



Science

THE EFFECTS OF VARIATION OF CATALYST CONCENTRATION ON BIODIESEL PRODUCTION

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Abstract

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, which conform to ASTM D6751 specifications for use in diesel engines. Fuel-grade biodiesel must be produced to strict industry specifications in order to ensure proper performance. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. From the production and characterization of biodiesel via the alkaline transesterification of coconut oil using different concentrations homogeneous catalyst (sodium hydroxide), oil to methanol molar ratio of 1:6, reaction temperature of 550C and reaction time of 60 min. Biodiesel can serve as a potential feedstock for the production of biodiesel owing to its high conversion rate and relatively low FFA content. At a catalyst concentration of 1% w/w oil NaOH catalyst, optimum yield of up to 96% was achieved. It is interesting to note that the viscosity of the biodiesel obtained falls within the limit as specified by ASTM D445 (2003). A flash point of 154.2 was obtained for the coconut biodiesel. This shows that the biodiesel is safe for handling as the flash point exceeds the minimum stipulated by the ASTM (93min). The transformation of the triglycerides present in most oils into methyl ester was confirmed by FT-IR studied. Further investigation regarding the profile of the acid methyl esters present in the oil was confirmed using GC-MS analysis.

Keywords: Coconut Oil; Sodium Hydroxide; Transesterification; Biodiesel; And Purification.

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1. Introduction

The increased use of fuel resulted in depletion of the fossil reserve. This triggers for many initiatives to search for alternative fuel, which can supplement or replace such fossil fuel. In recent years, research has been directed to explore plant based fuels and plants oils and fats as such have bright future (1). With the growth of modern civilization and industrialization in worldwide, the demand for energy is increasing day by day. Majority of the world’s energy needs are met through fossil fuels and natural gas. As a result, the amount of fossil fuels is on diminishing from year to

year. Since the fossil fuel is non-renewable, so fuel price is gouging as a consequence of spiraling demand and diminishing supply (2). At present the power generation of our country is mainly depends on imported fossil fuels. To reduce the dependency on imported fuel, the use of renewable sources has become more popular. In Bangladesh coconut is widely growing tree (3). Especially in the southern part of the country a large area will be found where coconut tree is considered as natural asset. The most common that is been developed and used is biodiesel, which is fatty acids methyl esters and of seed oil and fats have already been found to be environmentally safe, nontoxic and biodegradable (4). The raw materials being exploited commercially by the developed countries constitute the edible fatty oils derived from rape seed, soya bean, coconut, palm, sun flower, linseed etc (5).

Fuel and energy crisis and the concern of the society for the depleting world's non-renewable energy resources led to a renewed interest in the quest for alternative fuels. One of the most promising alternatives fuel is the vegetable oils and their derivatives. The first use of vegetable oil in a compression ignition engine was first demonstrated through Rudolph Diesel who used peanut oil in his diesel engine (3,6). The use of oils from coconut, soybean, sunflower, safflower, peanut, linseed, rapeseed and palm oil amongst others have been attempted. The long term use of vegetable oils led to injector coking and the thickening of crankcase oil which resulted in piston ring sticking. Therefore, vegetable oils are not used in SI engines because of endurance issues (7). Long list of trees, shrubs and herbs is available plenty in Nigeria, which can be exploited for fuel production (8). The production of biodiesel is usually achieved via transesterification reaction as shown in Figure 1.1.

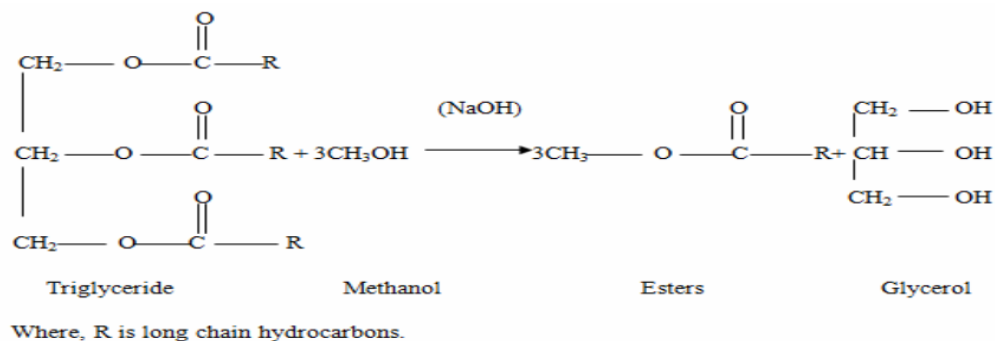


Figure 1.1: Transesterification reaction

It worthy to state that for many years researchers have been making a lot of effort in alternative for fossil fuels energy resources and replacing it with a non-fossil fuel. All of these were done as an effort to reduce the global warming which is largely caused by our dependence on fossil fuels. Petroleum diesel has gained a bad reputation for being a pollutant fuel. It is non-environmentally friendly biodiesel from coconut oil (8). In this study, coconut oil will be utilized for the biodiesel production process and fuel property will be characterized to access the suitability of the different methyl esters. The aim and objectives of this research include among others.

- 1) To determine the optimum conditions of biodiesel production by varying catalysts concentration.
- 2) To investigate the effects of catalysts concentration on the production of biodiesel from coconut oil.
- 3) To characterize the biodiesel to be produced.

2. Materials and Methods

2.1. Materials

The reagents and equipment used for the production and characterization of the biodiesel consist of coconut oil, methanol, sodium hydroxide, hydrogen tetraoxosulphate (VI) acid, distilled water, flash point tester, pour and cloud point tester, magnetic stirrer, reflux system, thermometer, separator funnel, round bottom flask, viscometer, bomb calorimeter, FT-IR spectrophotometer, gas-chromatography-mass spectrometer.

2.2. Method

2.2.1. *Extraction of Coconut Oil*

Coconut can be extracted from coconut oil through various means, but for the purpose of this research, mechanical method of extraction was used, through wet milking. The coconut flesh was first sliced into small pieces, washed, and crushed mechanically. The juice obtained was subjected to heating for a number of hours, where the oil formed at the top was collected and allowed to cool and stored for biodiesel production.

2.2.2. *Alkali-catalysed Transesterification Process*

Alkali-catalyzed transesterification process was carried out using a reactor which consists of a stirrer, and a thermometer. The magnetic stirrer was used to stir the mixture inside the screw-capped vessel. The vessel was kept in a water bath to maintain the temperature. The mixture was stirred at a speed of 300 rpm for all test runs. After the transesterification reaction, the product mixture was poured into a separating funnel and then allowed to settle into two phases. Since methanol has boiling point of 65⁰C, higher reaction temperature of 60⁰C was used, in most cases the temperature was kept below the normal boiling point of the methanol (65⁰C), so that the reactor does not need to be pressurized. As per stoichiometry reaction carried out at 3:1 methanol to oil molar ratio, the reaction is a reversible one, hence, an excess of methanol is necessary to drive the equilibrium towards methyl ester formation. Therefore actual experimental tests were carried out at higher molar ratio. Further by keeping required temperature constant, the mixture of methanol, sodium hydroxide solution will be added into the batch reactor where stirrer having speed 350 rpm was used to stir the mixture. The concentration of the catalyst used was varied seven (7) times during subsequent productions.

The catalyst used was sodium hydroxide; it was dissolved completely in the alcohol, and since the ratio of methanol to oil is 6:1, was also used during the production processes. The catalyst concentrations used were varied as (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4%w/w of oil) and quantity of catalyst used was calculated by percentage weight. After dissolution of catalyst in methanol, it was then added to the oil and placed in the reactor, for 60 minutes, with the stirrer at 350 rpm, and the temperature at 55⁰C. After the reaction, the sample was placed in a separating funnel and allowed to stay for 24 hrs where two distinct layers were formed, the biodiesel or methyl ester formed at the top and the glycerol at the bottom, which was latter separated and the biodiesel collected.

2.2.3. Washing and Purification of Biodiesel

The biodiesel produced contains some amount of soap and methanol so washing of the biodiesel thoroughly carried out. The biodiesel was washed with warm water to remove residual methanol, free glycerin, soap, and catalyst (9). Moreover, purification of biodiesel via water washing affords reduction of free glycerol contents that is ranked among the key important factors to determine if the biodiesel produced meets the biodiesel standard specifications for use in diesel engines. Biodiesel was mixed with warm water (around 10% volume of ester) to remove the catalyst and then allowed to settle under gravity for another 24h. The washing process was done multiple times until clean biodiesel was obtained (10, 11). The purified biodiesel was then dried and analysed.

2.3. Characterization of Biodiesel Base for their Physical Properties

The biodiesel produced was characterized for its physical properties such as density, viscosity, cloud point pour point, flash point and octane number. The properties of the biodiesel were measured using mainly the American Society for Testing and Materials (ASTM), 1980. The physical properties of biodiesel were determined according to the standard test methods are shown in Table 2.1.

Table 2.1: Determination of Physical and Chemical Properties using Standard Methods

Property	Unit	Biodiesel standard	Test method
Flash point	K	130(min)	ASTMD-93
Moisture content		0.050(max)	ASTMD-2709
Kinetic viscosity	g/ml	1.9-6.0	ASTMD-445
Cloud point	K	-	ASTMD-2500
Specific gravity	-	0.860-900	-
Pour point	K	-	ASTMD-97

3. Results and Discussions

Biodiesel was produced via acid esterification and alkaline catalysed transesterification of coconut oil with methanol. During the production [rprocess, the following variables were employed: sodium hydroxide, oil to alcohol ratio of 1:6, reaction temperature of 55⁰C and a uniform stirring intensity of 350rpm. Further, the effect of catalyst concentrations (0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4% w/w) on the properties and yield of biodiesel was investigated. The results obtained were discussed as follows:

3.1. FT-IR Spectra of Coconut Oil

The FT-IR spectra in the mid-infrared region have been used to identify functional groups and the bands corresponding to various stretching and bending vibrations in the samples of oil and biodiesel. The position of carbonyl group in FT-IR is sensitive to substituent effects and to the structure of the molecule (12). From the FT-IR spectra above ester functional group is present which was represented by the strong semi sharp peak at 2924.79cm⁻¹ (Figure 3.1). Such peak disintegrates into two sharp peaks upon transesterification accompanied with the formation of a methyl ester functional group.

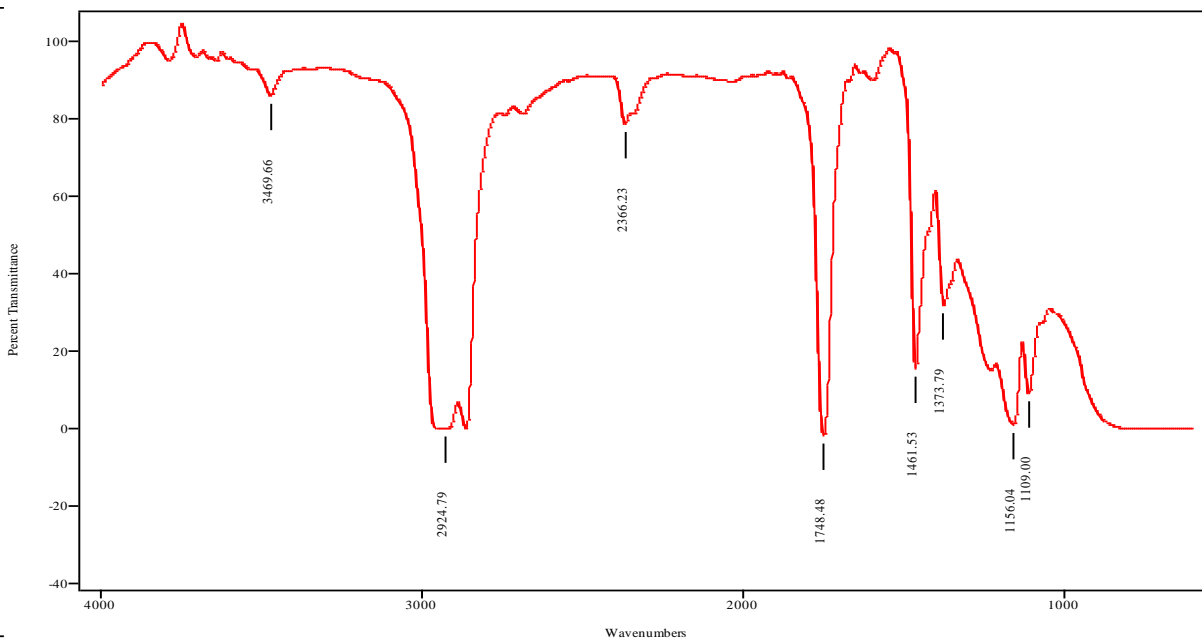


Figure 3.1: Showing IR spectra of crude coconut oil

3.2 FT-IR Spectra of Biodiesel Produced from Coconut Oil

The peak analysis of both spectra (crude coconut oil and coconut biodiesel) showed significant differences. This was marked by a change from ester functional groups to methyl esters, which is the most significant transformation in the infrared studies of oils and its methyl esters. All the aspects regarding the carbonyl groups are intact and visible. The ester functional group is the $R_1-C(OR)=O$ in oils and $R_1-C(OCH_3)$ in the biodiesel. Where R_1 represents long chains of hydrocarbons. All groups regards the CH_2-O are reduced and new signals are visible belonging to CH_3-O - vibrations in biodiesel. The most influence of the transesterification is observed in the new signal at 1435cm^{-1} which is definitely the methyl ester group with its deformation vibration. The next visible transformation is in the ester signal at approximately 1200cm^{-1} . The strong broad signal at 2924cm in the oil will separate into two concrete signals at 2929.54cm and 2861.45cm (Figure 3.2). The averaging of the energy over the triple ester group of the triglycerides is gone. Same happens to signal at 961cm which is the CH_2 wagging frequency (a deformation vibration of the $RO-CO$ group).

3.2. The Effects of Catalyst on the Yield of Biodiesel Produced

The effect of catalyst concentrations (0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4% w/w oi) on the yeild of biodiesel was investigtedl. The results obtained were summerized in Table 3.1. From the data above, it was observed that biodiesel yield of 52%w was lowest at a catalyst concentration of 0.2% w/w of oil. The effect of catalyst variation on conversion efficiency is shown in figure 3.3. Maximum biodiesel yield of 96%w was observed at a catalyst concentration of 1% w/w, and after that the yield was decreased due to (emulsion formation. The initial low conversion was due to insufficient catalyst, however, at higher catalyst amounts, saponification was favoured (13), and this led to low biodiesel yields.

Table 3.1: Effect of variation of catalyst concentration on biodiesel yield (oil to alcohol ratio 1:6, tempt. 60⁰C and stirring intensity of 350rpm.)

Catalyst conc. %w/w	biodiesel mass(g)	Yield (w%)
0.2	104.6	52.3
0.4	134	67
0.6	162	81
0.8	167.4	83.7
1.0	192	96
1.2	184	92
1.4	174	87

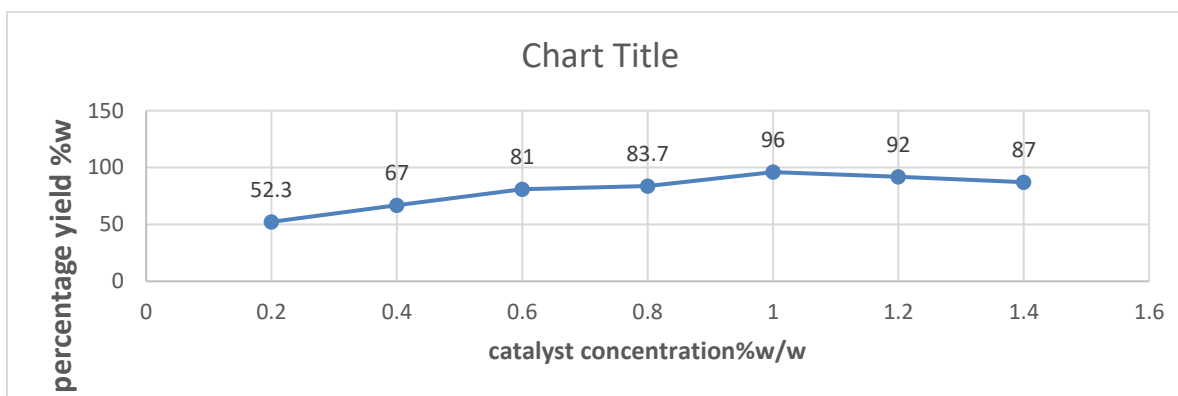
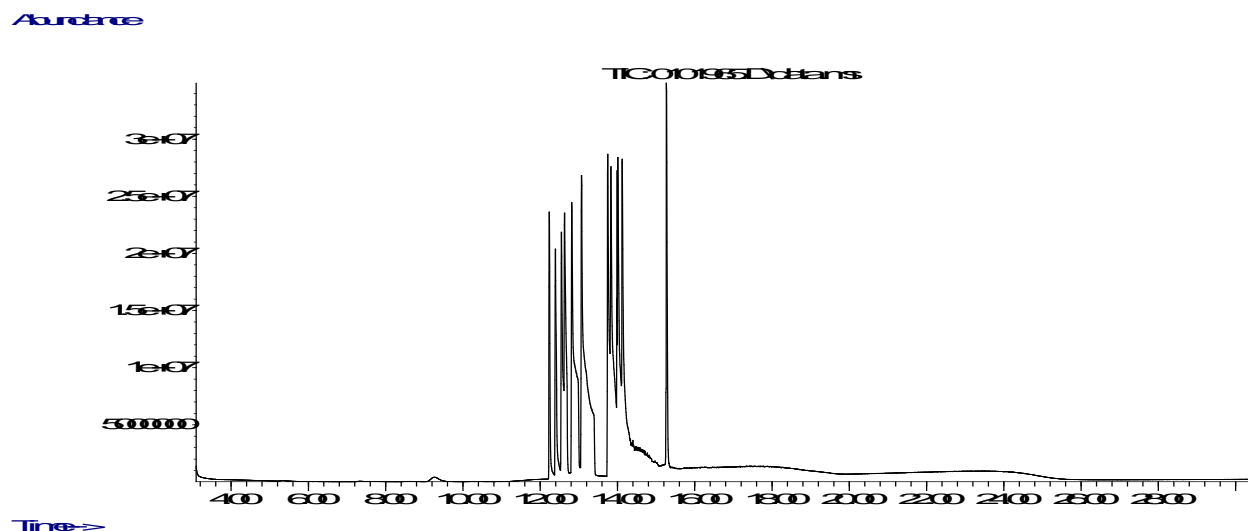


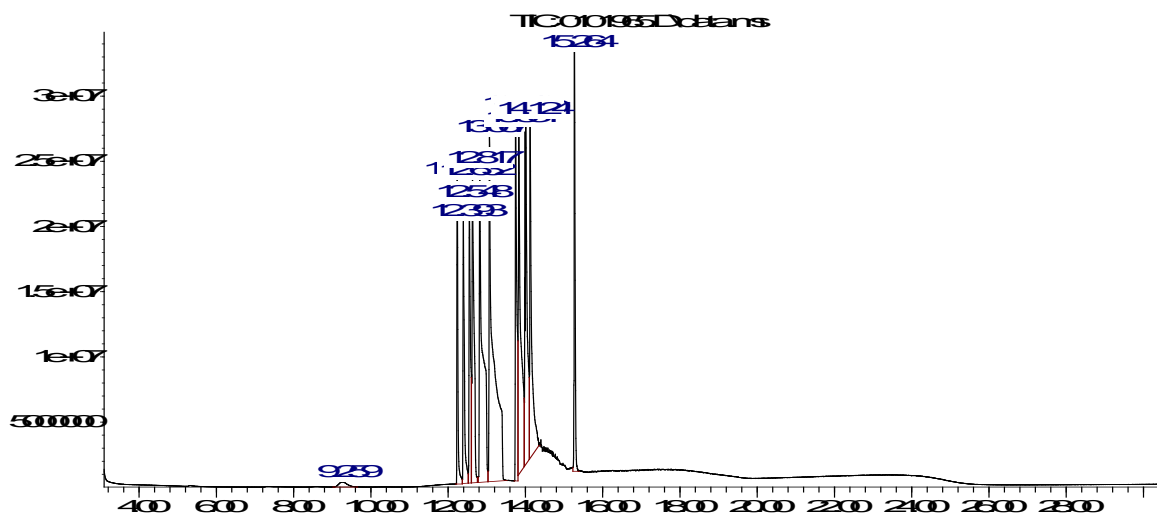
Figure 3.3: Graph showing the effect of catalyst concentration on biodiesel yield from coconut oil. Reaction time=60⁰C, 350rpm, 60min reaction time and NaOH catalyst in methanol.

3.3. Gas-Chromatography Mass Spectrometry Analysis. (GC-MS)

GC-MS analysis was used to explore the methyl ester profile of the biodiesel produced. To verify the formation of the fatty acid methyl ester, GC-mas analysis was conducted. The specific acid methyl ester present in the oil was also ascertained. The mass spectra of biodiesel from coconut seed oil biodiesel are given Figure 3.4.



Abundance



Time->

Figure 3.4: Mass spectra of biodiesel produced from the methanolysis of coconut oil at 60°C, 1:3 oil to alcohol molar ratio, 1%w NaOH catalyst with mixing speed of 350rpm.

3.4. Fuel Properties of Coconut Oil Biodiesel

The fuel properties of the biodiesel produced was analysed. The data presented in Table 3.2 was based on the optimum operating conditions.

Table 3.2: Properties of Biodiesel produced from Coconut Oil

Properties	ASTM D6771- 02	CBD
Specific gravity at 15°C	0.95max	0.84
Viscosity at 40°C (mm ² /s)	1.9-6	2.583
pH	-	-
Pour point(°C)	-35 to -16	-5
Cloud point		-2
Flash point (°C)	130min	154.2
Ash content (%)	0.1max	0.06
Density (g/cm ³)	-	0.73
Heat of combustion(mj/kg)		37.52

3.4.1. Kinematic Viscosity

The potential of vegetable oils to be used as fuel substitute in diesel engines have been envisaged right from the advent of diesel engines, however, due to its high viscosity such oils are transesterified in order to reduce the viscosity (14). From the results (Table 3.2) obtained, the viscosity of both the crude oil and the biodiesel showed a uniform decrease with increase in temperature. The result agrees with grounded theories which postulated a decrease in viscosity with increase in temperature. For the no-esterified coconut oil, the kinematic viscosity drops down from 3.945mm²/s² to 2.009mm²/s² within the temperature range of 30 and 50C. However, lower viscosity values were recorded for coconut oil methyl esters. It was observed that the viscosity

($3.101\text{mm}^2/\text{s}$ at 40°C) of coconut oil methylester generated was within the limit ($1.9\text{-}6\text{mm}^2/\text{s}$) specified by the American Society for Testing Materials Standards (2003). The biodiesel produced has a viscosity were within the values stipulated by ASTM D445 and D874, 2007. This goes to show that the biodiesel produced from coconut oil under the above conditions had enhanced fluidity as fuel for diesel engines.

3.4.2. Density

The importance of the density of a diesel fuel can never be overemphasized as it gives an indication of the delay between the injection and combustion of the fuel in a diesel engine (ignition quality) and the energy per unit mass (15). The density of coconut oil biodiesel using hygrometer, for testing specific gravity at 15°C , and was found to be $0.73\text{g}/\text{cm}^3$ (Table 4.2), which is less than density of diesel ($0.83\text{g}/\text{cm}^3$). This shows the potential use of coconut oil biodiesel as an alternative to fossil diesel fuel.

3.4.3. Flash Point

One of the most important characteristics of any fuel is its flash point. Flash point is the lowest temperature at which the diesel fuel ignites. It indicates the overall flammability hazards in the presence of air; higher flash points make for safe handling and storage of biodiesel (3). The Flash Point of the coconut oil biodiesel produced was determined via flash point tester and it was to be 154.2°C which is above the ASTM D6751-07b, D93 minimum standards for biodiesel fuel of about 93°C (Table 4.2). This makes the biodiesel sample safe for use and storage (16). Fuels with lower flash point which tend to ignite at lower temperatures are highly dangerous if not stored and used properly. Most non-edible based seeds oils flash point are higher than fossil diesel (17).

3.4.4. Pour and Cloud Point

The pour point is the lowest temperature at which the oil/fuel sample can flow. This property is related to the use of biodiesel in colder region (18). Coconut oil biodiesel has a pour point of -5°C and a cloud point of -2°C (Table 3.2). These values clearly indicate that the use of coconut oil methyl esters in colder regions where temperature reaches as low as below -5°C is limited. However, this value is also indicative of the high potential of this fuel as biodiesel particularly in Northern Nigeria where temperature is always above 20°C , a temperature at which the oil is fluid.

3.4.5. Ash Content

The ash content describes the amount of inorganic contaminants such as abrasive solids and catalyst residues, and the concentration of soluble metal soaps contained in a fuel sample (1,20). The biodiesel samples produced from coconut oil had ash content ranging from 0.06% and were lower compared to that of the crude oil which was obtained as 0.079% (Table 3.2). The measure of the amount of metal contained in the fuel is the ash content. Therefore, this result showed that the use of coconut biodiesel as a fuel would reduce injector nozzle clogging, combustion deposits and injector system wear compared to the crude coconut oil and Automated Gas Oil (AGO) which had higher ash content of 0.12%.

3.4.6. Heat of Combustion

Heat of combustion is the energy released as heat when biodiesel undergoes complete combustion with oxygen under standard conditions. It is the measure of the amount of energy released in the form of heat when one mole of a substance is burnt. The heat of combustion coconut oil biodiesel (37.52mj/KJ) was measured using a bomb calorimeter.

4. Conclusions and Recommendations

4.1. Conclusions

From the production and characterization of biodiesel via the alkaline transesterification of coconut oil using different concentrations homogeneous catalyst (sodium hydroxide), oil to methanol molar ratio of 1:6, reaction temperature of 55⁰C and reaction time of 60 min, the following conclusions were drawn:

Biodiesel can serve as a potential feedstock for the production of biodiesel owing to its high conversion rate and relatively low FFA content. At a catalyst concentration of 1%w/w oil NaOH catalyst, optimum yield of up to 96% was achieved. It is interesting to note that the viscosity of the biodiesel obtained falls within the limit as specified by ASTM D445 (2003). A flash point of 154.2 was obtained for the coconut biodiesel. This shows that the biodiesel is safe for handling as the flash point exceeds the minimum stipulated by the ASTM (93min). The transformation of the triglycerides present in most oils into methyl ester was confirmed by FT-IR studied. Further investigation regarding the profile of the acid methyl esters present in the oil was confirmed using GC-MS analysis. These results are consistent with those of other researchers and agree with international standards.

4.2. Recommendations

Coconut oil has been used mostly for cooking purposes over the years. However, with its discovered potential as biodiesel feedstock, more attention should be given to its cultivation. The Government of Nigeria should enact policies that would favor the farming or production of coconut on a large scale.

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