EFFECT OF INITIAL CATALYST AMOUNT ON PRODUCTION OF BIO-DIESEL FROM *JATROPHA CURCAS* SEED USING *IN-SITU* TECHNIQUE

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Abstract:

The effect of initial catalyst amount(0.3 - 1.5%) on the *in-situ* production of biodiesel from raw *Jatropha Curcas* seed was studied at a reaction temperature of 60^0C and reaction time of between 120min. Central composite experimental design was applied to evaluate effect catalyst amount (0.3 – 1.5%). Initial catalyst amount was found to have significant (P<0.05) positive influence effects on the yield up to a value of between 0.9 and 1.20 g/g after which there was a significant reduction in the yield of biodiesel produced. Due to formation of by-products (soaps) caused by excessive amount of catalyst there was a general reduction in *Jatropha Curcas* ethyl-ester as levels of catalyst amount increased. A cubic quadratic model was obtained to predict the yield as a function of catalyst amount. The model predicted well the observed data with a R^2 value of 0.939 and a non-significant Lack-of-Fit (P<0.05). The optimal value for initial catalyst amount was obtained as 1.01g/g. The biodiesel obtained at

optimal catalyst amount compared favorably with the ASTM D6751-02 standard for biodiesel.

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Key Words: *In-situ*, trans-esterification, *Jatropha Curcas* seed, biodiesel, response surface, bio-mass

1.0   Introduction

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 lays 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.

Openshaw (2000) described *Jatropha Curcas* (**Linnaeus**) as 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).

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 on yield of *Jatropha Curcas* biodiesel at temperature of $60^{o}C$ with a reaction time of 120min, and also to develop a model describing the influence catalyst amount on the yield.

2.0   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 $78^{o}C$; therefore, a reaction temperature of $60^{o}C$ 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 2^oC accuracy connected together with a T-type thermocouple and a mercury-in-glass thermometer.

2.1   Oil extraction and oil content

The seed kernels were ground, using a mechanical grinder, and defatted in a soxhlet apparatus, using hexane (boiling point of $40 – 60^oC$). 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 40^oC. Extracted seed oil was stored in freezer at$-2 \circ C$ for subsequent physicochemical analysis.

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.

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

   i.   400g of ground *Jatropha Curcas* seed was charged from the top into the reactor with the same quantity amount of alcohol (800g) at ambient conditions ($29 – 32^oC$).

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

 iii.   The catalyst at quantities of (0.3, 0.45, 0.60, 0.75, 0.90, 1.05, 1.20, 1.35, 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^oC with a calibrated thermostat attached to the heating system.

   v.   At 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 three 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 according to experimental design for all levels of catalyst amount as indicated in (iii) above.

2.3   Experimental design

A one-factor response surface design was used for the study, where the yield of Jatropha biodiesel was taken as the response variable and catalyst amount as independent variable. The design involved 21 experimental units with three replicates.

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.

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

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.

2.4   Statistical analysis

A non-linear regression procedure of Design Expert 7.0 (Stat Ease, 2007) following a cubic quadratic model (Eq. 2) was used to fit the data obtained from the in-situ experimental runs. The Analysis of variance (ANOVA) was 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.

$$Y = \beta_1 + \beta_2 X + \beta_3 X^2 . + \beta_3 X^3 ....2$$

Where βi are coefficients of model and X is initial catalyst amount

3.0   Results And Discussions

The oil content of *Jatropha Curcas* kernel was determined to be 53.16%, this was 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 initial catalyst amount was analyzed and fitted equation 2 to obtain model coefficients as shown in equation 3. The analysis of variance (ANOVA) for the regression is shown in Table 2. The ANOVA revealed a highly significant model (p-value < 0.05) with an F-value of 87.21 at 95% confidence level and a coefficient of determination (R^2) of 0.939. 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.

$$Y = 79.110 - 0.323X_1 + 31.855X^2 - 20.941X^3 ....3$$

where X = initial catalyst amount.

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

Coded Value Catalyst Amount	Actual Value Catalyst Amount	Experimental Yield (%)	Predicted Yield (%)	Residuals
-1	-0.01	81.3	81.31	4.31
-1	0.76	82.07	81.31	-0.98
-1	-0.79	80.52	81.31	0.48
-1	0.04	81.35	81.31	2.05
-1	0.81	82.12	81.31	-0.96
-1	-0.72	80.59	81.31	-1.24
-0.5	-0.09	85.77	85.86	-1.34
-0.5	0.5	86.36	85.86	-2.00
-0.5	-0.68	85.18	85.86	-0.67
0	-0.07	89.29	89.36	-1.22
0	0.53	89.89	89.36	1.50
0	-0.07	89.29	89.36	4.31

0.5	1.24	89.65	88.41	-0.98
0.5	0.24	88.65	88.41	0.48
0.5	-1.76	86.65	88.41	2.05
1	-0.57	79.05	79.62	-0.96
1	1.65	81.27	79.62	-1.24
1	-2.67	76.95	79.62	-1.34
1	-0.11	79.51	79.62	-2.00
1	1.28	80.9	79.62	-0.67
1	0.5	80.12	79.62	-1.22

Table 2. Regression ANOVA table for production of Jatropha biodiesel using in-situ methodology.

Source	Sum of Squares	Df	Mean Square	F value	p-value
Model	310.26	3	103.42	87.21	<0.0001 S
X	11.32	1	11.32	9.55	0.0066
X^2	291.95	1	291.15	246.19	<0.0001
X^3	15.35	1	15.35	12.94	<0.0022
Residual	20.16	17	1.19		
Lack of Fit	0.10	1	0.10	0.084	0.7763 NS
R^2	0.939				

The amount of catalyst significantly affected the biodiesel yield, with increased ester yield resulting from increased catalyst amount from 0.3 to 1.20 as shown in Figure 1. The increase in yield with initial catalyst amount is in conformity with findings of other researcher that rate of trans-esterification to produce ester is increased by the amount of catalyst starting the reaction. However, at higher levels of catalyst amount (>1.20%) 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 2.36mg KOH/g.   The high amount 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).
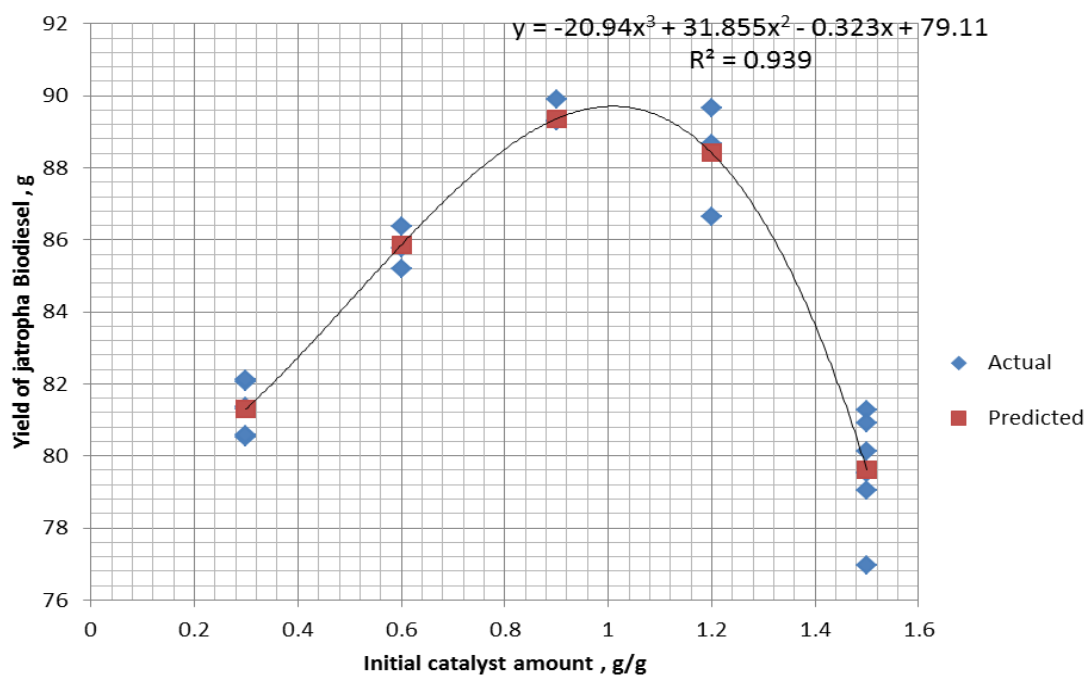
Fig 1. Effect of initial catalyst amount on Jatropha biodiesel production at

Optimum value of catalyst amount was obtained from the model given by equation (3). This was found to be 1.01g/g of catalyst predicted to produce 89.79g of Jatropha ethyl-ester. The fuel properties at this optimum condition were obtained using standard methods of the ASTM. 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 at optimal catalyst amount (1.01g/g). 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 fossil 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 study was able to reduce the viscosity value before trans-esterification from 6.85mm^2/s to 4.91mm^2/s. Additionally, the high flash point of *Jatropha Curcas* biodiesel (198 ^{o}C) compared to petroleum diesel (74 – 80°C) makes it safer to store, use and handle; the flash point is the temperature at which fuels will ignite when exposed to a flame. The heating value was obtained as 36.5 MJ/kg, which is comparatively lower than that of diesel fuels (about 45 MJ/kg).

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Conclusion

In this study ethyl-ester (biodiesel) from raw *Jatropha Curcas* oil seed using *in-situ* trans-esterification method was produced at various levels of initial catalyst amount. Initial catalyst amount had a significant positive effect on the yield and was able to reduce the viscosity to an acceptable level within the ASTM Standard. Due to formation of by-products (soaps) caused by excessive amount of catalyst there was a general reduction in *Jatropha Curcas* ethyl-ester as levels of catalyst amount increased from 1.10g/g. The optimum level of catalyst amount was found to be 1.01g/g. According to this study, the biodiesel obtained at optimum catalyst amount compared favorably with the ASTM D6751-02 standard. A cubic quadratic model with a coefficient of determination (R^2) of 0.939 was used to describe the effect of catalyst amount on the yield of biodiesel produced.

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