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Production of Bio-Diesel from Jatropha Curcas Seed Using In-Situ Technique: Effect of Catalyst Amount and Alcohol-Seed Ratio

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ABSTRACT

The effects of alcohol seed ratio (0.5, 1.5 & 2.0) and initial catalyst amount (0.5, 1.0 & 1.5%) on the *in-situ* production of biodiesel from raw *Jatropha Curcas* seed were studied and evaluated at a reaction temperature of 60^0C and reaction time of 120min using the Central Composite experimental Design. Initial catalyst amount and alcohol seed ratio were found to have significant ($P<0.05$) effects on the yield of biodiesel produced. Initial catalyst amount was the more important factor and had a positive influence on the yield than alcohol seed ratio which does not significantly affect the yield as a single factor. Due to formation of by-products (soaps) caused by excessive amount of catalyst and excess alcohol leading to difficult ester separation from glycerol, there was a general reduction in *Jatropha Curcas* ethyl-ester as levels of catalyst and alcohol seed ratio increased. A second-order quadratic model was obtained to predict the yield as a function of both factors. The model predicted well the observed data with a R^2 value of 0.985 and a non-significant Lack-of-Fit ($P<0.05$). The biodiesel obtained, compared favorably with the ASTM D6751-02 standard for biodiesel.

Keywords: *in-situ*, trans-esterification, *Jatropha Curcas* seed, biodiesel, response surface, bio-mass

INTRODUCTION

Jatropha Curcas (***Linnaeus***) is a multipurpose bush/small tree belonging to the family of Euphorbiaceae. It is a plant with many attributes, multiple uses and considerable potential. The plant can be used to prevent and/or control erosion, to reclaim land, grown as a live fence, especially to contain or exclude farm animals and be planted as a commercial crop. The wood and fruit of *Jatropha Curcas* can be used for numerous purposes including fuel. The seeds of *Jatropha Curcas* contain viscous oil, which can be used for manufacture of candles and soap, in cosmetics industry, as a diesel/paraffin substitute or extender. *Jatropha Curcas* oil cannot be used for nutritional purposes without detoxification making its use as energy or fuel source very attractive as biodiesel (Akbar *et.al*., 2009; Openshaw, 2000).

Biodiesel is generally defined chemically as a mono-alkyl ester of long chain fatty acids derived from renewable biological sources such as vegetable oils and animal fats. Biodiesel has received renewed significant attention in recent times both as a renewable fuel and as an additive to

existing petroleum based fuel. However, the use of vegetable oil and animal fats for biodiesel production has recently become a great concern because of the competition with food materials. As the demand for vegetable oil increase tremendously in recent years, it has become impossible to justify the use of these oils for fuel production in several developing countries who are struggling to meet their food requirements. The choice of seed oil preferably those that do not compete with food, under-utilized and inedible seed that can grow in the large arable land available in these developing countries will probably provide the panacea for this problems of developing countries including Nigeria *Jatropha Curcas, a* non-edible vegetable seed oil has not been known to compete for food uses and hence can be considered as a viable feedstock for biodiesel production in Nigeria.

The most commonly used method of biodiesel production is trans-esterification, which is the reaction of an alcohol with oil (triglyceride) in the presence of a catalyst to produce biodiesel (ester) and glycerol as a by-product. The i*n-situ* trans-esterification process uses the oil (triglycerides) in the seed directly without the need for initial extraction, thereby removing processes such as oil expression, purification and degumming (Dairo *et.al*, 2012). This would reduce the production cost and providing a favourable comparison with available fossil diesel (Haas and Scot, 2007). A recent study by Dairo *et.al* (2012) has shown that initial catalyst amount has a significant effect on biodiesel production from Jatropha using *in-situ* but several researchers (Dairo *et.al*, 2011; Zeng *et.al*., 2009; Khalil and Leite, 2006; Obibizor *et.al*., 2002) have also reported the interactive effect of other factors with initial catalyst amount on biodiesel production using in-situ method. The in-situ method has been reportedly influenced by ratio of seed to alcohol, amount of catalyst, reaction temperature, time and moisture content of seed by several researchers.

The objective was therefore to study the interactive effect of initial catalyst amount and alcohol–seed weight ratio and on yield of *Jatropha Curcas* biodiesel at temperature of 60^{o}C with a reaction time of 120min using response surface methodology and also to develop a model describing the influence of both factors on the yield.

MATERIALS AND METHODS

Local *Jatropha Curcas* seeds were purchased from an open market in Ogun State, Nigeria. The seeds were hand threshed after which the damaged seeds were discarded. Whole unbroken seeds in good condition were cleaned and shelled. Initial moisture contents of the seed samples were determined and were further reduced by sun drying in single layers for three to five days. The dried seeds were then passed through a Tyler sieve set to remove impurities, chaffs and other foreign matter.

The seed were ground in a blending machine to reduce its size and consequently increase its surface area. The ground seeds were divided into specified weights, sealed in double polythene bags and stored in the refrigerator prior to use.

The ethanol used has a boiling point of 78^{o}C; therefore, a reaction temperature of 60^{o}C was used as widely available in literature, however Van Gerpen *et.al*. (2004) reported that reaction temperature for trans-esterification must be below the boiling point of alcohol used. Sodium hydroxide of analytical grade (Aldrich Chemical Co. Ltd, England) was used as the catalyst, while the *in-situ* reactor was a 1.25 litre wet and dry mill multi-speed Osterizer blender(pulsematic, model Cycleblend 10, Pulsematic UK) with an incorporated 500W electric

heating element(240V, Semyem Electronics). The blender has a clear glass with stainless steel cutting blades. The temperature was monitored and controlled with a temperature controller (Model KZ 200DT) of 2^{o}C accuracy connected together with a T-type thermocouple and a mercury-in-glass thermometer.

Oil extraction

The seed kernels were ground, using a mechanical grinder, and defatted in a soxhlet apparatus, using hexane (boiling point of 40 – 60^{o}C). The extracted lipid was obtained by filtering the solvent lipid contained to get rid of the solid from solvent before the hexane was removed using rotary evaporator apparatus at 40^{o}C. Extracted seed oil was stored in freezer at −2^{O}C for subsequent physicochemical analysis.

Oil Content

The weight of oil extracted from 10 g of seeds powders was measured to determine the lipid content. Result was expressed as the percentage of oil in the dry matter of seed powders.

Acid value, % FFA

Acid value of seed oil was determined according to AOAC Official Method Cd 3a- 63.

Production of biodiesel (*Jatropha Curcas* ethyl-ester)

Laboratory procedure for production of biodiesel was similar to the approach of Dairo *et.al*. (2011) as follows.

i. 400g of ground *Jatropha Curcas* seed was charged from the top into the reactor with the amount of alcohol (200g, 600g & 800g) at ambient conditions (29 – 32^{o}C).
ii. Seed and alcohol were mixed for 20 minutes to obtain a homogeneous suspension.
iii. The catalyst at quantities of 2g,4g and 6g representing 0.5, 1.0 and 1.5% by weight of seed (was then added to the homogeneous mixture while still stirring).
iv. The temperature of the homogenous suspension in the reactor was raised and kept constant at 60^{o}C with a calibrated thermostat attached to the heating system.
v. At the end of the reaction time (120min), the reaction was stopped by adding ethanoic acid (1:1) to neutralize the catalyst (Ma *et.al*., 1998). The hot mixture was decanted and filtered into the solid and liquid phases.
vi. The solid phase was removed from the filter and dried to remove excess alcohol. The decanted liquid was allowed to settle into the heavy phase (glycerol) and the light phase (ethyl-ester) in a sealed glass jar.
vii. The ethyl-ester was transferred into a plastic bottle for washing to remove contaminants such as ethanol, glycerol or catalysts. Washing was done for four times or when water below the ethyl-ester became clear.
viii. The washed biodiesel was weighed and weight recorded to determine the yield.
ix. The above procedure was performed in triplicates for all levels of experimental variables as indicated above according to experimental design.

Experimental design

The Central Composite Design (CCD) of the Response Surface Methodology (RSM) is an experimental design useful for building a second order model for responses without the need to use a complete three-level factorial experiment. According to Box and Hunter (1978), this

design allows seeing interactions among experimental variables within the range studied, leading to better knowledge of the process. Alcohol seed weight ratio and catalyst amount were taken as the independent variable and the yield obtained from Equation 1 was taken as the response. The CCD design matrix obtained from Design Expert 7.1 software (Stat-Ease, 2007) is as shown in Table 1.

$$Y = \frac{W_{ester}}{W_{oil}} x100 \quad \text{.....1}$$

where

Y is the yield (%), W_{ester} is the weight of washed ester(g) and W_{oil} (g)is the weight of expressible oil in seed.

Statistical analysis

Multiple regression procedures following a second order polynomial equation (Equation 2) was used on data obtained from the *in-situ* experimental runs using Design Expert 7.1 (Stat-Ease, 2007)

$$Y = \beta_0 + \sum_{i=1}^{2} \beta_i x_i^1 + \sum_{i=1}^{2} \beta_{ii} x_i^2 + \sum \sum_{i<j=1}^{2} \beta_{ij} x_i x_j \quad \text{.....2}$$

where

Y is the response (yield), x_i (initial catalyst amount) and x_j (alcohol seed ratio) are the un-coded independent variables and β_0, β_i, β_{ii} and β_{ij} are intercepts, linear, quadratic and interaction coefficients respectively.

The Analysis of variance (ANOVA) and the lack-of-fit statistics were used to determine whether the constructed model was adequate to describe the observed data. The lack –of-fit test is performed by comparing the variability of the current model residuals to the variability between observations at replicates settings of the process factors. The Coefficient of Determination (R^2) statistic is a measure of the percentage of the variability of the parameter that is explained by the model, the higher the R^2 value the better the model.

RESULTS AND DISCUSSION

The data collected from the study of the physical and chemical properties of the test samples showed that oil content of *Jatropha Curcas* kernel was 50.6%. The oil content was found lower than the value of 63.16% reported by Akbar *et.al* (2009) and 53.16% reported by Dairo *et.al* (2012) both for *Jatropha Curcas*. The high oil content of *Jatropha Curcas* is an indication that the seed would be suitable as a non-edible vegetable oil feedstock. *Jatropha Curcas* has been reported to produce 2000 liter/ha oil per annual (Azam *et.al*., 2005).

The result obtained for trans-esterification is presented in Table 1 at various levels of alcohol-seed ratio and initial catalyst amount. The result was analyzed and fitted to the second order polynomial equation given by equation 2. The coefficients of Equation 2 were determined by multiple regression analysis procedure of Design Expert software. The regression included

Table 1. Experimental and Predicted Result from the Effect of Alcohol seed ratio and Catalyst amount on production of *Jatropha Curcas* ethyl ester

Alcohol Seed Ratio (x_1)	Catalyst Amount X_2(%)	Experimental Yield (%)	Predicted Yield (%)	Residuals
(-1)0.5	(-1)0.5	75.05	70.74	4.31
(-1)0.5	(0)1	83.70	84.67	-0.98
(-1)0.5	(+1)1.5	85.31	84.83	0.48
(0)1.25	(-1)0.5	80.56	78.51	2.05
(0)1.25	(0)1	87.50	88.45	-0.96
(0)1.25	(0)1	87.21	88.45	-1.24
(0)1.25	(0)1	87.12	88.45	-1.34
(0)1.25	(0)1	86.45	88.45	-2.00
(0)1.25	(0)1	87.78	88.45	-0.67
(0)1.25	(+1)1.5	83.41	84.63	-1.22
(+1)2	(-1)0.5	83.51	82.00	1.50
(+1)2	(0)1	86.64	87.97	-1.33
(+1)2	(+1)1.5	80.56	80.15	0.41

* mean of three replicates and 5 centre points

the two experimental variables and interactions regardless of their significant levels. The ANOVA revealed a highly significant model (p-value < 0.05) with an F-value of 98.67 at 95% confidence level and a coefficient of determination (R^2) of 0.985. The model was also evaluated by the lack-of-Fit as determined by the ANOVA (p-value >0.05) which was not significant, indicating that the response model represented the actual relationships of experimental factors well within the ranges of experimental study. The model obtained from the analysis is presented in Equation 3 in terms of actual variables.

$$Y = 48.04 + 16.86X_1 + 51.73X_2 - 8.801X_1X_2 - 2..63X_1^2 - 18.66X_2^2 .....3$$

where
Y is the yield of biodiesel (g), X_1 is initial catalyst amount (g) and X_2 is alcohol seed ratio (g)

The amount of catalyst(X_1) significantly affected the biodiesel yield, with increased ester yield resulting from increased catalyst amount from 0.5 to 1.25% for all levels of alcohol seed ratio as shown in Figure 1. However, at higher levels of catalyst amount (>1.25%) the yield decreased, indicating that optimum value of catalyst amount would between 0 and 1.25%. This value is close to the value of 1.01g/g of seed observed in an earlier study on single effect of initial catalyst amount by Dairo *et.al* (2012). The influence of catalyst amount could be attributed to the fact that initial catalyst amount determines the rate of reaction (production of ethyl ester), thus as the catalyst amount was increased, side reactions such as the formation of by products like soaps. The formation of these byproducts such as soap may have been influenced by the high acid value (2.35± 0.12) as more viscous fluids were observed at higher levels of catalyst amount. The soap formation has also been severally reported to also consume catalyst

consequently reducing the amount of catalyst available for the ethyl ester production (Dairo *et.al*., 2011, 2012; Zeng *et.al*., 2009; Meher *et.al*., 2006).
The soaps are also dissolved into the glycerol during phase separation because of the polarity of the soap; the dissolved soap increases the solubility of ethyl-ester in the glycerol resulting in additional losses of ethyl-ester. The neutralization of the free fatty acid (FFA) of the oil favoured by increased catalyst amount may also be another reason for decreased yield at higher levels of initial catalyst amount. This might also have resulted in decreased yield of *Jatropha Curcas* ethyl-ester.

The alcohol in the experiment was acting as both the solvent for the reaction as well as the transporting medium. As a singular factor, alcohol seed ratio was significant ($P< 0.05$) in the multiple regression procedure and coefficient of the model. Alcohol Seed Ratio(X_2) at low level had a slightly positive effect on the yield but as the level increased, the effect became slightly negative on the yield. This effect of alcohol can be attributed to the fact that as the alcohol amount increases, the ester produced continue to dissolve in the excess alcohol thereby leading to a reduced yield. Typically, excess alcohol displaces the ethanolysis reaction to ester formation; however, excessive amount of alcohol makes glycerol (a byproduct) difficult to separate from the product due to the increasing solubility of glycerol in the alcohol. Accordingly, the glycerol when kept in solution displaces the reaction to the left hand side of the chemical reaction resulting into a decreasing ester yield. Similar observations were reported by Sherma *et.al*, (2008); Dairo *et.al*,(2011); Enciner *et.al*, (2002).

The yield of *Jatropha Curcas* ethyl-ester general increased with increasing levels of catalyst amount and alcohol seed ratio, but progressively decreases at higher levels of both factors indicating an interaction of both factors on the yield of biodiesel produced as shown in the response surface plot of Fig. 1as obtained from the response model (Equation 3). This finding may be explained by the formation of by-products, possibly due to triglycerides saponification processes, side reactions, production of sodium salt, which are favored at high catalyst amount and the excess amount of alcohol.

The specific gravity, heating value, flash point and the viscosity were measured as fuel properties of the biodiesel samples produced. These parameters were compared with the ASTM standard D6751-02 (ASTM, 2004) for biodiesel. The specific gravity ($0.911 g/cm^3$) was greater than the ASTM standard (D6751-02) of 0.880 g/cm3; and value(0.88 g/cm3), obtained by Raheman and Phadatare(2004) for Jatropha biodiesel. Sherma *et.al* (2008) has reported that high specific gravity of biodiesel may be due to presence of impurities due to inadequate washing. The viscosity of biodiesel produced ($5.01 mm^2/s$) was within the specified range of the ASTM standard ($1.9 – 6.0 mm^2/s$) but higher than the value ($4.84 mm^2/s$) obtained for Jatropha biodiesel by by Raheman and Phadatare (2004). The greatest difference in using *Jatropha Curcas* oil as compared to diesel is the higher viscosity which could contribute to higher carbon deposit in the engines and also cause some durability problems. Additionally, the high flash point of *Jatropha Curcas* biodiesel (210^oC) obtained as compared to fossil diesel ($74 – 80^oC$) provides a safer product to use and handle than petroleum diesel. The flash point is the temperature at which biodiesel will ignite when exposed to a flame. In consonance with literature and reports of several researchers the heating value (39.6 MJ/kg) obtained was lower in comparison to that of fossil diesel fuels (45.0 MJ/kg).

CONCLUSION

In the present work, the response surface methodology was applied to produce ethyl-ester (biodiesel) from raw *Jatropha Curcas* oil seed using *in-situ* trans-esterification method. Initial catalyst amount was the more important factor with a positive influence on the yield in comparison to alcohol seed ratio which does not significantly affect the yield as a single factor, but was involved in significant interactions with catalyst amount. Due to formation of by-products (soaps) caused by excessive amount of catalyst and excess alcohol leading to difficult ester separation from glycerol, there was a general reduction in *Jatropha Curcas* ethyl-ester as levels of catalyst and alcohol seed ratio increased due to interactions between both experimental factors. A second order response model in terms of both factors with a coefficient of determination (R^2) value of 0.985 and a non-significant ($p>0.05$) lack of Fit were obtained. The model was used to obtain a response surface plot revealing the interactions of the two variables on the yield of biodiesel produced. The obtained model together with other statistical methods can be used to determine the optimum operating process factor conditions for the industrial process using a minimal number of experiments with the attendant economic benefit. According to this study, the biodiesel obtained, compared favorably with some of the ASTM standard.

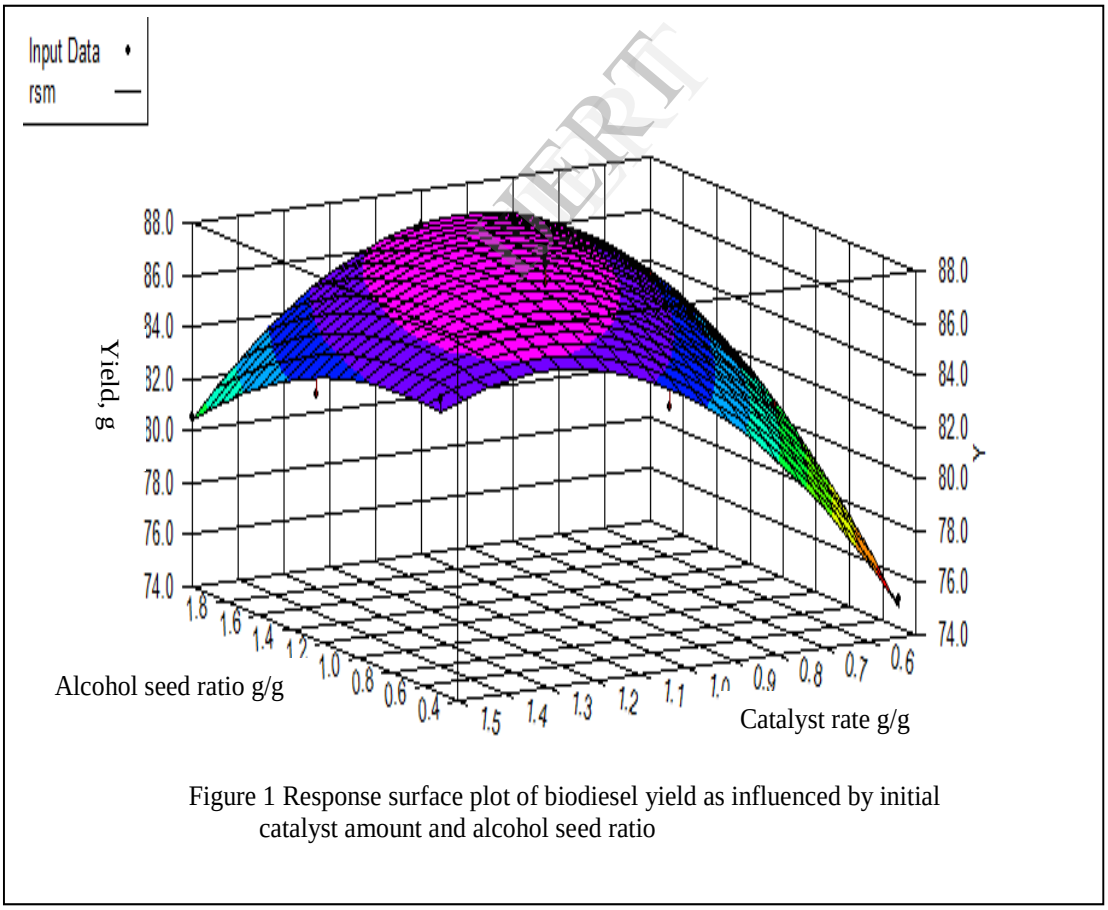

Figure 1 Response surface plot of biodiesel yield as influenced by initial catalyst amount and alcohol seed ratio

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