

Optimization of biodiesel production via methyl acetate reaction from cerbera odollam

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Abstract. Cerbera Odollam (sea mango) is a proven promising feedstock for the production of biodiesel due to its high oil content. Fatty acid methyl esters (FAME) were produced as the final reaction product in the transesterification reflux condensation reaction of sea mango oil and methyl acetate (MA). Potassium methoxide was used as catalyst to study its reacting potential as a homogeneous base catalyst. The initial part of this project studied the optimum conditions to extract crude sea mango oil. It was found that the content of sea mango sea mango oil was 55%. This optimum amount was obtained by using 18 g of grinded sea mango seeds in 250 ml hexane. The extraction was carried out for 24 hours using solvent extraction method. Response surface methodology (RSM) was employed to determine the optimum conditions of the reaction. The three manipulated variables in this reaction were the reaction time, oil to solvent molar ratio, and catalyst wt%. The optimum condition for this reaction determined was 5 hours reaction time, 0.28 wt% of catalyst and 1:35 mol/mol of oil: solvent molar ratio. A series of test were conducted on the final FAME product of this study, namely the FTIR test, GC-FID, calorimeter bomb and viscometer test.

Keywords: cerbera odollam; biodiesel; methyl acetate; potassium methoxide

1. Introduction

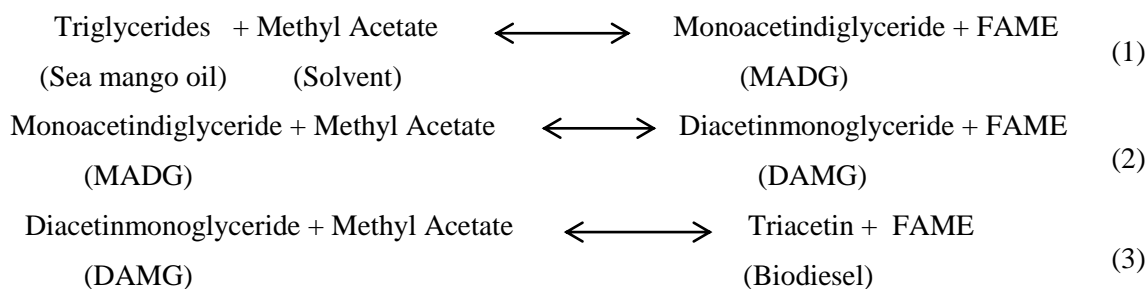
Depletion of fossil fuels has become a main topic recently. A need to search for alternative methods to replace these geologic deposits of organic materials has become important as it provides clean and recyclable energy. From the many renewable energy sources, biodiesel has been receiving much attention due to its potential in substituting diesel fuel in terms of vehicle engine usage. New researches were carried out only to discover many non-edible feedstocks for the production of biodiesel. The several advantages of non-edibles as diesel fuels are, its biodegradability, it is readily available, it has lower sulphur and aromatic content and it is renewable (Bhuiya *et al.* 2014).

Biodiesel is scientifically known as fatty acid methyl esters (FAME). They are derived from lipid substances originated from oil, fats, waste oil and many more (Palash *et al.* 2015, Masjuki *et al.* 2015). Generally, biodiesel feedstock can be categorized into four main categories, which are

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non-edible vegetable oil, edible vegetable oil, waste or recycle oil, and animal fats. Non-edible oils are regarded as second generation biodiesel while edible oils are of first generation. In production of biodiesel, a huge amount of glycerol is produced when methanol and ethanol is used as a solvent.

However, when a comparison is made between methanol and ethanol as solvents in biodiesel production, methanol is preferred. Methanol is easier to recover, while ethanol forms an azeotrope with water making it expensive to purify during recovery. In addition, methyl acetate (MA) as a solvent produces a glycerol-free process instead. Triacetin is formed in place of glycerol. Triacetin produced can be used as an addition to biodiesel without any negative side effects (Wu *et al.* 2014). Tan *et al.* (2010) successfully produced FAME using supercritical fluid method from triglycerides and MA instead of alcohol. In another research, Casas *et al.* (2011) used MA and sunflower oil only to produce a yield of 76.7% biodiesel and 17.2% triacetin at a temperature of 50°C and a compatible base catalyst. The single reaction consists of three steps where the first reaction produces monoacetindiglyceride, then diacetinmonoglyceride and finally the last step yields triglycerides and FAME. The steps are shown in Eqs. (1) to (3).



Study on the reaction between triglycerides and methyl acetate is still very limited. Moreover, many studies have been done using supercritical method where extremely high pressure and temperatures are used. Limited literatures are provided on a method that conserves energy by using lower temperatures. Advantages to supercritical methods are that its reaction time is much shorter than conventional methods. Moreover, it is a catalyst free process. However, the reflux condensation method is a typical lab experiment set up equipped with a reflux condenser where the solvent, methyl acetate (MA) is refluxed to the reactor when it is condensed. The reflux method helps reduce loss of MA solvent used (Casas *et al.* 2013). Having a boiling point of 57°C, methyl acetate evaporates easily and escapes the reaction. Having the reflux condenser, cool water condenses the evaporating solvent, hence minimizing solvent loss.

Previously, many researches were carried out using base /alkali catalyst and they have shown promising results in transesterification process. Some experimental studies reveal that base catalyst requires more reaction time and higher reaction temperature. Nevertheless, there are many advantages to base catalysed transesterification reaction and one of them is producing high yield FAME (Deshmane *et al.* 2013).

Deshmane and Adewuyi (2013) in their research used calcium methoxide solid base catalyst, methanol and soybean oil to produce a biodiesel yield of 90%. Metallic hydroxides are frequently used as catalysts due to its low price but they have lower catalytic activity when compared to alkoxides. However catalyst like potassium methoxide being a homogeneous base catalyst has to be separated from FAME after the reaction.

Potassium methoxides are derived from potassium (K⁺) and methanol (CH₃OH). When compared to common hydroxide catalysts, methoxides are preferred. A major drawback when

using base catalysts is a formation of soap as side product of the reactions. The amount of methoxide catalyst needed in a reaction is smaller. Hydroxides are lost in soap formation during reaction, hence a lesser yield FAME is obtained. Formations of soap when methoxides are used as catalyst are at its minimal amount, thus there is no lost in catalyst during reaction due to soap formation.

2. Methods

2.1 Materials

Methyl acetate (99%), used as a solvent, n-Hexane and Methanol (99%) was purchased from Fisher Scientific Malaysia. Methyl heptadecanoate (used as internal standard) and various methyl esters (methyl palmitate, methyl stearate, methyl oleate and methyl linoleate, which were used as standard references) were obtained from Fluka Chemical, Malaysia. Phosphoric acid used to neutralize the reaction was purchased from RCI Labscan, Malaysia. Sea mango fruit was collected from around Kampar, Malaysia, and the oil was extracted.

2.2 Pre-treatment of cerbera odollam seeds

First the seeds were placed in a metal tray after being cleaned, and dried in an oven at a constant temperature of 80°C for 24 hours to remove its moisture content. The oven temperature was not set too high to prevent the seed from decomposing at high temperatures (>100°C). Once the seed were obtained from the fruit, it was instantly placed for drying to prevent oxidation from occurring. As a result, keeping the seed for too long might show a less promising reading in the oil extraction amount. Once dried, the seed was grinded in a mechanical grinder into small powder form particles. Then oil is ready to be extracted.

2.3 Extraction of cerbera odollam oil

The extraction method used was solvent extraction process, where n-hexane was employed in this process. Several thimbles were used to store the grinded seeds and it was placed in a 250 mL beaker. The solvent n-hexane was added in the beaker. All beakers were covered to prevent solvent lost and the process was left to occur for 24 hours. The maximum amount of seeds that could be stored in the thimbles was 20 g and 200 ml of hexane was utilized to extract the oil. Increasing the volume of hexane in the extraction process was found to contribute negligible amount of oil extracted. Therefore, the volume of hexane was fixed at 200 ml. Subsequently, oil was recovered via the employment of a rotary evaporator where the hexane was recollected and reused for other extraction processes.

2.4 Reflux condensation methyl acetate method

For the condensation process to take place, a 250 ml round bottom flask, thermometer, retort stand and the coil condenser was set up accordingly. While the experimental setup is in progress, the catalyst used in this reaction was prepared by diluting 3 g of potassium hydroxide in methanol. Potassium hydroxide pallets are prepared in access for complete dilution in methanol forming

potassium methoxide. The catalyst preparation was done using a magnetic stirrer to provide agitation for a faster dissolving rate.

Depending on the oil to solvent molar ratio, required amount of solvent was added into the round bottom flask to initiate a reaction with 10 ml of *Cerbera Odollam* oil extracted earlier. In some reactions, molar ratio of 1:35 mol/mol is used, proposing that for 10 ml of oil, 32 ml of solvent is used. This is calculated using molecular weights of MA and stoichiometric equations. Once the oil and solvent are mixed in the round bottom flask, heater is turned on and the reaction starts to occur. Catalyst is added in immediately after the solvent and the reaction column is sealed to avoid losses of MA due to evaporation.

A thermometer was fitted into the round bottom flask to monitor its boiling temperature. Once the reaction starts to take place, running tap water is turned on to complete the reflux reaction. As methyl acetate evaporates and comes in contact with the cool water running through the coil condenser, it refluxes back in to the round bottom flask where reaction is taking place. This way, there is minimum solvent loss.

After each run, phosphoric acid is added to neutralize the reaction since a strong base is used as catalyst. Phosphoric acid is added into the reaction to quench the heated solution, producing salts. After quenching, the solution is placed into a centrifuging tube and centrifuged to remove salts. The solution is then heated to evaporate remaining solvent, leaving behind the final product of FAME. Impurities are important to be removed to avoid further reaction from taking place while evaporating excess solvent. The amount of phosphoric acid used in each run differs due to the catalyst amount used.

2.5 Product analysis

GC-2010 Plus Shimadzu was used to carry out the analysis of diluted samples to identify the amount of FAME produced. The gas chromatography was equipped with Nukol™ capillary column (15 m×0.53 mm, 0.5 μm film) and Flame Ionization Detector (FID) as the detector. Nitrogen gas was used as the carrier with an initial oven temperature of 120°C (held for 5 minutes) and raised to 260°C (held for 8 minutes) at a rate of 20°C/minute. Apart from that, the temperature of injector and detector were set at 230°C and 260°C respectively. For the GC test, samples were prepared in a vial and diluted using n-Hexane and Methyl heptadecanoate (internal standard). The internal standard, methyl heptadecanoate was dissolved in hexane to achieve a 1 g/L mixture. The diluted samples were injected into the GC column and the peak areas of each individual components and internal standard were recorded. According to the modified EN 14103 standards, the content of all the components are calculated using its areas from the peak. FAME content was calculated using Eq. (4).

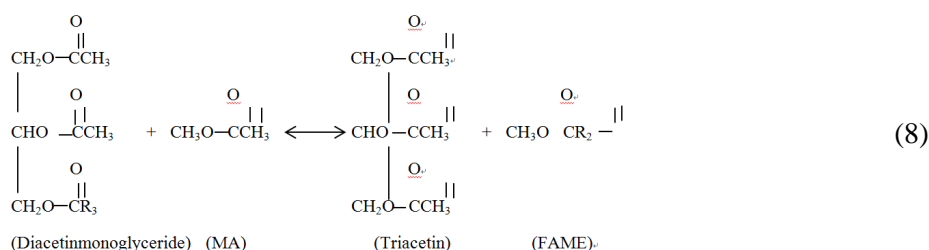
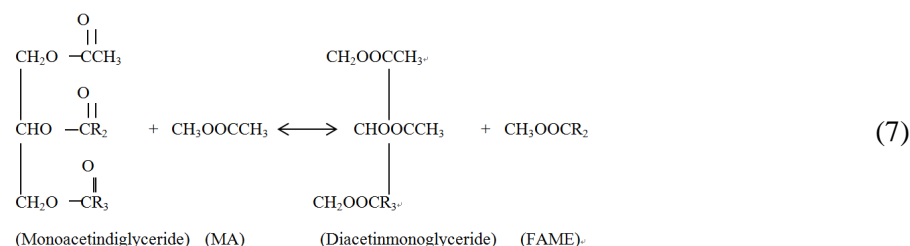
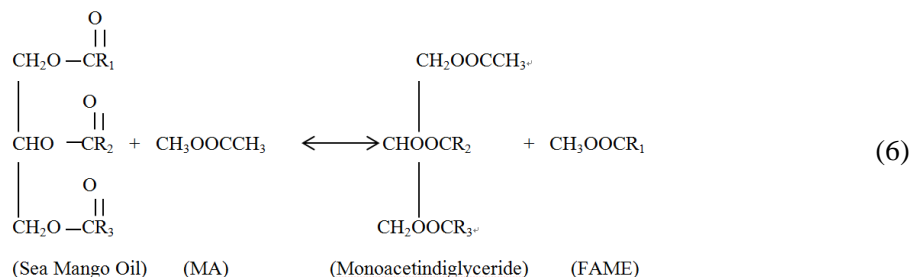
$$C = \frac{\sum A - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m} \times 100\% \quad (4)$$

Individual component content was calculated using Eq. (5).

$$C_i = \frac{A_i}{\sum A - A_{IS}} \times 100\% \quad (5)$$

2.6 Design of experiment

In this study, the Design-Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used to optimize responses for the experiment. Response Surface Methodology (RSM) was responsible for optimizing responses for the reactions. This design method analyses statistical data and optimizes desired responses for experimental runs. The three major steps that are involved in the design of these experiments are statistical design experiment, validation of mathematical model with response prediction and optimization of response. To study the influence of operating parameters (independent variable) on the transesterification of Cerbera Odollam into FAME (response), the central composite design (CCD) was chosen as the experimental design. Optimum operating parameters were generated and used from the software to determine the maximum yield (response) of FAME from the transesterification process performed. Three independent variables studied in this experimental design were reaction time (A), oil to Methyl Acetate molar ratio (B) and catalyst weight percentage (C). Proposed reaction route are shown by Eqs. (6) to (8).



3. Results and discussion

3.1 Sea mango oil extraction

Extraction of Cerbera Odollam oil was carried out using solvent extraction method. A thimble, n-Hexane and grinded seeds are needed for this extraction process. This process was used to

Table 1 Results of oil extraction for 250 ml hexane used within 24 hours

Sample no.	Mass of seed (g)	Mass of sea mango oil extracted (g)	Oil content (%)
1	8	3.50	43.75
2	10	4.82	48.00
3	12	6.10	50.80
4	15	8.00	53.00
5	18	9.91	55.05
6	20	11.00	55.00

Table 2 Experimental design matrix and results for reflux condensation reaction

Run no.	Reaction time (hours)	Catalyst weight (%)	Oil: Solvent molar ratio (mol/mol)	Yield (%)
1	3.30	0.20	35.00	44
2	4.00	0.15	20.00	25
3	4.00	0.25	20.00	35
4	4.00	0.15	50.00	45
5	4.00	0.25	50.00	48
6	5.00	0.12	35.00	45
7	5.00	0.20	35.00	58
8	5.00	0.28	35.00	66
9	5.00	0.20	9.77	15
10	5.00	0.20	60.23	41
11	6.00	0.25	50.00	40
12	6.00	0.15	20.00	32
13	6.00	0.25	20.00	30
14	6.00	0.15	50.00	38
15	6.40	0.20	35.00	53
Repeated runs				
16	5.00	0.20	35.00	55
17	5.00	0.20	35.00	59
18	5.00	0.20	35.00	60
19	5.00	0.20	35.00	58
20	5.00	0.20	35.00	62

determine the maximum amount of oil extracted from the seed. In this research, three variables were manipulated to determine the optimum crude oil extracted namely, the mass of seeds, amount of hexane and extraction time. 250 ml of n-hexane was used for each 20 g thimble. The extraction details are described in Table 1.

The optimum extraction of sea mango seed oil is at 24 hours extraction time, with 250 ml n-hexane and 18 g of seed to yield 55% crude sea mango oil.

3.2 Statistical analysis

Table 3 Sequential model sum of square for reflux condensation reaction

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob>F	
Mean	41587.20	1	41587.20			
Linear	815.53	3	271.84	1.61	0.2272	
2FI	58.38	3	19.46	0.095	0.9612	
Quadratic	2331.75	3	777.25	24.51	>0.0001	Suggested
Cubic	129.97	4	32.49	1.04	0.4583	Aliased
Residual	187.18	6	31.20			
Total	45110.00	20	2255.50			

Table 4 Analysis of variance (ANOVA) reflux condensation reaction

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob > F	
Model	3205.65	9	356.18	11.23	0.0004	significant
A	629.59	1	629.59	19.85	0.0012	
B	183.05	1	183.05	5.77	0.0372	
C	2.88	1	2.88	0.091	0.7693	
A2	2181.45	1	2181.45	68.78	< 0.0001	
B2	109.57	1	109.57	3.45	0.0927	
C2	250.78	1	250.78	7.91	0.0184	
AB	1.12	1	1.12	0.035	0.8544	
AC	36.12	1	36.12	1.14	0.3109	
BC	21.13	1	21.13	0.67	0.4334	
Residual	317.15	10	31.75			
Lack of Fit	295.65	5	59.13	13.75	0.0664	not significant
Pure Error	21.5	5	4.30			
Cor Total	3522.80	19				

In this study, 3 independent variables were used to determine the optimum conditions in this condensation reaction. A mathematical model produced from the response as a function to independent variables allows the desired optimum yield of reflux condenser process to be determined. Eq. (9) portrays a general quadratic equation of 3 independent variables.

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} x_i x_j \quad (9)$$

Furthermore, ANOVA which is the analysis of variance and correlation coefficient (R^2) was used to check the quality of the proposed model and test the lack of fit of the model respectively. There are two-dimensional and three-dimensional plots available to ease the study between the interactions of independent variables used. Another statistical analysis used here was the sequential model sum of squares. Tables 2 and 3 describe the experimental design matrix and results as well as the sequential model sum of squares, respectively.

From Table 3, it is known that the quadratic model was suggested as the best model to optimize

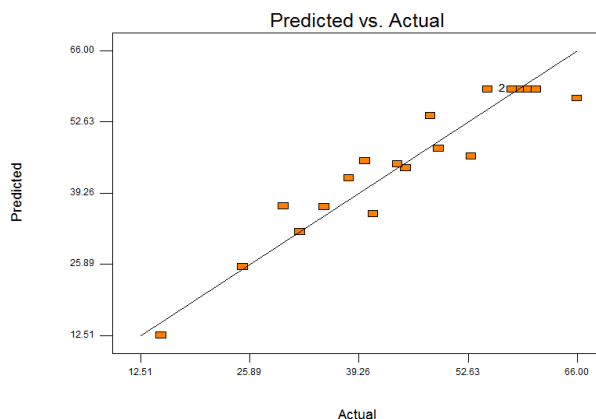


Fig. 1 Predicted yields (%) against actual yields for reflux condensation method

this experimental reaction as it fits the studied range of operating parameters with a ‘Prob>F’ value equal to 0.0001.

Then, an analysis of variance model (ANOVA) is used to evaluate the fitness of the model and also to determine the interactions of the models from the F value. The model is considered to be significant if the ‘Prob>F’ value is smaller than 0.05. Hence in this research conducted, the ‘Prob>F’ value is calculated to be 0.0004. This indicates that the models A, A2, C2, are significant model terms. Values of ‘Prob>F’ larger than 0.1 is insignificant and will not be taken into account of it will be eliminated. There are many insignificant terms in a model, thus model reduction improves a model. Table 4 shows the analysis of variance model (ANOVA).

3.3 Regression model equation

There is a range of FAME yield produced, from the lowest yield of 15% to the highest of 66% depending on experimental conditions. These figures can be fitted in to a quadratic model in which is developed after elimination of insignificant terms. The coded units are given in Eq. (10).

$$\text{Yield} = 58.73 + 6.79(A) + 3.66(B) - 0.46(C) - 12.30(A^2) - 2.76(B^2) - 4.17(C^2) - 0.37(AB) - 2.13(AC) - 1.63(BC) \quad (10)$$

From Eq. (10) it is known that significant terms existing has a great influence on the FAME content. Those insignificant is eliminated and neglected. From the equation, there are both positive values and negative values existing. Positive symbols imply synergistic effect while the negative is antagonistic effect. From the equation, molar ratio of solvent to oil (A) and catalyst percentage (%) have high coefficient, which means they play an important role as a variable affecting the FAME content in this research.

Through a predicted vs experimental plot, the quality of the model which was developed is determined by the correlation coefficient (R^2). In this study, the R^2 value is 0.9100 which means that 91% of the total variation of results was from the studied variables in this research. Fig. 1 shows the predicted yield vs experimental yield of this research. The straight line slope compares the regression model with the theoretical one. There is a fairly good achievement in experimental yield although not very promising, since the regression model is almost nearing the value 1. The higher the value of R^2 , the higher the accuracy of the model generated.

3.4 Process variable interactions

Interactions amongst each variable are important and significant in the study of biodiesel production as it affects the yield of FAME produced. Single variable studies are not necessary anymore when there is optimization of variables involved. Fig. 2 illustrates the effects of molar ratio (A) and catalyst ratio (B) on the FAME content. Increment in molar ratio of MA supposedly helps to increase the yield of FAME. Limitation of reaction equilibrium and difficulties in separating excessive MA from FAME and triacetin results in a decrement in FAME yield (Tan *et al.* 2009).

In this research, the illustration in Fig. 4 shows an increment in yield as the catalyst amount increases from 0.15% to 0.25% and methyl acetate molar ratio of 20-35 mol/mol. As the molar ratio increases beyond 1:35 mol/mol, FAME yield gradually decreases regardless of the catalyst amount. Tan *et al.* (2009) explains the effects in productivity when there is too much access of methyl acetate in the reaction. Reaction temperature was not discussed in this research due to the already known reaction optimum temperature of 60°C. Higher temperatures degrade the catalyst being used (Casas *et al.* 2012).

Fig. 3 shows the effect of oil: methyl acetate molar ratio (A) and time of reaction (C) on FAME yield for reflux condensation method used in this study. From previous researches it is stated that longer time in a reaction promotes higher activity till it reaches equilibrium (Tan *et al.* 2010). Once it reaches equilibrium at an optimum reaction time, the activity starts to decrease. Similarly in this study, reaction time with highest FAME yield is at 5 hours.

From Fig. 3, as the molar ratio increases from 1:20 mol/mol to 1:50 mol/mol, the yield in FAME increases. The lowest yield was obtained with 4 hours of reaction time and 1:20 mol/mol oil: solvent molar ratio. From this interaction, it is observed that molar ratio plays a bigger role in this research as compared to reaction time.

At reaction time of 4 hours and molar ratio of 1:50 mol/mol, the yield of FAME obtained is higher than when compared to the same reaction time and a molar ratio of 1:20 mol/mol. It is also observed that the FAME content decreases when molar ratio passes 1:35 mol/mol and reaction time of 5 hours. The effect of molar ratio on the reaction time is most prominent at 1:35 mol/mol in 5 hours of reaction time.

Lastly, Fig. 4 shows the effect of amount of catalyst used (A) and reaction time (C). Wu *et al.* (2014) stated that an insufficient amount of catalyst would result in a longer reaction time in which an equilibrium conversion would be obtained. Also, the effect of an increasing catalyst decreases

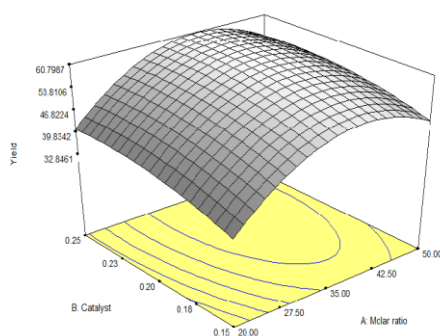


Fig. 2 Effects of molar ratio (A) and catalyst (B) in FAME content in reflux condensation method

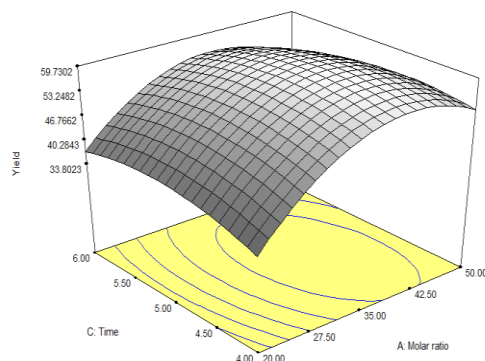


Fig. 3 Effects of oil: MA molar ratio (A) and reaction time (C) on the yield of FAME in reflux condensation reaction

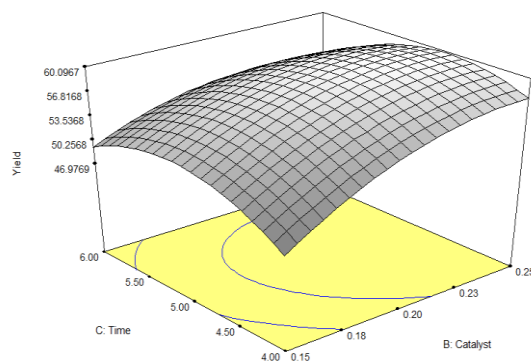


Fig. 4 Effect of catalyst (A) and reaction time (C) on FAME yield for reflux condensation reaction

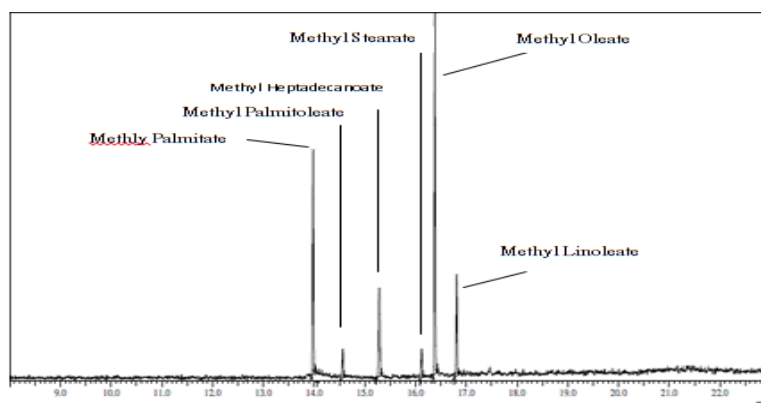


Fig. 5 Gas chromatography analysis

for a long reaction time. Based on Wu *et al.* (2014) study which comes in agreement with this research, a high concentration of catalyst was chosen and a medium reaction time perfected for the optimum yield of FAME. From Fig. 6 the FAME yield deteriorates with a longer reaction time. It is not at its highest performance even when the reaction time is too short for a complete

conversion. At 4 hours of reaction time, the yield is at its lowest. As the reaction time increased from 4 hours to 4.5 hours and finally 5 hours, FAME yield increased with the increment in catalyst amount. As the reaction time increased further beyond 5 hours, FAME yield starts deteriorating.

Comparison of the same amount of catalyst used at different reaction time can be done from Fig. 4 as well. It is observed that at 5 hours and 6 hours of reaction time, the same amount of catalyst used (0.20%), has a different effect on FAME yield. For the run with 5 hours of reaction time and 0.20% catalyst, FAME yield is observed to be higher than the 6 hours run reaction with the same amount of catalyst. Hence the optimum time of reaction suggested is at 5 hours and 0.28% catalyst.

3.5 Comparative results

RSM analysis is employed in this research to aid in the optimization of process variables in FAME production of Cerbera Odollam. Numerical features of the design software used to identify a perfect combination of optimizing variables needed to achieve a desired FAME yield throughout this research. The variables used in this study are (A) reaction time in hours, (B) the oil: methyl acetate molar ratio (mol/mol) and (C) the amount of catalyst used (%). All these variables are fixed between the lowest range of (-1) and highest range of (+1) while the FAME content was set to a maximum value. The optimum yield content and proposed optimum conditions to achieve this desired yield is shown in Table 5.

A comparison between predicted results and actual experimental results is shown in Table 6.

3.6 Characterization tests

Gas Chromatography results reveal the presence 6 substances in the FAME content. Fig. 5 shows the GC-FID graph obtained.

3.6.1 Calorific value and viscometry test

FAME sample was tested with calorimeter bomb to identify its calorific value or its heating value. Table 7 shows comparisons between previous studies conducted and this current study.

Using test method EN14214, the calorific value for petroleum diesel is 45.825 MJ/Kg. This shows that the FAME produced is suitable and able to replace petroleum diesel.

The ASTM standard requires the kinematic viscosity of FAME to be at 1.9 mm²/s to 6 mm²/s.

Table 5 Proposed optimum conditions and optimum yield of reflux condensation reaction

Conditions	Reflux condensation reaction
Reaction Time (A), hours	5
Oil: Solvent Molar Ratio, mol/mol	1:35
Catalyst, % wt	0.28
Predicted FAME yield, %	62

Table 6 Comparison of predicted and experimental yield in reflux condensation method

Run	Predicted FAME Content (%)	Experimental FAME Content (%)	Error (%)
1	62	66	6.45

Table 7 Comparison of calorific value between previous studies and current study

	Previous study by Silitonga <i>et al.</i> (2013)	Previous study by Ong <i>et al.</i> (2014)	Current study	Average calorific values	Percentage error (%)	Petroleum diesel calorific value
Calorific value (MJ/Kg)	40.226	39.90	39.76	39.96	0.5%	45.825

Table 8 Kinematic viscosity comparisons

	Previous study by Silitonga <i>et al.</i> (2013)	Current study	Petroleum diesel	ASTM standard (D 6751)
Viscosity (mm ² /s)	4.86	5.10	2.91	1.9-6.0

Test method D 6751 was used to determine the kinematic viscosity range of FAME. Table 8 illustrates kinematic viscosity findings from previous research and this current study.

4. Conclusions

A simple solvent extraction method successfully extracted 55% of sea mango oil with 250 ml n-Hexane and 24 hours extraction time. The optimum conditions for FAME production using reflux condensation method is 5 hours reaction time, 0.28 wt% catalyst and oil: MA molar ratio of 1:35 mol/mol. Calorific value obtained was 39.76 MJ/Kg which is almost the petroleum diesel value. Finally according to ASTM standards by comparison, the kinematic viscosity value obtained which is 5.10 mm²/s is in the range. The research was conducted successfully with good results.

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