

BIODIESEL PRODUCTION FROM CASTOR BEAN SEED: AN OPTIMIZATION PROCESS USING RESPONSE SURFACE METHODOLOGY

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Abstract

Castor plant grows naturally in the wild over a wide range of geographical regions in Nigeria and it has an oilseed which has no much use. Production of biodiesel from this oil bearing plant offers potential of converting this waste seed that contain between 35 to 55 % of oil to useful product that is environmental friendly. In this study, the effects of process variables such as reaction time and reaction temperature on the transesterification of the castor oil to biodiesel were investigated. Methanol with potassium hydroxide (KOH) as a homogenous catalyst was used for the transesterification process at a different reaction temperature of 50^oC, 55^oC, 60^oC, 65^oC and 70^oC while reaction time was varied from 0.5 to 2.5 hours and the corresponding volume of the biodiesel produced were recorded for each of the variations. The Analysis of Variance (ANOVA) results of the Response Surface Methodology showed that the quadratic coefficients were significant ($p = 0.05$). The R^2 and R^2 adj. value of 0.9594 and 0.9304 respectively indicated that the regression model was a good one and verification experiment confirmed the validity of the predicted model. The experimental results suggested the optimal condition of 65 °C and 1.87hours; reaction temperature and time respectively to achieve a maximum biodiesel yield of 96.2%. In addition the fuel properties of the biodiesel produced which include; specific gravity, density, kinematic viscosity, pH, ash content, carbon content, acid value, flash point, fire point and calorific value were investigated and compared with the standards.

Keywords: Biodiesel, Castor oil, transesterification, Optimization, Renewable, Response Surface Methodology, Vegetable oil seed.

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1. INTRODUCTION

Petroleum based fuels are non renewable and with present power consumption rate and increase in number of transport vehicles the coal pits are going to empty within short period of time. The world at present heavily depends upon petroleum fuels for transportation and for operating agriculture stationary machineries. Diesel engines dominate the field of transportation and agriculture machinery on account of its superior fuel efficiency. The consumption of diesel in most developing nations is several times higher than that of petrol consumption. Reserves appear to grow arithmetically while consumption is growing geometrically. Under this situation world will be leading to an industrial disaster (Sreenivas *et al.*, 2011). The diesel engine is a major contributor to air pollution especially within cities and along urban traffic routes. In addition

to air pollution that causes ground level ozone and smog in the atmosphere, diesel exhaust also contains particulate and hydrocarbon toxic air contaminants. Now society has become more aware of harmful effects of the various exhaust emission coming out of the engines and there is tremendous pressure on researchers to reduce exhaust emissions. Various harmful effects of exhaust emission are already established and known to today's society. Carbon monoxide, if inhaled, enters into the blood stream and causes hypoxia, which leads to further health problems. Hydrocarbon emissions are irritant and odorants and some of them carcinogenic. Oxides of nitrogen are found to be responsible for many of the pulmonary diseases (Fan *et al.*, 2011). Developing alternative energy is an unavoidable choice for harmonious coexistence

of human and environment as well as for sustainable economic growth in human society. Many renewable energy sources have drawn the attention of researchers. Among the renewable energy sources that have drawn the attention of researchers, biofuel is the most popular choice. Recently, the development of biofuel is being considered to be a major substitute for fossil diesel worldwide with particular reference to the biodiesel as a clean-burning alternative source of fuel produced from vegetable oils (Tonkin, 2009).

Biodiesel is produced by transesterification of the vegetable oil with methanol in the presence of a catalyst (usually sodium hydroxide or Potassium Hydroxide) but the resulting product may contain not only the desired methyl esters (biodiesel) but also glycerin and residual methanol. The production of biodiesel starts with the choice of feedstock. The feedstock's for biodiesel production are primarily categorized into four main groups; vegetable oils (edible and non-edible), animal fats such as tallow, yellow grease, chicken fat and by-products from fish oil, waste or recycled cooking oil and algae (Kumar and Chauhan, 2013).

The use of vegetable oils as biodiesel fuel dated back to 1900 by Rudolf Diesel, when he first used peanut oil for demonstration of his newly developed compression ignition (CI) engine (Bobade and Khyade, 2012). Today, there are more than 350 potential vegetable oil crops that could be used as the main conventional feedstocks for biodiesel production such as soybean, canola, and sunflower among others, depending upon the climate and soil conditions (Sreenivas *et al.*, 2011).

Castor is considered to be one of the most promising nonedible oil crops, due to its high annual seed production and yield, and since it can be grown on marginal land and in semiarid climate. Few studies have been done regarding castor fuel-related properties in pure form or as a blend with diesel fuel, primarily due to the extremely high content of ricinoleic acid. (Patel *et al.*, 2016). No matter what kind of catalysts or approaches were applied, all those studies

aimed to produce high yield of biodiesel by optimized reaction conditions based on optimized parameters in terms of alcohol/oil molar ratio, catalyst concentration, reaction temperature, and time. However, nearly in all studied cases, there existed complex interactions among the variables that remarkably affected the biodiesel yield. Moreover, it seems unrealistic to optimize the process by the traditional 1-factor-at-a-time approach, which is time-consuming and nearly impossible to achieve the true optimal condition. Alternatively, response surface methodology (RSM), an experimental strategy described first by Box and Wilson for seeking an optimal condition for a multivariable system, is an efficient technique for processing optimization (Kong *et al.*, 2004). In this study, Response Surface Methodology was employed to optimize the transesterification of crude castor oil with methanol in the presence of potassium hydroxide to produce biodiesel with the highest yield.

2. MATERIALS AND METHODS

The castor seed was collected from the wild in Ilorin, Kwara State, Nigeria. The reactants for the experiment include anhydrous methanol, potassium hydroxide (KOH), and the castor oil. Methanol was selected as reagent because it is cheap, low cost, react fast, renewable and biologically less objectionable in the environment while potassium hydroxide was selected because it is cheaper and has better performance than other catalysts available.

2.1 Equipment Used

The following equipment used for the work are:

- (a) Electronic weighing balance (*Mettler Toledo PL203*): accuracy 0.001g
- (b) Water bath machine (*Genlab Ltd*): for vaporization
- (c) Hot plate magnetic stirrer
- (d) Density meter (*Rudolph Research Analytical*: DDM 2911 Automatic Density Meter) for measuring the relative density and specific gravity

- (e) Digital Viscometer (NDJ – IB Rotational Viscometer; *Shanghai Chamgji*) for the determination of the kinematic viscosity
- (f) Handheld pH meter: for pH value
- (g) Bomb calorimeter (IKA Calorimeter, System C200 Basic Control): for evaluation of the calorific value biodiesel

2.2 Experimental Methodology

Central composite rotatable design of response surface methodology was employed as reported by Montgomery (2005). Roasting temperature (A) and roasting duration (B) were considered as main factors influencing oil yield from castor seeds. The choice variables levels were fixed based on information from the literature and trial experiments (Akinoso and Oni, 2012). The five levels of roasting temperature were (83.18, 90, 100, 110 and 116.82 °C) and roasting duration (6.59, 10, 15, 20 and 23.41 minutes) . Analysis of variance (ANOVA) was used to determine the significant effect of the parameters using the Design Expert 6.0.6. The objective function were related to the two process conditions with constraints defined by the stated values of the lower and upper limits as the boundaries conditions .The correlation between the operating parameters (independent variables) and the dependent response (oil yield) was determined using a quadratic model of a second-order polynomial as it is shown in Eq. (1)

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} x_i x_j \quad (1)$$

where, Y represents the predicted response; β_0 is the constant coefficient; β_i is the linear coefficient; β_{ii} is the quadratic coefficient; β_{ij} is an interaction coefficient; x_i and x_j are the coded values of the independent variables.

2.3 Transesterification Procedure

The extraction of oil from the processed castor bean seeds was produced using screw extraction for the mechanical expression of the oil. The collected clear transparent liquid oil was trans-esterified using methanol as alcohol and Potassium Hydroxide (KOH) as the catalyst. Every 250 ml of castor oil required

62.3 ml of methanol and the amount of Potassium Hydroxide was 1% by weight of the Methanol used. The catalyst was kept dry in an airtight container during the storage since water promotes saponification. The required amount of catalyst was measured and dissolved in the alcohol before pouring into the corresponding volume of the castor oil. The mixture was stirred and covered to avoid evaporation of the alcohol into the atmosphere and left to settle for 24 hours after which there was a clear distinction of biodiesel at the top and glycerin which settled at the bottom. The alcohol (methanol) reacted with the fatty acids in the Castor oil in the presence of the catalyst (Potassium Hydroxide) to form mono alkyl (Biodiesel) and glycerin, Fig. 1– 4 shown fuel preparation using magnetic stirrer and separation of biodiesel and glycerin.

2.4 Optimization of Transesterification

The purpose of the optimization is to determine the best combination of reaction temperature and reaction time to produce the highest yield of biodiesel. Methanol to castor oil molar ratio of 1:4 was used, and a catalyst (KOH) of 0.5g was also used for each of the molar ratios. Optimization was carried out at a different temperature of 55.0, 57.5, 60.0, 62.5 and 65.0 °C while reaction time was varied from 1.0 to 2.0 hours at step wise of 0.25 hour and the corresponding volume of the biodiesel produced was recorded for each of the variations.

Hemant *et al.*, (2011) stated that extraction of biodiesel from castor oil, in the presence of the catalysts produced faster with methanol as the transesterification agent compared with ethanol. The maximum yield of esters depend on the reaction time were recorded. The independent variables used for the study were reaction temperature and reaction time while response was product fractions.

2.4.1 Determination of the Yield of Esters

Biodiesel yield was determined using equation Eq. (2).



Fig. 1: Trans-esterification process



Fig. 2: Separation of biodiesel and glycerin



Fig. 3: Washing of Biodiesel



Fig. 4: Biodiesel Produced

$$\text{Biodiesel yield} = \frac{\text{Volume of biodiesel produced}}{\text{Volume of oil used}} \times 100\% \quad \text{Eq. (2)}$$

2.4.2 Separation and Washing of the Biodiesel

After transesterification and overnight settling, results showed methyl esters and glycerin distinctively separated. Glycerin is denser and therefore settled at the bottom of the container. The mixture needed to be separated and this was done by sucking out the biodiesel from the top of the container and leaving glycerin at the bottom to be disposed off.

Fig. 2 shown separation of Biodiesel from glycerin

2.4.3 Biodiesel Drying

After gently washing three times with warm water, the biodiesel was left overnight in the

open for the evaporation to take place and by the following day, all the water had evaporated and biodiesel was ready for blending and testing.

2.5 Characterization of Biodiesel produced from castor oil

Physicochemical properties of biodiesel produced from oil extracted from castor bean seed were characterized. The relative density and specific gravity was measured using Density meter (Rudolph Research Analytical: DDM 2911 Automatic Density Meter). Iodine value was determined using the method employed by Akpan *et al.*, (2006). The kinematic viscosity was measured using Digital

Viscometer (NDJ – IB Rotational Viscometer; Shanghai Chamgji) while the pH was determined using handheld pH meter and the calorific value was measured using Bomb calorimeter (IKA Calorimeter, System C200 Basic Control).

3. RESULTS AND DISCUSSION

The values of the physicochemical properties of biodiesel produced from oil extracted from castor bean seed were as presented in Table 1. Density, cloud point and pour point of castor oil were found higher than diesel. Higher cloud and pour point reflect unsuitability of castor oil as diesel fuel in cold climatic conditions. The flash and fire points of castor oil was quite high compared to diesel. This indicates that castor oil could be extremely safe to handle (Rao *et al.*, 2009). Higher carbon residue from castor oil may possibly lead to higher carbon deposits in combustion chamber of the engine. Low sulphur content in castor oil results in lower SO_x emissions. Presence of oxygen in fuel improves combustion properties and emissions but reduces the calorific value of the fuel (Zamora *et al.*, 2001). Castor oil has higher calorific value compared to diesel. Nitrogen content of the fuel also affects the NO_x emissions. Higher viscosity is a major problem in using vegetable oil as fuel for diesel engines. The investigation reduced viscosity by transesterification process. Viscosity of castor biodiesel is 6.5 mm²/s at 40 °C. It was observed that viscosity of castor oil decreased remarkably after transesterification of the oil. The experimental model equation based on the coded values (X₁ and X₂ as reaction temperature and reaction time, respectively) for the biodiesel yield from castor oil was expressed by Eq. (3).

The result of statistical analysis of variance (ANOVA) was carried out to determine the significance and fitness of the quadratic model as well as the effect of significant individual

terms and their interaction on the chosen responses. Coefficient of determination (R²= 0.9594) revealed that there are excellent correlations between the independent variables. The values of F-test (12.63) and estimated Error (0.37) also showed that the model satisfactorily fitted to experimental data. It was found from Table 2 that A, B, A², AB are significant model terms that influence biodiesel yield response.

Multiple regression analysis of the experimental data gave the following second order polynomial equation on terms of Biodiesel yield.

The positive sign of the coefficient in the model equation indicates that an increase in A, B, and A², will increase Y. However the negative signs in the model equation B² and AB all indicate that a decrease in these terms will decrease Y. The measured R² is (0.9594), adjusted R² (0.9304), predicted R² (0.7175). The R² implies that the model can explain 95.94% variability in the process. The R² and the adjusted R² are close to 1 which implies that the model fits the data well. According to the results, the experimental model confirmed the validity of the predicted model as indicated by the model equation 3 for the biodiesel yield.

Table 1: Physicochemical Properties of Castor Biodiesel

Sample	B100
Density at 20 ⁰ C,(g/cm ³)	0.95363
Specific Gravity	0.9554
Carbon (g/100g)	21.1469
Ash (g/100g)	1.22006
Saponification value (mgKOH/g)	241.5532
Acid Value (mgKOH/g)	13.9109
Ph	7.0
Flash point (°C)	280
Fire point(°C)	335
Kinematic Viscosity, (mm ² /s)	10.9
Calorific value, (MJ/Kg)	38,470

$$Y = 269.22319 + 9.40133X_1 + 59.09132 X_2 + 0.060150 X_1^2 - 2.41500 X_2^2 - 0.77000 X_1 X_2 \quad \text{Eq. 3}$$

Table 2: ANOVA for Response Surface Quadratic Model for Biodiesel

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	306.98	5	61.40	33.06	< 0.0001	Significant
A	211.49	1	211.49	113.89	< 0.0001	
B	63.76	1	63.76	34.34	0.0006	
A ²	15.73	1	15.73	8.47	0.0226	
B ²	2.54	1	2.54	1.37	0.2808	
AB	14.82	1	14.82	7.98	0.0256	
Residual	13.00	7	1.86			
Lack of Fit	12.63	3	4.21	45.76	0.0015	Significant
Pure Error	0.37	4	0.092			
Cor Total	319.98	12				

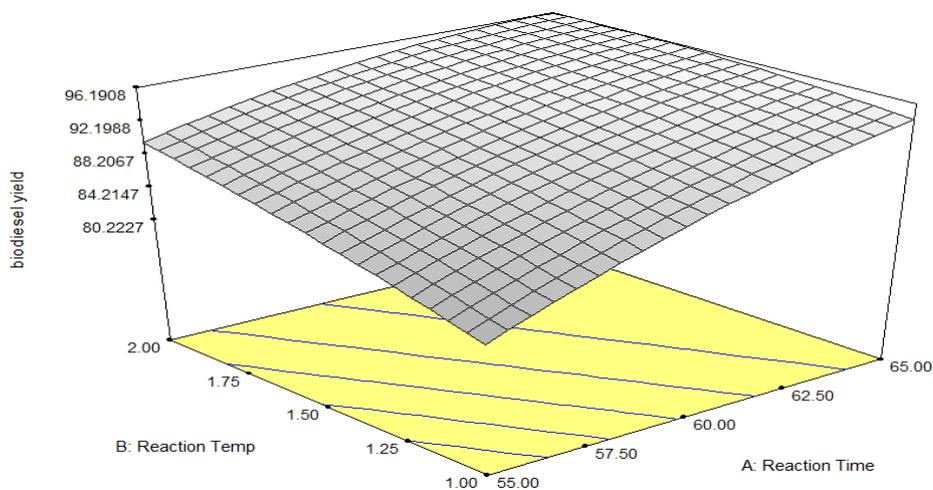


Fig. 5: Response surface plots showing effect of reaction temperature and reaction time and their interactive effect on the biodiesel yield

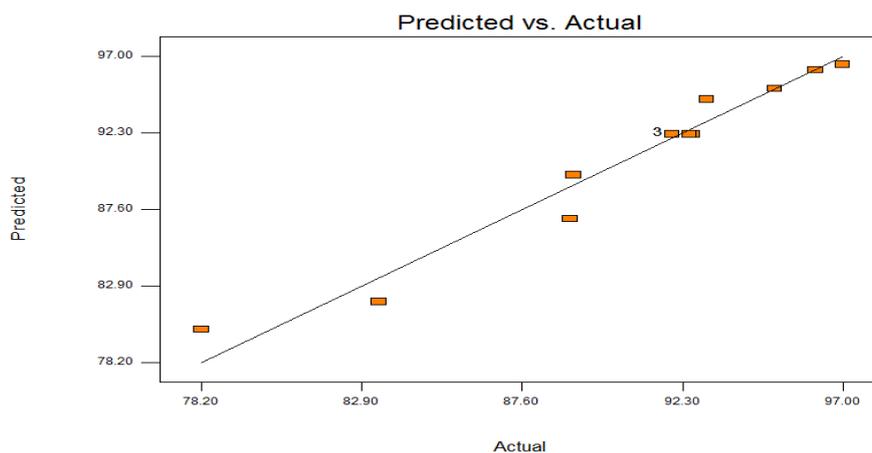


Fig. 6: Predicted Biodiesel yield versus experimental Biodiesel yield

3.1 Response surface plots showing effect of reaction temperature and reaction time and their interactive effect on the biodiesel yield

Figure 5 shown the effect of reaction temperature and reaction time and their

interactive effect on the biodiesel yield illustrates three-dimensional relationship between reaction time, temperature and biodiesel yield. These constant levels are at the central levels of that variable in their respective ranges. The figures indicate that biodiesel

increases as reaction time and temperature increase to the optimum values. This observation implies that the two variables were mutually dependent and showed direct influence on the percentage of biodiesel recovery.

The interactive effects of the reaction time and temperature on biodiesel yield indicated biodiesel yield varying from 80.22 to 96.19 %. The experimental results suggested the optimal condition of 65.00 °C and 1.87 hours; reaction temperature and time respectively to achieve a maximum biodiesel yield of 96.19% (Fig. 5).

3.2 Validation of the model

The relationship between predicted and experimental values of biodiesel yields is shown in Fig. 6. It can be seen that there is a high correlation ($R^2=0.9594$) between the predicted and experimental biodiesel yields. It means that the data fit well with the model and give a convincingly good estimate of response for the system in the range studied.

4. CONCLUSIONS

A central composite design (CCD) of RSM was employed to statistically evaluate and optimized the process parameters for biodiesel production using transesterification method. The Analysis of Variance results showed that the quadratic coefficients were significant; indicated that the regression model was a good one and verification experiment confirmed the validity of the predicted model. The effects of the temperature and reaction time during production of biodiesel suggested the processing condition of 65.00 °C and 1.87 hours of the reaction temperature and time, respectively to achieve a maximum biodiesel yield of 96.19 %. In addition the fuel properties of the biodiesel produced were investigated and compared with the standards.

5. REFERENCES

- [1] Sreenivas. P., Mamilla, V. R. and Sekhar, K. C. (2011). "Development of Biodiesel from Castor Oil, International Journal of Energy Science", 1(3): 192 - 197.
- [2] Fan, X., Wang, X. and Chen, F. (2011). "Biodiesel Production from Crude Cottonseed Oil: An Optimization Process Using Response Surface Methodology"; *The Open Fuels & Energy Science Journal*, 2011, Volume 4.
- [3] Tonkin I. (2009). "Global biodiesel Production Reaches Record High". Available from <http://www.roadtransport.com/>.
- [4] Kumar N, Varun, A. and Chauhan, S. R. (2013). "Performance and Emission Characteristics of Biodiesel from Different Origins: A Review". *Renew Sustain Energy Rev.* 21(0): 633 – 638. <http://dx.doi.org/10.1016/j.rser.2013.01.006>.
- [5] Bobade S. N. and Khyade V. B. (2012). Detail Study on the Properties of Pongamia Pinnata (Karanja) for the Production of Biofuel, *Research Journal of Chemical Sciences*, 2(7): 16-20.
- [6] Patel, V. R., Dumancas, G. G., Viswanath, L. C. K., Maples, R. and Subong, B. J. J. (2016). Castor Oil: Properties, Uses, and Optimization of Processing Parameters in Commercial Production. *Lipid Insights*. 9: 1 – 12. doi: 10.4137/LPI.S40233.
- [7] Kong, Q., He, G.Q., and Chen, Q.H.; Chen, F. (2004). "Optimization of medium composition for cultivating clostridium butyricum with response surface methodology". *J. Food Sci.*, 69: M163-M168.
- [8] Montgomery, D. C. (2005). "Design and Analysis of Experiment: Response Surface Method and Designs", John Wiley and Sons, Inc., New Jersey (USA).
- [9] Akinoso, R. and Oluwaseyi, O. P. (2012). "Optimization of Solvent Extracted Melon Seed oil using RMS", *Eur. J. Lipid Sci. Technol.* 114: 607-611.
- [10] Hemant Y. Shrirame, N. L. Panwar, and B. R. Bamniya. (2011). "Bio Diesel from Castor Oil - A Green Energy Option" College of Agricultural Engineering and Technology, Dr. B. S. Konkan Krishi Vidyapeeth, Maharashtra, India, *Low Carbon Economy*. 2: 1 - 6, doi:10.4236/lce.2011.21001
- [11] Akpan, U. C., Jimoh, D, and Mohammed, A. D. (2006). "Extraction, Characterization and Modification of Castor Seed Oil", *Leonardo J Sci.* 8: 43 -52.
- [12] Rao, P Reaction Temperature (°C) V. (1991). Vegetable Oils and their methyl esters as Fuels for Diesel Engines. *Indian J Technol.* 29(6):292 – 297.
- [13] Zamora, E., Sobalvarro, R., Norori, G. (2001). Trans-esterification of *Jatropha curcas* oil. *Biomass and Bioenergy*. 16: 54–62.