Single-Step extraction-esterification process to produce Biodiesel from Palm Oil Mill Effluent (POME) using microwave heating: a circular economy approach to making use of a difficult waste product.

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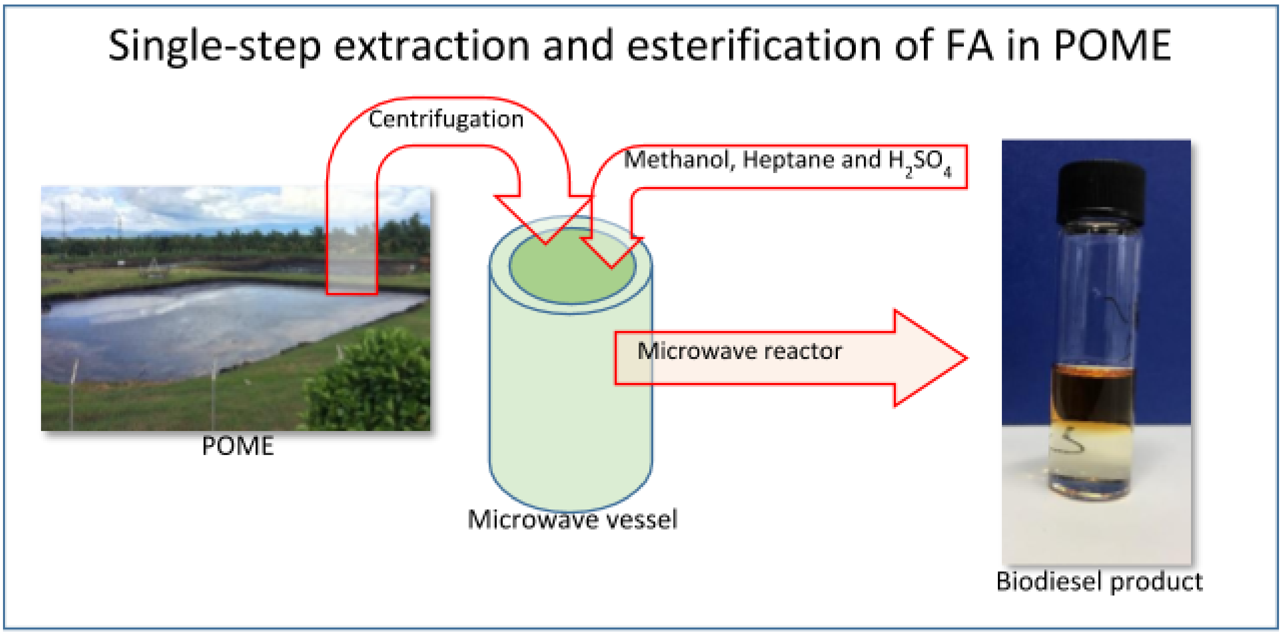
Abstract:

This investigation explores single step biodiesel synthesis using Palm Oil Mill Effluent (POME) as a feedstock. Normally considered a waste product from the extraction process of palm oil, POME treatment is difficult and can cause significant environmental pollution if discharged directly into watercourses. Fatty acids (FAs) present in POME were extracted and subsequently esterified in situ to FA methyl esters (FAME) suitable for use as biodiesel. The process of simultaneous extraction and esterification was performed under microwave irradiation in a sealed vessel which has been shown to reduce both time of reaction and energy use considerably in other reactions. The simultaneous extraction and esterification results in an 89% yield of biodiesel from the available FAs in the POME solids. The facile separation of biodiesel products from the reaction mixture augments the process and here presented is a potential route to making economic use of this difficult feedstock.

KEY WORDS: Biodiesel, palm oil mill effluent, microwave, esterification, circular economy

STATEMENT OF NOVELTY: The use of single step combined extraction and esterification microwave accelerated method for producing biodiesel directly from POME solids.

Graphical abstract:



The statement of novelty

Here presented is a method optimised by response surface methodology (RSM) to leverage the benefits of microwave processing upon the extraction and synthesis of biodiesel with the purpose of producing biodiesel from palm oil mill effluent (POME). The advantages of the microwave processing technique used in this investigation include the rapid and simultaneous extraction and esterification of fatty acids (FA) from the POME solids, followed by the facile separation of the biodiesel fraction. The RSM investigation undertaken was used to maximise the yield of biodiesel whilst minimising the amount of catalyst and methanol required for the reaction. This unique application of microwave processing for both the high pressure and temperature extraction and subsequent in-situ acid catalysed esterification in a single-vessel act as pilot study in to a method that could make use of this most difficult of biodiesel feedstocks.

1. Introduction

The circular economy (CE), whereby resources are kept in economic circulation for as long as possible and waste minimised, is currently a hotly debated concept in academic and policy circles. CE initiatives, such as recovery, recycling, and re-use, are seen as promoting carbon emissions reductions, resource security and economic competitiveness.[1] Successfully implemented, CE approaches could make a substantial contribution to the United Nations' Sustainable Development Goals, though that is presently largely a matter for speculation.[2, 3] Cognisant of the wider social and economic context, this research tackles a specific, currently environmentally problematic, residue stream of an industry of significance to a number of countries in the Global South. Approaches to the CE, as with the earlier concepts on which it builds, need to take into account geographic context industries and nations start with certain circumstances (e.g., dependence on particular industries), which may more constructively be adapted rather than abandoned.[4]

Since its introduction in the early 1900s from West Africa, the oil palm *Elaeis guineensis* has become the most valuable crop for countries in South East Asia. By 2007, palm oil had become the most consumed oil globally unseating soybean oil.[5, 6] Oil palm production has attracted much criticism on environmental grounds, with attention focusing on the prevention of further deforestation. There has also been research and policy activity into how to make existing production more efficient and less polluting. The Malaysia government, for example, introduced regulations mandating the capture of carbon emissions from POME that are typically left to microbial action in ponds open to the atmosphere.[7] Palm oil has helped lift Malaysia's economy to the ranks of upper-middle income countries, and the programme of increasing efficiency of production is part of the Malaysian government's drive to reach high income status (aiming at 2020). An existing technology for managing POME is anaerobic digestion, which implies decomposition in a controlled environment (minimising leakages to air or water) and generation of energy from the methane. This paper, however, pursues a higher value and more mobile form of energy, i.e., biodiesel. Pollution from the extraction of palm oil is mainly found in the waste water that is created; this is primarily the discharge from the sterilisation process and separator hydrocyclones known as Palm Oil Mill Effluent (POME).[8, 9] The harmful characteristics of POME can be summarised by its low pH and exceptionally high chemical and biological oxygen demand (COD and BOD respectively) that cause significant damage to watercourses if directly discharged. [10-12] During the rapid expansion of the Malaysian Palm Oil industry, which has seen the number of palm oil mills rise sharply from 10 in 1960 to 410 in 2008, there has also been a corresponding increase in the quantity of POME produced.[13] It is estimated that for every tonne of crude palm oil produced, around 3 tonnes of POME is also created leading to large volumes requiring treatment. For example, in 2009 43.8 million cubic metres of POME was generated in Malaysia alone.[9, 12, 14, 15]

However, due to the oil content present in POME, there is emerging interest in the utilisation of this material as a feedstock for Biodiesel production. Biodiesel is a synthetic fuel commonly defined as the alkyl esters of long chain FAs sourced from organic biomass such as vegetable oils or animal fats.[16] Biodiesel produced from waste products has become a focus of research in contemporary times. This approach offers several key advantages; chief among which is the reduction in competition for raw materials e.g. food.[7, 17-19] In addition, waste products are generally abundant, cheap and potentially difficult to dispose of currently; therefore any potential use is advantageous both to the producer of the waste and the environment as a whole.[20, 21] Even when the considering the low oil content of POME, the potential biodiesel yield could be significant. The use of POME as a biodiesel feedstock is a relatively new area with few publications at the time of writing, mainly concerning biological conversion methods.[22, 23]

The difficulties of using POME include the relatively low oil concentration in addition to the complex mix of surface-active particles as well as the variable composition of the POME from mill to mill. One potential avenue for the treatment of POME is the field of microwave chemistry. Since the seminal paper in 1986 by *gedye et. al.* microwave processing has been successfully applied to many organic chemical reactions; with reports of high yields and very short processing times the primary advantages.[24, 25] As well as numerous applications in the field of organic chemistry, microwave technology has been successfully applied to process of solvent extraction, known as microwave assisted extraction (MAE). First explored by Ganzler *et. al.* MAE makes use of the direct heating of the sample / solvent with microwave radiation to enhance extraction yields and lower both extraction times and energy usage.[26-28] The single step, single vessel extraction and esterification reactions being performed in this investigation represent a novel integrated method for the direct conversion of POME to biodiesel. By combining the advantages microwave technology has both in material extraction and organic reactions to the difficult feedstock that is POME, this investigation has increased the economic viability of waste treatment; thus, incentivising the removal of polluting FAs from the waste stream.

2. Methods and materials

Raw POME was sourced from Langkon Palm Oil Mill in Sabah, Malaysia and stored in sealed containers for transportation and storage. Methanol, heptane, magnesium sulphate and sulfuric acid were obtained from VWR chemicals.

For the following experiments raw POME was used. Samples used for experimentation were taken from an agitated sample; representing freshly discharged, unsettled, POME.

2.1 Extraction and esterification of fatty acids present in POME:

15ml of POME was centrifuged at RCF 3.0 (4400 RPM) in an Eppendorf 5702 centrifuge for 30 minutes. The supernatant was put aside and the pellet was transferred to a temperature-controlled microwave vessel. The organic solvent and acid catalyst were then added, the vessel sealed and placed in a Milestone Ethos EX microwave. Microwave heating was performed for 15 minutes at a constant temperature of 150°C. After the heating period the system was allowed to cool to room temperature. Once cooled the reaction mixture was transferred to a separating funnel and the organic layer removed. The organic layer was diluted 1:1 with BSTFA + TMCS (99:1) derivatisation agent and concentrations of FAs and methyl esters (MEs) analysed by GC-MS performed on a Hewlett Packard 6890 Plus fitted with a Thames Restek Rxi-17Sil MS moderate polarity column.

2.2 Determination of the initial oil content of the POME sample:

For the purpose of the evaluation of microwave reactions; the oil content of the raw POME sample was initially determined. A modified extraction procedure as set out in ISO standard 9377-2 was performed in addition to GC-MS quantification of the extracted materials. Briefly, 50ml of POME was acidified to pH 2, sealed in a vessel and stirred with the heptane extraction solvent for 30 minutes. Afterwards, Magnesium sulphate was added and the organic layer removed. A sample of the organic layer was diluted 1:1 with BSTFA + TMCS (99:1) derivatisation agent and concentrations of FAs quantified by GC-MS as above.

2.3 Water content of POME solids

An Ohaus MB23 moisture content determination apparatus was used to accurately quantify the water content in the centrifuged POME used for biodiesel production experiments. A sample of centrifuged POME (around 1.0 g) was placed onto a pre-weighed aluminium disc and placed onto the cradle of the MB23. The apparatus was activated and the device tracked the mass of the sample as the temperature is increased by an infra-red heating element present above the sample disc. After no additional change in temperature is recorded, the system reports the difference in mass between the initial and final reading as a percentage of the initial mass. This is equivalent to the mass lost as water vapour from the sample.

2.4 Statistical optimisation methods

The experimental conditions matrix was designed using analysis of variance (ANOVA) software Design Expert 11 using Response Surface Methodology (RSM) coupled with Central Composite

Design (CCD) to form a of this experimental design strategy that enables the embodiment of advantages of performing a specific number of experiments from otherwise performing unnecessary experiments, while fully considering the multivariate nature of any novel process parameters (factors), as well as consideration of the definite interactions between parameters (factors: volume of methanol, H_2SO_4 concentration, stirring), and their impact on the response yield (ME and FA concentrations).

3. Results and discussion

3.1 Initial fatty acid concentration in POME

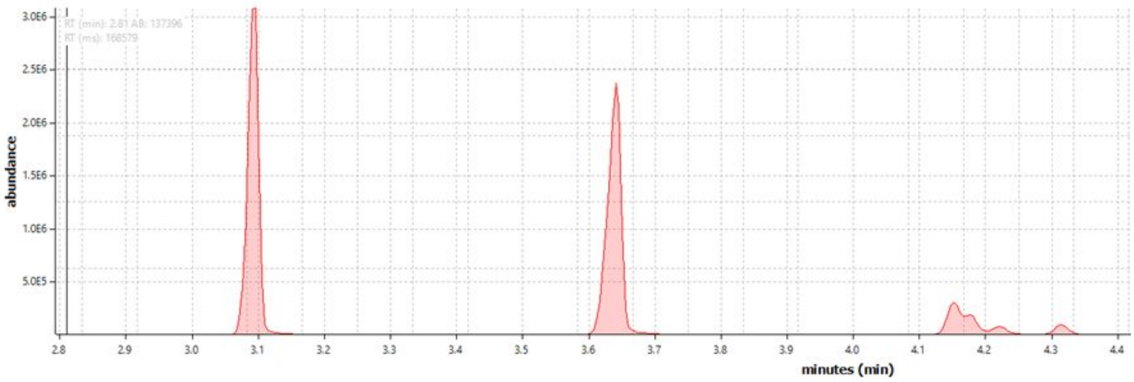


Figure 1 Chromatogram of Derivatised POME components as extracted according to the procedure above and analysed by GC-MS.

The principle components identified in the solvent extraction of raw untreated POME were FAs, principally palmitic acid, and to a lesser extent oleic acids and isomers thereof. Trace amounts of other FAs were detected as expected. For easy comparison the concentration of palmitic acid was used to evaluate the extraction efficiency and the esterification yield in this investigation. The concentration of palmitic acid in the raw pome sample was found to be 1.16 mg/ml. All extractions and reactions will be compared to this reference value for the purpose of determining yield and conversion to biodiesel. Figure 1 represents the make-up of oil extracted from raw POME according to the ISO method detailed in the previous section. The first and largest peak present at a retention time (RT) of 3.1 minutes is palmitic acid, unsurprisingly the most abundant component of POME. The peak at RT 3.65 minutes is the internal standard, docosane, used for accurate quantitation. The series of peaks between 4.1 and 4.4 minutes RT are the various C18 fatty acids, including primarily oleic acid itself (cis-9-Octadecenoic acid) as well as linoleic acid (9,12-octadecadienoic acid) as well as the saturated stearic acid (octadecanoic acid). The solvent extraction produces a remarkably clean extraction profile with only fatty acids being extracted.

3.2 Water content of POME solids

The water content of the POME sample was determined The POME analysed was centrifuged to be representative of the POME used in the biodiesel production experiments. The water content of the centrifuged POME was found to be 97.9 ± 0.3 %. Even after centrifugation, the water content of the centrifuged POME solids is still high, with almost the entire mass of the sample being water. Despite this, the appearance of the POME is that of a fibrous paste. The temperature of the water determination apparatus was set at a mild 120°C in order to prevent the volatilisation of any fatty acids or other organics that could detrimentally affect the accuracy of the water content determination.

3.3 Comparison between microwave and bench heating

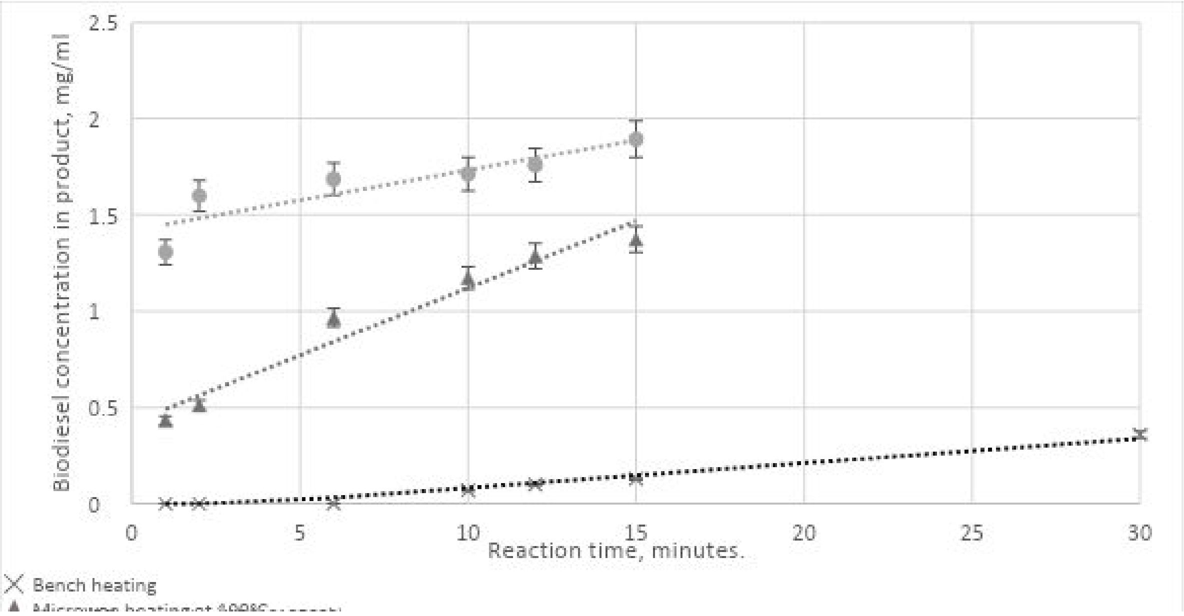


Figure 2 FAME concentration of reactions comparing microwave and bench heating

In order to assess the rate enhancement possible when working with microwave heating system, 3 identical reaction mixtures containing pure palmitic acid were heated with methanol and a H_2SO_4 catalyst. The first reaction was performed under reflux heating whereas the second and third were performed in a sealed microwave vessel at 100 and 150°C respectively. Figure 2 shows the FAME concentration after only one minute of microwave heating is significantly higher than the 30-minute FAME concentration from standard bench heating. The microwave heating was conducted at two temperatures in order to show the effect temperature has upon the esterification reaction taking place. As the reaction mixture contains 10 ml of both methanol and heptane, this approaches the azeotropic ratio resulting in a boiling point of the benchtop reaction of around 59.1°C at atmospheric pressure. The modest increase of reaction temperature used in the 100°C microwave reaction gives a significantly higher concentration of FAME, the 150°C reaction further increased the concentration of FAME produced in the 15-minute reaction window. The additional 50°C in reaction temperature between the two microwave reactions has a large effect on the resultant FAME concentration. This may be explained by the increase in pressure imparted upon the reaction by the heating of the solvent mixture far in excess of the azeotropic boiling point. As shown Figure 2 as well as increasing the rate of extraction / esterification, the higher temperature microwave reactions also increased the total amount of FAME after the 15-minute heating period. To investigate how the increased temperature (and microwave power) can increase not only the rate but more importantly the yield of FAME through increased extraction of FA, SEM images of the POME solids before and after microwave treatment were taken. A marked increase in porosity as demonstrated by the appearance of holes in the POME solids structure. Figure 3 shows the structure of the POME solids under 200x magnification. The image shows the flaky nature of the substrate. Figure 4 shows two images of POME solids taken after the microwave reaction. The appearance of pores, holes and tears in the flakes of the POME solids could be responsible for the increased quantity of oil extracted from the POME solids in the microwave reactions by increasing the surface area of the solid as well as by breaking down the physical structure that could be retaining oils. The temperature of the microwave heated reactions is controlled through the means of a PID loop that controls the microwave power delivered by the magnetron to the samples based on the setpoint temperature and the current sample temperature. In the case of the 150°C microwave samples, not only was the temperature achieved by the microwave 50°C hotter than the 100°C reaction, the average incident power used to achieve and maintain this temperature would have been higher too. In addition, the reported temperature by the microwave control software can only refer to the bulk temperature inside of the vessel (due to the proxy measurement of temperature via a thermowell). Therefore, a value for the temperature of the individual constituents of the reaction vessel cannot be determined. It is a known phenomenon that solid particles in microwaves may experience super-heating and form ‘hot-spots’ as a function of very strong microwave absorbance in a localised area, and, this could be used to explain how the modest increase in bulk microwave reaction temperature (from 100°C to 150°C) could result in a significantly higher yield of oils liberated from the solid structure.[29]

The higher incident power delivered by the microwave control software in the case of the hotter reaction could lead to an increased level of porosity developing as a result of the breakdown of the organic POME solids as a function of the increased level of superheating.

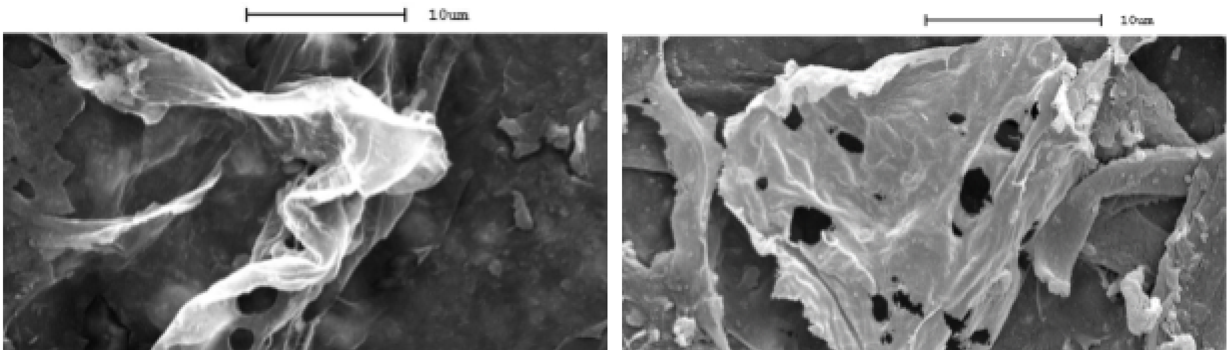


Figure 3 SEM image of POME solids showing new holes and tears formed during microwave treatment at 150°C (Mag. X1000)

Figure 4 SEM image of POME solids pre microwave treatment (Mag. X200)

3.4 CCD model and RSM analysis

A central composite design (CCD) model was used to estimate the impact of methanol, H_2SO_4 concentration and stirring on the yield of biodiesel and the quantity of fatty acids extracted from POME. In this initial design, the temperature and time of reaction was fixed at 150°C and 15 minutes. The reason for this was to more accurately attribute the effects of methanol to oil ratio and acid concentration to the yield of biodiesel. The factors and their minimum and maximum values for the optimisation are presented in Table 1

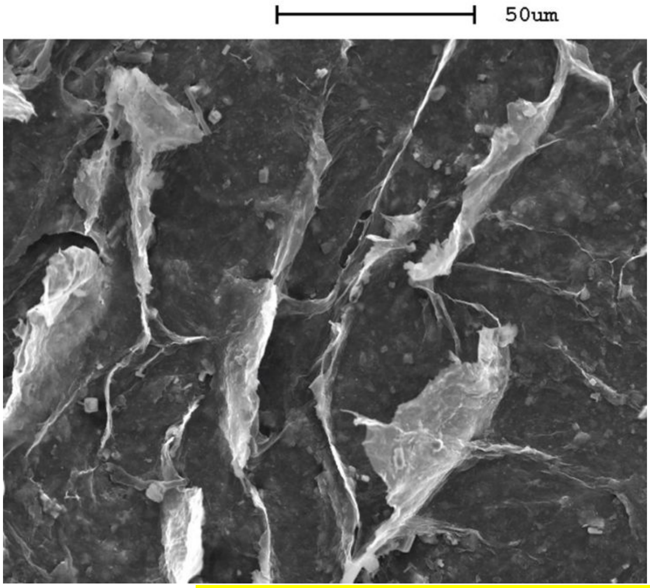


Table 1 Factors and ranges of experimental conditions used for the optimisation investigation.

Factor	**Name**	**Units**	**Type**	**Minimum**	**Maximum**	**Mean**	**Std. Dev.**
A	Methanol:Heptane vol ratio	Ratio	Numeric	0.1000	0.5000	0.2929	0.1585
B	H_2SO_4 concentration	Molar	Numeric	0.0010	0.0400	0.0198	0.0155
C	Stirring	%	Numeric	20.00	100.00	58.57	31.71

In this investigation, both the concentration of biodiesel in the final product as well as the concentration of fatty acid were studied. The purpose of this is to investigate simultaneously the performance of fatty acid extraction from POME as well as the secondary step of esterification. This is done by back-calculating the concentration of fatty acid using the present concentration of the methyl ester and adding this to the value retuned from GC-MS of the unreacted (residual) fatty acid. The methanol to heptane volume ratio was varied between 0.1 and 0.5, with a fixed 10 ml volume of heptane being used for the extraction.

Table 2 Reaction variables and responses

	Factor 1	**Factor 2**	**Factor 3**	**Response 1**	**Response 2**
	Experimental conditions			**Result**	
Run	A: Volume of methanol	B:H_2SO_4 concentration	C: Stirring	FAME concentration	FA concentration (equivalent)
	ml	Molar	%	mg/ml	mg/ml
1	5	0.021	60	1.01	1.01
2	5	0.040	20	1.09	1.05
3	3	0.021	60	0.22	0.90
4	3	0.021	60	0.20	0.86
5	3	0.021	60	0.20	0.87
6	1	0.021	60	0.00	0.79
7	5	0.040	20	1.07	1.04
8	5	0.001	20	0.00	0.68
9	3	0.040	60	0.45	0.95
10	3	0.001	60	0.00	0.81
11	1	0.001	20	0.00	0.79
12	3	0.021	60	0.21	0.88
13	5	0.001	20	0.00	0.67
14	1	0.040	100	0.08	0.83
15	1	0.001	20	0.00	0.77
16	1	0.040	100	0.07	0.83
17	3	0.021	60	0.20	0.89
18	1	0.001	100	0.00	0.74
19	5	0.001	100	0.00	0.68
20	3	0.021	60	0.21	0.88
21	1	0.001	100	0.00	0.81
22	5	0.001	100	0.09	0.74
23	3	0.021	100	0.37	0.86
24	3	0.021	60	0.21	0.91
25	1	0.040	20	0.08	0.78
26	1	0.040	20	0.05	0.80
27	5	0.040	100	1.08	1.05
28	3	0.021	20	0.65	0.91

Table 2 shows the 28 reactions for the RSM study incorporating a CCD design. The effect of stirring, sulfuric acid concentration and methanol present in the reaction was investigated in order to study the extraction of FAs from the centrifuged POME matrix and the subsequent esterification of the extracted FAs to biodiesel. The experimental variables and responses from the CCD are given in Table 2. The highest 3 concentrations of FAME in the trial were from runs utilising the maximum values for methanol content and H_2SO_4 concentration. In some runs there was an unquantifiable concentration of FAME in the sample post-reaction. The runs exhibiting zero FAME were almost exclusively characterised by the low H_2SO_4 concentration stressing the importance of acid in the esterification component of the extraction-esterification process occurring in the microwave vessel. This trend is also observed in similar extraction/reaction experiments.[30, 31] In terms of the fatty acid concentration, relating to the extraction component of the extraction-esterification process, the highest concentrations of FA were also found from runs utilising the maximum values for methanol:heptane volume ratio and H_2SO_4 concentration suggesting a role for both the acid and methanol in the initial extraction of the fatty acid from the POME matrix.

Table 3 Fit statistics for the model

Parameter	FA concentration	FAME yield
Std. Dev.	0.0239	0.0991
Mean	0.8486	0.2693
C.V. %	2.82	36.81
R^2	0.9742	0.9616
Adjusted R^2	0.9502	0.9259
Predicted R^2	-0.1485	-5.9939
Adequate Precision	22.5356	17.6275

The fit statistics as shown in Table 3 above can be used to evaluate the applicability of the model for both the FA extraction and the subsequent esterification to create FAME. A high R2 close to 1.00 for both models show that the fit of is good when compared to the experimental data. The modest difference between the predicted R^2 and adjusted R^2 could be used to indicate a block effect. However, the large value retuned for adequate precision means that the model is significantly representative of the data and can be used for the intended purpose to navigate the design space.

3.5 Fatty acid extraction performance using RSM

Table 4 is an excerpt from the ANOVA performed on the relationship between the model variables and the FA concentration and is used to determine the significance, or lack of significance of each model term. An F value for the entire model of 40.62 implies significance, with a 0.01% chance this value being due to noise. P values lower than 0.05 indicate model terms that are significant to the model. In this case, methanol quantity, A, and H_2SO_4 concentration, B, are deemed to be significant.

Stirring, C, with a P value of 0.1998 is not deemed to have a significant effect upon the Fatty acid concentration.

Table 4 ANOVA table for fatty acid extraction [Type III - Partial]

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**
Model	0.3016	13	0.0232	40.62	< 0.0001
A-Methanol:Heptane vol ratio	0.0237	1	0.0237	41.47	< 0.0001
B-H2SO4 concentration	0.0093	1	0.0093	16.35	0.0012
C-Stirring	0.0010	1	0.0010	1.81	0.1998

The 3D surface in Figure 5 shows the concentration of extracted FA at all levels of H_2SO_4 concentration and methanol. As can be seen, FA concentration peaks when both the levels of levels of H_2SO_4 concentration and methanol are at their maximum. The peak value of 1.05 mg/ml represents a 90.5% yield of all available oil in POME when compared to the ISO method used for determination. This high value is obtained after only 15 minutes of extraction at 150°C degrees and using only the centrifuged POME solids as opposed to the raw POME that the reference extraction was performed on.

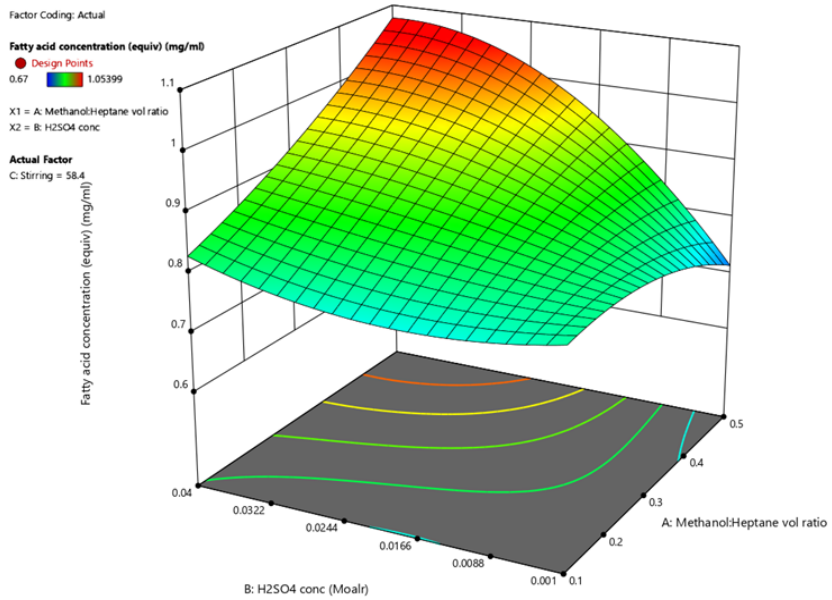


Figure 5 Effect of H2SO4 concentration and methanol on the extracted FA concentration. Colour represents FAME concentration from 0 (blue) to 1.05 mg/ml (red)

The extraction of the FAs from the centrifuged POME solids was found to be dependent on both the concentration of H_2SO_4 and the volume of methanol present. As shown, even with all factors at their lowest the extracted FA concentration is still above 0.75 mg/ml, over 64% of the oil extracted according to the reference ISO method; this must be attributed to the action of the high temperature

of the microwave and the heptane that is also present in the vessel. The methanol content of the reaction has the strongest effect on the FA concetration suggesting some solubility of palmitic acid in the methanol or perhaps the methanol-heptane azeotrope that would be formed in reactions containing the 5 ml of methanol. The next most significant factor was the H_2SO_4 concentration.

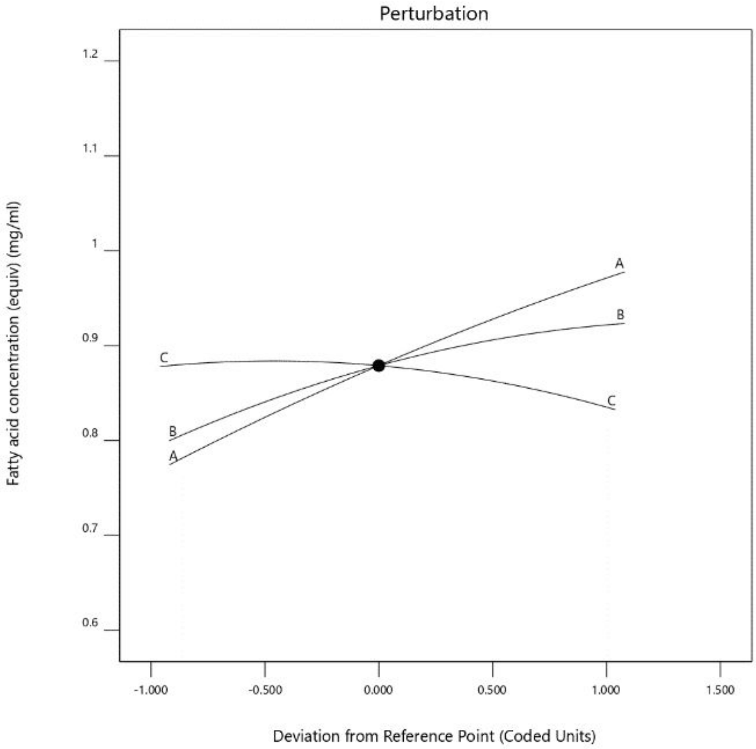


Figure 6 Perturbation plot showing the influence of all factors on the FA concentration

Whilst this was added ostensibly as an esterification catalyst (for the second step of the reaction) the effect of acid upon the POME solids may act to break down the solid structures allowing increased penetration of the extraction solvents, and subsequently, a higher amount of FA extracted. The least significant factor for FA extraction is the stirring which has a mildly detrimental effect on FA extraction. Figure 6 is a pertubation plot showing the effect of the three factors upon the FA concentration. The horizontal dimension of each line represents the range of values used in the experiments. Line A represents effect of the methanol volume on the extraction and ranges from 1 to 5 ml, line B represents the effect of H_2SO_4 concentration upon the extraction when varied from 0.001 mg/ml to 0.04 mg/ml and line C represents the stirring rate used in the microwave reactor as a unitless value and was adjusted between 20% and 100% of the maximum. As can be seen, A is the steepest gradient showing that the amount of methanol is most important to this initial extraction step.

3.6 Biodiesel production performance using RSM

Table 5 ANOVA table for biodiesel esterification [Type III - Partial]

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**
Model	3.44	13	0.2648	26.96	< 0.0001
A-Methanol:Heptane vol ratio	0.5101	1	0.5101	51.92	< 0.0001
B-H2SO4 concentration	0.1012	1	0.1012	10.31	0.0063
C-Stirring	0.0392	1	0.0392	3.99	0.0656

The esterification of the extracted palmitic acid to methyl palmitate (FAME) was also analysed through RSM as the final yield of biodiesel from the POME is the most important factor in this study overall. As shown in Table 5, and in common with the FA extraction model, methanol quantity (A) and H_2SO_4 concentration (B) are deemed to be significant. Stirring, C, with a P value of 0.0656 is not deemed to have a significant effect upon the FAME concentration. Figure 7 is a 3D surface showing that a high

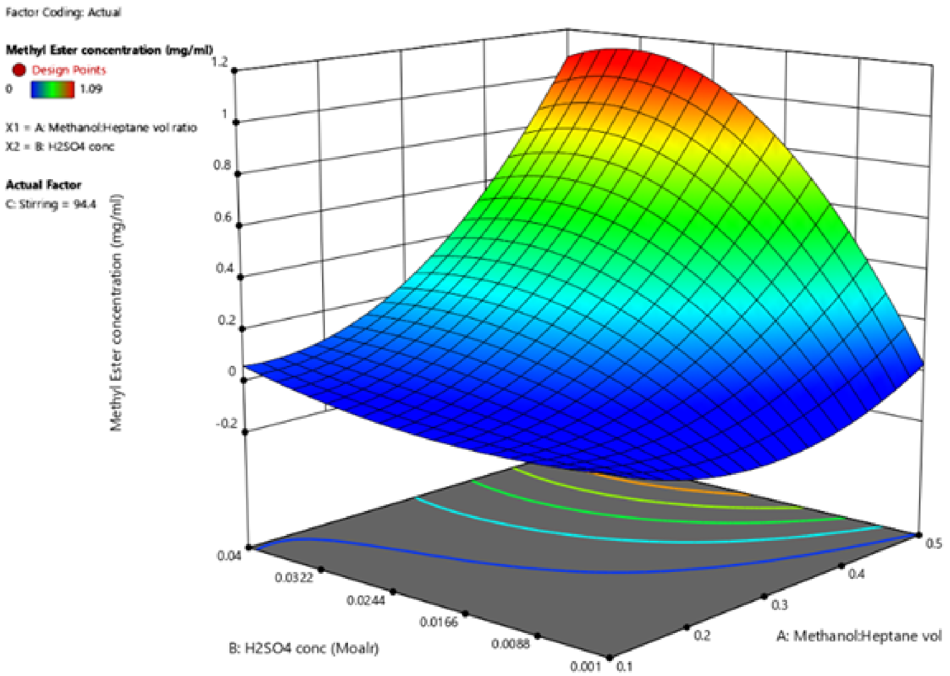


Figure 7 Effect of H2SO4 concentration and methanol on the FAME concentration. Colour represents FAME concentration from 0 (blue) to 1.09 mg/ml (red)

yield of biodiesel is only produced under conditions with the highest amount of acid and methanol. However, under these circumstances the peak yield of biodiesel when compared to the available FAs in raw POME is 89%. Whilst conditions used for the reaction were somewhat harsh and a high amount of methanol used, this can be recovered from the reaction mixture in a simple way

through distillation. The amount of methanol used could be reduced if the POME solids were dried prior to reaction however with only mild centrifugation this method can achieve a high biodiesel yield with only a 15-minute reaction time.

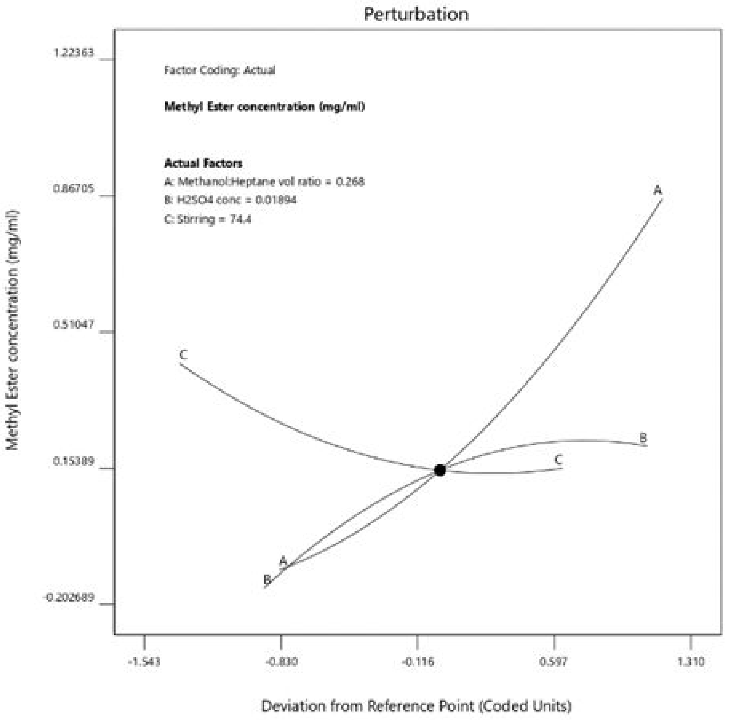


Figure 8 Perturbation plot showing the influence of all factors on the Biodiesel concentration

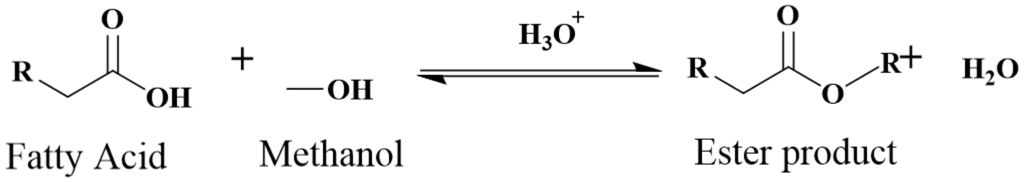


Figure 9 Equilibrium formed between reactants and products in the production of esters.

Further study into optimising the reaction with respect to temperature and reaction time could yield even more impressive results for the exploitation of this difficult feedstock. The perturbation plot, Figure 8, shows the magnitude of the contributions of the factors to the final concentration of FAME in the product. As shown, the most significant factor to biodiesel concentration is the methanol content in the reaction. This can be explained by the dynamic equilibrium present in the esterification reaction between reactants and products as shown in Figure 9. An excess of methanol will help to drive the equilibrium towards the biodiesel; this is especially important due to the residual water present in the centrifuged POME that will work in favour of the reverse reaction. The effect of H_2SO_4 concentration on the yield of biodiesel is the second most significant factor in this series of reactions. As the esterification catalyst it would be expected that the reaction responds well to an increase in acid concentration. In addition, H_2SO_4 also acts to dehydrate the reaction, diminishing the disruptive effect of residual water on the dynamic equilibrium formed between the biodiesel product and reactants in the reaction. As seen with the FA extraction, stirring had a modest albeit negative effect upon the final biodiesel concentration. Possible reasons for this could be that the increased agitation causes mixing of the organic and aqueous layer leading to increased contact between FAME molecules and water present in the reaction leading to acid hydrolysis of the product.

3.7 RSM insight in to maximising biodiesel yield

A useful output from a statistical model is the ability to attribute relative (and actual) contributions from each factor to deconvolute the relationships and possible interactions between factors in order to optimise the reaction conditions towards minimising energy use or amount of materials used for example. Table 6 is a table of factor coefficients that estimate the contributions from not only the individual factors but the interactions between factors (compound factors) represented by the multiple letter entries. A positive value for the estimated coefficient represents a positive relationship between increasing the value of the factor and a resultant increase in response value. For example, factor B, H_2SO_4 concentration has a positive coefficient meaning that an increase in H_2SO_4 concentration will give a higher biodiesel yield. Whereas factor C, stirring has a negative coefficient meaning that in order to maximise the response, stirring should be minimised.

Table 6 Factor coefficients for biodiesel esterification yield

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**
Intercept	0.2782	1	0.0321	0.2094	0.3470
A-Methanol:Heptane vol ratio	0.5050	1	0.0701	0.3547	0.6553
B-H2SO4 concentration	0.2250	1	0.0701	0.0747	0.3753
C-Stirring	-0.1400	1	0.0701	-0.2903	0.0103
AB	0.2488	1	0.0263	0.1925	0.3052
AC	0.0063	1	0.0263	-0.0500	0.0627
BC	-0.0024	1	0.0263	-0.0588	0.0539

A^2	0.1025	1	0.0590	-0.0241	0.2291
B^2	-0.1775	1	0.0590	-0.3041	-0.0509
C^2	0.1075	1	0.0590	-0.0191	0.2341
ABC	-0.0049	1	0.0263	-0.0613	0.0514
A^2B	0.0588	1	0.0748	-0.1017	0.2194
A^2C	0.1488	1	0.0748	-0.0117	0.3094
AB^2	-0.2449	1	0.0748	-0.4055	-0.0844

Actual reaction equation

Equation 1 can be used to predict the actual methyl ester concentration from the model when variables are entered using the same units as used in the model.

Predicted methyl ester concentration = $0.050599 + (2.51617A) - (21.66933B) - (0.003557C) + (152.49966AB) - (0.054369AC) + (0.006367BC) - (4.56470A^2) + (499.33209B^2) + (0.000067C^2) - (0.031617ABC) + (75.40736A^2B) + (0.093011A^2C) - (3220.69398AB^2)$

Where: A = Methanol:Heptane volume ratio

B = H2SO4 Concentration

C = Stirring rate

Equation 1 Predicted methyl ester concentration calculated from model terms

4. Conclusion

This study has shown the potential for conversion of fatty acids from POME into biodiesel. In keeping with circular economy principles, this provides a route to extracting further value from an industrial residue. Once implemented, this approach would provide a financial incentive to mill operators to capture and manage POME without leakages to the environment. It also offers an additional relatively high value output in the context of rural economies in a developing country. FAs were extracted and esterified in a single reaction vessel from centrifuged POME and converted to biodiesel with a peak yield of 89% at 150°C and a reaction time of 15 minutes. This high efficiency reaction could provide a method to obtain large quantities of biodiesel from a waste material, reducing the environmental impact of the free FA component of POME. Further studies could include the scale-up of the batch-based microwave technique to a larger flow system more suited to the continuous nature of POME production at palm oil mills.

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