

Optimization of *in-situ* Biodiesel Production from Raw

Castor Oil-Bean Seed

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Abstract

Optimization of *in-situ* biodiesel production from raw castor oil-bean seed was carried out from raw castor bean oil seed (37.9% oil content) by alkaline catalyzed *in-situ* trans-esterification with Sodium hydroxide as catalyst and ethanol as the solvent in a laboratory batch processor. Response surface methodology and central composite experimental design was applied to evaluate effects of reaction time (30 -120 min), alcohol/seed weight ratio (0.5 – 2.0), Catalyst amount (0.3 – 1.5%) and reaction temperature (40 – 70°C). Catalyst amount, reaction temperature and time all had significant main effects ($p < 0.05$) while Alcohol-seed ratio had only slight effects on yield of castor biodiesel as a main effect but was significantly involved in interactions with other factors. A modified statistical model comprised of all significant factors and interactions ($p < 0.05$) obtained by multiple regressions predicted that the highest yield of castor ethyl-ester was 99.5% of expressible oil at the following optimized reaction values; alcohol/seed weight ratio of 0.5, a catalyst./seed weight ratio of 1.31, reaction temperature of 60.33°C, and reaction time of 81.7minutes. A Taguchi L9(3⁴) optimization experimental design used to confirm the modified model at optimum point and two other points within experimental region produced yield that was significantly comparable to model predictions at 95% confidence level using a paired t-test. Measured properties of the castor ethyl-ester such as viscosity(5.78mm²/s), pour point (-21.5 °C), flash point (177.12 °C), calorific value (47.76MJ/kg), acid value (0.34 mg KOH/g) and cetane number (48.73) were within the ASTM standard D6751-02 but specific gravity.

Keywords: Castor oil-bean seed, biodiesel, *in-situ* trans-esterification, response surface methodology, optimization, Castor ethyl-ester

1. Introduction

Several scientific Design of Experiments (DoE) techniques can be used to explore which variables and at what level of the variable will maximize a particular output. These techniques have been widely used in all spheres of science including bio-technology to manufacturing industries as a means of maximizing output for a given input of resources (Chitra *et al*, 2005). Optimization procedures usually applied are factorial designs, response surface methodology, uniform experimental design, Taguchi orthogonal design, one variable at a time (OVAT) method and several others.

Biodiesel a renewable fuel with lesser exhaust emissions is one of the alternative sources of energy that is presently of interest worldwide, hence, researchers have focused on the development and the optimization of the processes of biodiesel production to meet the standards and specifications needed for the fuel to be used commercially without compromising on the durability of engine parts. Various oils have been in use in different countries as raw materials for biodiesel production owing to its availability, Soybean oil is commonly used in United States and rapeseed oil is used in many European countries for biodiesel production, whereas, coconut oil and palm oils are used in Malaysia for biodiesel production. In developing countries like Nigeria, edible oils are not sufficient produced locally to satisfy the requirements of the food sector and are usually expensive because

of high import bills, consequently Nigeria and other developing countries would be more comfortable in production of non-edible crops that can sustain the renewable fuel in the large arable land usually available in these developing countries. Castor oil bean seed is one of such non-edible vegetables oil seeds and viable feedstock for the production of renewable, biodegradable and nontoxic fuel (biodiesel).

Different methods to produce biodiesel exist, but all methods have the same underlying chemical reaction which has severally being reported to have two inputs: vegetable oil and alcohol, and creates two outputs: ester and glycerol (Van Gerpen et al. 2004). Trans-esterification is the most commonly used method of reducing the viscosity of vegetable oil. Trans-esterification is the reaction of a lipid with alcohol to form esters and a by-product, glycerol. By trans-esterifying vegetable oils, alkyl monoesters of the fatty acids present in the vegetable oil are obtained. These esters are commonly referred to as biodiesel. A catalyst is usually required to speed up the reaction; this may be basic, acidic or enzymatic in nature. The variables involved in determining the optimum conditions for trans-esterification are temperature, catalyst, triglyceride to alcohol ratio, rate of ignition, water content of alcohol used and the amount of excess alcohol (Pinto *et al.*, 2005). 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.

Optimization of experiments has been reported by Robert, *et al.* (2002) as a way of experimentation leading to useful savings of scientific resources. Considerable numbers of researches have been done to optimize process variables in the production of biodiesel from various crops using both conventional and *in-situ* methods (Alamu *et al.*, 2007), however, optimization of experimental conditions for biodiesel production from ethanolysis of castor oil bean seed using *in-situ* method is scarce in literature; therefore this study was aimed at optimizing the condition of trans-esterification of castor-oil- bean seed into biodiesel through reaction variable such as alcohol-seed ratio, catalyst amount, reaction temperature and reaction time.

2. Materials and methods

Castor bean seeds used for the research work were procured from the experimental field of the Forestry and Wildlife department of the University of Agriculture, Abeokuta Ogun State, Nigeria. Initial moisture contents of the seed samples were determined and this was further reduced by sun-drying. The dried seeds were hand threshed, passed through a Tyler sieve set to remove impurities, chaffs and other foreign matter. Clean seed were ground in a food blending machine to reduce its size and consequently increase its surface area. The ground seeds and clean whole seeds were divided into specified weights, sealed in double polythene bags and stored in the refrigerator prior to use.

The ethanol used had a boiling point of 78°C; therefore, a reaction temperature of 60°C was used as widely available in literature (Van Gerpen *et al.*, 2007). Reaction temperature for trans-esterification must be below the boiling point of the alcohol used. The catalyst quantity usually used were between 0.1 and 1.5% weight of oil (Van Gerpen *et al.*, 2007) while reaction times between 30min and 2h has been reported (Chitra *et al.*, 2005). Therefore a reaction time of between 30 and 120 min was selected. 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 Cycle blend 10, Pulsematic UK) with an incorporated 500W electric heating element (240V, Sony Electronics, Japan). The blender has a clear glass with stainless steel cutting blades. The temperature was monitored and controlled with a temperature controller of 2°C accuracy connected together with a T-type thermocouple and mercury-in glass thermometer.

2.1 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 and provides information about interactions among experimental variables within the range studied, leading to better knowledge of the process (Box and Hunter, 1978). The relationship between the coded values and the actual values obtained by Eq. (1) is given in Table 1. The CCD design was randomized and replicated thrice at each experimental condition.

$$x_k = 2 \left(\frac{X_k - \overline{X_k}}{R} \right) \quad (1)$$

where x_k is the coded value, X_k is the actual value of variable k, $\overline{X_k}$ is the midpoint value of variable k and R is the range of variable k.

The use of the RSM required a confirmatory experimental run, this was performed using the Taguchi L9(3⁴) experimental design as obtained from Design Expert 7.1 software (Stat-Ease, 2007). The Taguchi design experimental variables in terms of coded and actual values are as shown in Table 2. The three levels of factors included the optimum values obtained from the RSM experimental runs and two other points that were within the experimented region (but not values used for the central composite design of Table 1).

2.2 Statistical analysis

Multiple regression procedures following the second order polynomial equation given by Eq. (2) was used on data obtained from the experimental runs.

$$y = \beta_0 + \sum_{i=1}^4 \beta_i x_i^1 + \sum_{i=1}^4 \beta_{ii} x_i^2 + \sum_{i < j=1}^4 \beta_{ij} x_i x_j \quad (2)$$

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. Analyses of Variance (ANOVA), and t-test were also used in the data analysis.

2.3 Production of castor biodiesel (castor ethyl-ester)

The method as described by Dairo *et. al* (2011) was used in the laboratory production of biodiesel with 400g of ground castor bean seed and the required weight of alcohol (200,500& 800g) charged from the top of the reactor into the reactor at ambient conditions (29 – 32°C). Both seed and alcohol were mixed for 20 minutes to obtain a homogeneous suspension. The catalyst at quantities (0.5, 0.9 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 the desired temperature (55, 60 and 65°C) with a calibrated thermostat attached to the heating system. At the end of the reaction time (30, 75 and 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 (Alamu *et al.*, 2007).

The washed biodiesel was weighed and weight recorded to determine the yield according to Eq. (3). The above procedure was performed in triplicates for all levels of experimental variables according to experimental design.

The Yield was taken as the percentage ratio of the weight of washed castor ethyl ester to that of the expressible weight of oil in castor bean seed, Eq. (3).

$$Y = \frac{W_{ester}}{W_{oil}} \quad (3)$$

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

2.4 Confirmatory experimentation

The response surface model obtained from the study was tested using the Taguchi experimental design for process optimization at experimental points (Table 2) following the earlier described procedure with replication.

3. Results and discussion

The yield of biodiesel obtained for the experimental points of the central composite design matrix configuration is shown in Table 3 in terms of experimental coded values and coded values. The yield data obtained from Eq. (3) was fitted to a second order quadratic polynomial (Eq. 2), comprising of all process factors by using multiple regression procedure of Design Expert 7.1. 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.

Two full quadratic models consisting of all experimental variables were obtained in terms of coded experimental variables and actual experimental variables using Design Expert 7.1 software. The ANOVA for the full quadratic model revealed a highly significant model with coefficient of determination (R^2) value of 0.940 however, not all the process factors significantly affected the response variable. One main effect; the Alcohol Seed Ratio(X_1), and interactions of Reaction Temperature and Reaction Time (X_3 - X_4), Catalyst Amount and Reaction Temperature (X_2 - X_3), and quadratic term of Alcohol-seed ratio(X_1)² were not significant factors in the model at 95 % confidence level.

A modified quadratic model was thereafter obtained after eliminating the non-significant factors using the stepwise elimination procedure, but Alcohol Seed Ratio (X_1) which was a main factor and was also significantly involved in interactions was included into the modified model as a forced factor. The modified model in terms of actual variables shown in Eq. (4) comprised of an intercept, Alcohol/Seed weight Ratio(X_1), Catalyst Amount(X_2), Reaction Time(X_3), Reaction Temperature(X_4), interactions of Alcohol Seed Ratio – Catalyst Amount (X_1X_2), Alcohol Seed Ratio – Reaction Temperature (X_1X_3), Alcohol Seed Ratio – Reaction Time (X_1X_4), Catalyst Amount - Reaction Time (X_2X_4) and the quadratic terms of Catalyst Amount (X_2^2), Reaction Temperature (X_3^2) and Reaction Time (X_4^2).

$$Y = -0.56 + 0.09x_1 + 0.055x_2 + 0.026x_3 + 0.009x_4 - 0.10x_1x_2 - 0.001x_1x_3 + 0.0007x_1x_4 + 0.0004x_2x_4 - 0.206x_2^2 - 0.0002x_3^2 - 0.0001x_4^2 \quad (4)$$

The coefficient of Determination (R-Squared) value was 0.941 indicating that the model represented well the actual relationships of experimental factors within the range of experimental study.

The numerical optimization of the modified yield model produced series of optimized solutions at various levels of experimental factors, however, for maximization of response (yield) while maintaining experimental factors within experimental region; Alcohol Seed Ratio (0.5), Catalyst Amount (1.31%), Reaction Temperature (60.3°C) and Reaction Time (82 minutes) with a predicted yield of 0.995 was selected as the optimized parameter points.

The confirmatory tests using Taguchi optimization design at the optimized experimental points and two other points within the experimental region but were not part of the initial experimental points, produced yield of castor ethyl-ester that were not significantly different ($p = 0.301$) from the prediction of the modified yield model using a 2-tail t-test at 95% confidence level. This is a confirmation that the modified second order yield model (Eq. 4) described well the yield of castor ethyl-ester within the experimental region studied.

Fuel properties such as viscosity, specific gravity, flash point, pour point, Cetane number, and heating value of biodiesel produced at the optimum variable levels were compared to ASTM standards to determine the suitability of the sample as biodiesel fuel. The biodiesel (Castor ethyl-ester) produced at optimized parameters level had viscosity (5.75mm/s²) which met the ASTM standard (<6.00) flash point (177.3°C) also met the ASTM standard (>130°C). The Acid value of 0.34 mg KOH/g obtained was within the ASTM limit (<0.8) while the Cetane Number of 48.7 was higher than the required ASTM standard (>47), the higher the Cetane number the better the fuel. The pour point (-21.1°C) was lower than value for fossil fuel (-18°C) indicating the fuel would require a lower temperature for it to cease to flow through the fuel system showing the suitability in cold region. The specific gravity (0.932kg/cm³) was higher than the ASTM standard (0.870 kg/cm³) hence did not meet this criterion, this might probably be an indication of impurity in the fuel or incomplete washing of the biodiesel that have added to its specific weight of the fuel.

4. Conclusion

A Second order response surface modified models consisting of statistically significant ($P < 0.001$) process variables were obtained in terms of actual experimental variables to describe the *in-situ* trans-esterification of castor oil-bean seed based on yield of castor ethyl-ester. The optimized modified yield model had a Coefficient

of Determination (R^2) of 0.941.

The Catalyst Amount(X_2) and Reaction Time(X_4) are the two most important process variables influencing the yield of Castor biodiesel (ethyl-ester) and consequently the *in-situ* trans-esterification of castor oil bean seed, while the Alcohol Seed Ratio (X_1) does not significantly ($P>0.05$) influence the ethanolysis of castor bean seed as a main effect, but was significantly involved in interactions with other process factors.

Optimized parameters of the modified yield model were obtained as Alcohol Seed Ratio (0.5), Catalyst Amount (1.31%), Reaction Temperature (60.3°C), and Reaction Time (82minutes) with a predicted yield of 99.5% of expressible oil from seed.

Measured properties of the castor ethyl-ester such as viscosity(5.78mm²/s), pour point (-21.5 °C), flash point (177.12 °C), calorific value (47.76MJ/kg), acid value (0.34 mg KOH/g) and cetane number (48.73) were within the ASTM standard D6751-02 but specific gravity.

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Table 1. Experimental, predicted and residual values of biodiesel yield obtained at various experimental levels

Alcohol/Seed Ratio (X_1)	Catalyst Amount, % (X_2)	Reaction Temperature ($^{\circ}\text{C}$) (X_3)	Reaction Time (min) (X_4)	Weight of Ethyl Ester *(g)	Yield *	Residuals
-1	-1	-1	-1	0.578	0.551	0.0273
-1	-1	1	-1	0.648	0.619	0.0287
-1	1	-1	-1	0.684	0.728	-0.0440
-1	1	1	-1	0.819	0.796	0.0223
0	0	0	-1	0.728	0.772	-0.0440
1	-1	-1	-1	0.602	0.615	-0.0133
1	-1	1	-1	0.612	0.636	-0.0243
1	1	-1	-1	0.628	0.617	0.0110
1	1	1	-1	0.674	0.638	0.0363
1	0	0	0	0.967	0.952	0.0150
0	0	0	0	0.961	0.952	0.0083
-1	0	0	0	0.920	0.953	-0.0330
0	1	0	0	0.941	0.934	0.0073
0	0	0	0	0.905	0.952	-0.0477
0	0	-1	0	0.926	0.882	0.0440
0	0	1	0	0.911	0.927	-0.0153
0	-1	0	0	0.844	0.823	0.0213
-1	-1	-1	1	0.584	0.592	-0.0087
-1	-1	1	1	0.615	0.660	-0.0460
-1	1	-1	1	0.827	0.812	0.0157
-1	1	1	1	0.895	0.880	0.0147
0	0	0	1	0.954	0.881	0.0727
1	-1	-1	1	0.742	0.749	-0.0067
1	-1	1	1	0.791	0.770	0.0210
1	1	-1	1	0.769	0.794	-0.0253
1	1	1	1	0.777	0.815	-0.0377

* Mean of three replicates

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