

Determination of Optimal Yield of Biodiesel from Coconut (*Cocos Nucifera*) Seed Oil.

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Abstract

Coconut seeds were investigated for its use as biodiesel feedstock. 67.2% oil was extracted using soxhlet extraction. Biodiesel synthesis was developed and optimized using Box-Behnken design in Response Surface Methodology to study the effect of experimental variables such as methanol to oil ratio, catalyst concentration, reaction temperature and reaction time on the extracted oil from coconut seeds. The model shows optimum conditions of biodiesel yield of 79% were found at 6:1 alcohol/oil ratio, 1% catalyst concentration (KOH), reaction temperature of 65°C and reaction time of 40 min. respectively. At the end of experimental design it was found that the catalyst concentration and reaction time significantly affect the biodiesel yield than molar ratio among others under the range of values studied. The produced biodiesel was analyzed for its physicochemical and fuel properties all of which are within ASTM specification except for cetane number and sulphur content indicating suitability as an alternative source of fuel.

Keywords: Biodiesel, Response Surface Methodology, Optimization, ASTM Specification.

1. Introduction

The replacement of mineral fuel by biodiesel is one of the effective ways of solving the problem of saving and effective usage of energetic resources. Biodiesel is becoming an increasingly acceptable alternative to fossil diesel because of narrowing gap between worldwide oil production and consumption. Also Nigeria's vegetation and rainfall regime support agrarian activities that can produce feedstock for Biofuel production. Sustainable biofuel production will create more jobs and stimulate related industries thus improving the socio-economic industries of the country (Itodo *et al.*, 2010).

The surge of interest in biodiesel has highlighted a number of positive environmental effects associated with its use. These potentialities include reduction in greenhouse gas emission, deforestation, pollution and the rate of biodegradation (US department of energy, 2003).

Biodiesel is a non-petroleum based fuel made from virgin or used vegetable oil (both edible and non-edible) and animal fat. The main sources or biodiesel can be non-edible oils obtained from plants species available in different countries. Direct application of vegetable oils as

fuel for diesel engine is not possible due to its higher viscosity; hence reduction of vegetable oil viscosity is an urgent need. Transesterification is the process of biodiesel Production which involves the reaction of fat/oil with alcohol in the presence of acidic, basic or enzymatic catalyst to form esters and glycerol (Agarwal, 2007). This study tends to investigate the impact of reaction variables (Molar Ratio/Oil, Catalyst Concentration, Reaction time and Temperature) on Biodiesel production from *Cocos nucifera* seed oil and also analyzed fuel properties of the produced Biodiesel produced for use as an alternative to fossil fuels.

2 Experimental

2.1 Sampling and Sample Treatment.

The Coconut seeds were obtained from vendors at kasuwar Daji in Sokoto metropolis, Sokoto State, Nigeria. The shell of the seed was removed after which the seeds were sun dried then cut into smaller pieces and put into a blender in order to reduce its size and hardness. The smashed sample was then powdered in the blender and later taken for oil extraction. Oil was extracted from the powdered samples using n-hexane as extraction solvent using soxhlet extractor.

2.2 Physicochemical Analysis of Extracted Oil.

Acid value, Moisture content, Saponification values, Ester value and Iodine Value of the extracted oil were determined according methods by Verma, 2001.

2.3 Optimization Of Transesterification Process Using Response Methodology Surface (RSM).

The seed oil was pre-heated up to 65°C in the reaction flask, the oil was allowed to cool at room temperature, A 6:1 molar ratio of methanol to coconut oil methylation process was carried out by dissolving KOH (2.25g) in methanol (198cm³) then mixed with the extracted oil (375g) in a round bottom flask (500cm³) fitted with a cork, the content was stirred on magnetic stirrer for 5min., then heated on a water bath at 65°C for 40min. The mixture was poured into separating funnel and allowed to settle under gravity for 12 hours. Two distinct layers were observed a dark yellow layer (glycerol) at the bottom and a light yellow layer (biodiesel) at the upper layer. The glycerol was separated from the biodiesel which was then measured and recorded (Dalai, 2004).

The biodiesel was mixed with warm distilled water to remove residual catalyst and allowed to settle in a separating funnel under gravity for 12 hours and then separated. The separated biodiesel was dried using silica and then weighed.

The same method was adopted for the Transesterification of 3:1 and 9:1 methanol to oil ratio (optimization process) using catalyst concentration 0.1-1%, reaction time 40-60 min at temperatures 55-65°C. Ten milligrams of oil was used throughout, the experiments and biodiesel yield was calculated using the formula below;

$$\text{Biodiesel Yield} = \frac{\text{Weight of the Biodiesel} \times 100}{\text{Weight of the oil}}$$

(Xuejen *et al.*, 2006).

Determination Of Fuel Properties Of Fame From Cocos nucifera seed oil.

The specific gravity, Kinematic viscosity, Flash point, cloud point, pour point, Aniline point and color scale of fatty methyl ester produced were determined according to ASTM Methods.

API gravity of the produced biodiesel was calculated using equation below as reported by Gerpen *et al.* (2004).

$$\text{API gravity (}^\circ\text{C)} = \frac{141.5 - 131.5}{\text{SG at } 15/4^\circ\text{C}} \dots\dots\dots (1)$$

$$\text{S.G at } 15/4^\circ\text{C} = 0.904 \text{g/cm}^3$$

ASTM D611 method was used to calculate the diesel index using equation.

$$\text{Diesel Index} = \frac{\text{Aniline point (}^\circ\text{F)} \times \text{API gravity} \dots\dots\dots (2)}{100}$$

Cetane number was calculated from the diesel index and a constant using the equation below:

$$\text{C.N} = \text{D.I} \times 0.72 + 10 \dots\dots\dots (3)$$

$$\text{D.I} = \text{Diesel index}$$

$$0.72 + 10 = \text{API constant.}$$

2.4 Experimental Optimization Of Biodiesel.

The synthesis of biodiesel from coconut seed oil (transesterification) process were developed and optimized using the Box-behnken design (BBD) in response surface methodology. Box-behnken design helps in investigating linear, quadratic cubic and cross product effect of the four reaction condition variables on biodiesel yield. The four independent variables studied were molar ratio, catalyst concentration, reaction temperature and reaction time. Considering limits for the experiment set up and working conditions for each chemical species, each run was triplicate. The complete design matrix of the experiment employed and their result are given in Table 2. The experiment sequence was randomized to minimize the effect of uncontrolled factors. Design and results analyses as well as optimization were done using statistical design on MINITAB 15 software. The range of the four variables studied under three different levels are molar ratio (g) 3-9,

catalyst concentration (g) 0.1-1%, reaction temperature (°C) 55-65 and reaction time (min) 40-60.

2.5 Results and Discussion.

The quality of oils expressed in terms of the physicochemical properties such as Moisture content, Saponification, Iodine and Ester value are shown in table 1. The moisture content of the coconut oil is 1.0 ± 0.54 which suggest that the sample seeds can dry well and be stored for a long time and will not favor any microbial growth in storage tank (Gerpen *et al.*, 2004).

When the saponification value was determined a value of 72.65 ± 0.13 and is good enough since high Saponification value implies the possible tendency to soap formation and difficulties in separation of products if utilized for biodiesel production. (Ofoefule *et al.*, 2013). The Iodine value was determined to know degree of unsaturation in oil and is expressed as the percentage by weight of iodine absorbed by an unsaturated fat or oil, for an oil to be regarded as having a high degree of unsaturated fatty acids, it has to have an Iodine value of ≥ 115 mg iodine/g. Hence coconut oil with iodine value of 85.22 ± 0.16 has low composition of unsaturated fatty acid can be classified as a non drying oil. In a similar work with rubber seed oil, Ndana *et al.* (2011) obtained a value of 76.80. The difference in Iodine value of the two oils may be due to nature and ester composition of the feedstock.

Table 1: Physiochemical properties of Coconut seed oil and biodiesel.

Parameter	Value
Colour	Light yellow
% Oil yield	67.2
% Biodiesel yield	85
Free fatty acid (mgKOH/g)	1.17
Moisture content (%)	1.0 ± 0.54
Saponification value (mgKOH/g)	72.65 ± 0.13
Iodine value (mgKOH/g)	85.22 ± 0.16
Acid value (mgKOH/g)	2.33
Ester value (mgKOH/g)	70.32 ± 0.08

Key: Values are mean of 3 (three) trials

3.2 Optimization process of Coconut Oil

In the optimization process, the box-behnken design (BDD) was able to function as an optimal design for the desired response based on the model obtained and the input criteria. The optimization of biodiesel yield was carried out based on four transesterification variables which are in the range of experimental runs. Response surface regression analysis was carried out to fit the response variable that predict the biodiesel yield. The regressors or terms incorporated in model are those statistically tested to be significant. The “p” value less than 0.05 indicated the particular term was statistically

significant. The analysis showed that catalyst concentration, reaction time, molar ratio*molar ratio, time*time and molar ratio*catalyst concentration and reaction time significantly affect the biodiesel yield. The molar ratio, temperature, catalyst concentration*catalyst concentration, temperature*temperature, molar ratio*temperature, molar ratio*time, catalyst concentration*temperature, catalyst concentration*time and temperature*time were found to be statistically insignificant as shown in Appendix 1. Appendix 2 shows the effect of those transesterification variables that were found to be significant. As can be seen, the model developed was successful in capturing the correlation between the transesterification condition variables to the biodiesel. The result of regression analysis suggests that biodiesel yield was only significantly affected by molar ratio, catalyst concentration and reaction time. Significant interaction terms were found to exist between the main factors catalyst concentration and reaction time.

Figure 1: Contour Plot of Yield vs. time, catalyst concentration.

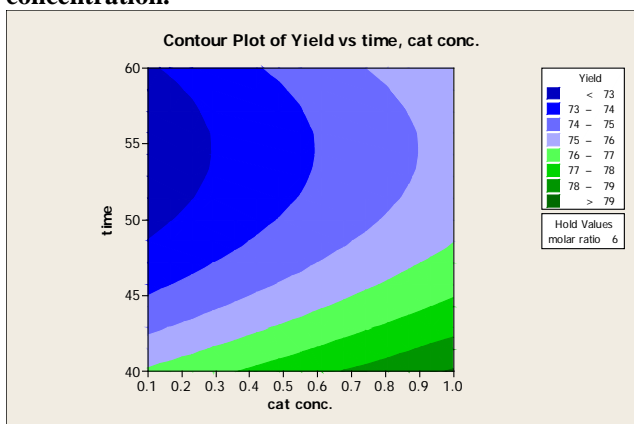


Figure 1 is a contour plot of Transesterification condition variables (catalyst concentration and reaction time) when the reaction period was prolonged to 60 min. and at low catalyst concentration of 0.1g, the biodiesel yield increase but as the amount of catalyst increases the biodiesel yield decreases because high amount of catalyst increase the formation of soap than the esterification of triglycerides into biodiesel. At low reaction time the biodiesel yield is low due to incomplete reaction which reduce molecular interaction between the triglycerides and methanol. It is suggested that for an optimum yield, the amount of reaction time be reduced to the barest minimum of 40min. and optimum catalyst concentration of 0.1g in order to save time as well as cost of catalyst.

Optimal condition for biodiesel was obtained when the molar ratio, catalyst concentration, reaction temperature and reaction time were at 6:1, 1%, 65°C and 40min. respectively. With a predicted yield of 80% close to

experimental value (79%), it is clear that optimization of biodiesel production could be achieved through regression analysis using a known catalyst and other reaction variables.

Table2. Optimization Process For Biodiesel Production.

Methanol to oil	Catalyst (%)	Reaction temp (°C)	Reaction time (min.)	% Yield
3:1	0.1	60	50	68.67
3:1	0.55	60	40	67.4
3:1	0.55	60	60	60.67
3:1	0.55	65	50	70.0
3:1	0.55	65	50	64.67
3:1	1.0	60	50	73.3
6:1	0.1	55	50	69.4
6:1	0.1	60	40	74.38
6:1	0.1	60	60	73.55
6:1	0.1	65	50	69.7
6:1	0.55	55	40	77.4
6:1	0.55	65	40	84.48
6:1	0.55	55	60	73.4
6:1	0.55	65	40	72.6
6:1	0.55	65	60	79.38
6:1	1.0	55	50	72.54
6:1	1.0	60	40	80.8
6:1	1.0	60	60	76.67
6:1	1.0	65	50	80.0
9:1	0.1	60	50	68.87
9:1	0.55	50	60	63.06
9:1	0.55	55	50	77.1
9:1	0.55	65	50	68.04
9:1	0.55	60	40	72.54
9:1	0.55	60	60	70.7
9:1	1.0	60	50	58.68

Key: Values in the table are means of three (3) trials.

The value for specific gravity of the biodiesel from coconut oil is 0.904g/cm³ and is close to the value obtained in similar oil (0.92g/cm³) reported by Gajendra *et al.* (2010). The values are within the acceptable unit of 0.80-090 recommended by ASTM for a B100 type biodiesel as shown in table 3. The difference in value of the same oils may be due to free fatty acid or water content of the sample. This property allows biodiesel to be blended with diesel fuel in various proportions so as to improve diesel engine performance and emission properties as observed by Weiksner *et al.* (2006).

The kinematic viscosity of coconut methyl ester is 4.37mm²/s and within the 1-6mm²/s recommended for biodiesel by ASTM and 3.5-5.0mm²/s recommended for BIS standard. This value is higher than 2.83mm²/s reported for coconut oil biodiesel (Gajendra *et al.*, 2010) but lower than the 5.31 for coconut oil by Ofiofule *et al.* (2013). The difference in Kinematic Viscosity for the

same oils may be due to the increasing degree of saturation of either the fatty acid or alcohol in fatty acid methyl esters (FAME). This indicates that the biodiesel is suitable for use as a direct fuel in diesel engine.

The flash point of the biodiesel was found to be 126°C and is slightly higher than that of coconut methyl ester of 123°C reported by Ofoefule *et al.*, 2013 and but lower than 20% blend diesel (128°C) reported by (Barnwal *et al.*, 2005). The differences in the same oils may be due to methanol content of the sample. The value is within the recommended limit of ASTM standard for flash point D93 which should be 100°C and above. This shows that the biodiesel produced have a good flash point and its use will eliminate the fear of fire outbreaks on storage.

The pour point obtained is 8.9°C, is more than the -12°C reported for coconut methyl ester by Gajendra *et al.* (2010) but within the ASTM stipulated range for fuel grade biodiesel. But the COME could result in plugging of fuel pump in extremely cold conditions.

The cloud point of 10°C obtained is higher than that of Coconut methyl ester (-3°C) by Gajendra *et al.* (2010) but slightly lower than palm methyl ester (13°C) by Barnwal *et al.* (2005) but is within the ASTM standard limits for biodiesel. The difference in cloud point with the same sample may be due to presence of saturated fatty methyl ester (FAME) in the sample.

The coconut oil methyl ester indicate an aniline point at 36.1°C (97°F) which is slightly higher than the 35°C (95°F) reported for castor methyl ester by Ndana *et al.* (2011). This property indicates its miscibility with other aromatic fuels and will burn to generate a good amount of energy.

The API gravity of the coconut oil methyl ester is 25.03, and is low when compared to 36.40 reported for groundnut seed methyl ester (Galadima *et al.*, 2008) which predicts the tendency to have high heating value (that is the amount of heating energy released by the combustion of a unit value of fuels) and improve fuel economy.

The COME has a diesel index of 24.28 which is higher than 19.98 reported for castor methyl ester and lower than 26.79 reported for soy beans methyl ester reported by Ndana *et al.* (2011). The oils are all below the diesel index limit (47) specified for commercial fuels. Note that ignition quality of the fuel found to correlate with approximately to the cetane number of commercial fuels.

Cetane number is found to correlate approximately to diesel index which indicates the ignition quality of the fuel. The CN of COME was found to be 27.48 and is lower than 51 reported for coconut oil (Gajendra *et al.*, 2010). The difference in value of the same oils may be due to oxygen content of the samples. Lower values will result in smoky exhaust. Therefore cetane improver can be added to enhance their ignition quality.

The COME has a sulphur content of 0.06% and is the same as that reported for rubber methyl ester by Ndana *et al.*

(2011) but slightly lower than 0.61% reported for coconut oil by EPA (2009) which is slightly above the specific value given by ASTM D2622 OF 0.05%. This indicates the diesel could emit permissible SO_x upon combustion that have no environmental implication.

The ASTM color of the COME value is 0.5 and is the same as that of Jatropha Methyl Ester but lower than that soy oil methyl ester (1.0) by Ndana *et al.* (2011). This value is low and falls within the standard range of 0.5-0.8 on ASTM color scale and indicates that the biodiesel produced is of high grade, possess light color and has not undergone auto-oxidation that may suggest possible contamination and the formation of insoluble sediment.

Physical properties of COME (Coconut Oil Methyl Ester).

Parameter	Values
Specific gravity (g/cm ³) at 15°C	0.904
K.V at 40°C (Cst)	4.37
FlashPoint(°C)	126
PourPoint(°C)	8.9
CloudPoint (°C)	10
Aniline Point (°C)	36.1
DieselIndex	24.28
CetaneNumber	27.48
SulphurContent % wt	0.064
ASTMColor	0.5

4. Conclusion

An appreciable quantity of coconut oil (67.2%) was extracted from coconut seed using n-hexane as solvent to produce biodiesel using an optimization process developed by Box-behnken design which gave the highest yield of 79% at 6:1 molar ratio, 0.5% catalyst concentration, 65°C reaction temperature and 40 min. reaction time and furthermore the physicochemical properties of the oil indicate it possesses attractive properties of alternative fuels.

The fuel properties falls within the acceptable specification limit of ASTM for biodiesel and diesel fuel such as high flash point is suitable as alternative fuel, low kinematic viscosity for lubrication purpose, low moisture content for preventing corrosion, pour point for preventing gelling problem. The fuel properties of the biodiesel are strongly influenced by the amount of the individual fatty esters in biodiesel.

Biodiesel produced from coconut oils have more compatible properties as convectional diesel engines when economic conditions permits, some anti-gelling additives may be needed to improve the cold flow properties. Similarly, it can be blended with diesel fuel to increase diesel engine performance. As a source of income for Nigerian farmers especially in coconut producing areas in the south as well.

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