Optimization of Transesterification of Nigerian *Jatropha Curcas* oil Using Response Surface Methodology

Ibrahim A. Mohammed, Umaru Musa, Eyitayo A Afolabi, Muhammad M Sadiq, Aliyu M. Aliyu, and Salihu Abdul

***Abstract*—** The major challenge associated with the commercial production of biodiesel is the high cost of edible vegetable oil. This necessitates the use of non edible oil such as *Jatropha curcas* oil for the production of biodiesel. The research presents the report of optimization of alkaline transesterification of *Jatropha curca*s oil using Response Surface Methodology. A central composite design (CCD) technique consisting of 20 experiments was employed to study the effect of process variables: catalyst concentration (0.25g - 0.75g), methanol to oil ratio (3:1-9:1) and reaction time (60 - 120 min). Statistical analysis of the variables and their interactions were carried out which lead to the development of a regression model. The maximum yield of 98.80 % was obtained at methanol to oil ratio of 6:1, catalyst concentration of 0.75g and reaction time of 90 min. The result of simulation of model equation shows a close agreement with the experimental value. It was deduced that methanol to oil ratio had a higher effect on the biodiesel yield than catalyst concentration and reaction time. Characterization of the biodiesel revealed that it compares favourably with the ASTM standard.

***Keywords*—**Jatropha curcas oil, Transesterification, Optimization, Biodiesel, Variables

I. Introduction

The world demand for energy has been on the continuous increase due to gradual increase in human population and increasing level of industrialization [1]. The alarming growth of these emerging industries, transportation, agricultural activities and other human needs are to a large extent purely dependent on petroleum derived fuel. At present the world fossil fuel resources are rapidly depleting [2]. Emissions from the combustion of these fuels are the greater contributor to global warming [3].

Nigeria as a developing country depends strongly on the global nature of oil price [4]. In 2007 Nigeria was reported to have imported about 80 % of its petroleum requirement and this has lead to increasing cost and quite a number of uncertainity; the latest been the fuel subsidy crises. The centre of oil extraction in Nigeria (the Niger Delta region) has been neglected over years in an attempt to hasten the oil development of oil and gas industry. Quite unfortunately this has lead to severe environmental degradation, generated militancy from the local communities making the task of successful oil prospecting almost impossible for the multinational companies in the country. These have kept the cost of oil exploration on continuous increase [5]. There is therefore the urgent need for alternative renewable energy sources [6]. Vegetable oil has been recognized as a feedstock for the production of biodiesel which can be use as a possible substitute for mineral diesel [7].

Biodiesel, vegetable alternative diesel fuel derived from variety of vegetable oil or animal fats through transesterification has enjoyed wide acceptability in recent times due to renewable nature, biodegradability, non toxicity, less emission of gasses and particles [8]. However the use of edible oil for commercial production of biodiesel may be expensive [9]. The high cost of edible oil and its limited availability are critical issues in the biodiesel industry, non edible vegetables oil are therefore perceived to be effective feedstocks for commercial viability of biodiesel production [1].

Numerous non edible feedstock have been identified for biodiesel production. Among all Jatrophacurcas oil appears to be a potential energy crop that is globally taking the centre stage as the most viable feedstock for competitive and commercial production [9]. Jatropha is a small tree or shrub belonging to the family of Euphorbiaceae. It has drought tolerant resistance, it is found in the sub-tropical region of the land, can grow on semi-arid and marginal lands [1]. Jatropha seed can yield up to 40 % oil content, non edible and its price is not distorted by competing food uses. The plant grows well in Nigerian and is already planted by farmers mainly for border demarcation of small farm holdings [9]. The

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improvement of the production technologies, through controlling the reaction parameters that affect the reaction rate and mechanism are also reported to help minimized cost of biodiesel production [10].

According to Fan *et al.*, [8], irrespective of the experimental condition studied, the aim is to produce biodiesel with high yield. It is unrealistic to optimize the biodiesel production process by the traditional 1-factor at-a-time approach, which is time consuming and almost impossible to achieve true optimal condition. The author added Response Surface Methodology (RSM) an experimental strategy first described by Box and Wilson. It is a useful statistical technique which has been applied in research for complex variable systems. It has advantage of limited number of experimental runs required to generate adequate information for statistically acceptable results [1]. It is an effective tool for process optimization [8]. RSM has been of recent proved to be successfully applied for optimization of biodiesel in fats and oil from different feed stocks. Hence the aim of this work is to optimize the production of biodiesel from Jatrophacurcas using response surface methodology (RSM).

II. METHODOLOGY

A. Acid Pretreatment

The crude Jatropha oil was poured into a conical flask and heated to a temperature of 60 ^{0}C. A mixture of concentrated H_2SO_4 (1 % w /w) with methanol (30 % v/v) was separately heated at (60 ^{0}C) and then added to heated oil in the flask. The mixture was stirred for 1 hour and allowed to settle over the night.

B. Base Catalyzed Transesterification

50 ml of the pretreated Jatropha oil was measured and poured into a 150 ml conical flask and heated to a temperature of 60 ^{0}C. A solution of potassium methoxide was then prepared in a 250 ml beaker using 0.25 g (i.e. catalyst concentration of 0.5 %) of potassium hydroxide pellet and 6 ml (i.e. mole ratio of oil to methanol of 1:3) of methanol. The solution was properly agitated until the potassium hydroxide pellet was completely dissolved. A known amount of potassium methoxide solution was then poured into the warm Jatropha oil and agitated vigorously for 60 minutes using a water bath agitator and the mixture was allowed to settle for 24 hours in a separating funnel. After settling the upper layer which was the biodiesel was decanted into separate beaker while the lower layer which comprised of glycerol and soap was collected from the bottom of separating funnel. The quantity of biodiesel collected was measured and recorded. Same procedure was followed for the other experiments.

III. RESULT AND DISCUSSION

A. Effect of Individual Parameters on the Biodiesel Yield

Stoichiometrically, three moles of methanol are required for individual mole of triglyceride, but in practice, a higher molar ratio is required in order to drive the reaction towards completion and produce more FAME as products. Figure 1 shows that the methanol-to-oil ratio showed positive influence on methyl ester yield. But the yield started to decrease as the ratio much increased beyond 6:1. The decrease in the yield may be due to the separation problem resulted from excessive methanol. Higher ratio of methanol used could also minimize the contact of access triglyceride molecules on the catalyst active sites which could decrease the catalyst activity. From Figure 2, it was observed that the catalyst concentration affected the biodiesel yield in a positive manner up to a certain concentration (0.75g). Beyond this concentration, the biodiesel yield decreased. When the catalyst concentration was increased, the interactive (active) site of the catalyst was increased; thus, the transesterification reaction was accelerated and biodiesel yield was increased.

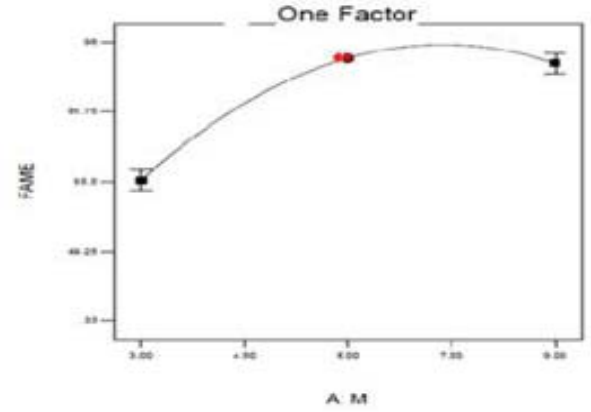

Fig. 1 Effect of Methanol to Oil ratio

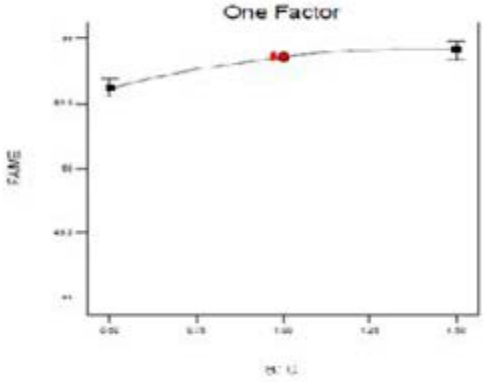

Fig. 2 Effect of Catalyst Concentration

The increase in reaction time affected the biodiesel yield in a positive manner until 90 min was attained, after this time there was a decrease (Figure 3). The increase in the yield of FAME at higher reaction time is due to higher rate of reaction. Hence, its effect on the biodiesel is almost constant.

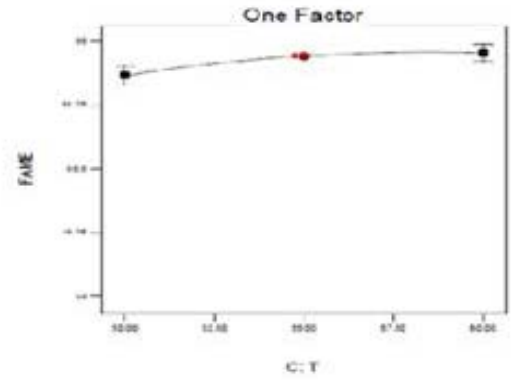

Fig. 3 Effect of Reaction Time

Equation 1 below clearly shows all the linear terms to be having positive coefficients, whereas the quadratic terms and the interaction terms having negative coefficients. Hence, an increase in temperature, catalyst concentration and methanol to oil molar ratio to a certain extent could result in a higher %FAME. However, a reduction in the %FAME could be obtained when using too high catalyst concentration, temperature and methanol to oil molar ratio.

B. Effect of Interactive Parameters on Biodiesel Yield

Figure 4 showed the strong interaction between methanol/oil molar ratio (M) , and KOH catalyst concentration (C). This can also be confirmed by the high p-values of the interaction parameters. It could also be seen from Figure 4 that the FAME yield increased with increasing catalyst concentration at first. However, when the catalyst concentration reached a certain level, (0.75 g) the reverse trend was observed. The similar pattern was followed when increasing methanol/oil molar ratio. This was because the positive coefficient for the linear parameters (M,C, and T) played the main role when the KOH catalyst concentration and methanol/oil molar ratio were at lower level, while at higher level, the interaction terms and the quadratic terms showed more sign insignificant effect, leading to the decrease of the yield. However, when the catalyst concentration was too high, soap could be quickly formed which made the separation of glycerol from biodiesel more difficult, thus reducing the yield.

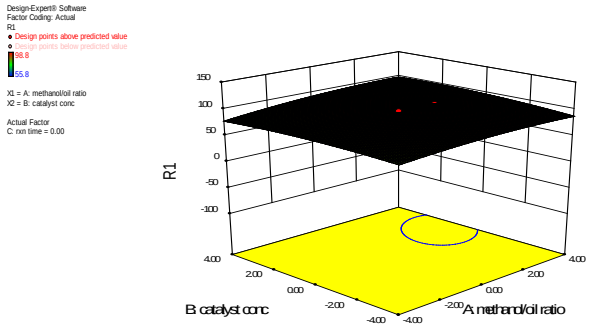

Fig. 4 Methanol to Oil ratio and Catalyst Concentration at 90 min

Increasing of the methanol amount, on one hand, will drive the reaction to the right since the transesterification reaction is an equilibrium process; on the other hand, excess methanol will increase the solubility of glycerol resulting in the reaction driven to the left, thus decreasing the yield. Figure 5 showed the effect of methanol/oil ratio and the reaction time when the level of catalyst concentration was fixed. At low methanol to oil ratio, %FAME increased with in reaction time to certain level.

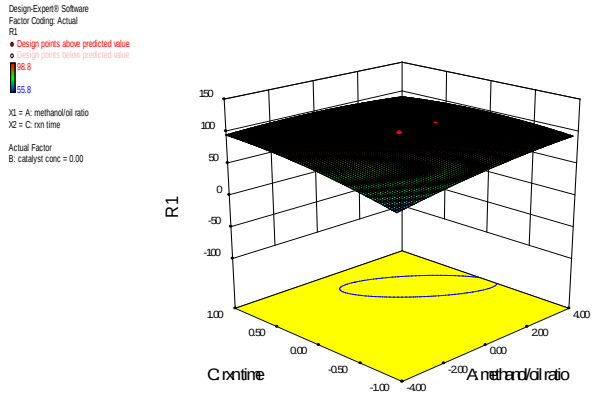

Fig. 5 Methanol to Oil ratio and Time at 1% Catalyst Concentration.

Figure 6 showed the effect of reaction time and catalyst concentration on the methyl ester yield when the level of methanol/oil molar ratio was fixed. At a certain level of catalyst concentration, the increase in reaction time increases the methyl ester yield. This is attributed to the fact that at a higher initial reaction time results in faster settlement of glycerol [11]. The reaction time was observed to affect the FAME yield in a positive manner until 90 min. After that the effect was negative. This could be explained by the higher p-value, and the negative coefficient for the interactive and quadratic term in the model, indicating the non-significant effect.

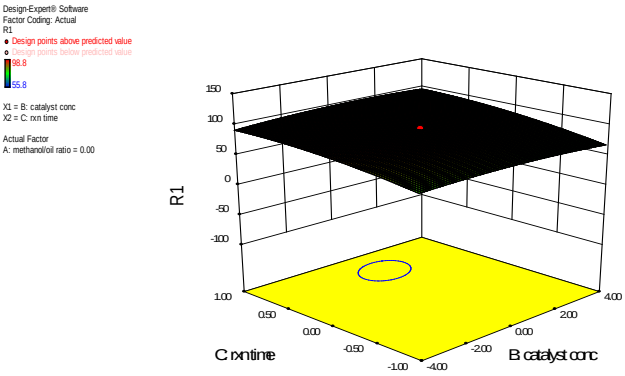

Fig. 6 Catalyst Concentration and Reaction Time at Molar ratio 6:1

TABLE I
RESULT FOR 2^3 RSM MATRIX DESIGN

RUN	CODED FACTOR			ACTUAL FACTOR			FAME (%)	
	X_1	X_2	X_3	M	C	T	A	P
1	-1	-1	-1	3:1	0.25	60	56.40	61.30
2	-1	-1	+1	3:1	0.25	120	86.20	88.28
3	-1	+1	-1	3:1	0.75	60	55.80	51.80
4	-1	+1	+1	3:1	0.75	120	88.60	90.27
5	+1	-1	-1	9:1	0.25	60	92.40	91.54
6	+1	-1	+1	9:1	0.25	120	76.80	81.61
7	+1	+1	-1	9:1	0.75	60	91.60	90.33
8	+1	+1	+1	9:1	0.75	120	96.00	91.91
9	0	0	-1.68	6:1	0.5	40	70.40	71.52
10	0	0	+1.68	6:1	0.5	140	97.80	95.53
11	0	-1.68	0	6:1	0	90	90.00	83.89
12	0	+1.68	0	6:1	1.00	90	79.60	84.56
13	-1.68	0	0	1:1	0.5	90	66.80	64.43
14	+1.68	0	0	12:1	0.5	90	90.00	91.23
15	0	0	0	6:1	0.5	90	98.80	98.00
16	0	0	0	6:1	0.5	90	96.40	98.00
17	0	0	0	6:1	0.5	90	98.60	98.00
18	0	0	0	6:1	0.5	90	97.20	98.00
19	0	0	0	6:1	0.5	90	98.20	98.00
20	0	0	0	6:1	0.5	90	98.60	98.00

Where M = Methanol to Oil Mole Ratio, C = Catalyst Concentration, T = Reaction Time, A = Actual Experimental Yield, P = Predicted Yield

The model for percentage of biodiesel content (yield %) in terms of the actual factors is shown in predictive Equation below;

$$R_1 = 97.99947 + 7.13789 * M + 0.19839 * C + 7.96798 * T + 2.87500 * M * C - 9.22500 * M * T - 5.11702 * M^2 - 4.86954 * C^2 - 7.13228 * T^2 \quad (1)$$

Table 1 show the experimental matrix X_1, X_2 and X_3 which corresponds to the un-coded value for methanol / oil ratio, catalyst concentration and reaction time. All the factors Methanol/oil ratio, catalyst concentration and Reaction time show a significant influence on the reaction. The analysis of variance showed that this model was adequate to express the actual relationship between the response and significant value, with a satisfactory coefficient of determination, $R^2 = 0.9139$ which indicate 91% of variability. From the ANOVA statistical analysis, the model F-value of 23.40 implies the model is significant. Values of prob>f, both less than 0.0500 indicate model term are significant, in this case A, B, AC, A^2 B^2 and C^2 are significant model terms, values greater than 0.1000 indicate the model terms are not significant.

TABLE II
ANALYSIS OF VARIANCE TABLE

Source	SS	DF	MS	F-Value	P-Value Prob>F
Model	3568.59	9	396.51	23.40	<0.00001
A	695.81	1	695.81	41.06	<0.00001
B	0.54	1	0.54	0.032	0.8622
C	867.06	1	867.06	51.17	<0.00001
AB	66.13	1	66.13	3.90	0.0764
AC	680.80	1	680.80	40.18	<0.00001
BC	34.45	1	34.45	2.03	0.1844
A^2	377.34	1	377.34	22.27	0.0008
B^2	341.73	1	341.73	20.17	0.0012
C^2	733.09	1	733.09	43.26	<0.00001

Where SS = Sum of Square, DF = Degree of Freedom, MS = Mean Square

TABLE III
FUEL PROPERTIES OF JATROPHA CURCAS OIL BIODIESEL

Fuel property	This work	A	B	ASTM
Kinematic viscosity at 40^0C (mm^2/s)	5.62	-	4.42	1.9-6.0
Specific gravity g/ml at 15^0C	0.91	0.840	-	0.88
Boiling Point (^{0}C)	189	201	192	182-338
Flash Point (^{0}C)	152	128	113	140-170
Cloud Point (^{0}C)	12	8	4.6	-3-12
Iodine Value ($gI_2/100g$)	147	-	-	
Pour Point (^{0}C)	8	-2	-20	-15-10
Saponification Value (mgKOH/g)	144.1	150	160	140-180
Cetane Number	52	50	62	48-65

A = (Raja et al., 2011), B = (Ohanejo and Umukoro, 2011)

The results of characterization of the methyl ester produced from Jatropha curcas oil shown in Table 3 show quantitative and qualitative agreement with the ASTM standard and also observe an appreciable consistency with other reported literatures. The slight variation obtained in term of properties could be attributed to variation of species of plant oil seed and geographical location in which the seed was obtained.

IV. CONCLUSION

RSM was successfully employed to study the effects of process variables, such methanol-oil ratio, catalyst concentration, and reaction time at a constant temperature, rate of mixing for the production of biodiesel from the crude Jatropha curcas oil. An empirical model equation was developed for the methyl esters yield as a function of the variable investigated. The experimental results show that the optimal condition were as follows: methanol/oil molar ratio of 6:1; time of 90 min; catalyst concentration, of 1.0%. The optimized condition gave an actual yield of 98.80 %. All the individual process variables show a positive effect on biodiesel yield. The properties of the biodiesel produced compares favourably with ASTM standard and other reported literatures.

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