oil properties. Furthermore, the chemical and physical properties of coffee oil could indicate the quality of oil that could be developed for the renewable energy industrial areas.

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