Optimization and Modeling of Process Variables of Biodiesel Production from Marula Oil using Response Surface Methodology

[1] Christopher C Enweremadu* and [2] Hilary L Rutto

[1]*Department of Mechanical and Industrial Engineering, University of South Africa, UNISA Science Campus, Florida, Private Bag X6, Florida 1710, South Africa.*
[2]*Department of Chemical Engineering, Vaal University of Technology, Private Bag X021, Vanderbijlpark 1900, South Africa.*
enwercc@unisa.ac.za*

Summary: This paper presents an optimization study in the production of biodiesel production from Marula oil. The study was carried out using a central composite design of experiments under response surface methodology. A mathematical model was developed to correlate the transesterification process variables to biodiesel yield. The transesterification reaction variables were methanol to oil ratio, x_1 (10-50 wt %), reaction time, x_2 (30-90 min), reaction temperature, x_3 (30-90 °C) stirring speed, x_4 (100-400 rpm) and amount of catalyst, x_5 (0.5-1.5 g). The optimum conditions for the production of the biodiesel were found to be: methanol to oil ratio (29.43 wt %), reaction time (59.17 minutes), reaction temperature (58.80°C), stirring speed (325 rpm) and amount of catalyst (1.02 g). The optimum yield of biodiesel that can be produced was 95 %. The results revealed that the crucial fuel properties of the biodiesel produced at the optimum conditions met the ASTM biodiesel specifications.

Keywords: Central composite design, Marula oil, Modeling, Optimization, Process variables, Response surface methodology.

Introduction

The world is no longer endowed with new sources of low cost energy fossil fuels and even as the energy demands including for petroleum-based energy has been increasing due to growing industrialization. According to the International Energy Outlook of 2011 [1], the world use of liquid fuels will increase from 85.7 million barrels per day in 2008 to 112.2 million barrels per day in 2035. Due to the growing number of transportation, agricultural and construction vehicles, petroleum is the single largest energy resource that has been consumed by the world's population, exceeding natural gas, coal, nuclear energy and renewable materials.

In addition, the transport sector will account for 82% of the total increase in liquid fuel use, with the remaining growth attributed to the industrial sector [1]. Because of the progressive depletion of oil resources in combination with increasing energy consumption and the negative environmental impact of fossil fuel use, there has been a shift toward alternative sources of energy that are renewable, sustainable, efficient, cost-effective and generate reduced emissions [2, 3]. Biodiesel is among the most viable liquid transportation fuels for the foreseeable future and can contribute significantly to sustainable development in terms of socioeconomic and environmental concerns [4].

Various feedstock from edible and non-edible oils, waste and used vegetable oil, yellow grease and animal fat have been used in biodiesel production and found to be a good diesel substitute [5-8]. One of the alternative sources of biodiesel which has not been considered can be from marula tree (*Scelerocarya birrea)*, of subspecies *caffera*, which is a deciduous tree that grows naturally in many parts of South Africa, Botswana and Namibia [9]. The natural marula nuts contain active anti-oxidants which is likely to improve the oxidation stability of the biodiesel produced from it.

Several optimization studies have been carried out in the production of biodiesel. Meher *et al.*, [10], found that the yield of methyl ester from karanja oil under the optimal condition is 97–98%. The optimization of biodiesel production has been done using response surface methodology with different oils [11-15].

Response surface methodology (RSM) is a mathematical/statistical based technique which is useful for analyzing the effects of several independent variables on the response [16]. The eventual objective of RSM is to determine the optimum operating conditions for the system, or to determine the region, which satisfies the operating specifications. Almost all RSM problems utilize one or both of these approximating polynomials [17].

RSM has an important application in the process design and optimization as well as the improvement of existing design.

Although biodiesel has been produced using non-edible and edible oils, no study has been found on the production of biodiesel from marula oil. The main objective of this work is to produce biodiesel from marula oil using transesterfication process. A central composite design (CCD) was used to study the effects of five transesterification process variables: methanol to oil ratio, reaction time, reaction temperature, stirring speed, and amount of catalyst on the yield of biodiesel. A mathematical model was developed and used to correlate the transesterification process to the yield of biodiesel. Numerical optimization was used to determine the optimal conditions that can be used for the biodiesel production. Some of the important fuel properties of biodiesel produced at optimum conditions were compared with fuel properties of biodiesel using ASTM standard.

Experimental

Marula oil was supplied by Marula Pty Ltd. The fatty acid composition of marula oil is given on Table-1. Sodium methoxide and methanol were purchased from Rochelle Chemical Suppliers, South Africa and were of analytical grade. A reference standard of fatty acid methyl ester FAME Mix (C8-C24) catalogue number (18918.1 AMP) was purchased from the Sigma Chemical Co. Ltd.

Table-1: Fatty acid composition of Marula oil (wt %).

Fatty acid	Marula oil
Saturated:	
Palmitic C16:0	**10.2±2.31**
Stearic C18:0	**6.3±3.58**
Eicosanoic C20:0	**1.6±1.07**
Monounsaturated:	
Palmitoleic C16:1	**1.1±0.59**
Oleic C18:1	**74.1±3.56**
Polyunsaturated:	
Linoleic C18:2	**2.4±1.41**
Alpha Linolenic C18:3	**1.2±0.71**

Values are mean ± SD of triplicate determinations

Design of experiment

A Central Composite Design (CCD) was used to investigate the linear, quadratic, cubic and cross-product effects of the five experimental parameters on the yield of biodiesel. Table-2 lists the range and levels of the five independent variables studied. The CCD comprises of a two-level full factorial design (2^4), eight axial or star points and five center points. In CCD the value of α was held at 2^{18}. The complete design matrix of the experiments employed and results are presented on Table-3.

The experiment sequence was randomized in order to minimize the effects of the uncontrolled factors. Each response of the biodiesel yield (Y) was used to develop a mathematical model that correlates the yield of biodiesel to the experimental variables through first order, second order, third order and interaction terms, according to the following third order polynomial equation.

$$Y = \beta_O + \sum_{j=1}^{4} \beta_j X_j + \sum_{i,j=1}^{4} \beta_{ij} X_i X_j + \sum_{j=1}^{4} \beta_{jj} X_j^2 + \sum_{k,i,j=1}^{4} \beta_{kij} X_k X_i X_j + \sum_{j=1}^{4} \beta_{jjj} X_j^3 \quad (2)$$

where β_0 is offset term, β_j is linear effect, β_{ij} is first-order interaction effect, β_{jj} is squared effect, β_{kij} is second-order interaction effect.

The experiments were repeated four times and the average result was chosen.

Table-2: Levels of transesterification process variables.

Variable	Coding	Unit	Levels				
			-2	-1	0	1	2
Methanol-oil ratio	x_1	wt %	10	20	30	40	50
Time	x_2	min	30	45	60	75	90
Temperature	x_3	ºC	30	45	60	75	90
Stirring speed	x_4	rpm	100	175	250	325	400
Amount of catalyst	x_5	g	0.5	0.75	1.0	1.25	1.5

Production of biodiesel

The marula oil was heated to 100 °C to eliminate residual water and speed up the transesterification reaction. As there was no adequate information on biodiesel synthesis from marula, the alkali transesterification and the "foolproof" methods were tested. The foolproof method is essentially a two-step transesterification process. As the alkali transesterification method was not successful due to the high free fatty acid content, a two-step acid-alkali production method was adopted. Transesterification of waste vegetable oil was carried out in a temperature-controlled hot plate equipped with a reflux condenser and magnetic stirrer. During the acid-catalyzed stage, the amount of methanol used was 20% of the volume of oil plus 60% excess methanol. One liter of marula oil and 40% of the required volume of methanol was measured and added to the heated marula oil at 60ºC. The mixture was stirred gently for 5 min using a magnetic stirrer until it becomes murky. 1 ml of 95% sulfuric acid was added to the mixture. Holding the temperature at 60ºC, the mixture was stirred gently for 1hr at 500-600 rpm. The heat was removed and stirring continued for another hour after which the mixture was allowed to settle for 2 hrs. The free fatty acid content was measured and found to be below 2 %. The normal alkali transesterification process followed. The experiments were carried out according to experimental design matrix shown in Table-3.

Table-3: Experimental design matrix and results.

Process variables					
Methanol-oil ratio (wt %)	Time (hr)	Temperature (°C)	Stirring speed (rpm)	Amount of catalyst	Biodiesel yield (%)
20	45	45	175	1.25	61.29±1.20
40	45	45	175	0.75	66.92±1.15
20	75	45	175	0.75	61.65±0.77
40	75	45	175	1.25	64.85±1.51
20	45	75	175	0.75	64.23±1.40
40	45	75	175	1.25	63.25±1.26
20	75	75	175	1.25	65.50±1.06
40	75	75	175	0.75	66.34±1.33
20	45	45	325	0.75	67.61±1.08
40	45	45	325	1.25	69.39±0.81
20	75	45	325	1.25	69.65±1.51
40	75	45	325	0.75	61.80±1.25
20	45	75	325	1.25	65.64±1.48
40	45	75	325	0.75	60.25±1.12
20	75	75	325	0.75	60.40±1.15
40	75	75	325	1.25	62.85±1.32
10	60	60	250	1	55.67±1.00
50	60	60	250	1	57.42±1.03
30	30	60	250	1	59.25±0.98
30	90	60	250	1	61.67±1.18
30	60	30	250	1	49.25±0.70
30	60	90	250	1	58.50±1.01
30	60	60	100	1	90.25±1.56
30	60	60	400	1	93.60±1.43
30	60	60	250	0.5	46.65±0.83
30	60	60	250	1.5	46.40±0.73
30	60	60	250	1	94.66±1.71
30	60	60	250	1	93.85±1.66
30	60	60	250	1	94.67±1.33
30	60	60	250	1	94.89±1.18
30	60	60	250	1	94.56±1.28
30	60	60	250	1	95.39±1.02

Values are mean ± SD

Gas Chromatography method

The analysis of biodiesel produced was done by a Varian Gas Chromatography (model number CP3400) equipped with an auto sampler (model no CP3800). A poly-siloxane coated column of length (30 m), internal diameter (0.3 mm) and film thickness (0.53 μm) was used. The oven temperature was kept 160 °C for 1 min., increased at 4 °C /min up to 220°C and held for 17 min. The injector temperature was started at 250 °C while the detector temperature was maintained at 280°C thorough out the reaction. Nitrogen was used as a carrier gas. The samples were prepared using hexane as solvent and 1 μl were injected into the gas chromatography. Calibration standards were prepared from a known concentration methyl esters solution, and then the standards were used to plot a calibration curve which was used in the determination of the methyl esters. Each experiment was performed in triplicate. The biodiesel was measured using the following equation:

$$\text{Biodiesel yield(wt\%)} = \frac{\text{Amount of FAME(g)}}{\text{Amount of oil used (g)}} \times 100\%$$

(3)

Characterization of fuel properties of marula biodiesel

The biodiesel produced at optimal conditions was characterized according to the ASTM biodiesel standard. The following parameters were determined: acid value, by color indicator titration according to ASTM D974; iodine value, by volumetric titration using Wijs reagent, according to the ISO standard 3961; kinematic viscosity of sample was measured with the help of a Red Wood No. 1 viscometer at a temperature of 40 °C; density was determined with a density meter at 25 °C; water content was determined by coulometric Karl Fischer titration method; pour point and cloud point were determined using the tilt and cloud and pour point apparatus following ASTM standards D2500 and D93 respectively. The flash point was measured according to ASTM D93 using Pensky-Martens

apparatus. Each experiment was conducted in triplicate and the data reported as mean ± standard deviation.

Model fitting and statistical analysis

Design Expert (Version 6.0.6, StatEase, Inc., USA) software was used as regression analytical tool to fit experimental data to the third order polynomial regression model. The evaluation of statistical significance of the model was developed.

Results and Discussion

Development of regression model equation

The final equation in terms of actual values after excluding the insignificant terms was identified using Fisher's test as shown in Eq. (1):

The negative sign in front of the terms indicates antagonistic effect, while the positive sign indicates synergistic effect. The quality of the model could be evaluated from the coefficient correlation. The coefficient of determination, R^2 for Eq. (2) was 0.922. A high value of predicted R^2 is an indication of reasonable significance of the model. This implies that 92.2 % of the total variation in the transesterification responses is explained by the model. Similar observations have been made by Rashid *et al.* [18].

The analysis of variance (ANOVA) is used to check the adequacy of the model is presented in Table-4. Using a 95% confidence level, the cubic model was tested to be significant as the theoretical $F_{0.05\ (20.9)}$ is much lower than the computed F value of 5.62. This indicates that the regression model is reliable in predicting the biodiesel yield. From Table-4, it was observed that generally the five individual variables studied, methanol to oil ratio (x_1), the reaction time (x_2), reaction temperature (x_3), stirring speed (x_4) and amount of catalyst (x_5) have very little effect on the biodiesel yield. The quadratic terms x^2_5, had enormous effect on the biodiesel yield compared to the variables x^2_1, x^2_2, and x^2_3; while the x^2_4 variable had very little effect on the biodiesel yield. The cubic

terms did not affect the biodiesel yield. Generally the effect of interaction between the variables was minimal on biodiesel yield. The predicted versus the experimental values of biodiesel yield plotted against a unit slope is presented in Fig. 1. The results show that the regression model equation provided a very accurate description of the experimental data.
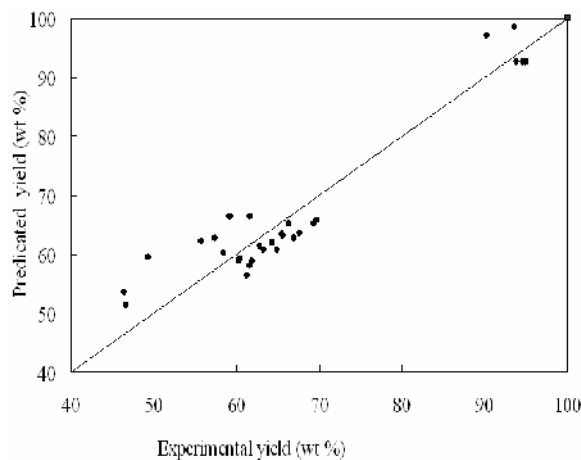

Fig. 1:   Predicted versus the experimental values of biodiesel yield.

Effect of Transesterification on the Process Variables

The three-dimensional plot in Fig. 2 shows the response surface of biodiesel yield with varying temperature (x_3) and methanol to oil ratio (x_1). The reaction time (x_2), stirring speed (x_4) and the amount of catalyst (x_5) were held at 60 min, 250 rpm and 1 gram respectively. As could be observed from the Fig., the biodiesel yield was slightly lower at 45 °C compared to 75°C. Also, when the temperature was held at 45°C and 75°C the biodiesel yield increased with increase in methanol to oil ratio but as the methanol to oil ratio reached about 30 wt % there was a sharp decrease in the biodiesel yield at both temperatures. The reason could be that the higher quantity of methanol might have increased the solubility of glycerine in the reaction mixture causing a reverse glycerolysis reaction to occur [6].

$$Y = -374.0 - 5.20x_1 + 3.34x_2 + 4.67x_3 - 0.02x_4 + 297.50x_5$$
$$- 0.076x_1^2 - 0.029x_2^2 - 0.037x_3^2 + 2.28\text{x}10^{-4}x_4^2 - 161.01x_5^2 - 1\text{x}10^{-3}x_1x_2 \qquad (1)$$
$$- 2.433\text{x}10^{-3}x_1x_3 - 1.48\text{x}10^{-3}x_1x_4 - 0.079x_1x_5 + 2.49\text{x}10^{-3}x_2x_3$$
$$- 6.02\text{x}10^{-4}x_2x_4 + 0.201x_2x_5 - 1.33\text{x}10^{-3}x_3x_4 - 0.019x_3x_5 + 0.072x_4x_5$$

Table-4: Analysis of variance ANOVA for the regression model equation and coefficients after removing the insignificant terms

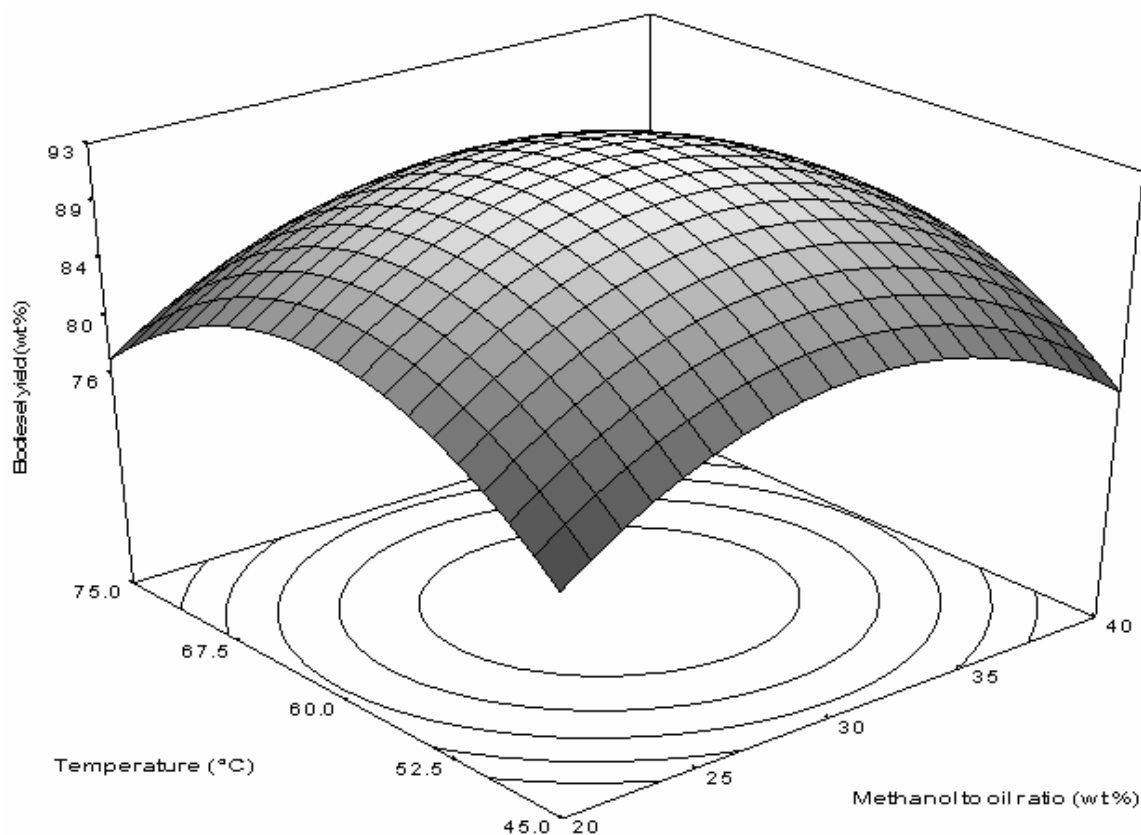| Source	Sum of squares	Degrees of freedom	Mean of squares	F-test
Model	**6854.7**	**20**	**342.74**	**6.52**
x_1	0.42	1	0.42	8.01E-03
x_2	0.02	1	0.02	3.88E-04
x_3	0.6	1	0.6	0.011
x_4	4.39	1	4.39	0.083
x_5	6.74	1	6.74	0.13
x^2_1	1675.8	1	1675.8	31.87
x^2_2	1269.9	1	1269.9	24.15
x^2_3	1984.86	1	1984.86	37.75
x^2_4	48.56	1	48.56	0.92
x^2_5	2970.65	1	2970.65	56.5
x_1x_2	0.36	1	0.36	6.85E-03
x_1x_3	2.13	1	2.13	0.041
x_1x_4	19.58	1	19.58	0.37
x_1x_5	0.62	1	0.62	0.012
x_2x_3	5.04	1	5.04	0.096
x_2x_4	7.34	1	7.34	0.14
x_2x_5	9.15	1	9.15	0.17
x_3x_4	35.76	1	35.76	0.68
x_3x_5	0.087	1	0.087	1.66E-03
x_4x_5	29.48	1	29.48	0.56
	578.34	11	52.58	-

Fig. 2a: Effect of amount of temperature and methanol to oil ratio on the transesterification process response surface plot
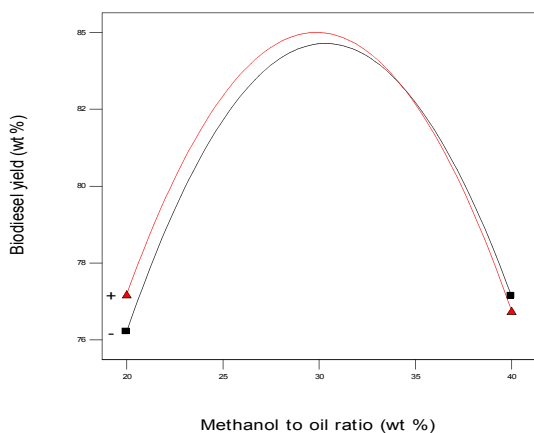
Fig. 2b: Effect of amount of temperature and methanol to oil ratio on the transesterification process: two-dimensional drawing where the temperature is held at (+) 75°C and (-) 45 °C.

The changes in biodiesel yield with stirring speed and the reaction time are presented in Fig. 3. The reaction temperature, the amount of catalyst and the methanol to ratio were held at 60°C, 1 g and 30

wt %, respectively. The stirring speed at 325 rpm gave a higher biodiesel yield when compared to 175 rpm. As the reaction time increases the biodiesel yield increases to a maximum of about 60 minutes, thereafter there was a sharp decrease in biodiesel yield at both stirring speeds. Saponification process caused by reversible reaction occurs when reaction time was above 60 minutes might have led to the reduction in the biodiesel yield [19].

The changes in the yield of fatty acid methyl ester with varying temperature and the amount of catalyst are plotted in Fig. 4. The reaction time, methanol to oil ratio and stirring speed were held at 60 minutes, 30 wt % and 250 rpm respectively. The amount of catalyst at 1.25 g has a slightly higher biodiesel yield compared to 1 gram. The effect of increasing temperature depicts a minimax behavior on the biodiesel yield; the maximum yield occurring at about 60°C but above this temperature, the biodiesel yield decreases significantly. Higher temperature accelerates the loss of methanol in the vapour phase; similar result has been reported by [20].
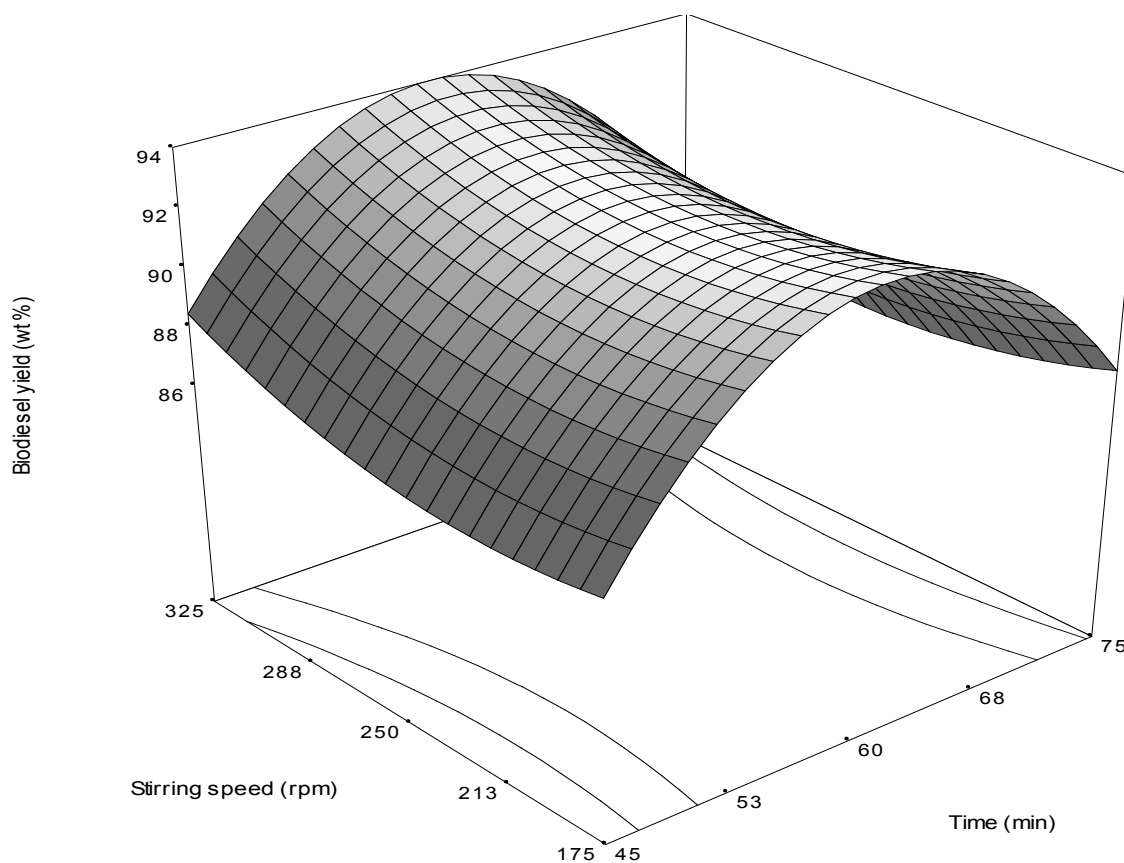

Fig.3a. Effect of stirring speed and time on the transesterification process: response surface plot.
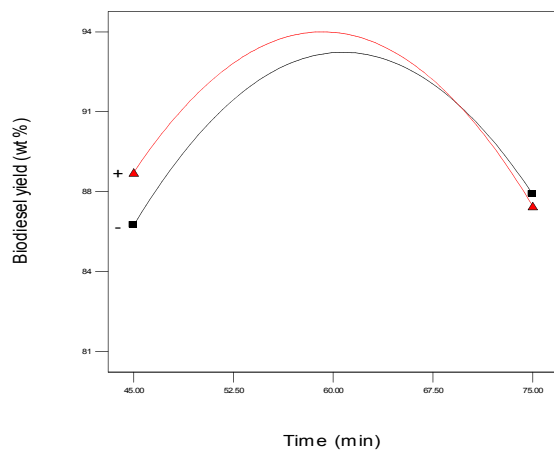
Fig.3b. Effect of stirring speed and time on the transesterification process: two-dimensional drawing where the stirring speed is held at (+) 325 rpm and (-) 175 rpm.
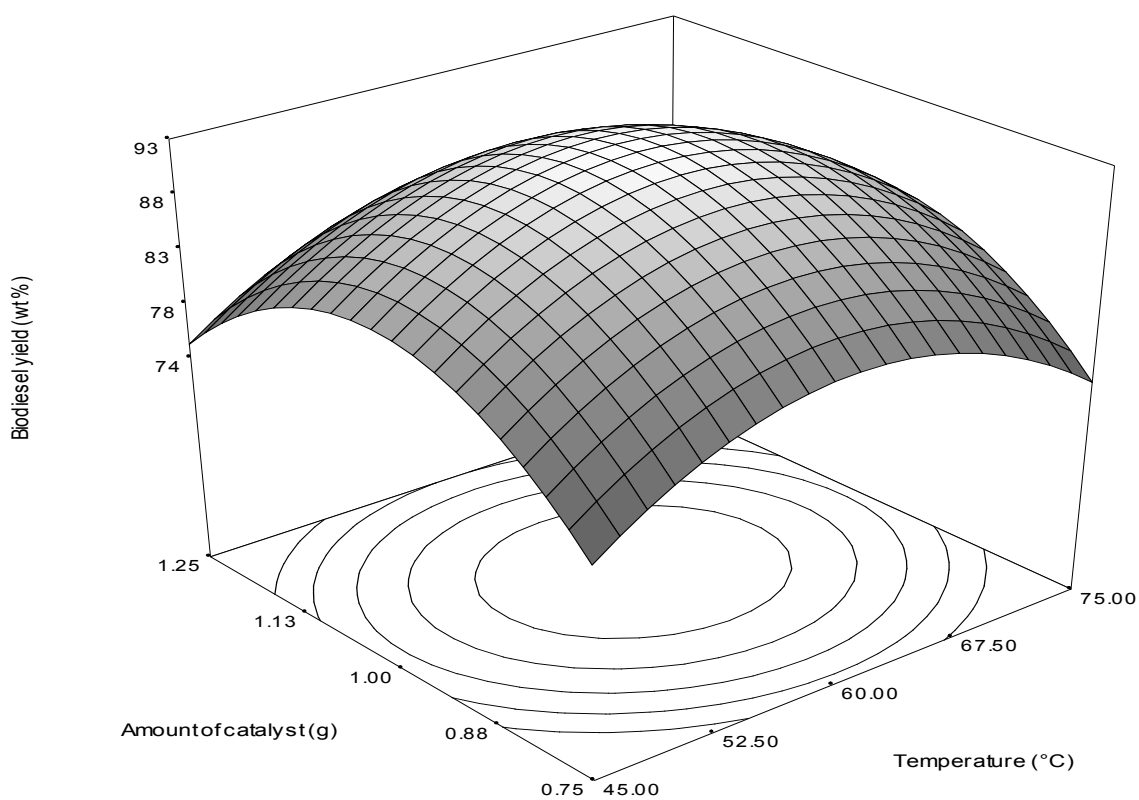

Fig.4a. Effect of amount of catalyst and temperature on the transesterification process: response surface plot
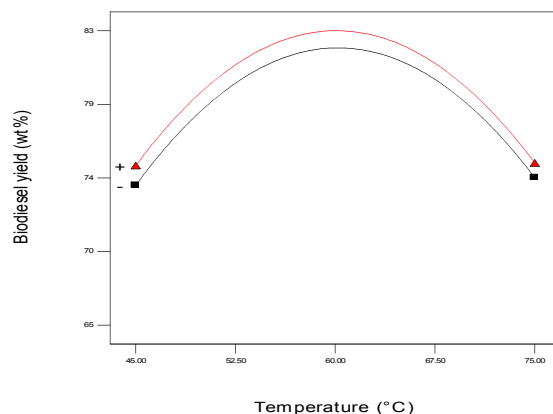
Fig.4b: Effect of amount of catalyst and temperature on the transesterification process: two-dimensional drawing where the catalyst is held at (+) 1.25 g and (-) 0.75 g

Table-5: Fuel properties of Marula biodiesel compared to other biodiesel and ASTM specifications4

Parameter	Marula	Soybean	Jatropha	Palm	ASTMD6751
Density at 25°C (kg /m^3)	877±15.74	885	880	864.4	-
Viscosity at 40°C (mm²/ s)	4.12±0.03	4.2	4.4	4.5	1.9-6.0
Flash point (°C)	171±2.95	160	163	176	130 min
Pour point (°C)	3±0.025	-7	0	15	-
Cloud point (°C)	6±0,09	4	4	16	-
Oxidation stability (hr)	8.4±2.86	1.3	3.23	13.37	3 min
Cetane number	58±1.04	49	57.1	61	47 min
Higher heating value (MJ/kg)	37.9±0.09	41.28	41	41.24	-
Iodine value (gI$_2$/100g)	96.40±0.04	128	105.1	57	-
Acid value (mgKOH/g)	0.32±0.03	0.15	0.48	0.12	0.5 max
Free glycerol (wt %)	0.01±0.001	0.07	0.01	0.01	0.02
Total glycerol (wt %)	0.12±0.02	0.00	0.02	0.06	0.24
Water content(% vol)	trace	-	-	-	0.05 max

Values are mean ± standard deviation of triplicate determinations

Optimum operating conditions

The response surfaces from the three-dimensional plots (Figs. 2-4) showed minimax and saddle behavior; therefore the optimum conditions can be obtained by applying numerical optimization using design expert software. The optimum conditions for the production of biodiesel were as follows: methanol to oil ratio (29.43 wt %), reaction time (59.17 minutes), reaction temperature (58.80 °C), stirring speed (325 rpm) and amount of catalyst (1.02 g). The optimum biodiesel yield that can be produced was 95.39 %. Similar results have been obtained from the study by Joeng *et al*. [21], who used response surface methodology (effects of five level three factors interaction) and reported optimal values of the variables as follows: reaction catalyst amount of 1.26% (w/w), temperature of 65.0°C, and lard-to-methanol molar ratio of 1:7.5, with a 20 min reaction time the optimum yield of fatty acid methyl ester was 98%. Also, in the present study the optimized biodiesel yield (95.39%) was marginally higher than the yield (94%) obtained by the transesterification of moringa oil with methanol but performed poorer when compared with 98.5%

obtained by methanolysis of sunflower oil by Rashid *et al*. [22, 23].

Fuel properties of marula biodiesel compared to other fatty acid methyl esters

Some fuel properties of methyl esters produced from marula oil were determined and compared to that of soybean, jatropha and palm oil methyl ester [24-26] (Table-5). Generally the fuel properties of biodiesel are influenced by fatty acid methyl ester profile [27].

The fuel properties of methyl ester synthesized from marula oil are within the ASTM standards for biodiesel. High cloud and pour point values can be explained by the amount of unsaturated and saturated methyl ester [28]. The higher cloud and pour points of marula biodiesel compared to biodiesel from soybean and jatropha could be explained by the higher saturated FAME of marula oil which have higher melting point than unsaturated FAME [29]. The more the saturated molecules, the higher the cetane number as in the case of palm biodiesel. The lower iodine value of marula oil biodiesel compared to soybean biodiesel could be that soybean biodiesel

have more unsaturated FAME and therefore a higher iodine value of which does not meet the biodiesel ASTM standard.

Conclusions

This study has demonstrated the possibility of producing biodiesel from marula using a two-step acid-alkali catalyst technique. The response surface technique was used to determine the optimal conditions for the transesterification process. The optimum conditions for the production of biodiesel were as follows: methanol to oil ratio (29.43 wt %), reaction time (59.17 min), reaction temperature (58.80°C), stirring speed (325 rpm) and amount of catalyst (1.02 g). The optimum yield of biodiesel that can be produced was 95 %. It was found that the important fuel properties of the biodiesel produced at optimum condition met the biodiesel ASTM D-6751 specifications.

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