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Research article

Optimization of biodiesel production from non-edible seeds of Delonix regia *(*Gul Mohr*)*

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Abstract

Concerns on the ever increasing cost of fossil fuel, fast depletion of world reserves and the impact on environmental pollution has necessitated the search for alternative energy sources. Consequently, biofuels (biodiesel, bioalcohol and biogas) have been identified as sustainable substitutes. The use of food crops for biodiesel production has been very much criticized as they affect food supply. As a result, scientists are now focusing on the utilization of non-edible feedstock for biodiesel production. It is on this background that *Delonix regia* (flame of the forest) is being investigated as possible feedstock for the production of biodiesel in Akwa Ibom State, Nigeria. *D. regia* is a prolific bearer commonly grown as an ornamental. Extracted oil was upgraded by transesterification using sodium methoxide as catalyst. An optimal biodiesel yield of 87% was obtained within 60min at 60^{o}C by using 6:1 molar ratio (methanol: oil), 0.7% w/v catalyst concentration and 600rpm agitation. Biodiesel analysis showed comparable results with ASTM standards in terms of acid value, kinematic viscosity, free fatty acid, density, colour, ash and water contents, as well as flash, pour and cloud points. The overall results show that *Delonix regia* oil can serve as a veritable feedstock for the production of biodiesel that can effectively be utilized in diesel engines.

Keywords: biodiesel, transesterification, optimization, non-indigenous Delonix regia,

1. Introduction

Vegetable oils have attracted considerable attention as a possible renewable energy source for the production of a substitute for petroleum-based diesel. Different products from vegetable oil such as neat vegetable oil, mixtures of vegetable oil with petroleum diesel as well as biodiesel have been proposed as useful alternatives [1,2,3]. Results from these studies indicated that although, vegetable oil can be used directly as diesel engine fuel, these engines will require some amendments due to high viscosity, poor thermal/hydrolytic stability and ignition qualities of the oil. As a result of these undesirable characteristics, it is necessary to chemically process vegetable oils in order to convert them into biodiesel. While, there are many processes that can achieve this goal, transesterification is considered the most viable [4,5]. Through this process, the large branched molecular structure of vegetable oil is transformed into smaller, straight chained molecules similar to those of standard diesel hydrocarbons. Transesterification is therefore, a process that exchanges the organic group R" of an ester with the organic group R' of an alcohol.

Although, these are common well-established chemical reactions in which alcohols react with triglycerides of fatty acids in the presence of a base or acid catalyst, there are often possible variations in yield of biodiesel, and thus, the need to optimize the reaction process. Molar ratio of alcohol: oil, catalyst concentration, purity of reactants as well as reaction time and temperature are some of the factors that could affect the rate of transesterification and thus, biodiesel yield. Temperatures ranging between 45^{o}C and 65^{o}C have been tested with optimal results obtained at 50^{o}C and 60^{o}C respectively [6,7]. Optimal alcohol: oil molar ratios of 6:1[6] and 5: 5 [8] have also been reported. The type and concentration of catalysts employed are also critical in transesterification reactions. Both acid and alkaline catalysts have been tested, however, alkaline catalysts such as NaOH, and KOH are preferred because of their less corrosive nature. In addition, alkali metal oxides such as sodium methoxide can also be used as catalyst. Catalyst concentration range of 0.5-1% (w/w) has been reported with conversion rates ranging between 70-99% [8].

In an attempt to reduce the price of biodiesel, a number of non-edible seeds such as those from *Jatropha, Cocos nucifera,, Azadirachta indica*, *Prunus amygdalus, Canabis sativa,* etc. have been tested in different parts of the world. In Nigeria, *Jatropha* is also reported to be promising since the plant grows well in most parts of the country and can produce seeds for almost fifty years [9]. Currently, *Jatropha* farms are being established in some states of the middle belt for biodiesel production. Although, *Jatropha* can grow well in most parts of the country, it's cultivation in Akwa Ibom is particularly hindered by high acid soils and excessive rain. It is therefore, necessary to search for indigenous non-edible seeds that can be effectively used as feedstock for biodiesel production. This study is aimed at evaluating the prospects of producing biodiesel from *Delonix regia* (flame of the forest).

2. Materials and methods

2.1 Seed Preparation, oil extraction and characterization

Dry fruits of *Delonix regia* were collected from different areas in Akwa Ibom State. Fruits were split opened to obtain the seeds which were sun dried and stored in dry bottles until when needed. De-shelled seeds were ground with a mechanical grinder and 200g of the grinded seeds were packed in filter paper which was then inserted into a wheaton soxhlet extractor using 150ml of hexane as extracting solvent at 60^{o}C. This process was carried out for 9hrs and the solvent was recovered by simple distillation. The oil was filtered using a cartilage filter to remove solid debris and the distilled residual oil was heated at 100^{o}C for 1hr in order to remove any water molecules. The oil was then cooled and stored in sealed plastic bottles until when required. Four physical properties (kinematic viscosity, density, flash point and total acid content) of the seed oil were determined. The ASTM D1298 and D445 were used in measuring the density and viscosity respectively while flash point and the acid content were determined using ASTM D93 and ASTM D methods respectively [10].

2. 2 Preparation of sodium methoxide and potassium methoxide

20g of methanol was mixed with 0.8g of NaOH alkaline pellets with stirring continuously until all the pellets have dissolved. This reaction forms sodium methoxide. Caution was taken in handling the oxide. Since alcohols can evaporate easily, the flask was covered with aluminium foil during shaking to reduce the loss of alcohol. This covering was also to prevent the alcoxide from absorbing water from the air. The above process was adopted for the preparation of potassium methoxide.

2.3. Basic Titration

This is carried out to determine the number of grams of NaOH that will be used per litre of oil in the transesterification process. With this process a rough estimate of the quantity of catalyst to be used for optimization. A 0.1 solution of NaOH was prepared by dissolving 1g of NaOH in 1litre of water. In another beaker, 1ml of *Delonix* oil was dissolved in 10ml of pure isopropal alcohol. The content was warmed gently in hot water stirred until all of the oil had dissolved in the alcohol and the mixture turned clear. 2 drops of phenolphthalein solution was used as indicator. With the help of a burette, 0.1% NaOH solution was added drop by drop with stirring until the solution stays pink for 10 seconds. The number of mls of 0.1% NaOH solution used added to 5.0 will give the number of NaOH to be used per litre of oil [11].

2. 4 Transesterification process and separation of ester

Transesterification of the first batch of *D. regia* seed oil was carried out with methanol in the presence of NaOH as catalyst. The method of [10] was employed in this investigation. Reactions were conducted in batches at 6:1 methanol to oil molar ratio, 1% catalyst and 65^{o}C temperature. The oil was first heated to this temperature in an oven with stirring at intervals. 240g of seed oil was charged into a 500ml rector and then heated in a water bath to the desired temperature. 40g of methanol and NaOH (1% weight of oil) were mixed and heated to the desired temperature in a separate container. This mixture was then poured into the reactor placed in an electric mixer and magnetic stirrer. The stirring speed was maintained at 400rpm and the reaction was carried out for 5hours. After the reaction the contents were allowed to cool under air current. This solution was then poured into a separating funnel and separation was allowed to take place under gravity for 10 hours. The methyl ester (biodiesel) was found floating on top while the denser glycerine, excess alcohol, catalyst, impurities and traces of un-reacted oils settled at the bottom of the funnel. Solidified glycerine in the funnel was removed by reheated just enough to liquefy it. The separated biodiesel layer was then mixed and washed with warm distilled water to remove un-reacted alcohol, oil and catalyst. Before washing for the first time, a small amount of dilute acetic acid was added to neutralize possible effects of any NaOH that may be present in the biodiesel. The biodiesel obtained was then used for characterization. Before, characterization of produced biodiesel, the percentage conversion of the oil to biodiesel was determined using the equation:

$$\% \text{ Conversion} = \frac{\text{Volume of biodiesel produced}}{\text{Volume of oil used}} \times 100$$

2. 5 Characterization analysis

2.5.1 Biodiesel Characterization

The physical and chemical properties of biodiesel were investigated. The parameters assessed included; colour, viscosity, density, acid value, flash and clod points, pour point, sulphur, moisture and ash content, carbon residues as well as gross heat of combustion. Biodiesel colour was determined using the ASTM D method while the density and kinematic viscosity were measured using ASTM standards D1298 and D445 respectively. Cloud, pour and flash points were determined using the ASTM methods D5949, D5773 and D 93 respectively. The Total acid number was measured using the ASTM D method while the carbon residue and gross heat of combustion were assessed using the ASTM D189/IP 13, ASTM 4868 and ASTM D482/IP respectively. The sulphur, moisture and ash contents were determined using Acq method sulphur M, ASTM D and ASTM D482/IP methods respectively [11, 12].

2.6 Optimization of reaction conditions

With respect to optimization, five parameters; molar ratio of alcohol: oil, temperature, catalyst concentration, reaction time and rate of agitation were investigated. The effect of each factor was assessed by varying one of the above parameters while keeping the others constant. The molar ratio of alcohol: oil was determined at 7.1, 6:1, 5:1, 4:1 and 3:1 while, temperature was examined at 45^{o}C, 50^{o}C, 55^{o}C, 60^{o}C and 65^{o}C. Catalyst concentration was tested at 0.6%, 0.7%, 0.8%, and 0.9%. The reaction time was investigated at 30, 40, 50, 60 and 70min, while, the effect of agitation was studied at 700, 600, 500, 400 and 300 rpm. All experiments in this study were conducted in three replicates and results analysed using ANOVA.

3 Results and Discussion

3.1. Basic Titration

Since the amount of catalyst to be used in this experiment varies with oil, it was necessary to get a rough idea of this quantity. This was achieved through titration and the mean value of 6.5g of NaOH was used for 1000ml of oil (table 1).

Table 1: Titration Results

	Volume of NaOH (ml)			
Samples	Initial	Final	Vol used	Required mass
A	55.0	56.4	1.7	7.0
B	50.0	51.3	1.3	6.2
C	60.0	62.8	1.6	6.5
Average	55.0	56.8	1.5	6.5

3.2. D. regia seed oil characterization

The prospects of utilizing non-edible seed oil from *D. regia* as feedstock for biodiesel production was investigated. Results on four physical properties of the oil indicated very high acid content, viscosity and flash point (table 2) which clearly makes it unsuitable for use in combustion engines. In order to make this oil suitable as biofuel, it has to undergo the process of transesterification. This process was therefore, employed to convert the *D. regia* oil into biodiesel by transforming the large branched molecular structure of the vegetable oil into smaller, straight chained molecules [12]. It must be noted that the high values recorded for *D. regia* oil are not peculiar since similar results have been reported for *Jatropha* and other non-edible seeds [1,6,8].

Table 2: Physical characteristics of seed oil

Property	D. regia oil	ASTM biodiesel values
Total Acid Number Mg of NaOH/g	0.96	0.128
Flash Point (^{o}C)	197	78.0
Density @25 ^{o}C	893	820-870
Kinematic viscosity @ 25^{o}C (mm^{2}/s)	38.45	1.6-5.5

3.3 Biodiesel characterization

The physical and chemical properties of the biodiesel produced from *D. regia* were determined and compared with ASTM specifications for petroleum diesel (table 3). The results obtained from this study with respect to density, kinematic viscosity, flash, cloud and pour points, total acid number, carbon residue, sulphur, ash and moisture contents as well as gross heat of combustion were found to be within ASTM ranges and comparable with those of biodiesel obtained from other non-edible plants such as *Jatropha* [12]; palm oil [13] and soyabean oil [14]. *D. regia* oil was found to contain low acid level which considerably enhanced their conversion efficiency into biodiesel. It is on this basis that *D. regia*, *Jatropha* , Rubber seed, Neem, Bitter almond seed oils are being preferred to edible oils as feedstock for biodiesel production [12, 14]. The zero sulphur content of *D regia* biodiesel (table 3) also makes it an environmentally friendly fuel. Similar results were reported for *Jatropha*, and soybean [12, 14].

Table 3: Biodiesel characteristics

Parameters	Values	
	Experimental	ASTM for diesel fuel
Colour	2.6	3.5
Density (kg/m^3)	859	820-870
Kinematic viscosity (mm^2/s)	4.0	1.6-5.5
Pour point (^{o}C)	-21	-27.5
Cloud Point (^{o}C)	4.4	2.6
Flash point (^{o}C)	110	78
Cross heat of Combustion (MJ/kg)	37.2	45.218
Total Acid Number (mg of NaOH/g)	0.30	0.128
Carbon residue	0.04	0.06
Biodiesel yield (%)	87	97.4
Sulphur content (ppm)	Nil	0.5
Moisture content (%)	0.044	0.5 max
Ash content (%)	Nil	0.5

Density is an important parameter in fuel performance since it affects heating values and octane number. Results obtained in this study indicate a density value for *D. regia* biodiesel that is within recommended limits for biodiesel fuels by ASTM [15]. Although, the calorific value of *D. regia* biodiesel is lower than that of petroleum diesel, this value is close to those of *Jatropha, and rubber* biodiesel but higher than those of palm oil and palm kernel oil. This may be due to higher oxygen content of palm oil and palm kernel oil which as reported by [16] improves combustion properties and emission but reduces calorific value. Low calorific values can also result in high carbon residue in engines. It therefore, follows that biodiesel from *D. regia*, *Jatropha* and rubber are preferred to that from palm oil and palm kernel.

Viscosity, being a measure of the internal flow of resistance of a liquid would obviously affect injection lubrication and fuel atomisation. High viscosity will increase engine deposits. Thus, the 4.0 mm^2/s viscosity recorded for *D. regia* oil compared to the 5.5 ASTM value makes it a better alternative to petroleum diesel (table 3). In addition, a highly viscous oil would also help in lubricating the engine. The pour, cloud and flash points are also important parameters in fuel performance. While, the pour point is the lowest temperature at which fuel can still be moved before it gels, the cloud point is the temperature at which small solid crystals are first visually observed as the fuel cools down. The flash point on the other hand, is the lowest temperature at which the vapour above the fuel becomes flammable. These three parameters therefore, describe the different temperatures at which fuel can be moved or safely stored. The pour, cloud and flash points reported for *D. regia* biodiesel (table 3) are generally higher than those of ASTM petroleum diesel but in agreement with earlier reports on biodiesel from non-edible seeds in Nigeria [16, 17]. It therefore, follows that biodiesel is safer to use than petroleum diesel.

3.4 Optimization conditions

Optimization results obtained in this study show that all of the reaction variables investigated, molar ratio, catalyst concentration, temperature, reaction time and rate of agitation, positively influenced biodiesel production from *D. regia* oil. The percentage biodiesel yield increased with increase in alcohol: oil molar ratio giving an optimal yield of 85.0% at 6:1 ratio (Fig.1). Similar results have been reported using other feedstock [11,15, 17]. It is also observed in this study that a molar ratio above 6:1, does not necessarily result in an increase in biodiesel yield but could rather increase the cost of production and hence the pump price of biodiesel. Catalyst concentration also affected biodiesel yield (Figure 2**).** Keeping other variables constant, a

0.7% (w/v) concentration was found to be optimal since an increase in concentration above this point produced a comparatively lower yield. This could be due to soap formation and gelatinous layer in the reaction mixture, factors that would obviously affect transesterification process. Increasing catalyst concentration above the optimal is therefore not profitable since this could result in increase residues on the biodiesel and thus, increase cost of washing.

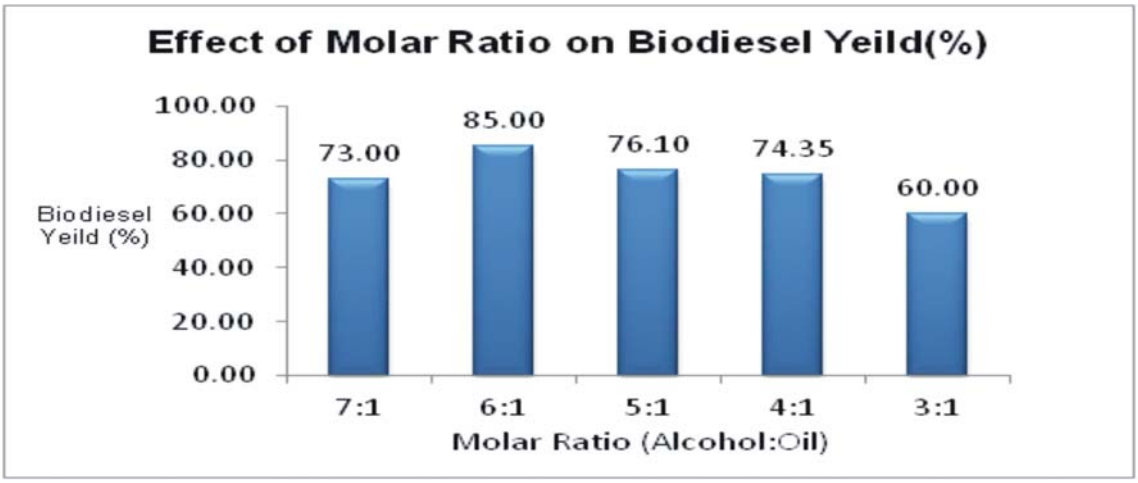

Figure 1: Effect of molar ratio (alcohol: oil) on biodiesel yield

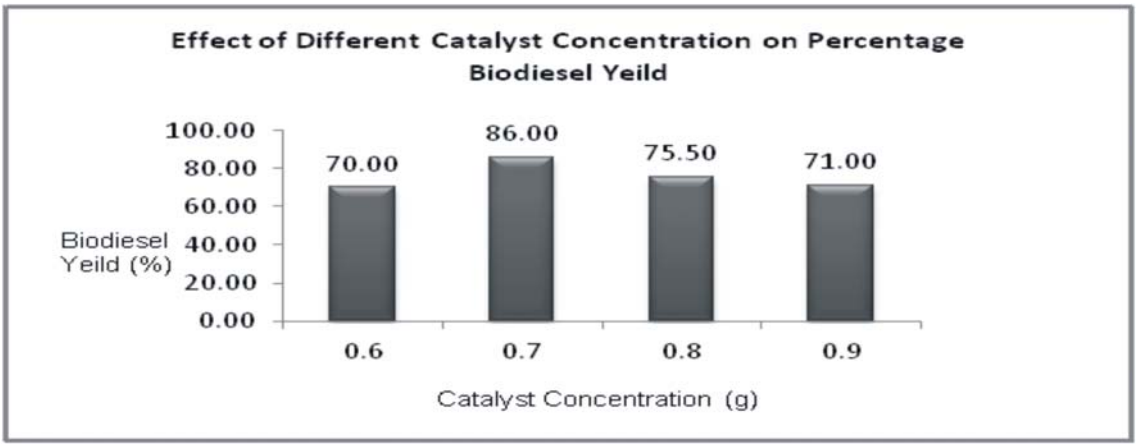

Figure 2: Effect of catalyst concentration on biodiesel yield (%).

Biodiesel yield was also affected by reaction temperature (table 4). Generally, an increase in temperature had a corresponding increase in yield up till 60^{o}C when it declined. Although, all the temperature levels tested gave good yield, an optimal of 86% was recorded at 60^{o}C. The increase in biodiesel yield with increase in temperature may be attributed to the reduction in viscosity which could increase the solubility of oil in methanol and thus, increase in biodiesel yield. While, biodiesel can be produced at room temperature, this reaction will take a longer time before completion [12] and therefore, increase in cost of production.

Table 4: Percentage yield of biodiesel with varying temperatures (^{o}C)

Temperature (^{o}C)	**Parameters**				
	Catalyst (%w/v)	**Methanol: Oil Ratio**	**Reaction Time (hr)**	**Rate of Agitation (Rpm)**	**Biodiesel yield (%)**
45	0.7	6:1	1	600	78.3

50	0.7	6:1	1	600	80.9
55	0.7	6:1	1	600	82.4
60	0.7	6:1	1	600	86.0
65	0.7	6.1	1	600	80.0

Reaction time also affected the percentage of biodiesel yield from *D. regia* seed oil (Figure 3). Increase in reaction time positively affected percentage yield up to 60 min before a decline set in. This implies that 60 min is the optimal time with a yield of 87% (Figure 3). However, 30 min recorded the lowest yield. It can be argued that since, yield decreased after 60 min, it would be unprofitable to increase the time of reaction above the optimal point.

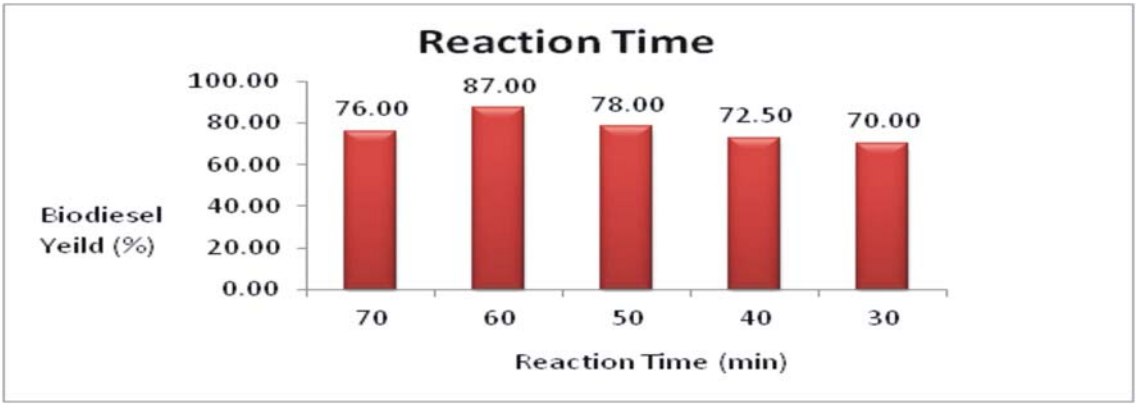

Figure 3: Effect of reaction time on biodiesel yield (%).

Biodiesel yield was found to increase with increase in rate of agitation up to a point and then decreased. 600rpm produced the highest percentage yield (86%) while 300rpm produced the lowest yield of 68% [Figure 4]. Mixing is an important factor in transesterification reactions, because oils are immiscible with alkaline-alcohol solutions. Agitation therefore, facilitates the mixing of the different reactants and thus increases the rate of the reaction. This explains why yield increased with increase in rate of agitation. However, once the single phase is established, mixing becomes inconsequential and increase in agitation no longer increase the rate of reaction.

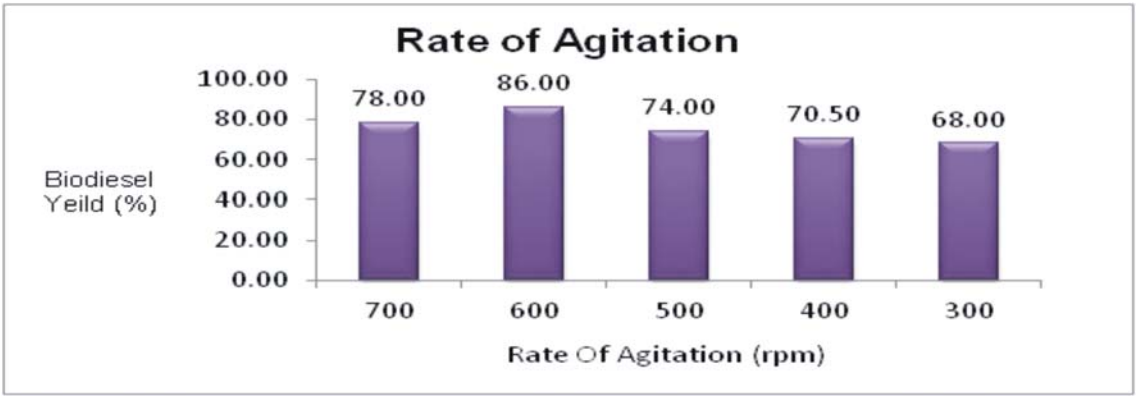

Figure 4: Effect of rate of agitation on percentage biodiesel yield.

4. Conclusion

It is established from this study that biodiesel can be successfully produced from crude *Delonix regia* oil through alkali-catalyzed transesterification. Results indicated that all the variables tested had positive effect on the reaction. The optimal conditions for biodiesel production were; 6:1 molar ratio, 60^{o}C temperature, 0.7%

catalyst concentration, 600rpm agitation and 60min reaction time. Under these conditions, biodiesel yield of 87% was achieved. Characterization of the biodiesel showed properties that conform with ASTM limits. Due to the relative lost cost of NaOH, methanol, and the high percentage yield, it is profitable to use *D. regia* seeds as a non-edible feedstock for biodiesel production. Since this plant is a prolific bearer and commonly grown as ornamental in most cities in Nigeria, its availability is guaranteed. However, commercial production can be undertaken in marginal lands in order not to affect agricultural production. On the other hand, the commercial production of biodiesel from palm oil and palm kernel oils may not be feasible since Nigeria has not been able to meet the food requirements of this food crops

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