CHEMICAL ENGINEERING TRANSACTIONS
VOL. 96, 2022
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: David Bogle, Flavio Manenti, Piero Salatino

ISBN 978-88-95608-95-2; **ISSN** 2283-9216
DOI: 10.3303/CET2296027

Optimisation of Fuel-Grade Hydrocarbons' Production from Spent Coffee Grounds Using Green Processes

Bhekuyise Mkhonto*, Manimagalay Chetty

Department of Chemical Engineering, Durban University of Technology, South Africa

21448990@dut4life.ac.za

The present study focused on the optimisation of production of fuel-grade hydrocarbons using lipids or oil extracted from spent coffee grounds (SCGs). The oil was extracted from SCGs using 2-methyltetrahydrofuran as a green solvent and calcium oxide synthesised from chicken eggshells was used as a green catalyst during the SCGs oil transesterification. Calcium oxide was doped with lithium (Li-$CaO_{(s)}$) to improve catalyst activity. The oil extraction and the transesterification processes were optimised using the design of experiment (DoE). The response surface methodology (RSM) and the Box-Behnken design were used to optimise both processes. The combination of extraction time and solvent-to-solids ratio were optimised for the oil extraction process. The combination of reaction time and catalyst loading were optimised for the transesterification process. Fourteen 14 experiments were predicted by Box-Behnken design for both the oil extraction and transesterification processes. The model predicted that the optimum extraction conditions were, 1:18 (w/v) SCGs-to-solvent ratio and 4.5 h extraction period, providing a maximum of 25.10 wt% oil yield. The model predicted optimal yield was confirmed experimentally, obtaining an oil yield of 24.60 wt%, which was 0.5 wt% lower than the value predicted by the model. During transesterification the reactor temperature was maintained at 65 °C, a SCGs oil-to-methanol molar ratio of 1:12 and 165 rpm mixing speed. The model predicted the optimum reaction time of 2 h, 5 wt% of the oil used catalyst loading, providing 98.21 wt % oil conversion. The predicted optimal yield was confirmed experimentally, achieving an oil conversion of 97.81 wt%, which was 0.4 wt% lower than the predicted by the model.

1. Introduction

According to Giller et al. (2017), 2.25 billion cups of coffee are consumed everyday world wide, and its beans are one of the largest traded commodity together with petroleum-based products. This high coffee consumption generates an enormous amount of waste referred to as spend coffee grounds (SCGs). There has been a number of attempts to valorise SCGs, these attempts include using SCGs as a source of antioxidant, fertiliser, absorbent for the removing cationic dyes in wastewater treatments, and as source of fermentable sugars, however these attempts have not gained large scale application (Efthymiopoulos et al., 2018). Currently the majority of the SCGs are sent to landfills where they decompose and release greenhouse gases (GHG) to the atmosphere and acidic leachate containing ecotoxic compounds, which contaminates ground water (Kookos, 2018). The use of SCGs as a substrate for the production of fuel-grade hydrocarbons, heating pallets and heating logs have recently gained a lot interest (Bio-bean, 2021). SCGs have been reported to contain between, 6 – 27.80 wt% of oil on a dry basis, with most researchers reporting, 11 – 20 wt% of oil on a dry basis (Campos-Vega et al., 2015). The quantity of lipids extracted from SCGs is strongly affected by the extraction method and the extraction conditions (Caetano et al., 2014). SCGs oil mainly contains triglycerides, usually above 80 wt% of the total lipid, small quantities of diglycerides and free fatty acids (FFA). The glycerides' part accounting for, 80 - 95 wt% of the total oil in the SCGs (Pichai and Krit, 2015). SCGs lipids are a readily available feedstock for production of fuel-grade hydrocarbons, which are a mixture of long-chain fatty acid alkyl esters (FAME) obtained transesterification of biobased lipids such as animal fats or vegetable oil. Fuel-grade hydrocarbons can be used in a compression ignition engine, without any engine modification (Murugesan et al., 2009). Recently, fuel-grade hydrocarbons have become more alluring due to their biodegradability, non-toxicity, environmentally friendly

Paper Received: 24 January 2022; Revised: 14 July 2022; Accepted: 10 August 2022
Please cite this article as: Mkhonto B., Chetty M., 2022, Optimisation of Fuel-grade Hydrocarbons' Production from Spent Coffee Grounds Using Green Processes, Chemical Engineering Transactions, 96, 157-162 DOI:10.3303/CET2296027

nature and can be produced from any material containing fatty acids attached to other molecules or FFA (Haile, 2014). SCGs have been successfully used as a source of lipids for the production FAME, however the use of fossil-based solvents such as hexane for oil extraction and the use of non-reusable sodium and potassium hydroxide as catalysts during the transesterification of the SCGs oil renders the fuel-grade hydrocarbon production process environmentally unfriendly.

The aim of the present work was to determine the optimal oil extraction condition from SCGs and oil transesterification conditions using design of experiments (DoE). DoE is a method used to evaluate a relationship between parameters affecting a process and the process outputs. In general, it is utilised to discover cause and-effect relationships. This information is required for monitoring process inputs and optimising the process output. In recent years, the use of DoE has drastically increased, and it has been used for the optimisation of a wide range of industrial processes, such machining, chemical mixing, and biochemical processes, to determine the best conditions. The present study was aimed at optimising process conditions such as solids-to-solvent ratio, oil extraction duration for oil recovery from SCGs using 2-methyltetrahydrfun and optimising the transesterification process conditions such as reaction time, catalyst loading using calcium oxide doped with lithium oxide (Li-$CaO_{(s)}$) synthesised from chicken eggshells as green catalyst.

2. Materials and methods

Chicken eggshells were collected, washed and dried in the sun for two days. Wet SCGs as source oil, were collected from a local coffee street vendor, the wet SCGs were dried on the sun for a period of 7 days. 2-MeTHF (99.95 % purity) as green solvent for oil extraction, Methanol (99.97 % purity).

2.1 Oil extraction and Transesterification

The extraction of the oil from SCGs was conducted using a Soxhlet extraction unit. The dried SCGs sample (30 g) were placed in cellulose thimble. 2-MeTHF was placed in the bottom round flask. The heating mantle temperature was set to 80 ℃, which is the boil temperature of 2-MeTHF. The molar mass of the SCGs oil was found to be,862.80 g/mol (Rocha et al., 2014).

The catalyst ($CaO_{(s)}$) was prepared by crushing and calcining the dried chicken eggshells in a kiln at 900 °C for 5 h, the resulting with powder (which is 95 wt% CaO). The white powder was doped with 1 wt% lithium oxide, at 600 °C for 3 h in a kiln. The resulting Li-$CaO_{(s)}$ was used as a catalyst in the one-step transesterification experiments. The reactor conditions were ,65 °C,165 rpm mixing speed,1:12 oil to methanol ratio and 35 g of SCGs oil per experimental run. Catalyst loading was administered as per DoE prediction for a particular experimental run. Eq (1) was employed to estimate the amount of methanol used.

$$C_{57}H_{104}O_6 + 3CH_3OH \rightarrow 3\,C_{19}H_{36}O_2 + C_3H_8O_3 \quad (1)$$

The reactor content was than discharged into a separating funnel, and were allowed to settle for 24 h, where two distinct layers were observed. The top layer on the separating funnel was subjected to batch distillation to remove the excess methanol. After distillation the weighed using a balance (Mettler AE 200). The extent of SCGs oil conversion was estimated using Eq (2).

$$\text{SCGs oil conversion} = \left(\frac{\text{Mass of FAME Produced (g)}}{\text{Mass of SCG Oil Used (g)}}\right) 100\% \quad (2)$$

2.2 Response Surface Methodology (RSM)

Design-Expert software version 11 (DX11) was used to study and optimise the experimental data. Analysis of variables (ANOVA) and the RSM component of the software was employed. To optimise the process parameters in question for both oil extraction and transesterification processes, the Box–Behnken experimental design was used. If all independent variables are quantifiable and can be repeated with insignificant error, the response surface can be expressed using the model presented by Eq (3):

$$Y = C_0 + \sum_{i=1}^{k} C_i X_i + \sum_{i=1}^{k} C_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{i=i-1}^{k} C_{ij} C_{ij} \quad (3)$$

With regards to the present study; Y (wt%) is the oil extraction yield or fuel grade hydrocarbons yield depending on the experiment being conducted, X_1, X_2 are process parameters to be optimised, C_o is the constant C_i the coefficients of the linear terms, C_{ii} is the regression coefficients for the quadratic terms and of C_{ij} is the coefficient

of the interaction effects and k is the number of input parameters presented. These major process parameters can be identified by reviewing previous literature or undertaking a preliminary investigation using a factorial or partial factorial design. For the extraction of oil from SCGs, parameters such as oil extraction time (X_1), solids-to-solvent (X_2) ratio and the type of solvents used plays a crucial role in the efficiency of the oil extraction process (Efthymiopoulos et al, 2018).

Concerning the oil transesterification, process parameters such as catalyst loading (X_2), reaction time (X_1), reactor temperature and stirrer speed plays a crucial role in the in-process efficiency (Mathiyazhagan and Ganapathi, 2011). The coded and uncoded levels of the Box–Behnken independent variables were presented in Table 2.

Table 2: Independent process variables and their experimental design levels for the SCGs oil extraction.

Variables					
Coded process parameter levels	-1	-0.50	0	0.50	1
Time (h)-X_1	1	2.50	4.50	5.50	8
SCGs-to-solvent ratio (w/v)-X_2	0.20	0.10	0.067	0.056	0.05

Table 3: Independent process variables and their experimental design levels SGCs oil conversion.

Variables					
Coded process parameter levels	-1	-0.50	0	0.50	1
Time (min)-X_1	60	90	120	150	180
SCG oil-to-Li-$CaO_{(s)}$ loading (wt%)-X_2	0.50	1	2	4	5

A maximum of 14 experiments were predicted for both the SCGs oil extraction and the for the SCGs oil conversion.

3. Results and Discussion

3.1 Oil extraction Optimisation

The ability of 2-MeTHF as solvent for extraction of oil from SCGs was investigated by (Mkhonto and Chetty, 2021), reporting a maximum of 28.20 wt% oil recovery. In this investigation, SCGs oil extraction was maximised by optimising two process parameters, namely, SCGs-to-2-MeTHF ratio and extraction time. The quadratic regression model was proposed after regression analysis was performed on Box-Behnken exploratory design results. Table 4 depicts the results obtained after 14 experimental runs, which were obtained by employing the quadratic regression model. The quadratic model with coded variables predicts the yield of SCGs oil, the model is depicted by Eq (4). Where Y is the SCGs oil yield, X_1, and X_2 represent the extraction time (h) and SCGs-to-solvent ratio (w/v).

Table 4: Design of experiment for the optimisation of extraction of lipids from SCGs

Run	Time (h)	SCGs-to-Solvent ratio (w/v)	Actual Yield (wt %)	Predicted Yield (wt %)
1	0	0	25.70	24.64
2	1	-1	15.40	14.95
3	0.5	0.5	24.60	25.09
4	-0,5	-1	13.10	14.69
5	0	0	26.10	24.64
6	0.5	-0.5	21.20	22.20
7	-1	-1	12.50	11.10
8	1	0	23.10	23.24
9	1	1	20.50	20.61
10	-0.5	1	17.10	18.23
11	-1	0	15.10	17.05
12	-1	0.5	17.40	16.52
13	-0.5	1	19.20	18.23
14	0	0	25.10	24.64

$$Y = (4.964 + 0.35X_1 + 0.26\,X_2 + 0.079X_1X_2 - 0.49X_1^2 - 0.62X_2^2\,)^2 \quad (4)$$

The surface response of the quadratic model was to used optimise the extraction of oil from SCGs was evaluated using NOVA for both extraction and SCGs oil conversion processes. The outcomes of this model are shown in Table 5. The p-value of the parabolic model was 0.0001, which was < 0.05, indicating that the quadratic regression model was significant. The model terms are said to be significant if the p-values are 0.05 and the model terms are said to be insignificant if the p-value is 0.10. The lack of fit "F-value "was estimated to be 0.17, which indicated that the lack of fit was not significant when compared to the pure error. The adjusted R^2 value of 0.90 and the predicted R^2 value of 0.74 have a different value of 0.16, which is < 0.2. This indicated that there was a good estimation between the experimental data and the quadratic model. The SCGs oil yield at the optimal extraction conditions of 1:18 (w/v) SCGs-to-solvent ratio and 4.5 h extraction period was predicted by the model to be 25.10 wt%. The predicted optimal oil yield was confirmed experimentally, obtaining a lipid yield of 26.71 wt% which was slightly higher but close to the predicted value.

Table 5: Analysis of discrepancies on the results for the quadratic regression model for SCGs oil extraction.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0359	5	0.0072	23.93	0.0001	significant
X_1-Time	0.0086	1	0.0086	28.73	0.0007	
X_2-SCGs-to-Solvent ratio	0.0044	1	0.0044	14.61	0.0051	
X_1X_2	0.0002	1	0.0002	0.825	0.3904	
X_1^2	0.0057	1	0.0057	18.91	0.0025	
X_2^2	0.0105	1	0.0105	34.95	0.0004	
Residual	0.0024	8	0.0003			
Lack of Fit	0.0020	5	0.0004	3.47	0.1673	not significant
Pure Error	0.0004	3	0.0001			
Cor Total	0.0383	13				

Figure 1(a) depicts the three-dimensional surface plot of time (h) vs SCGs-to-solvent ratio (w/v).

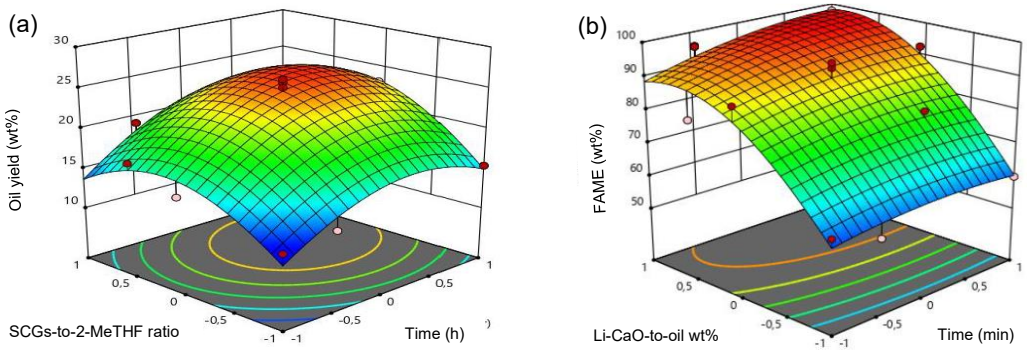

Figure 1: Illustration effect of the extraction time and SCGs-to-solvent ratio on the oil yield (a) and surface plot of time(min) against catalyst loading-to-SCGs oil (wt%) (b).

Figure 1(a) depicts possible combinations of process parameters that can be used to obtain a good oil yield. According to the slope of the 3-D plot (Figure 1(a)) and the coefficients of regression of the quadratic model (Table 5) the solids-to-solvent ratio was the more effective parameter on the oil extraction yield.

3.2 Transesterification optimisation

In this section investigation, the transesterification of SCGs oil was maximised by optimising two process parameters, namely, oil-to-catalyst loading and reaction time. The two parameters appeared to have the most effect on the conversion of SCGs oil to fuel grade hydrocarbons, advocating for their optimisation. The quadratic regression model was proposed after regression analysis was performed on Box-Behnken exploratory design results. Table 6 depicts the results obtained after 14 experimental runs, which were obtained by employing the

quadratic regression model. The quadratic model with coded variables predicts the yield of SCGs oil, the model is depicted by Eq (5).

Table 6: Design of experiment for the optimisation for SCGs oil conversion

Run	Time (h)	SCGs-to-Solvent ratio (w/v)	Actual Yield (wt%)	Predicted Yield (wt%)
1	0	0	92.54	89.49
2	1	-1	59.91	60.22
3	0.5	0.5	90.82	97.02
4	-0.5	-1	55.80	60.22
5	0	0	84.82	89.49
6	0.5	-0.5	79.74	77.97
7	-1	-1	61.00	58.37
8	1	0	92.54	90.06
9	1	1	97.81	98.21
10	-0.5	1	95.84	92.54
11	-1	0	88.74	84.27
12	-1	0.5	81.00	89.49
13	-0.5	1	95.65	92.54
14	0	0	94.09	89.49

$$Y = (9.46 + 0.16X_1 + 0.98X_2 + 0.095X_1X_2 - 0.12X_1^2 - 0.66X_1^2)^2 \quad (5)$$

The surface response of the quadratic model was used to optimise the conversion of SCG lipids to fuel grade hydrocarbons was evaluated using NOVA. The outcomes of this model are presented in Table 7.

Table 7: Analysis of discrepancies on the results for the quadratic regression model for SCGs oil conversion

Model	Sum of Squares	df	Mean Square	F-value	p-value	
X_1-Time	8.250	5	1.65	18.65	0.0003	significant
X_2-SCGs oil-to-catalyst loading	0.1756	1	0.1756	1.98	0.1965	
X_1X_2	6.300	1	6.30	71.25	< 0.0001	
X_1^2	0.0363	1	0.0363	0.4100	0.5399	
X_2^2	0.0365	1	0.0365	0.4130	0.5384	
Residual	1.200	1	1.20	13.52	0.0063	
Lack of Fit	0.7079	8	0.0885			
Pure Error	0.5691	5	0.1138	2.46	0.2447	not significant
Cor Total	0.1388	3	0.0463			
Model	8.960	13				

The lack of fit "F-value "was estimated to be 2.46, which indicated that the lack of fit was not significant when compared to the pure error. The adjusted R^2 value of 0.87 and the predicted R^2 value of 0.77 have a different value of 0.11, which is < 0.2. This indicated that there was a good estimation between the experimental data and the quadratic model. The conversion of the SCGs oil at the optimal reactor conditions of 3 h reaction time and catalyst loading-to-SCGs oil of 5 wt% was predicted by the model to give a maximum oil conversion of 98.21 wt%. The predicted optimal yield was confirmed experimentally, using the following reactor conditions, 65 °C and a stirrer speed of 165 rpm and a lipids conversion of 97.30 wt% obtaining, which was slightly lower but close to the prediction. Based on the slope of the 3-D plot, (Figure 1(b)) and the coefficients of regression significance of the quadratic model in Table 7, the reaction time was the most significant factor in the conversion of SCGs oil to fuel grade hydrocarbons between the two studied parameters.

4. Conclusion

The present study investigated the optimisation of Soxhlet, oil extraction from dry SCGs using 2-MeTHF as green solvent and the conversion of the oil to FAME in the presence of Li-$CaO_{(s)}$ catalyst synthesised from chicken eggshells. SCGs are an abundant source of oil which can be used for the production of fuel-grade hydrocarbons. Oil extraction yield was maximised by optimising the extraction time and solvent to solids ratio. A model was developed to predicts the oil yield for different combinations of solvent to solids ratio and extraction time, the model followed a quadratic regression. The model predicted the optimum extraction time of 4.5 h, and solvent to solids ratio of 18:1, providing 24.60 wt% oil yield, which were confirmed by experiments. A second model was developed for the oil transesterification process. The oil conversion was maximised by optimising the reaction time and oil to catalyst loading. The transesterification model predicted the optimum oil conversion time of 3 h and oil to catalyst loading of 5 wt%, yielding 98.21 wt% oil conversion, which was confirmed experimentally. The discrepancies between the predicted by the model and experiments were marginal.

References

Al-Hamamre, Z., Foerster,S., Hartmann,F and Kröger,M., 2012. Oil extracted from spent coffee grounds as a renewable source for fatty acid methyl ester manufacturing. Fuel , 96(1), pp. 70-76.

Bio-bean, 2021. Coffee Logs - bio-bean. [Online] Available at: Coffee logs. https://www.bio-bean.com/coffee-logs/ [Accessed 8 January 2022].

Caetano, N., Melo, A., Silva, V and Martins, A., 2014. Potential of Spent Coffee Grounds for Biodiesel Production and Other Applications. Clean Technologies and Environmental Policy, 16(7), p. 1423–1430.

Campos-Vega, R., Loarca-Piña, P., Vergara, H and Oomah, B., 2015. Spent coffee grounds: A review on current research and future prospects. Trends in Food Science &Technology, 45(1), pp. 24-36.

Efthymiopoulos, I., Hellier, P and Ladommatos, N., 2019. Effect of Solvent Extraction Parameters on the Recovery of Oil From Spent Coffee Grounds for Biofuel Production. Waste Biomass Valor, Issue 10, p. 253–264.

Giller, C., Malkani, B and Parasar, j., 2017. Coffee to Biofuels, s.l.: http://repository.upenn.edu/cbe_sdr/94.

Haile, M., 2014. Integrated volarization of spent coffee grounds to biofuels. Biofuel Research Journal, Issue 2, pp. 65-69.

Kookos, I. K., 2018. Technoeconomic and environmental assessment of a process for biodiesel production from spent coffee grounds (SCGs). Resources, Conservation and Recycling, Issue 134, p. 156–164.

Mathiyazhagan, M and Ganapathi, A., 2011. Factors Affecting Biodiesel Production. Research in Plant Biology,, 1(2), pp. 01-05.

Mkhonto, B and Chetty, M., 2021. 2-Methyltetrahydrofuran as a Potential Green Solvent for Lipids Extraction from Spent Coffee Grounds for Fuel Grade Hydrocarbons Production. CHEMICAL ENGINEERING TRANSACTIONS, 89(DOI: 10.3303/CET2189069), pp. 409 - 414.

Murugesan, A. et al., 2009. Production and analysis of bio-diesel from non-edible oils–A review. Renew. Sustain. Energy Rev, Issue 13, p. 825–834.

Pichai, E and Krit, S., 2015. Optimization of solid-to-solvent ratio and time for oil extraction process from spent coffee grounds using response surface methodology. Asian Research Publishing Network, 10(16), pp. 7049-7052 .

Rocha, M. et al., 2014. Ultrasound-assisted production of biodiesel and ethanol from spent coffee grounds. Bioresour. Technol, Volume 167, p. 343–348.