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 effect 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 was studied at a reaction temperature of 60^{0}C and reaction time of 120min. Central composite experimental design was applied to evaluate effects of alcohol-seed weight ratio (0.5 – 2.0) and initial catalyst amount (0.5 – 1.5%). Initial catalyst amount and alcohol seed ratio was found to have significant (P<0.05) effects on the yield. 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 model was obtained to predict the yield as a function of all 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 but the viscosity.

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

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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 chemically a mono-alkyl ester of long chain fatty acids derived from renewable biological sources such as vegetable oils and animal fats (Khan, 2002; Srivastava and Prasad, 2000). 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. Developing countries such as Nigeria and other do not have sufficient edible oil to fulfill the requirement of the food sector hence they are imported with attendant high cost. The solution for sustainable feedstock of biodiesel lies in 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. Fortunately, inedible vegetable oils, mostly produced by seed-bearing trees and shrubs can provide an alternative. *Jatropha Curcas* seed with no competing food uses is one of such non-edible vegetable seed oil and 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. This would reduce the production cost and providing a favourable comparison with available fossil diesel (Haas and Scot, 2007). Several researchers (Dairo et al, 2011; Zeng et al., 2009; Khalil and Leite, 2006; Obibizor et al., 2002; Ozgul and Turkay , 2003; Silver-Marinkovic and Tomosevic, 1988) have all reported the production of biodiesel 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 effect of initial catalyst amount and alcohol–seed weight ratio and on yield of *Jatropha Curcas* biodiesel at temperature of 60ºC with a reaction time of 120min using response surface methodology and also to develop a model describing the influence of factors on the yield.

MATERIALS AND METHODS

Local *Jatropha Curcas* seeds were purchased from a market in Ogun State, Nigeria. The seeds were hand threshed, according to their condition where damaged seeds were discarded before seeds in good condition were cleaned, shelled. Initial moisture contents of the seed samples were determined and were further reduced by sun drying in thin layers for three 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 78ºC; therefore, a reaction temperature of 60ºC was used as widely available in literature. Reaction temperature for trans-esterification must be below the boiling point of alcohol used (Van Gerpen et al., 2004). The sodium hydroxide was of analytical grade manufactured by Aldrich Chemical Co. Ltd, England. 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, Japan). The blender has a clear glass with stainless steel cutting blades. The temperature was monitored and controlled with a temperature controller (Kazuki, model KZ 200DT, Kazuki China) of 2ºC 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 – 60ºC). The extracted lipid was obtained by filtrating the solvent lipid contained to get rid of the solid from solvent before the hexane was removed using rotary evaporator apparatus at 40ºC. Extracted seed oil was stored in freezer at−2 ◦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)

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 – 32ºC).

Seed and alcohol were mixed for 20 minutes to obtain a homogeneous suspension.

The catalyst at quantities of 0.5, 1.0 and 1.5% by weight of seed was then added to the homogeneous mixture while still stirring.

The temperature of the homogenous suspension in the reactor was raised and kept constant at 60ºC with a calibrated thermostat attached to the heating system.

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.

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.

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.

The washed biodiesel was weighed and weight recorded to determine the yield.

The above procedure was performed in triplicates for all levels of experimental variables according to experimental design.

Experimental design

The Central Composite Design (CCD) of the Response Surface Methodology (RSM) was used for the study. The CCD is an experimental design useful for building a second order model for responses without the need to use a complete three-level factorial experiment. It allows seeing interactions among experimental variables within the range studied, leading to better knowledge of the process and therefore reducing research time and costs (Box and Hunter, 1978). Alcohol seed weight ratio and catalyst amount were taken as the independent variable and the yield as the dependent variable or the response. The CCD design matrix obtained from Design Expert 7.1 software (Stat-Ease, 2007) is as shown in Table 1.

The Yield, defined as the percentage ratio of the weight of washed Jatropha ethyl ester to that of the expressible weight of oil in Jatropha seed (Equation 1) was the dependent variable and referred to as the response.

$$Y = \frac{W_{ester}}{W_{oil}} x100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

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 DataFit 9.0.5 software (Oakdale, 2011)

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

where

Y is the response

x_i and x_j 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 53.16%. The oil content was found lower than the value of 63.16% reported by Akbar et al (2009) for *Jatropha Curcas*. It was however higher than reported values for linseed, soybean, and palm kernel which is 33.33%, 18.35% and 44.6%, respectively (Gunstone, 1994); Castor bean seed of 37.9% (Dairo, 2010). High oil content of *Jatropha Curcas* indicated that *Jatropha Curcas* are suitable as 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 DataFit 9.0.5 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.

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

where X_1 = initial catalyst amount and X_2 = alcohol seed ratio

The amount of catalyst 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%. 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 and the neutralization of the free fatty acid (FFA) of the oil favoured by increased catalyst amount occurred. The average acid value of the *Jatropha Curcas* oil was experimentally determined to be between 2.23 and 2.36 mg+KOH/g. This high value of acid value may have contributed to the formation of the soap, as was observed during experimentation. More viscous fluid was formed at higher catalyst amount. The soap formation also consumes catalyst consequently reducing the amount of catalyst available for the ethyl ester production. This might also have resulted in decreased yield of *Jatropha Curcas* ethyl-ester. 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. These observations are in consonance with researches of Dairo et al.,(2011); Zeng et al.,(2009); Meher et al.,(2006); Ramadhas et al.,(2005).

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); 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 these factors. 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 surface plot of ester yield versus alcohol seed ratio and catalyst amount obtained from the response model are plotted are shown in Figure 1. A careful examination of the plot showed interactive effects of these two factors on the yield at varying levels.

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 (0.901g/cm^3) was within the range of the ASTM standard (D6751-02), however the viscosity of biodiesel produced (4.91 mm^2/s) was higher than fosil diesel(2.0 – 3.0 mm^2/s) but was within the specified range of the ASTM standard(1.9 – 6.0 mm^2/s). Other parameters tested were within the limits of ASTM confirming that biodiesel produced from the study met the criteria for acceptable standards. 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. The study was able to reduce the viscosity to 4.91 mm^2/s. Additionally, the high flash point of *Jatropha Curcas* biodiesel(202^{o}C) makes it safer to store, use and handle than petroleum diesel; 202^{o}C is the temperature at which it will ignite when exposed to a flame while diesel is only 74 – 80^{o}C. The heating value was obtained as 37 MJ/kg, which is comparatively lower than that of diesel fuels (about 45 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 and had a positive influence on the yield than 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. According to this study, the biodiesel obtained, compared favorably with the ASTM D6751-02 standard and 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.

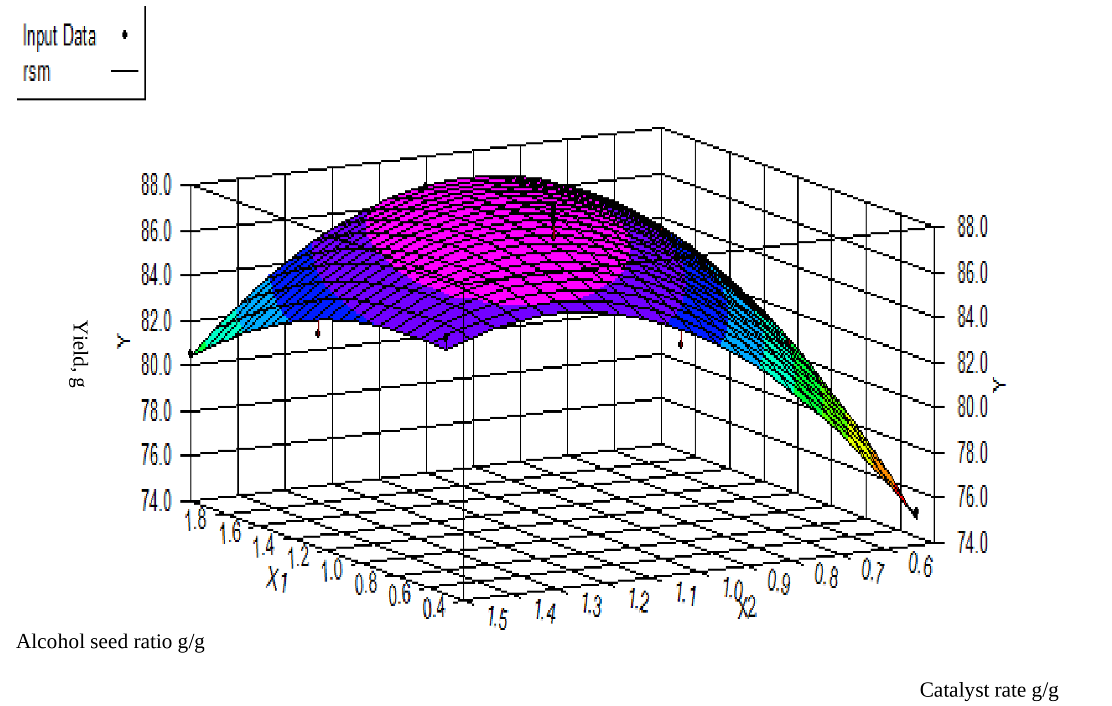

Figure 1 Response surface plot of biodiesel yield as influenced by initial catalyst amount and alcohol seed ratio

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