Microwave Irradiated Transesterification of *Croton Megalocarpus* Oil – Process Optimization using Response Surface Methodology

Anil Kumar, Abraham Chirchir, Saul S Namango, Henry K Kiriamiti

Abstract - Biodiesel is a renewable, biodegradable and environmentally friendly fuel which has the highest potential to replace petrodiesel. In Kenya, *Croton megalocarpus* oil has been shown to be a viable source of non-edible feed to produce biodiesel. Biodiesel is produced by transesterification of oil with an alcohol in the presence of a catalyst. Microwave irradiation is a superior heating mode as compared to conventional heating. Optimization studies for the transesterification of *Croton megalocarpus* oil employing homogeneous NaOH catalyst were carried out by conventional heating and microwave irradiation. Box Wilson Central Composite Design was used to optimize process variables of methanol-to-oil ratio, catalyst concentration, reaction temperature for the case of conventional heating; and methanol-to-oil ratio, catalyst concentration, reaction time for microwave irradiation. The yield of fatty acid methyl ester (FAME) was correlated as a function of the reaction variables in form of a quadratic equation. The correlation was plotted in response surface and contour plots to indicate the effect of operation variables and to identify areas of optimal yield. Croton oil was characterized by standard methods. Gas chromatography was used to obtain FAME yield. FAME was analyzed for properties as a biodiesel fuel and it satisfied the international standards.

Keywords biodiesel, microwave, response surface, optimization.

I. INTRODUCTION

According to American Society for Testing and Materials (ASTM), a biodiesel is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751. [1]. Studies using pure and petrodiesel blended biodiesels show that this biofuel can be used in diesel engine without any modification and is best suited to replace petrodiesel as a fuel [2].

Produced from biological sources, biodiesel is biodegradable. Biodiesel has lower environmental impact compared to petrodiesel as dramatic reductions are observed in the emissions of unburned hydrocarbons, carbon dioxide, carbon monoxide, sulphates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, ozone-forming hydrocarbons, and particulate matter [3]. *Croton megalocarpus* tree is indigenous to East Africa. In a study, vegetable oil production for five oil bearing plant species, *Aleurites moluccana, Croton megalocarpus, Jatropha carcas, Moringa oliphera* and *Pachira glabra*, were investigated as potential biodiesel feedstock. The multi-criterion-decision-analysis ranked *Croton megalocarpus* as the plant with the highest vegetable oil production potential, followed by *M. oliefera*, *J. curcas*, *A. moluccana*, and *P. glabra* [4]. Aliyu *et. al*. [5] also studied the potential of C*croton megalocarpus* and concluded that the croton oil had a strong potential as a source for biodiesel.

Biodiesel is produced by reacting a vegetable oil (or animal fat) with an alcohol in presence of a catalyst in a transesterification reaction. Transesterification is a reversible reaction and is supposed to occur in three steps. First is the conversion of triglycerides to diglycerides, followed by conversion of diglycerides to monoglycerides and lastly the conversion of monoglyceride to glycerol. Each step yields one molecule of alkyl ester, as given in reactions below:

$$\text{Triglyceride} + R'OH \overset{\text{catalyst}}{\rightleftharpoons} \text{diglyceride} + R'COOR_1$$

$$\text{Diglyceride} + R'OH \overset{\text{catalyst}}{\rightleftharpoons} \text{monoglyceride} + R'COOR_2$$

$$\text{Monoglyceride} + R'OH \overset{\text{catalyst}}{\rightleftharpoons} \text{glycerol} + R'COOR_3$$

In the above reactions, R' is the alkyl group for the alcohol whereas R_1 , R_2 and R_3 are carbon chain of fatty acid [6]. When methanol is used as the alcohol, the transesterification (or methanolysis) results in formation of fatty acid methyl esters (FAME). Catalysts for transesterification can be categorized into homogeneous and heterogeneous. Homogeneous catalysts are of acidic and basic type. Basic catalysts are more common as they perform better. The conventional homogenous basic catalysts are alkali such as sodium hydroxide, alkali metal alkoxides (such as sodium or potassium methoxide and ethoxide) and potassium hydroxide. Transesterification reactions are carried out using conventional heating (eg., waterbath) and microwave irradiation. Microwave irradiation drastically reduces the reaction time, leading to energy saving and better environmental impact. Reaction variables are heating mode, reactant ratio, catalyst concentration, reaction temperature and reaction time. For microwave reactors, the microwave power is also a variable. In the present study, process variables were methanol-to-oil ratio, catalyst concentration, reaction temperature for the case of conventional heating; and

Anil Kumar, Dept of Chemical & Process Engineering, Moi University (phone: +254733361291; e-mail: akumar@mu.ac.ke, anil3900@gmail.com).
Abraham Chirchir, Dept of Chemical & Process Engineering, Moi University (email: tabokiat@yahoo.com).
Saul S. Namango, Dept of Chemical & Process Engineering, Moi University (email: saul.namango@gmail.com).
Henry K. Kiriamiti, Dept of Chemical & Process Engineering, Moi University (email: kiriamiti@yahoo.com).

methanol-to-oil ratio, catalyst concentration, reaction time for microwave irradiation.

II. MATERIALS AND METHODS

A. ANOVA and regression analysis

A five-level, three-factor Box-Wilson Central Composite Design (CCD), was used for experiment design.
Independent variables for conventional heating are given in Table 1.

Table 1: Independent variables and their levels in CCD. Codes: X1 Catalyst amount (wt%), X2 Temperature (deg C), X3 Methanol:oil mole ratio

Codes	Variable levels				
	-α= -1.682	-1	0	1	+α= 1.682
X1	0.16	0.5	1	1.5	1.84
X2	43	50	60	70	77
X3	1	3	6	9	11

A total of 20 experiments, including 6 replications at the centre point, were conducted. Reaction time was kept constant at 2 h. Table 2 gives the independent variables for microwave irradiation.

Table 2: Independent variables and their levels in CCD. Codes: X1 Catalyst amount (wt%), X2 Time (s), X3 Methanol:oil mole ratio

Codes	Variable levels				
	-α= -1.682	-1	0	1	+α= 1.682
X1	0.16	0.5	1	1.5	1.84
X2	10	30	60	90	110
X3	4	6	9	12	14

For a full factorial rotatable design, $\alpha = [2^k]^{1/4} = [2^3]^{1/4} = 1.682$ [7].

Figure 1 shows a CCD for $k = 3$ factors. This design has $14 + n_C$ runs (usually $3 \leq n_C \leq 5$). Here n_C is the number of replicates at the centre point.

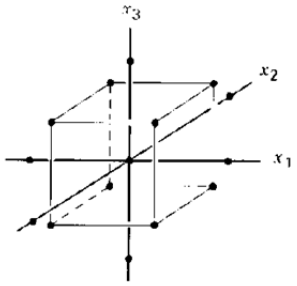

Fig.1 CCD for Three factors

A full quadratic model for biodiesel yield (Y) was tested.

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{1=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} X_i X_j \quad (1)$$

Design Expert 9® was used for ANOVA and regression analysis.

B. Experimental Procedure

Croton megalocarpus oil was obtained from Help Self-Help Centre Nairobi. Analytical grade sodium hydroxide pellets were obtained from Gelsup, Nairobi. Analytical grade methanol was from Sigma Aldrich. GC grade solvents n-heptane, hexane; GC standards methyl heptadecanoate, triolein, methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate were from Sigma Aldrich. Equipment included analytical balance, water bath (Stuart RE 300B, accuracy ± 1°C), mechanical stirrer (Stuart SS10, 0-2000 rpm), domestic microwave oven (Shivaki, SMW-103, 1300W), voltage regulator, magnetic stirrer (Hanna), thermocouple thermometer (Hanna HI9055), centrifuge (Hettich D-7200), Teflon® tubing, standard laboratory glassware. Experimental setup and procedure has been described elsewhere [8].

C. FAME Analysis

FAME was analyzed using a Gas chromatograph (MRC GC3420A) with flame ionization detector, capillary column Agilent CP-Sil 88 (60m x 0.25mm x 0.36mm, coating 0.2µm); carrier gas was nitrogen and other gases were hydrogen and air. Gases were of analytical grade. Data analysis was done using Peak-ABC chromatography data handling system. FAME content was calculated using the following formula (BRUKER Chemical Analysis Application Note # CA-270358):

$$\text{FAME} = \left(\frac{(\sum A) - AEI}{AEI}\right)\left(\frac{CEI \times VEI}{m}\right) \times 100\ \% \quad (2)$$

where, $\sum A$ = total peak area for methyl esters, AEI = peak area of methyl heptadecanoate (internal standard), CEI = concentration of methyl heptadecanoate solution (mg/ml), VEI = volume of methyl heptadecanoate solution (ml), m = mass of the sample (mg).

III. RESULTS AND DISCUSSION

Table 3 gives the observed characteristic properties of *Croton megalocarpus* oil.

Table 3: Croton oil properties

Property	Value
Density, kg m^{-3}	929.2
Dynamic viscosity, Pa.s	0.0265 (313K) 0.0066 (373K)
Refractive index	1.4737 (293K)
S content, wt%	0.0012
Water content, wt%	0.007
Ash, wt%	0.087
Acid value	2.00
Free fatty acid	1.00
Saponification value	192.1
Iodine value	139.2
Calorific value (gross), MJ kg^{-1}	41.0
Peroxide value	8.66
Fatty acid composition, wt%	
C8:0 Caprylic	0.09
C10:0 Caproic	0.08
C12:0 Lauric	0.09
C14:0 Myristic	0.26
C16:0 Palmitic	8.39
C18:0 Stearic	3.15
C18:1cis Oleic	12.16
C18;2cis Linoleic	70.97
C18:3n3 α-linolenic	3.89
Others	0.92

Table 4 gives the CCD matrix with experimental and predicted yields for conventional heating.

Table 4: CCD Matrix with Experimental and Predicted yields for Conventional Heating

Run	Level of variables [actual(coded)]			Expt Yield	Quadratic Model
	X1	X2	X3		Y
1	1(0)	60(0)	6(0)	96	95.6
2	1(0)	43(-1.68)	6(0)	83.5	83.7
3	0.5(-1)	70(1)	9(1)	85.1	85.8
4	1(0)	60(0)	11(1.68)	78.9	78.4
5	1.84(1.68)	60(0)	6(0)	82.9	82.2
6	1(0)	60(0)	1(-1.68)	86.8	87.2
7	0.5(-1)	50(-1)	3(-1)	90.6	90.7
8	1(0)	60(0)	6(0)	95.5	95.6
9	1.5(1)	70(1)	9(1)	91.1	91.1
10	1.5(1)	70(1)	3(-1)	84.01	84.8
11	1(0)	60(0)	6(0)	96	95.6
12	1.5(1)	50(-1)	3(-1)	85	84.4
13	0.16(-1.68)	60(0)	6(0)	82.6	83.1
14	1(0)	60(0)	6(0)	95.2	95.6
15	1.5(1)	50(-1)	9(1)	74.3	75.2
16	1(0)	60(0)	6(0)	96.2	95.6
17	0.5(-1)	50(-1)	9(1)	74.6	73.9
18	1(0)	77(1.68)	6(0)	94.6	94.2
19	1(0)	60(0)	6(0)	95.2	95.6
20	0.5(-1)	70(1)	3(-1)	88.1	87.2

Table 5 gives the CCD matrix with experimental and predicted yields for microwave irradiation.

Table 5: CCD Matrix with Experimental and Predicted yields for Microwave Irradiation.

Run	Level of variables [actual(coded)]			Expt. Yield	Quadratic Model
	X1	X2	X3		Y
1	1(0)	60(0)	9(0)	96.3	96.1
2	1(0)	10(-1.68)	9(0)	74.9	75.4
3	0.5(-1)	90(1)	12(1)	73.5	72.7
4	1(0)	60(0)	14(1.68)	75.1	75.3
5	1.84(1.68)	60(0)	9(0)	67.1	67.2
6	1(0)	60(0)	4(-1.68)	69.8	69.7
7	0.5(-1)	30(-1)	6(-1)	63.5	62.5
8	1(0)	60(0)	9(0)	95.5	96.1
9	1.5(1)	90(1)	12(1)	83.7	84.6
10	1.5(1)	90(1)	6(-1)	65.0	64.3
11	1(0)	60(0)	9(0)	95.8	96.1
12	1.5(1)	30(-1)	6(-1)	68.0	68.7
13	0.16(-1.68)	60(0)	9(0)	51.9	51.9
14	1(0)	60(0)	9(0)	95.9	96.1
15	1.5(1)	30(-1)	12(1)	83.1	82.0
16	1(0)	60(0)	9(0)	97.0	96.1
17	0.5(-1)	30(-1)	12(1)	48.3	48.9
18	1(0)	110(1.68)	9(0)	92.0	91.7
19	1(0)	60(0)	9(0)	96.3	96.1
20	0.5(-1)	90(1)	6(-1)	78.3	79.3

Table 6 gives the ANOVA for regression analysis for conventional heating for a full quadratic model.

Table 6: ANOVA for Response Surface Quadratic model-conventional heating

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	959.09	9	106.57	151.77	< 0.0001	significant
X1	*0.89*	*1*	*0.89*	*1.27*	*0.2866*	
X2	*132.12*	*1*	*132.12*	*188.17*	*< 0.0001*	

X3	*94.35*	*1*	*94.35*	*134.37*	*< 0.0001*	
X1 X2	*7.62*	*1*	*7.62*	*10.86*	*0.0081*	
X1 X3	*29.61*	*1*	*29.61*	*42.17*	*< 0.0001*	
X2 X3	*118.50*	*1*	*118.50*	*168.77*	*< 0.0001*	
X1^2	*300.36*	*1*	*300.36*	*427.78*	*< 0.0001*	
X2^2	*78.77*	*1*	*78.77*	*112.19*	*< 0.0001*	
X3^2	*295.73*	*1*	*295.73*	*421.18*	*< 0.0001*	
Residual	7.02	10	0.70			
Lack of Fit	*5.17*	*5*	*1.03*	*2.80*	*0.1416*	*not significant*
Pure Error	*1.85*	*5*	*0.37*			
Cor Total	966.12	19				

The Model F-value of 151.77 implied the model was significant. There was only a 0.01% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case X2, X3, X1.X2, X1.X3, X2.X3, X1^2, X2^2, X3^2 were significant model terms. Values greater than 0.1000 indicate the model terms are not significant. Although X1 was not significant, it cannot be dropped because it was part of model hierarchy.

The "Lack of Fit F-value" of 2.80 implies there was a 14.16% chance that a "Lack of Fit F-value" this large could occur due to noise. P-value for lack-of-fit was > 0.05, hence it was insignificant which implies that there was no evidence that the model did not fit.

The "Pred R-Squared" of 0.9519 was in reasonable agreement with the "Adj R-Squared" of 0.9962; i.e. the difference was less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 36.646 indicated an adequate signal. The model was: Yield, $Y = 95.59 - 0.26\ X1 + 3.11\ X2 - 2.63\ X3 + 0.98\ X1.X2 + 1.92\ X1.X3 + 3.85\ X2.X3 - 4.57\ X1^2 - 2.34\ X2^2 - 4.53\ X3^2$. (3)

Eqn. 3 was used to plot response surface and contours for optimization of FAME yield for conventional heating. Fig. 1 is a plot for Yield as a function of Temperature and Catalyst composition. The optima lies close to a temperature of 70°C and a catalyst concentration of 1.5 mass%. Fig. 2 gives a plot for Yield as a function of Methanol to oil mole ratio and Catalyst composition. The optima lies close to a mole ratio of 7 and a catalyst concentration of 1.5 mass%. Fig. 3 is a plot for Yield as a function of temperature and mole ratio. It indicates that a maxima corresponds to a temperature of 70°C and a mole ratio of 7. The observations made in the RSM plots therefore confirm that the experimental values were in good agreement with the predicted values.

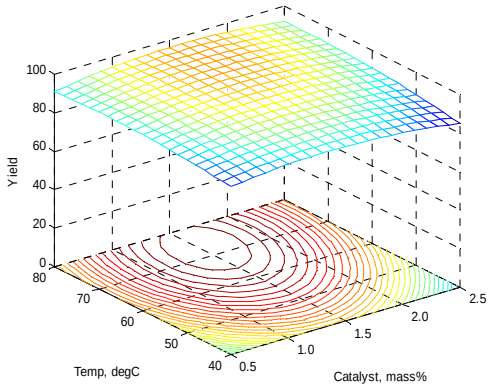

Fig 1 RSM plot: Effect of Catalyst conc. and Temperature on Yield –conventional heating

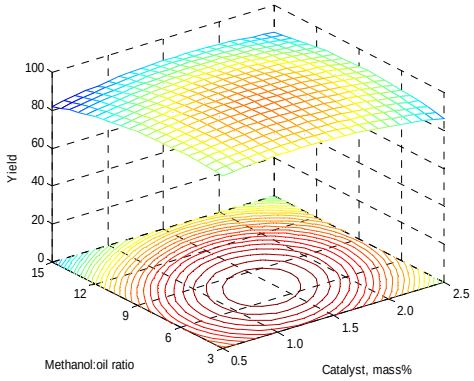

Fig 2 RSM plot: Effect of Catalyst conc. and Methanol:oil ratio on Yield- conventional heating

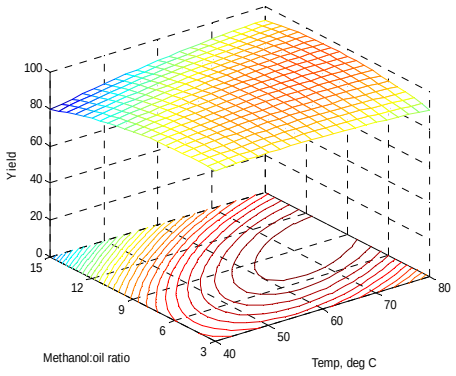

Fig 3 RSM plot: Effect of Methanol:oil ratio and Temp on Yield - conventional heating

Table 7 gives the ANOVA for regression analysis for microwave irradiation for a full quadratic model.

Table 7: ANOVA for Response Surface Quadratic model- Microwave Irradiation

Source	Sum of Squares	Mean Square	F Value	p-value Prob > F	
Model	4481.30	497.92	649.60	< 0.0001	significant
X1	*279.32*	*279.32*	*364.41*	*< 0.0001*	
X2	*320.80*	*320.80*	*418.53*	*< 0.0001*	
X3	*37.78*	*37.78*	*49.28*	*< 0.0001*	
X1.X2	*224.72*	*224.72*	*293.17*	*< 0.0001*	
X1.X3	*361.81*	*361.81*	*472.02*	*< 0.0001*	
X2.X3	*24.50*	*24.50*	*31.96*	*0.0002*	
X1^2	*2410.93*	*2410.93*	*3145.34*	*< 0.0001*	
X2^2	*285.25*	*285.25*	*372.14*	*< 0.0001*	
X3^2	*1006.17*	*1006.17*	*1312.67*	*< 0.0001*	
Residual	7.67	0.77			
Lack of Fit	*6.29*	*1.26*	*4.58*	*0.0602*	*not significant*
Pure Error	*1.37*	*0.27*			
Cor Total	4488.97				

The Model F-value of 649.60 implied the model was significant. There was only a 0.01% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicated model terms were significant. In this case X1, X2, X3, X1.X2, X1.X3, X2.X3, X1^2, X2^2, X3^2 were significant model terms. The "Lack of Fit F-value" of 4.58 implied there was a 6.02% chance that a "Lack of Fit F-value" this large could occur due to noise. The p-value for lack-of-fit was greater than 0.05, hence it was not significant.
The "Pred R-Squared" of 0.9869 was in reasonable agreement with the "Adj R-Squared" of 0.9968; i.e. the difference was less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. In this case, the ratio of 76.275 indicated an adequate signal. The full Quadratic model (Eqn 4) can therefore be used to predict the yield as a function of selected operation variables, Yield, Y = 96.13 + 4.52 X1 + 4.85 X2 + 1.66 X3 – 5.30 X1.X2 + 6.73 X1.X3 + 1.75 X2.X3 – 12.92 $X1^2$ – 4.45 $X2^2$ – 8.36 $X3^2$ (4)
Eqn 4 was used for response surface and contour plots for microwave irradiation. Fig 4 is a response surface and contour plot for FAME yield (Y) as a function of Catalyst concentration (X1) and Reaction time (X2). It shows that the maximum yield corresponds to a catalyst concentration of about 1%, and a time of about 50s. These values were close to experimentally observed values.

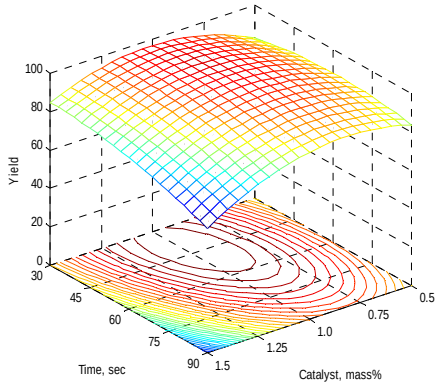

Fig 4 RSM plot- Effect of Catalyst conc. and Time on Yield- Microwave Irradiation
Fig 5 gives a response surface and contour plot for FAME yield (Y) as a function of Catalyst concentration (X1) and Methanol to oil ratio (X3). Optima lies at a catalyst concentration of 1-1.25%, and a methanol: oil ratio slightly above 9:1. This was in agreement with experimental observations.

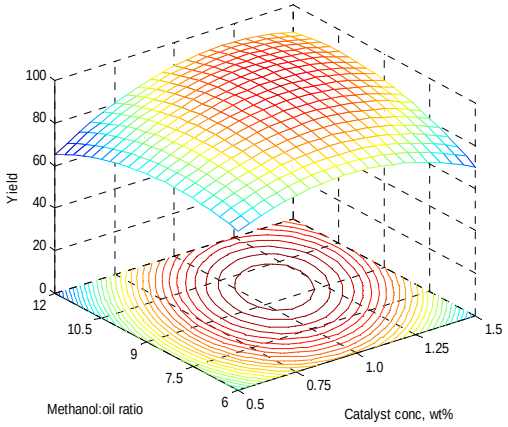

Fig 5 RSM plot- Effect of Catalyst conc. and Methanol:oil ratio on Yield- Microwave Irradiation
Fig 6 is a response surface and contour plot for FAME yield (Y) as a function of Reaction time (X2) and Methanol to oil ratio (X3). A methanol:oil ratio of 9:1, and a time of 45s corresponds to the maximum yield. These values were in agreement with the experimental observations.

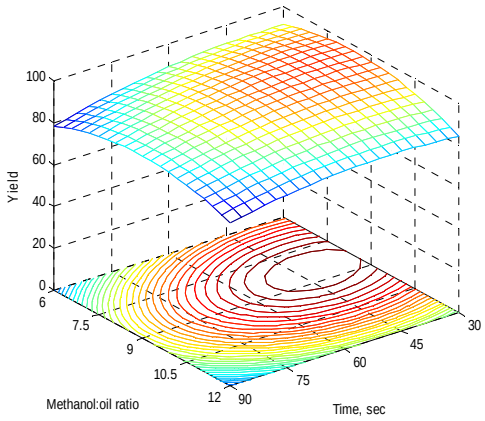

Fig 6: RSM plot- Effect of Time and Methanol:oil ratio on Yield –Microwave Irradiation

FAME was tested for characteristic fuel properties and it conformed to international standards. Table 8 gives the properties.

Table 8: Properties of Croton megalocarpus oil FAME

Property	Value	Standards: ASTM D6751
Density at 20°C (293K), kg m^{-3}	898.9	not specified
Kinematic viscosity at 40°C, mm^2 s^{-1} Absolute viscosity at 40°C, Pa.s	2.66 $2.397x10^{-3}$	1.9 – 6.0
Refractive index at 20°C (293K)	1.4673	not specified
Acid value, mg KOH/g	0.23	0.50 max
Water & Sediment	nil	0.050 vol% max
Sulphur, mass%	0.0012	S 15 Grade 0.0015% max, S500 Grade 0.05% max
Iodine value	143.6	not specified
Flash point, °C	183	130° C min
Distillation temperature (atmospheric equivalent) at 90% recovery by volume, °C	341.6	360° C max
Calorific value, MJ kg^{-1}	49.4	not specified

IV. CONCLUSIONS

In this paper a study of optimization of transesterification *croton megalocarpus* oil was carried out using conventional heating and microwave irradiation. FAME yield was correlated in a quadratic equation as a function of reaction variables. ANOVA showed that the correlations fitted the experimental data satisfactorily. Response surface and contour plots for conventional heating indicated that for conventional heating highest yield of 97% corresponded to a methanol to oil ratio of 6:1, catalyst concentration of 1mass%, a reaction temperature of 60-70°C for a reaction time of 2 h. When microwave irradiation was used, highest yield of 93% was obtained at 9:1 methanol to oil ratio, 0.5% NaOH catalyst, and reaction time of 1 min. Hence both heating methods gave a comparable yield but reaction the time was reduced from 2h to 1 min when microwave irradiation was used. Lower reaction time leads to faster production rate and energy savings. FAME produced met the requirements to be used as a diesel fuel.

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