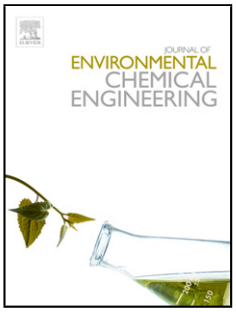

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PII: S2213-3437(17)30178-1
DOI: http://dx.doi.org/doi:10.1016/j.jece.2017.04.041
Reference: JECE 1591

To appear in:

Received date: 25-3-2017
Revised date: 21-4-2017
Accepted date: 22-4-2017

Please cite this article as: Vesna Najdanovic-Visak, Florence Yee-Lam Lee, Marcia T.Tavares, Alona Armstrong, Kinetics of extraction and in situ transesterification of oils from spent coffee grounds, Journal of Environmental Chemical Engineeringhttp://dx.doi.org/10.1016/j.jece.2017.04.041

Kinetics of extraction and in situ transesterification of oils from spent coffee grounds

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Abstract

Resource limits, environmental concerns and unstable petroleum costs have led to an increased effort to develop alternative liquid fuels. Purpose grown feedstocks are expensive and demand additional resources such as land and water. Spent coffee grounds (SCGs) are a good potential low-cost feedstock, however, processing times and costs must be lowered in order to be cost competitive with fossil fuels.

In this work, we investigated the kinetics of oil extraction from SCGs to explore if current methods of oil extraction could be hastened and an integrated process which couples oil extraction and conversion to biodiesel stages in one single step (in situ transesterification) which could significantly cut down biodiesel production costs.

Kinetics of oil extraction from SCGs using n-hexane as solvent was studied as a function of temperature, solvent to solid ratio and water content. We have found that oil extraction times could be significantly reduced to 10 minutes due to high diffusion coefficients. Further, we demonstrate, for the first time, the successful in situ transesterification of SCGs using different concentration of sodium hydroxide as catalyst and methanol to oil mole ratio, promising lower biodiesel production costs from a ubiquitous waste product around the world.

Keywords: biodiesel, coffee waste, coffee oil, direct transesterification, reactive transesterification, oil extraction.

1. Introduction

Decarbonisation of liquid fuels is necessary to avoid dangerous climate change. Biodiesel offers a viable alternative, however the growth of feedstocks render it economically uncompetitive with petroleum [1]. Moreover, the growth of biomass, both algal and terrestrial plants, requires resources that may be under pressure, for example land and water [2-4]. In addition there may be other detrimental impacts of land use change (both direct and indirect) for biodiesel feedstocks, for example increased greenhouse gas emissions [5-6]. Furthermore, the increased use of land and water generates waste with high levels of nitrogen containing compounds causing eutrophication, oxygen consumption, and toxicity. Therefore, it is required to remove such substances, usually by biological processes involving heterotrophic denitrifying bacteria through enzymatic reactions mediated by nitrate reductase, nitrite reductase and nitric oxide. One of the widespread technologies for the biological treatments is based on moving bed biofilm reactor (MBBR) [7-8].

As a result of these issues, research has focussed on the potential of waste products, transforming waste from a problem to a useful low cost resource for the production of valuable chemicals and biofuels.

In the last decade an effort was made in developing the use of agricultural waste as alternative raw materials for biodiesel production. The food industry produces enormous amounts of waste which are rich in carbohydrates, proteins, pectin and bioactive compounds, all potential sources of valuable chemicals and fuels [9]. As the biggest manufacturer in Europe, the food sector is increasingly focused on processing food waste in order to garner extra income and reduce waste and associated landfill [10]. Consequently, the potential of other non-agricultural waste products have been explored, including used cooking oil, organic municipal waste and olive stones [11-13].

With world coffee production in the region of 9.3 billion kilograms per year [14], spent coffee grounds (SCGs) is a promising biodiesel feedstock that currently has little or no commercial value. Furthermore, SCGs have a higher calorific value than many organic wastes [15]. On average, SCGs contain up to 20% of lipids [16] and lignocellulosic material, which can be used for bioenergy [17-19] along with various applications such as absorbents [20], activated carbon [21-23] support for catalyst [24], catalyst source of antioxidants [25-26], biodiesel [13-14] or biofuel pellets [15]. The production of biodiesel is an especially attractive prospect given the urgent need to decarbonise liquid fuels and the limited viable sources of low carbon liquid fuel.

Oil extraction from SCGs is an important process for their successful utilisation as biofuel. The limited studies that have assessed the oil content of SCGs report between 10 to 20 % dry mass using solvent extraction [17, 27-31] (Table 1). Most of the studies are based on n-hexane or ether as solvents and demand excessive time periods for extraction (Table 1). The kinetics of oil extraction from SCGs is essential to determine the production rate, energy consumption and process minimization (all important parameters to determine the industrial applicability), yet this information is not reported. Key variables that may impact the extraction kinetics are: temperature, solvent to solid ratio, the diffusion capacity of solvents and solutes as well as by size, shape and internal structure of the seed particles. Once the oil has been extracted transesterification is necessary to produce biodiesel [17,28,32] (Table 2). As it can be observed, the yields of biodiesel from extracted oil is rarely reported, with the limited studies reporting yields of 56% to 100%; comparable with the yields from other vegetable oil feedstocks.

Although the use of SCGs as a low-cost oil-rich feedstock can decrease the cost and environmental impact of biodiesel production, the processing costs remain inhibitive and must be lowered in order to be competitive with conventional oil fuels. The integration of the oil extraction and transesterification stages into one single step (in situ transesterification) has the potential to achieve this. In the in situ transesterification process, the SCGs are directly contacted with alcohol containing a catalyst, allowing simultaneous oil extraction and its conversion to produce fatty acid methyl esters (i.e. biodiesel). Prior studies have proven the viability of in situ transesterification method using various feedstocks, including sunflower seeds [33-34], soybean [35] and jatropha curcas [36]. The yields of in situ transesterification processes are influenced by various parameters, such as temperature, catalyst loading, oil to methanol ratio, particle size and moisture [37]. Further, significant differences in production yields have been observed for different feedstocks due to their varying structure.

Therefore, the aim of the present study was to: (1) determine if quicker oil extraction is possible be establishing the kinetics of oil extraction from SCGs using hexane as a solvent, and, (2) to determine if in situ transesterification of oils by methanol to produce fatty acid methyl esters (i.e. biodiesel) is viable and the influence of temperature, solvent to SCGs ratio and catalyst concentration.

2. Experimental section

2.1. Materials

Spent coffee grounds were provided by Pizzetta Republic, Lancaster University campus, and originated from roasted Arabica Atkinson & Co. Ltd espresso grounds coffee. All the chemicals used are listed in Table 3. These were supplied by Sigma-Aldrich and were used without further purification.

2.2. Methods

2.2.1. Characterization of spent coffee grounds

Collected SCGs were analysed for particle size and water and oil contents. The average particle size of coffee grounds was determined by the laser diffraction analyser (Malvern Mastersizer 3000E, accuracy better than 0.6%). The water content of SCGs immediately after collection was determined by measuring the mass before and after the SCGs were dried in an oven at 353 K until no further changes in mass were observed (AT201 analytical balance, Mettler, UK). Solvent n-hexane was used to determine the oil content of the dried SCGs by performing a Soxhlet extraction at 342 K (n-hexane's normal boiling point). Approximately 30 g of coffee grounds were used and the extraction was carried out for six hours. Hexane was subsequently evaporated in a rotary evaporator and the content of the extracted oil was determined gravimetrically using the analytical balance. Samples of the extracted oils were further analysed by titrations to determine acid, peroxide and iodine values.

2.2.2. Kinetics of oil extraction

Samples of the SCGs, approximately 25 g, were weighed using the Mettler AT201 analytical balance with stated repeatability of ± 3×10^{-2} mg and transferred to a one-litre three-neck Pyrex flask with a hemispherical base. The flask was fitted with a condenser to avoid evaporation, thermometer to monitor temperature and syringe to sample extraction mixture at regular intervals. Solvent, n-hexane, was used at various solvent to SCGs ratios (mLg^{-1}): 5, 8, 12, 15, 25 and 30. The known amount of n-hexane was heated in the flask while SCGs were heated separately at the desired extraction temperature (293.2 K, 313.2 K, 323.2 K and 333.2 K). When both materials reached the desired temperature, they were mixed and the extraction started. The flask was immersed in a temperature-controlled water bath equipped with magnetic stirrer to maintain in suspension the particles of the SCGs. The temperature was controlled within ± 0.1 K, monitored by a thermometer. Samples of the extraction mixture (1 mL), taken at regular intervals, were collected in pre-weighed vials. The amount of oil extracted in each time interval was determined gravimetrically by measuring the mass of the residue in the flask after evaporation of the solvent. Extractions were replicated at least twice for each of the experimental conditions. Extraction yield at any time (M_t) was calculated as:

$$M_t = \frac{\text{mass of oils extracted at time t}}{\text{mass of dry SCGs}} \qquad (1)$$

Before commencing the work, the time taken to reach saturation was estimated by measuring the extraction yield after 30 minutes, 1 hour, 2 hours and 3 hours to assure that few consecutive samples produced essentially the same extraction yield. In this way, it was determined that 1 hour was sufficient to reach saturation (M_{inf}). The repeatability of the extraction method was confirmed by carrying out replicas of the assays at random conditions. The average deviation of the extraction yield M_t was ±0.3.

2.2.3. In situ transesterification

In situ transesterification was carried out in 200 mL round-bottom flask connected with condenser to avoid evaporation. Methanol and sodium hydroxide were placed in the flask at the desired ratio and the flask was immersed in a water-bath at 333 K. Once the sodium hydroxide was completely dissolved in methanol at 333 K, a known amount of SCGs were added to the mixture. After a certain time, the SCGs were vacuum-filtered in Buchner funnel in order to separate meal and filtrate. To guarantee that the reaction has stopped, sodium hydroxide was neutralized by adding acetic acid (mole ratio NaOH:CH_3COOH = 1:1). Rotary evaporator was used to evaporate methanol from the filtrate. Further separation of fatty acid methyl esters and glycerol was performed by liquid-liquid extraction using n-hexane as a solvent. Mixing hexane and filtrate resulted in phase separation: bottom layer rich in glycerol and upper layer rich in hexane and fatty acid methyl esters (FAMEs). The extraction was repeated three times and the extracts were collected. Afterwards, the solvent was evaporated from the extracts and the mass of the obtained biodiesel was recorded. Samples were prepared for further analysis (Gas Chromatography and titrations). All transesterification experiments were repeated in triplicate, allowing estimation of standard deviations.

2.2.4. Gas Chromatography Analysis

The fatty acid methyl esters content of the extracted samples were determined by gas chromatography using a Trace^{TM} GC 1300 equipped with flame ionisation detector and on-column injection (Thermo Fisher Scientific, UK), as well as with a 30 m × 0.25 mm i.d. capillary column coated with a 0.25 μm thickness film from Thermo Scientific^{TM} – TR-BD(F) (UK). The operating conditions were set as the following: the carrier-gas was helium at constant pressure of 100 kPa; the oven temperature program was 120°C for 1 minute, followed by a 10°C min^{-1} ramp up to 220°C with a holding time of 10 min; the flame ionization detector was set at 380 °C. Peak identification was carried out using known standards (methyl palmitate, methyl linoleate and methyl oleate). Heptadecane was used as an internal standard. The data were processed with the software Chromeleon 7. All the results presented are the average of at least two replicate analyses.

2.2.5. Titrations

Titrations of the extracted oil and obtained biodiesel were carried out to determine acid, iodine and peroxide values.

Acid value: A 0.05 M NaOH in ethanol solution was prepared by dissolving NaOH pellets in ethanol. Two grams of sample (oil or biodiesel), 25 mL ethyl ether:ethyl alcohol (2:1 v/v) and two drops of phenolphthalein were added to a flask. The mixture was titrated against the 0.05 M NaOH in ethanol solution until the color changed from transparent to light pink. The procedure was repeated with a blank sample containing 25 mL of solvent and 2 drops of phenolphthalein, titrated with 0.05 M NaOH in ethanol until the solution changed color from transparent to light pink. The acid value was calculated as:

$$\text{Acid value} = \frac{\left(V_{NaOH} - V_{NaOH,0}\right) \cdot C_{NaOH} \cdot 40}{m_{sample}} \qquad (2)$$

where V_{NaOH} and $V_{NaOH,0}$ are the volume of the sodium hydroxide solution spent to neutralize sample of oil or biodiesel and the volume of the sodium hydroxide solution spent to neutralize blank sample, respectively. C_{NaOH} and m_{sample} stand for molar concentration of NaOH and mass of sample, respectively.

Iodine value: Approximately 0.2 g of the sample (oil or biodiesel) was weighed in a dry 250 mL stoppered bottle and 10 mL of Wij’s solution was added to the sample. A blank mixture was prepared by omitting the oil. Both flasks were placed in the dark for 30 minutes. Next, 15 mL of 10% potassium iodide solution and 10 mL of water were added to both flasks and mixed thoroughly. Such solutions were titrated with sodium thiosulphate solution using starch solution as an indicator. The Iodine value was calculated as:

$$\text{Iodine value} = \frac{\left(V_{Na_2S_2O_3} - V_{Na_2S_2O_3,0}\right) \cdot C_{Na_2S_2O_3} \cdot 127}{m_{sample}} \cdot 100 \qquad (3)$$

where $V_{Na_2S_2O_3}$ and $V_{Na_2S_2O_3,0}$ are the volume of $Na_2S_2O_3$ spent for the titration of sample of oil or biodiesel and the volume of $Na_2S_2O_3$ spent for the titration of blank sample, respectively. $C_{Na_2S_2O_3}$ and m_{sample} stand for molar concentration of $Na_2S_2O_3$ and mass of sample, respectively.

Peroxide value: Approximately 3 g of sample (oil or biodiesel) was weighed and transferred to a 250 mL Erlenmeyer flask. Then, 10 mL of chloroform was added to dissolve the sample. Volume of 15 mL of acetic acid and 1 mL KI solution (1.3 g potassium iodide in 1 mL of water) were added and mixed, in a dark place, for 5 minutes. Next, 30 mL distilled water and 1 mL starch indicator were added. The resulting solution was titrated against sodium thiosulfate (0.01 M) until the blue color disappeared. The procedure was repeated with a blank sample containing 10 mL chloroform, 15 mL acetic acid, 1 mL KI and 30 mL distilled water.

The Peroxide value was calculated as:

$$\text{Peroxide value} = \frac{\left(V_{Na_2S_2O_3} - V_{Na_2S_2O_{3,0}}\right) \cdot C_{Na_2S_2O_3}}{m_{sample}} \cdot 1000 \quad (4)$$

where $V_{Na_2S_2O_3}$ and $V_{Na_2S_2O_3,0}$ are the volume of the sodium thiosulfate solution spent for the titration of sample of oil or biodiesel and the volume of the sodium thiosulfate solution spent for the titration of blank sample, respectively. $C_{Na_2S_2O_3}$ and m_{sample} stand for molar concentration of $Na_2S_2O_3$ and mass of sample, respectively.

2.2.6. Models for kinetics of oil extraction

A modified model of Fick’s Law of diffusion in non-stationary state for spherical particle suspended in a homogeneous medium is given by:

$$\frac{M_t}{M_{\inf}} = 1 - A\exp(-B \cdot t) \qquad (5)$$

where M_{t} and M_{inf} represent the mass of the diffused oil (kg oil/kg dry meal) at time *t* and infinite time (extraction yields), respectively. Parameters *A* and *B* are constant coefficients. For spherical particles, parameter *B* can be expressed as:

$$B = \frac{D_e \pi^2}{R^2} \qquad (6)$$

where D_{e} and *R* stand for the effective diffusion coefficients ($\mathrm{m^2 s^{-1}}$) and particle radius (m), respectively. Variation of the effective diffusion coefficient with temperature can be represented with the Arrhenius-type equation:

$$D_e = D_0 \exp\left(-\frac{\Delta E_d}{R_g T}\right) \qquad (7)$$

where D_0, ΔE_d, R_g and *T* are constant ($\mathrm{m^2 s^{-1}}$), the activation energy ($\mathrm{Jmol^{-1}}$), the gas constant (8.314 $\mathrm{Jmol^{-1}K^{-1}}$) and absolute temperature (K), respectively.

The modified model of Fick’s Law given by equation (5) was applied to fit the experimental extraction data for different process parameters and the fitted coefficients *A* and *B* were obtained. This allowed the calculation of the effective diffusion coefficient (Eq. (6)) at different temperatures. Further, equation 7 was used to obtain the activation energy.

Another equation based on the empirical model proposed by Peleg for the sorption processes in foods was used to fit the experimental data:

$$M_t = \frac{t}{K_1 + K_2 t} \qquad (8)$$

where t stands for time while K_1 and K_2 are the model parameters.

The experimental and modeling results were compared in terms of the absolute average deviations (*AAD*) of the yields:

$$AAD(\%) = \frac{1}{NP}\sum_i \frac{\left|M_i^{calc} - M_i^{\exp}\right|}{M_i^{\exp}} \cdot 100 \qquad (9)$$

where M_i^{calc} and M_i^{exp} are the calculated and experimental extraction yields, respectively, while *NP* stands for the number of available experimental points.

3. Results and Discussion

The findings of this study highlight the potential to reduce both the time and cost of biodiesel production from SCGs. Specifically, for the first time, we determined the oil extraction kinetics of SCG, allowing the identification of the potential rapidity of oil extraction. Further, for the first time, we established the potential for in situ transesterification of SCG, a one-step biodiesel production method, reducing both the cost and time for biodiesel production. We undertook this research using SCGs with the characteristics, including those of the extracted oil, presented in Table 4. The oil yield was 14.2 g per g of dry SCGs which is in good agreement with the yields of Soxhlet hexane extraction from spent coffee grounds reported in literature (Table 1).

3.1 Oil extraction kinetics

Kinetics of the oil extraction from SCGs using n-hexane at various temperatures is given in Figure 1. In the beginning, the extraction process was controlled by a washing mechanism, whereby n-hexane rapidly solubilized the oil available on the particles' surface. After this initial stage, with an approximate duration of 10 minutes, the extraction rate decreased considerably, as oil diffusion from solid to surface became the predominant process. Both extraction rate in the initial stage and the final yield were enhanced by increased temperatures – the maximal obtained yield was 13.6 g oil extracted / g dry SCGs at 333 K.

To describe the extraction process, experimental data were fitted by two models: modified Fick's law (eq. (5)-(7)) and Peleg empirical model (Eq. (8)). Parameters of both models are presented in Table 5. The experimental and fitted results were compared in terms of the absolute average deviations (*AAD*) which varied from 0.43% to 0.76% for modified Fick's law and from 0.35% to 0.62% for Peleg empirical model.

The modified Fick's Law (eq.(5)) was applied to fit the experimental extraction data resulting in coefficients *A* and *B* for each temperature. Effective diffusion coefficient can be calculated using equation (6). An essential parameter for process design - effective diffusion coefficients at different temperatures were calculated according to equation (6) giving values in ranged from 2.14×10^{-11} m^2s^{-1} at 292.7 K to 3.97×10^{-11} at 333.2 K which is one order of magnitude higher than the effective diffusion coefficients of canola oil (1.3×10^{-12} m^2s^{-1} to 3×10^{-12} m^2s^{-1}) [**Error! Bookmark not defined.**] and sunflower oil (2.1×10^{-12} m^2s^{-1} to 5.0×10^{-12} m^2s^{-1})[1]. This might be due to the prior coffee processing with hot water.

Further, equation (7) was used to obtain the activation energy plotting straight line in ln(D_e) versus 1/*T* diagram. The slope of the line was taken and activation energy was calculated to be

12.7 $kJmol^{-1}$, similar to values of 19.1 $kJmol^{-1}$ and 11.3 $kJmol^{-1}$ reported for canola seeds and sunflower, respectively [33-34].

To evaluate the influence of the ratio of solvent volume to mass of dry SCGs and the potential to reduce costs through reducing solvent volumes, extractions were performed using various solvent to solid ratios (8, 12, 15 and 25 mLg^{-1}) at 333 K during 60 minutes. Increasing solvent to solid ratio from 8 mLg^{-1} to 15 mLg^{-1} significantly enhanced the extraction yields (Figure 2). This trend flattens out with further increase of the solvent to solid ratio suggesting a solvent to solid ratio of 15 mLg^{-1} was sufficient to extract the maximum yield of oil.

The moisture content of the SCGs was also critical, with a substantial decrease in the extraction yield with an increase in the initial moisture (Figure 3). This was expected since the presence of moisture decreases the solubility of oils in hydrophobic hexane. However, if upscaling to a commercial process a trade-off between the energy and economic costs of drying the SCG versus the increased extraction rate would need to be established

Together these results indicate the potential for a significant saving in time which could improve the viability of oil extraction from SCGs.

3.2 In situ transesterification

Both catalyst concentration and methanol to oil ratio influenced the yield of in situ transesterification performed at 333 K for 90 minutes (Figure 4). For each methanol to oil ratio, in situ transesterification yield was enhanced with increased catalyst concentrations until the maximum yield was obtained. Further rise of the catalyst concentration resulted in the decrease of the yield, which might be due to the reversible nature of the transesterification process. Higher concentration of the catalyst may have favoured the backward reaction - the formation of triglycerides. The maximum achieved yield was 96.0%, 82.6% and 71.5% for three different methanol to oil mole ratios - 400, 800 and 2400 mol/mol, respectively. Increasing the methanol to oil mole ratio had two simultaneously occurring opposite effects on the transesterification process: 1) it increased the yield since higher concentration of reagents (methanol) favour the forward reaction – production of fatty acid methyl esters (biodiesel); and, 2) it decreased the yield due to the significant reduction of the concentration of one of reactants (triglycerides) favouring the backwards reaction – production of triglycerides.

It is worth to noting that the maximum obtained reaction yield was attained for different catalyst concentrations depending on methanol to oil mole ratio. However, the construction of the yield as a function of catalyst to oil mole ratio (Figure 5) revels unlike trend – the maximum yield was observed for similar catalyst to oil mole ratio (approximately 3:1). This is expected since one molecule of triglyceride contains three ester groups which, in first instance, react with methoxide ion formed from sodium hydroxide and methanol.

Ultimately, the obtained biodiesel samples were analysed in terms of the acid content, amount of unsaturation in fatty acids and rancidity. Obtained values for acid, iodine and peroxide of obtained biodiesel were 1.50 (mg KOH)/(g oil), 76.3 (g I_2)/(100 g oil) and 20 (mmol O_2)/(kg oil). Both iodine and peroxide value were at acceptable levels for biodiesel, however the acid content was too high, suggesting that additional processing would be required.

Conclusions

We establish, for the first time, the oil extraction kinetics and that it is feasible to perform in situ transesterification of oils from spent coffee grounds for biodiesel production. The oil extraction kinetics allows the optimisation of oil extraction from SCGs, the products of which could then be converted into biodiesel. The maximal obtained extraction oil yield was 13.6 g oil per one g of dry SCGs at 333 K. Obtained data on kinetics of oil extraction process were fitted by modified Fick’s law and Peleg empirical model, giving the absolute average deviations lower than 0.8%. Calculated effective diffusion coefficients vary from 2.14×10^{-11} m^2s^{-1} at 292.7 K to 3.97×10^{-11} m^2s^{-1} at 333.2 K and activation energy was estimated to be 12.7 $kJmol^{-1}$.

Furthermore, our findings reveal that in situ transesterification, a single step biodiesel production process with significant cost savings potential might provide new industrial potential for the recovery of fuel from SCGs. The maximum achieved yield of in situ transesterification was 96.0% under following reaction conditions: methanol to oil mole ratios of 400, 333 K, catalyst concentration of 0.2 $molL^{-1}$ and 90 minutes.

These findings need to be up-scaled to a commercial level and the trade-offs between increased reaction temperature and dryness of SCGs determined to identify the optimal conditions in light of energy and cost requirements. Ultimately, biodiesel production from SCG offers a contribution to low carbon fuels across the world.

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Captions to Figures:

Figure 1. Yield of the extracted oil versus time at 293 K (filled circles), 313 K (empty circles), 323 K (filled squares) and 333 K (empty circles) in the solid-liquid extraction of dry spent coffee grounds using n-hexane as solvent. The volume of solvent to mass of SCGs ratio was 15 mL/g while the average particle size of SCGs was 415 μm. Lines correspond to the modified Fick's model given by equation (5) using the obtained parameters (Table 5).

Figure 2. Yield of the extracted oil as a function of the volume of solvent to mass of SCGs ratio. The extraction time and temperature were set to be 60 minutes and 333 K, respectively. The average particle size of SCGs was 454 μm.

Figure 3. Yield of the extracted oil as a function of the initial moisture content in spent coffee grounds. Extraction time, temperature and the volume of solvent to mass of SCGs ratio were set to be 60 minutes, 333 K and 15 mL/g, respectively. The average particle size of SCGs was 454 μm.

Figure 4. Yield of in situ transesterification of coffee oils from spent coffee grounds as a function of catalyst (NaOH) concentration for different methanol to oil mole ratio: 400 (circles), 800 (squares) and 2400 (triangles). All the reactions were performed at 60^{o}C using dried spent coffee grounds during 90 minutes.

Figure 5. Yield of in situ transesterification of coffee oils from spent coffee grounds as a function of catalyst (NaOH) to oil mole ratio concentration for different methanol to oil mole ratio: 400 (circles), 800 (squares) and 2400 (triangles). All reactions were performed at 60^{o}C using dried spent coffee grounds during 90 minutes.

Figure 1

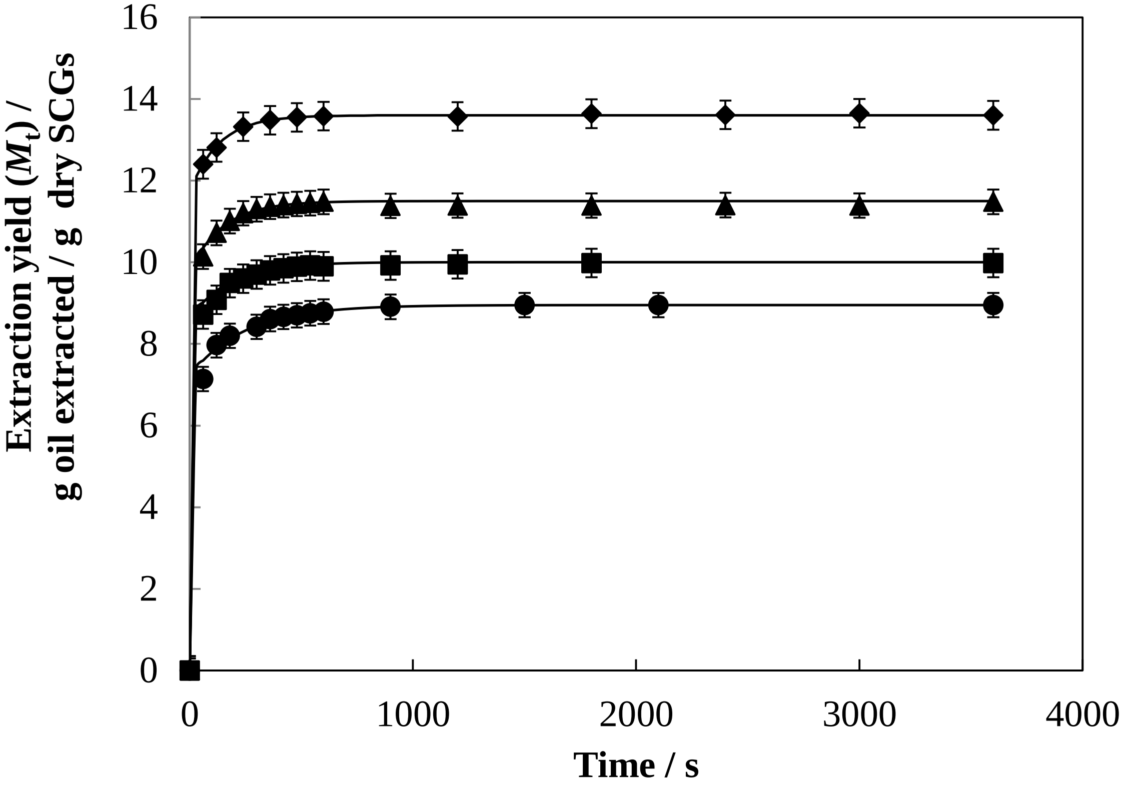

16
14
12
10
8
6
4
2
0
0
1000
2000
3000
4000
Extraction yield (M_t) / g oil extracted / g dry SCGs
Time / s

Figure 2

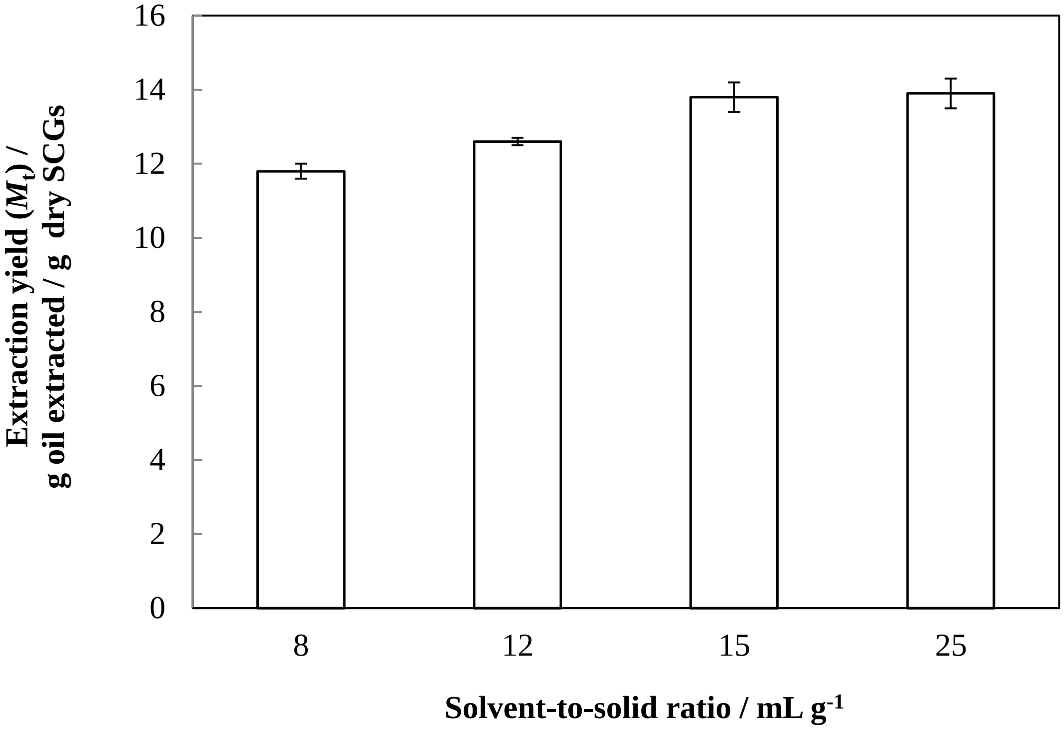
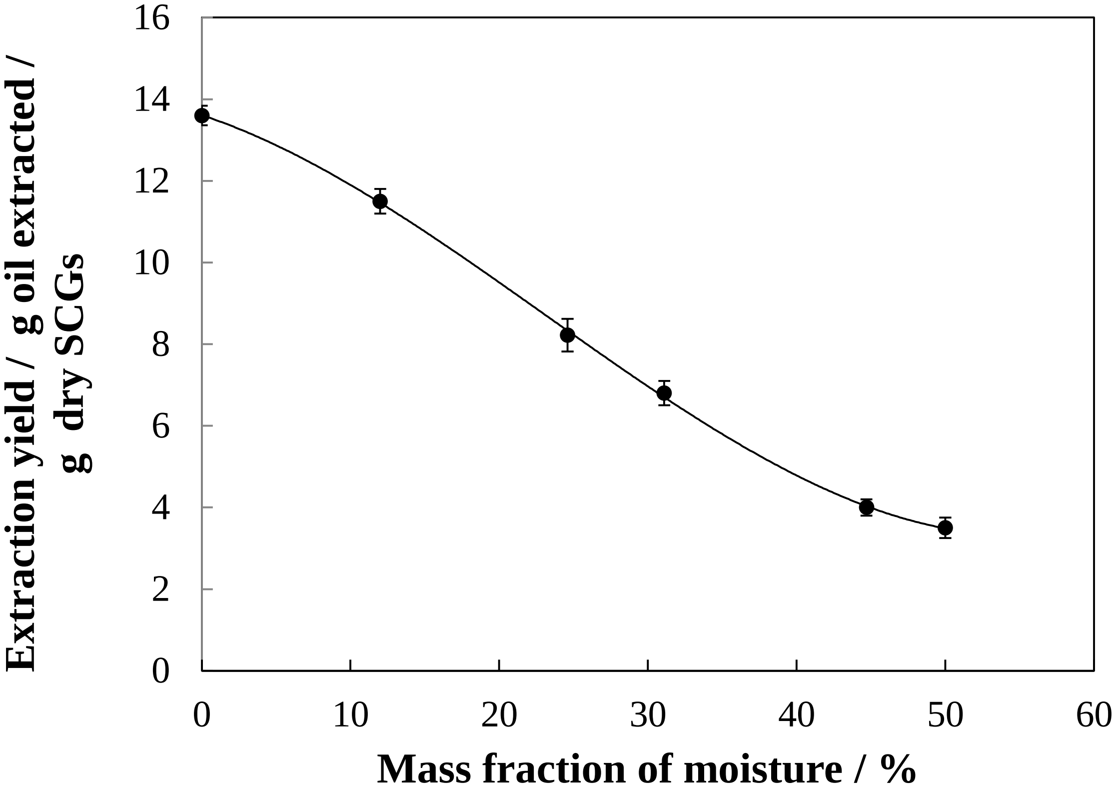

Extraction yield (M_t) / g oil extracted / g dry SCGs
0
2
4
6
8
10
12
14
16
8
12
15
25
Solvent-to-solid ratio / mL g^{-1}

Figure 3



16
14
12
10
8
6
4
2
0
0
10
20
30
40
50
60
Extraction yield / g oil extracted / g dry SCGs
Mass fraction of moisture / %

Figure 4

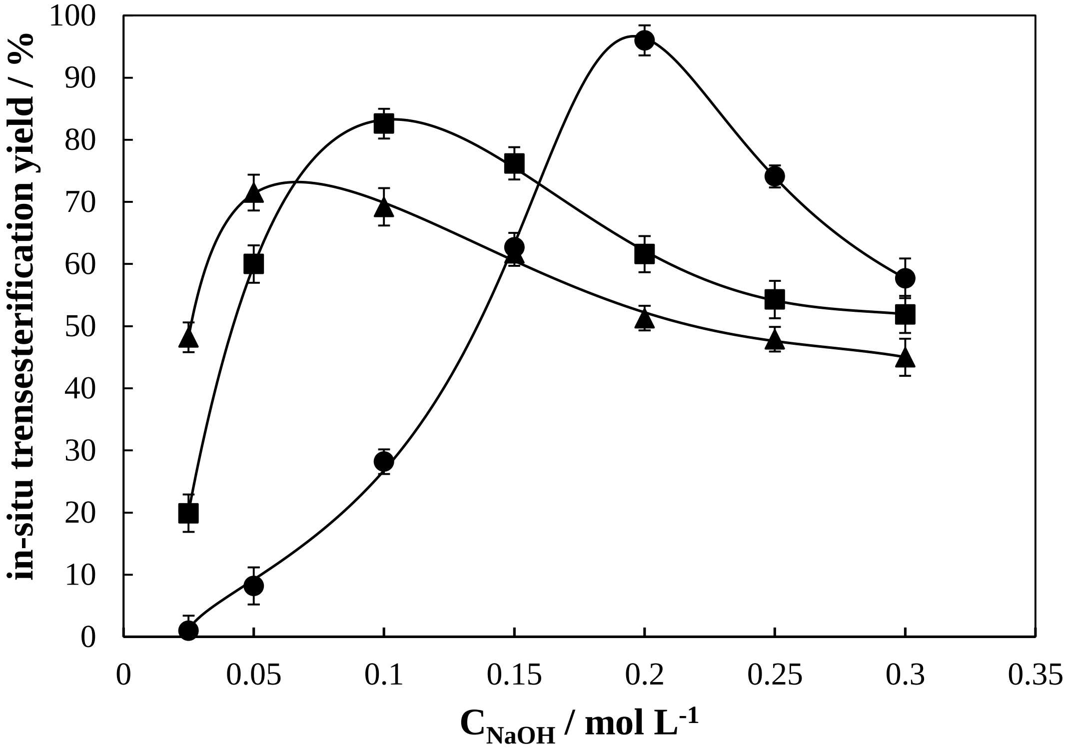

in-situ trensesterification yield / %
100
90
80
70
60
50
40
30
20
10
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
C_{NaOH} / mol L^{-1}

Figure 5

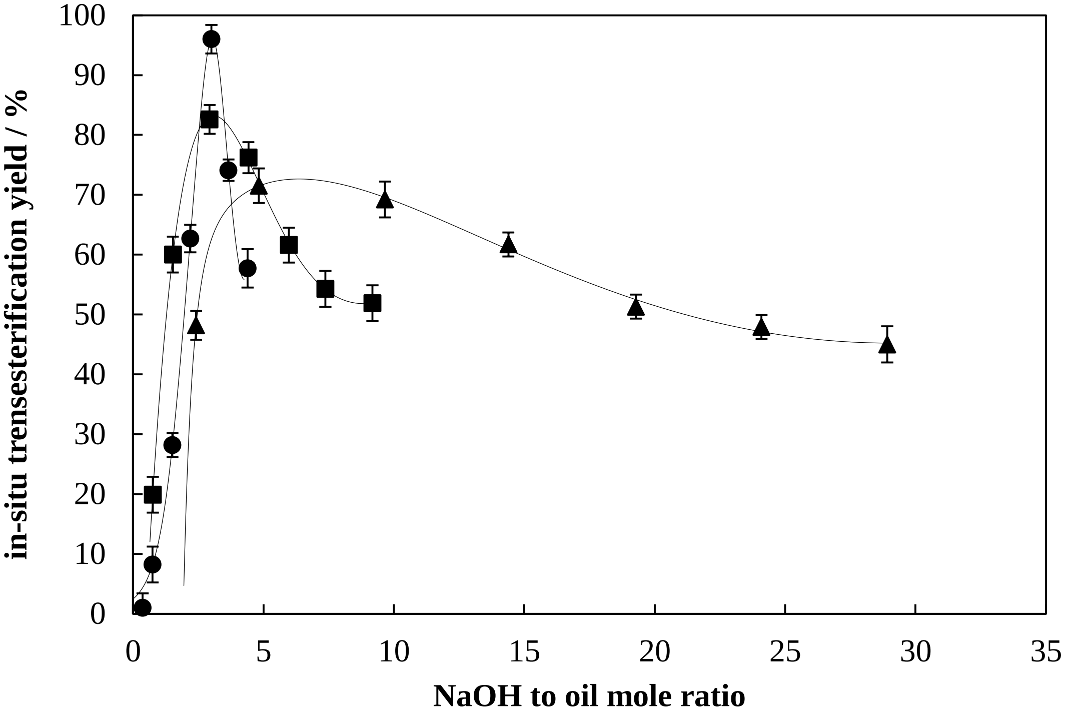

in-situ trensesterification yield / %
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
NaOH to oil mole ratio

Table 1. Reported Soxhlet solvent extraction of oils from spent coffee grounds

Solvent	**Solvent to SCGs ratio ml g^{-1}**	**Time h**	**Yield g oil extracted / g dry SCGs**	**Lit.**
Hexane	15.0	8	13.0	[27]
Hexane	4.2	0.5	15.3	[28]
Hexane	8.0	6	19.7	[29]
Petroleum ether	-	6	12.5	[30]
Hexane	15.0	6	11.0	[31]
Hexane	3	1	13.4	[17]

Table 2. Transesterification of extracted coffee oils from spent coffee grounds.

Temperature K	Oil:Methanol mol/mol	Time min	Yield %	Reference
338	1:5	150	56	[28]
338	1:5	240	69	
338	1:9	240	86	
358	1:5	150	63	
358	1:5	60	59	
358	1:9	60	80	
333	1:15	120	60.5	[32]
343	1:13	10	100	[17]

Table 3. Chemicals used in this study which were supplied by Sigma-Aldrich

Chemical	Purity / mass%	Purpose
n-Hexane	99.9	Oil extraction and post-transesterification extraction of FAMEs
Methyl stearate	99.5	Gas Chromatography
Methyl palmitate	99.0	
Methyl linoleate	98.5	
Methyl oleate	99.0	
Methanol	99.8	In situ transesterification
Sodium hydroxide	98	Catalyst and acid value
Ethanol	99.5	Acid value
Phenolphthalein 2% in ethanol	-	
Wij's solution (0.1 M)	-	Iodine value
Potassium iodide	99.5	Iodine and peroxide value
Sodium thiosulphate	98.5	
Starch solution 1% in water	-	
Chloroform	99.0	Peroxide value
Acetic acid	99	Peroxide value and neutralization of catalyst after in situ transesterification

Table 4. Characteristics of used spent coffee grounds and extracted oil

Spent coffee grounds	
Water content / % [(g water)/(g wet SCGs)]	49.3 ± 0.6
Oil content / [(g oil)/(g dry SCGs)]	14.1 ± 0.2
Average particle diameter / μm	454
Extracted oil	
Acid value / (mg NaOH) (g oil)$^{-1}$	1.8
Peroxide value / millimoles (kg oil)$^{-1}$	0.2
Iodine value / g (100 g oil)$^{-1}$	83.7

Table 5. Parameters of the modified Fick's law (eq.(5)) and Peleg empirical model (eq.(8)). Average particle size of SCGs was 415 μm while the volume of hexane per mass of SCGs was 15 mLg^{-1}.

***T* / K**	292.7	313.2	323.2	333.2
	Modified Fick's law			
A	0.194	0.139	0.150	0.138
B / s^{-1}	4.10×10^{-3}	5.72×10^{-3}	6.77×10^{-3}	7.60×10^{-3}
De / m^{2}s^{-1}	2.14×10^{-11}	2.99×10^{-11}	3.54×10^{-11}	3.97×10^{-11}
ΔE_d / kJmol^{-1}	12.7			
AAD / %	0.76	0.71	0.51	0.43
	Peleg empirical model			
K_1 / s	1.78	0.990	0.70	0.48
K_2 /	0.111	0.099	0.087	0.073
AAD / %	0.41	0.49	0.62	0.35