Effects of Process Variables and Petro-Diesel Blend on the Yield and Fuel Properties of Tiger Nut Oil Biodiesel

Umeuzuegbu J.C.

Abstract - Though, biodiesel is now gaining more grounds as the best alternative replacement for fossil fuel,this conception could only come true if the cost of biodiesel is competitive with that of fossil fuel. This research work focused on effects of process variables and petro-diesel blend on the yield and fuel properties of tiger nut oil fatty acid methyl ester (TNOFAME) or biodiesel. Tiger nut oil (TNO) was solvent extracted using n-hexane, and then characterized based on American Society for Testing and Materials (ASTM) method. The fatty acid profile was determined using gas chromatography mass spectrometry while the functional group of the oil was analyzed using Fourier transform infrared spectroscopy. The effect of process parameter on the yield of TNOFAME was investigated using one factor at a time method. The TNO was pretreated to reduce the free fatty acid below 1% and then transesterified using methanol in the presence of sodium hydroxide (NaOH) catalyst. The fuel properties of the TNOFAME produced were determined based on ASTM standards. The tiger nut oil biodiesel was blended with #2 diesel oil on a percentage volume ratio of biodiesel to diesel 0, 20, 40, 60, 80 and 100% designated as B0, B20, B40, B60, B80 and B100 respectively. The effect of petro-diesel blend on the fuel properties of TNOFAME was carried out by testing the fuel properties of different blends, B0, B20, B40, B60, B80 and B100 and comparing the properties with those of B100 and B0. The process parameters, methanol to oil molar ratio, catalyst concentration, reaction temperature, reaction time and agitation speed greatly affected the biodiesel yield as their increase resulted in the increase of biodiesel yield until the optimum parameter was attained when the yield started decreasing. The experimentally determined properties of the TNOFAME; density, kinematic viscosity, cetane number, flash point, cloud point, water and sediment, calorific value, iodine value, pour point, refractive index gave the values, 870Kg/m^3, 4.60mm^{2}s^{-1}, 61, 160^{0}C, 7^{0}C, 0.03%, 0.45, 36.2MJ/Kg, 65.2, gI$_2$/100g, 4^{0}C, 1.446 respectively. By blending of biodiesel, B100 with petro-diesel B0, both fuels impart their respective good fuel properties, low viscosity, low density, low cloud and pour point and high calorific value of petro-diesel, high cetane number, high flash point, high lubricity and biodegradable nature of biodiesel on the blends, B20 B40, B60, and B80. However at present only blends of low biodiesel content (≤ 20%) possess equivalent fuel properties of diesel and as such suitable for use in compression ignition engine without engine modification.

Key words: Tiger nut oil biodiesel, transesterification, characterization, ASTM method, process parameter, biodiesel yield.

I INTRODUCTION

The astronomical increase in world population coupled with high spate of industrialization has resulted to enormous increase in energy demand. The world has hitherto depend on fossil fuel , petroleum, coal and natural gas for its energy resources. The very rapid depletion of fossil fuel in addition to its environmental impact has led to the search for alternative, renewable and environmentally friendly fuel. Among the various alternatives investigated, biodiesel has proved to be the foremost for reduction of gas emission [1]. Biodiesel is a mono-alkyl ester of long chain fatty acid that has properties that approximate that of diesel with added advantages of high lubricity, high cetane number high calorific value and being highly biodegradable. It is a promising nontoxic alternative fuel used in the transport sector. Biodiesel is produced by the reaction of oil or fat with monohydric alcohol. Various processes have been adopted for biodiesel production from vegetable oil and animal fat, namely; micro-emulsion with alcohol, catalytic cracking, pyrolysis and transesterification [2, 3, 4, 5]. Among these methods, transesterification is the key and the most important process for production of a cleaner and environmentally safe biodiesel [6, 7].Transesterification means conversion of one type of ester to another. During transesterification a basic catalyst breaks the fatty acid from the glycerine one by one. If an alcohol typically methanol contacts a fatty acid, it will bond and form biodiesel [8].

A proper selection of feedstock for production of biodiesel is critical for viable alternative fuel to petro-diesel. Although, biodiesel is gaining popularity, more than 95% of the renewable resources used for its production are edible oils [9]. which will in a long term have serious implications on food availability and the cost of biodiesel as it may be more expensive than petro-diesel. Worldwide, biodiesel production is mainly from edible oils such as soya bean, sunflower, canola, palm oils etc as these oils contain less free fatty acid than non-edible oils and most times do not require esterification or pretreatment before transesterification. Much research efforts are now geared towards identifying and evaluating non-edible seed oils as suitable feed stock. However, the cost of non-edible oil biodiesel purification because of their high free fatty acid must be considered before making a good choice of the feedstock. The non-edible oils that are being studied and are

promising as suitable feedstock for biodiesel production are: neem (*A. indica*), jatropha tree (*J. curcas*), karanja (*P.pinnata*), tobacco seed (*N. tabacum L.*), rice bran, mahua (*M. indica*), rubber plant (*H. brasiliensis*), castor, linseed, and microalgae. Jatropha curcas oil plants have been widely studied with respect to biodiesel production from non-edible oils [10, 11] but the use of most of other non-edible oil plants such as rubber, neem, castor etc have not been intensely studied as Jatropha curcas.

This research work aims at investigating the effects of process parameters and petro-diesel blend on the yield and fuel properties of tiger nut oil biodiesel. The process parameters investigated are methanol to oil molar ratio, catalyst concentration, reaction temperature, reaction time, and agitation speed. Biodiesel blends, B0, B20, B40, B60 , B80 and B100 were investigated. The effect of process parameters on the yield of biodiesel from tiger nut oil biodiesel was investigated by using one factor at a time method where a factor is kept constant and others varied in turn. The effect of petro-diesel blend on the fuel properties of tiger nut oil biodiesel were investigated by characterizing and comparing the properties of the B0, B20, B40, B60 and B80 with B100 and B0.Tigernut variously known as ground almond, yellow nut-grass, Zulu nut, chufa, rush nut is a perennial herbaceous plant that probably originate from Egypt. Today they are cultivated in Spain, Africa , Australia, North and South America etc. In Nigeria it is called “aya”, “ofio” and “akihausa” by the Hausas, Igbos and the Yorubas respectively [12]. It grows well in well-drained sandy or loamy soil and its yield is specifically favored by the increase in surrounding temperature [13]. It is an easily grown plant that could thrive without application of fertilizer, maturing in 90 to 110 days

II Materials and Methods

2.1 Materials

Tiger nuts (plate 1), reagents, glass wares, equipments including gas chromatography mass spectrometer (GC-MS), Fourier transform infrared spectroscopy (FTIR), viscometer, magnetic hot plate, soxhlet extractor, , specific gravity bottle; electrostatic oven etc.

2.2 Experimental Methods

the moisture content. The dried nut was then grind with mechanical grinder and the sample kept for further analysis.

2.2.1 Sample preparation

The tiger nut used in this research work was purchased from Ogboete market Enugu, in Enugu State , Nigeria. 10kg of the tiger nut was sorted and washed with water to remove sand, dirt and other impurities. The nut was sundried for three days and further oven-dried at temperature of 50^0C for 5 days in other to eliminate

Plate1: Tiger nuts

2.2.2 Extraction of oil from the dry, grind tiger nut

Solvent extraction using n-hexane was employed for extraction of oil from the dried, grind tiger nut. The use of the solvent is in agreement with the findings of [14, 15, 16] who reported that tiger nut oil is extracted using n-hexane or super-critical carbon dioxide for enhanced yield of oil.

The oil content of the nut was evaluated using soxhlet extractor. For the oil used in the work, 3kg of the dried, ground tiger nut was measured into a plastic container containing 3 liters of n-hexane. The mixed content of the container were vigorously shaken after covering the container. The container was made air tight to prevent evaporation of the solvent and then kept to macerate for a day. Then the dissolved oil in n-hexane was decanted and the slurry filtered. The filtrate was then distilled to recover the solvent at 65^0C (AOAC 1990). The percentage oil yield was calculated as:

$$\%\ oil\ yield\ = weight\ of\ oil\ obtaind\ \div\ weight\ of\ seed\ sample\ x\ 100 \quad (2.1)$$

2.2.3 Characterization of tiger nut oil

The physiochemical properties of the oil extracted from tiger nut was characterized based on American Society for Testing Materials, ASTM 6751 (1973) method. Analytical equipments, GC MS (QP2010 plus Shimadzu, Japan) and FTIR (M530 Bulk scientific FTIR) were used to determine the fatty acid profile and the functional groups of the oil respectively.

2.2.4 Effect of process parameters on biodiesel yield

The effects of process parameter on biodiesel yield were investigated using one factor at a time method involving keeping a factor constant at a time and varying the others in turn. The five factors investigate are, molar ratio of methanol to oil, catalyst concentration, reaction time, reaction temperature and agitation speed.

2.2.5 Biodiesel Synthesis from tiger nut oil

The free fatty acid in tiger nut oil 2.52% is in excess of 1.0wt%, therefore the oil must first be esterified or pretreated with concentrated sulphuric acid and methanol to reduce the free fatty acid below 1.0wt % in other to avoid the formation of soap with direct transesterification with alkali. Then the oil is transesterified using sodium hydroxide and methanol

2.2.5.1 Pretreatment or esterification of tiger nut oil

Esterification involves heating the oil to a temperature of 110^0C for 10 minutes to remove most of the water present in the oil. The oil was cooled and then introduced into a 500ml three-necked round bottomed flask fitted with a condenser and a thermometer at the middle and side arms respectively. Then methanol of 60%w/w of oil mixed with concentrated sulphuric acid of 7% w/w of oil was added. The set up was heated to 60^0C for 60 minutes with a magnetic heating mantle and the agitation speed set at 400rpm. The reaction mixture after cooling was transferred into 250ml separating funnels where it settles and separate into water, pre-treated oil and methanol layers. The pre-treated oil after being tapped off was wet-washed and oven dried at 105^0C for complete evaporation of water.

2.2.5.2 Transesterification of tiger nut oil

The pre-treated oil was then transesterified using methanol and sodium hydroxide catalyst. The experimental transesterification set up is as shown in plate 2. A specified quantity of the pre-treated oil was run into a 500ml three-necked round bottomed flask fitted with a condenser, a thermometer and a receiver on the middle and the side arms respectively. Then a known amount of mixture of sodium hydroxide catalyst in methanol was added into the flask. The stirrer was switched on to a specified speed and the reaction mixture was heated and refluxed for the required reaction time. The reaction mixture was made to stand for a day in separating funnels where it separated into the upper biodiesel layer and the lower glycerol layer.

2.2.5.3 Purification of TNOFAME produced

After transesterification, the upper ester layer may contain traces of methanol and glycerol. The remaining un-reacted methanol has safety risk and might corrode engine components and glycerin within the biodiesel will lessen the fuel lubricity and cause injector coking and other deposits [17]. Such traces of methanol is soluble in water and therefore is removed by wet washing. A drop of 1M sulphuric acid was added to the biodiesel in a separating funnel. Hot distilled water was as well added and the mixture vigorously shaken. The mixture was allowed to settle when it separates into two, the upper layer consisting of the biodiesel and the lower layer consisting of water and water soluble impurities. The water was discarded after testing with three drops of phenolphthalein indicator. Washing was continued until the waste water was bright and does not turn pink when tested with phenolphthalein. The washed sample was dried by heating at 105^0C on a laboratory hot plate until all residual water molecules is evaporated. The percentage biodiesel yield is given by the expression

$$\%\ biodiesel\ yield\ = volume\ of\ biodiesel\ produced\ \div\ volume\ of\ oil\ used\ x\ 100 \quad (2)$$

2.2.6 Determination of the fuel properties of the TNOFAME produced

The fuel properties of the tiger nut oil biodiesel produced were characterized based on ASTM method. The properties characterized for include density, viscosity, iodine value, saponification value, cetane number acid value , free fatty acid , calorific value, flash point, cloud point, pour point etc.

2.2.7 Blending of TNOFAME with petro-diesel

The tiger nut oil biodiesel was blended with #2 diesel oil on a percentage volume ratio of biodiesel to diesel of 0, 20, 40, 60, 80 and 100% designated as B0, B20, B40, B60, B80 and B100 respectively. Direct blending of the required volumes of the biodiesel and diesel was carried out in conical flasks with continuous stirring to achieve uniformity of mixing.

2.2.8 Determination of the fuel properties TNOFAME blends

The fuel properties of the diesel and biodiesel blends B0, B20, B40, B60, B80 were similarly determined as that of the B100 based on ASTM method.

Plate 2: Biodiesel production by transesterification

III RESULTS AND DISCUSSION

3.1 Oil yield from tiger nut

Solvent extraction using soxhlet extractor gave the oil yield of tiger nut as 20.1%. This is in agreement with the findings of [15, 16], who reported the oil yield range of 15.1 to 41.2% for tiger nut. Tiger nut could therefore be graded as oil bearing, and in addition to its moderate saponification number is a suitable substitute for commercial biodiesel feedstock. The determined saponification value of the oil is moderate which makes it suitable for biodiesel production as it will not be prone to formation of soap compared with oils of high acid value. However, the oil content of tiger nut is quite less than that of some edible seed oils, 52.2% for melon seed [18], 41% for sunflower seed [19], but is equivalent to 18.5% for soya bean [20].

content of 3.86% for the oil is higher than the maximum 1% that is required for high yield of biodiesel. High free fatty acid and moisture content require the oil to be pretreated or esterified before transesterification. The relatively low saponification value of 190.2mgKOH/g for TNO is moderate , indicative of its suitability for biodiesel production as it will not be prone to formation of soap.

The kinematic viscosity measures the flow resistance of the fuel, while the density determines the quantity of the fuel metered as this is measured volumetrically. High density

3.2 Characteristics of TNO

3.2,1 Physiochemical properties of TNO

The summary of characteristics of tiger nut is as presented in table 1. From the table, it could be seen that the free fatty acid values of the oil is greater than 1%. The determined acid value of 5.04mgKOH/g and the free fatty acid value of 2.52% respectively for tiger nut oil are high and unacceptable for alkali transesterification reaction as the excess alkali give rise to soap formation and inhibition of ester separation from biodiesel [10]. Again the moisture and viscosity of TNO, 891kgm^{-3} and 32.50mm^{2}s^{-1} at 40^{0}C respectively will make its atomization in internal combustion engine difficult and has been associated with increased engine deposits hence it cannot be used directly as bio-fuel [21]. The determined iodine value of the oil, 86.50gI_2/100g oil does not strictly place TNO as a semi drying oil. Iodine value, a measure of degree of un-saturation of the oil obtained is below 100gI_2/100g oil, indicative of the oil being nondrying and therefore suitable for biodiesel production. High iodine value of oil corresponds to high degree of un-saturation of the fatty acid

in the triglyceride, and if heated, such an oil is prone to thermal oxidation and polymerization of the triglyceride causing formation of deposits. The peroxide value, an index of rancidity obtained as 1.50mEq/Kg was relatively low, ostensibly because of high antioxidant content of the nut, and indicative of high resistance of the oil to peroxidation during storage and handling [22]. The determined fire point and flash point of TNO are 201^0C and 183^0C respectively. The flash point in excess of 130^0C indicates that the oil is non-flammable for handling and storage.

The key flow properties for winter fuel specification are the cloud and pour point. The cloud point of 7^0C and pour point of 3^0C for TNO are moderately low and suitable for use in warm and temperate climates but not suitable for cold climatic condition. Oils of high cloud and pour points can readily congeal and faces difficulty of handling during cold weather.

3.2.2 Fatty Acid Profile of tiger nut oil (GC –MS)

The fatty acid profile of tiger nut oil was obtained with the aid of gas chromatography mass spectrometry (GC-MS). Figure1 shows the GC-MS spectra of tiger nut oil. The fatty acid composition of tiger nut oil is as shown in table 2 below. Tiger nut oil consist of 90.2% unsaturated fatty acid (myristic, oleic, linoleic and linolenic acids, and about 10% of saturated fatty acid (stearic and arachidic acids) The oil predominantly consist of about 76.1% oleic acid which agrees with the findings of [16] and [23]. Tiger nut oil is categorized as oleic oil akin to olive oil that consist of 56-85% oleic acid [24, 25].

Table 1 Physiochemical properties of TNO

Properties	**Unit**	**NSO**
Oil yield	%	20.1
Density	Kg/m3	891
Saponification value	mgKOH/g	190.2
Iodine value	(gI_2/100g oil)	86.5
Peroxide value	mEq/Kg	1.50
Kinematic viscosity	mm^2/s	32.5
Fire point	^{0}C	201
Flash point	^{0}C	183
Cloud point	^{0}C	7
Pour point	^{0}C	3
Refractive index		1.464
Specific gravity		0.891
Moisture content	%	2.86
Acid value	mgKOH/g	5.04
Free fatty acid	%	2.52
Calorific value	MJ/Kg	28.5

Table 2: Fatty acid profile of TNO

Common name	Systemic name	Lipid number	Concentration (%)
Myristic	Cis-9 tetradecanoic acid	C14:1	1.7
Palmitic	Hexadecanoic acid	C16:1	10.4
Stearic	Octadecanoic acid	C18:0	0.3
Oleic	Cis-9-octadecanoic acid	C18:1	76.1
Linoleic	Octadeca-9-12dienoic acid	C18:2	11.8
αlinoleic	Octadeca trienoic acid	C18:3	0.6
Arachidic	Eicosanoic acid	C20:0	0.1

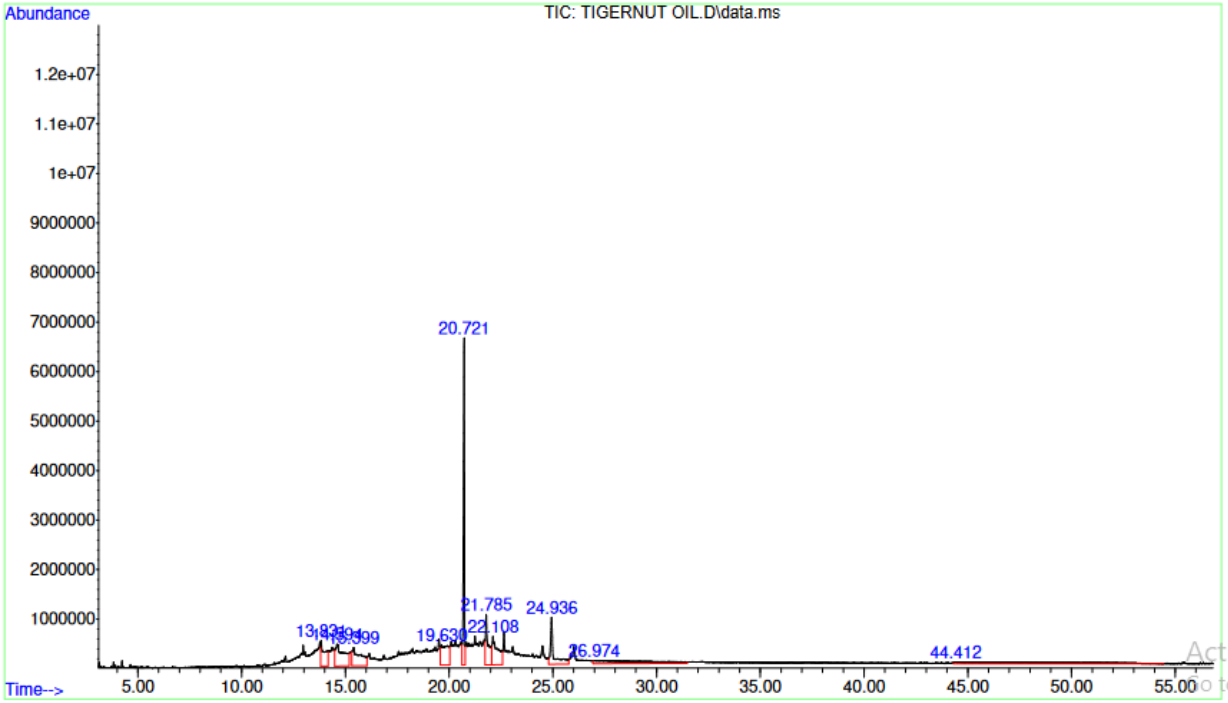

Figure 1: GC-MS plot of TNO

3.2.3 Fourier transform infrared spectra analysis (FTIR) of tiger nut oil

The Fourier transform infrared spectra of TNO was analyzed using Fourier transform infrared spectroscopy (M530 Buck scientific FTIR). This analysis was carried out in order to detect the various functional groups contained by the oil. The FTIR spectrum of TNO is as shown in figure2. The various functional groups detected at different wave numbers is as shown in table 3.

Table 3: FTIR functional group frequencies of APO

Frequency wave number (cm^{-1})	Types of Vibration	Functional Group
3429.525	Stretch	$-NH_2$(aromatics)
3162.679	Stretch	$-NH_3^+$(amino acid)
2553.132	Stretch	$-NH_3^+$amine hydro-halides
2446.047	Stretch	0-H (carboxylic acid)
2273.t14	Stretch	-PH (phosphines)
1843.498	Stretch	C=H β-lactone)
1618.791	Stretch	C=C vynile esthers
1444.479	Stretch	CH_3 (aliphatics)
1384.615	Stretch	$S0_2$ (Sulfonyl chloride
1176.327	Stretch	P=O (Phosphate
1019.8491	Stretch	C-O (Cyclic alcohol)
826.8491	Stretch	C-H (Benzene)
698.7069	Stretch	O-C=O (Carboxilic acid)

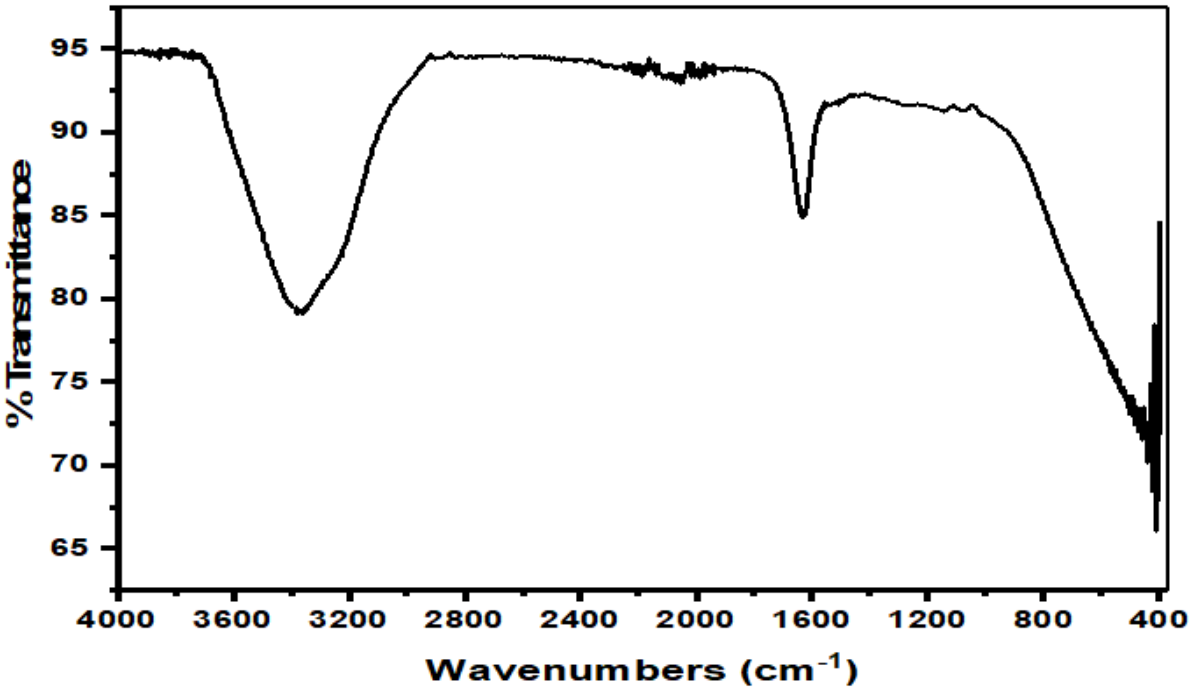

Figure 2: FTIR spectra of Tiger nut oil

3.3 Effects of Process Parameter on Biodiesel Yield

3.3.1 Effects of methanol to oil molar ratio on TNOFAME yield

Alcohol to oil molar ratio is one of the most vital factors that can affect the yield of esters. The stoichiometry of the transesterification reaction requires 3:1 methanol to oil molar ratio to yield 3 moles of ester and 1 mole of glycerol, but most researchers have found that excess alcohol was required to drive the reaction close to completion. In this work, the effect of methanol to oil molar ratio of 2:1 to 12:1 was investigated, when other process parameters catalyst concentration, reaction temperature, reaction time and agitation speed were kept constant. The yield of tiger nut oil biodiesel for the different molar ratio of methanol to oil is shown in Figure 3. The results indicated that methanol to oil molar ratio has significant effect on the FAME yield. The maximum ester yield was obtained at a methanol to oil molar ratio of 8:1 for TNO. The yield reduced when the molar ratio was higher than 8:1. This trend can be explained by the fact that while the increase in methanol to oil molar ratio favors transesterification reaction, very high methanol to oil molar ratio decreased the catalytic activity of the catalyst, resulting in the reduction of biodiesel produced. This is in agreement with the findings of [26] and [27]. It has also been reported by [28] that the use of excess alcohol for transesterification reaction increased the polarity of the reaction mixture and this increased the solubility of the glycerol. Increase of solubility of glycerol retards separation of glycerol from biodiesel and thus reduce the yield of biodiesel.

3.3.2 Effects of catalyst concentration on biodiesel yield

The alternative reaction pathways for breaking of bonds created by the use of catalysts most often involve lower activation energy. The effect of catalyst concentration on the yield of TNOFAME was investigated from 0.25 to 1.5%wt catalyst concentration as shown in figure 4. It was found that the yield of biodiesel increased with increase in catalyst concentration until an optimum yield was obtained at 1%wt. of catalyst when the yield starts declining. Decrease in biodiesel yield beyond the 1%wt. catalyst concentration can be explained by the fact that in the presence of excess catalyst above the optimum 1%wt., the excess catalyst react with the oil to form soap which increases the viscosity of the reaction mixture, hindering effective dispersion and mixing of the reactants and also separation of glycerol from biodiesel which gives rise to reduction of biodiesel production. This is in conformity with the findings of [29] and [30].

3.3.3 Effects of reaction temperature on biodiesel yield.

The rate of reaction is known to increase with increase in temperature. In order to investigate the effects of temperature on the yield of TNO biodiesel, the temperature was varied from 50^0C to 75^0C while the other parameters, catalyst concentration, methanol to oil to oil molar ratio, reaction time and agitation speed were kept constant as shown in figure 5. From the figure, it could be seen that biodiesel yield increased with increase in reaction temperature until a maximum yield was obtained at optimal temperature of 65^0C when the yield starts decreasing. The decrease in biodiesel yield beyond 65^0C may be explained by the fact that the boiling point of methanol is approximately 65^0C, and therefore on exceeding this temperature, the backward reaction is favored as most of

the methanol will be lost by evaporation, thus reducing the yield. This conforms with the findings of [31].

3.3.4 Effects of reaction time on biodiesel yield.

In this work, the effects of reaction duration from 15 to 90minutes on the yield of biodiesel from TNO was investigated. It was found that reaction time of 60 minutes was needed for a maximum yield of TNO investigated and beyond this time, the yield decreased as shown in Figure 6.

The decreased in yield after 60 minutes may be due to reversible reaction nature of transesterification resulting in loss of esters [32]. Also longer reaction time most times allows the fatty acid present to react with alkali and this will result to soap formation. The presence of soap retards the formation of ester [33].

3.3.5 ***Effects of agitation speed on biodiesel yield.***

In order to study the effect of agitation speed on the yield of TNO biodiesel, agitation speed was varied from 150rpm to 400rpm while keeping the other parameters, methanol to oil molar ratio, catalyst concentration, reaction temperature and reaction time constant as shown in figure 7. Agitation is particularly important during transesterification in order to ensure homogeneity within the reaction mixture. From the figure it could be observed that TNO biodiesel gradually increased with increase of agitation speed until an optimal value was attained at 300rpm when the yield starts decreasing. The decrease in yield on exceeding the optimal agitation speed of 300rpm may be explained by the fact that the backward reaction may have been favored when mixing intensity went beyond the optimal value of 300rpm.thereby retarding the formation of biodiesel. These results are in conformity with observations made by [33],who studied the effect of agitation speed on the transesterification of non-edible oil and concluded that higher agitation promoted the homogenization of the reactants and thus led to higher yield of biodiesel.

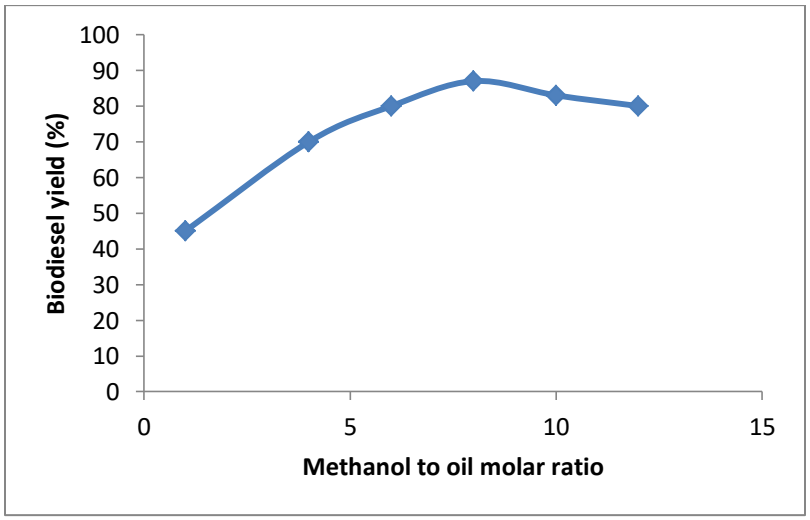

Figure 3: Effect of methanol to oil molar ratio on TNOFAME yield

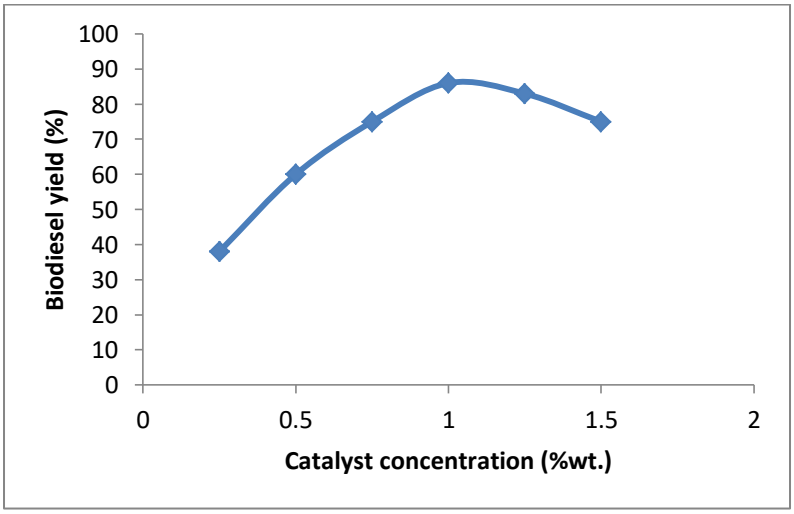

Figure 4: Effect of catalyst concentration on TNOFAME yield

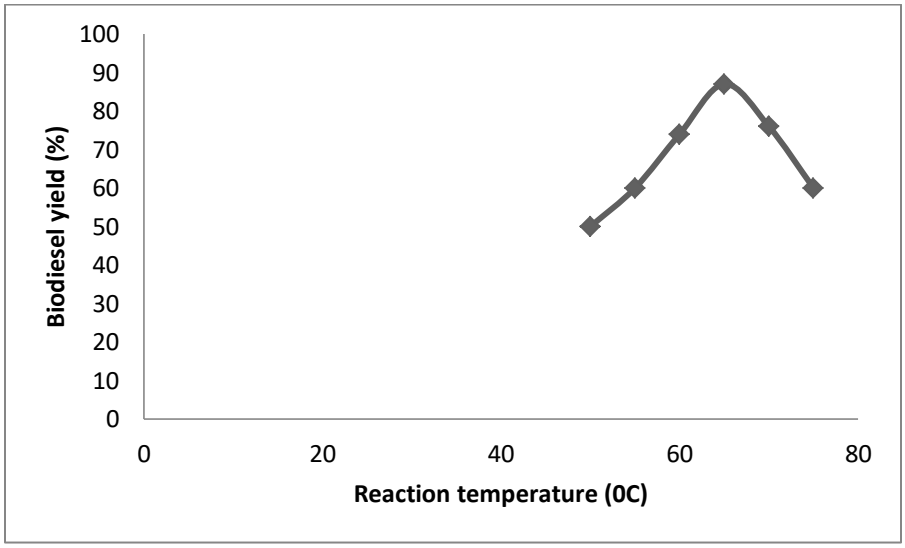

Figure 5 : Effect of reaction temperature on TNOFAME yield

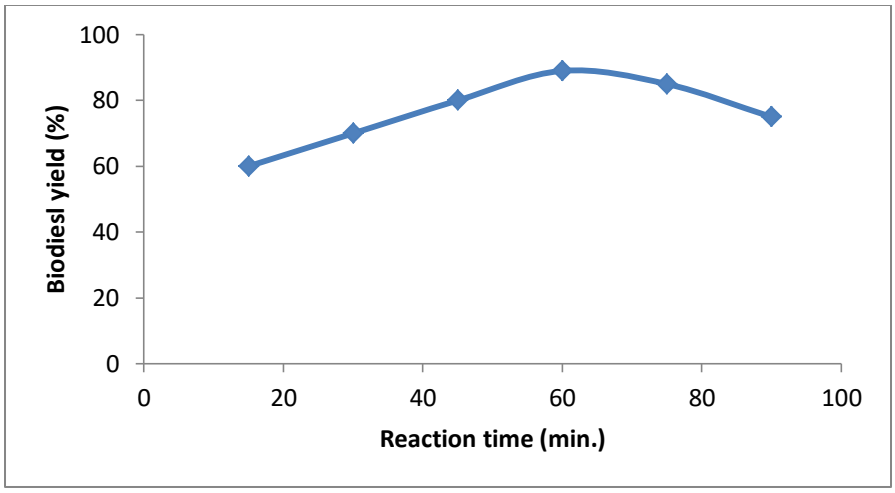

Figure 6: Effect of reaction time on TNOFAME yield

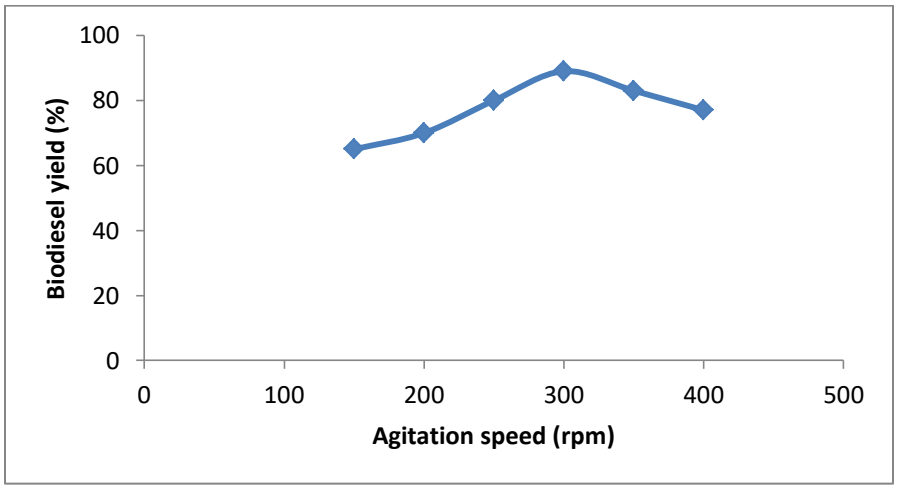

Figure 7: Effect of agitation speed on TNOFAME yield

3.4 Fuel Properties of the TNOFAME Produced.

Table 4 gives the summary of the fuel properties of TNOFAME studied in the course of this research work. Biodiesel generally has higher density than petro-diesel. This has a significant impact on fuel consumption as fuel introduced into the combustion chamber is determined volumetrically. The density of TNOFAME was evaluated as 870 kg/m^3, which is within the ASTM limits for biodiesel. The biodiesel has lower density compared to the density of TNO (891 kg/m^3). The value of kinematic viscosity obtained for the TNO biodiesel was 4.60mm^2/s as shown in table 4, and it could be observed that it is within the standard range of ASTM limit. Again this value is quite less than that of the TNO from which it was produced. The determined density and viscosity values are thus in agreement with literature findings [34] and [35]. High viscosity and density of fuel results in poor atomization in compression ignition engines, which may give rise to carbon deposits, plugging of fuel filter, and injector coking [36] and therefore reduction of the engine power output. Oils are transestrified in order to reduce the density and viscosity to a reasonable level to avoid the aforementioned problems. Low-viscosity fuel produces very subtle spray which cannot properly get into the combustion cylinder, thus forming a fuel-rich zone that give rise to formation of sooth [37] and [38]. From the result it could be inferred that FAME from TNO has a good injection and atomization performance.

The flash point is a determinant for flammability classification of materials. The typical flash point of pure methyl ester is ≥130^{0}C, classifying them as "non-flammable". However, during production and purification of biodiesel, not all the methanol, may be removed, making the fuel flammable and dangerous to handle and store if the flash point falls below 130^{0}C. The determined flash point of the TNOFAME is 160^{0}C. This falls within the ASTM standard as shown in table 4, indicative of its safety in handling and storage.

Cetane number serves as a measure of ignition quality of the fuel. This is the most pronounced change from vegetable oil to the transesterified product. Fuels with low cetane number show an increase in emission due to incomplete combustion. The lower limit for cetane number by ASTM standards is 47. The cetane number obtained for the TNO biodiesel was 61. Thus the obtained results which are within the acceptable ASTM limits indicates that the produced biodiesel possess good ignition response. Very low acid value 0.5mgKOH/g is required of biodiesel. The acid value of the TNOFAME obtained is 0.45mgKOH/g, being within the limit of the standard. High acid value is not permissible for good quality biodiesel as the excess alkali can corrode and damage the machine parts. The saponification number relays the degree of concentration of glycerides in the biodiesel and hence the quantity of alkali needed to saponify a gram of it. The calorific value obtained for TNOFAME was 35.4MJ/KG. TNOFAME calorific value is relatively low when compared to that of diesel 42.5MJ//KG. The moisture content of TNOFAME 0.03% is within the ASTM standard limit and conforms with the literature values [35]and [36].

The cloud point which is the lowest temperature of first appearance of wax-like material on cooling the biodiesel was determined as 7^{0}C for TNOFAME while the pour point which is the lowest temperature at which the fuel will still pour was determined as 4^{0}C. The cloud and pour points are not sufficiently low and might give rise to cold flow problems in cold season especially in the temperate and cold regions. This problem however could be overcome by the addition of suitable cloud and pour point depressants or by blending with diesel oil [36].The properties of the biodiesel produced are within the ASTM limit for biodiesel, as shown in table 5.

Table 4: Fuel properties of TNOFAME

Properties	Unit	TNOFAME	ASTM Standards	Test method
Density	Kgm^{-3}	870	860-900	D93
Kinematic viscosity	mm^{2}s^{-1}	4.60	1.9-6.0	D445
Cetane number		61	47min.	D613
Flash point	^{0}C	160	100 to 170	D93
Cloud point	^{0}C	7	-3 to -15	D2500
Water &sediment	%	0.03	0.05	D2709
Acid value	mgKOHg^{-1}	0.45	0.50	D664
Calorific value	MJKg^{-1}	35.4	42.06	D35
Iodine value	gI_2/100g oil	63	42-166	
Pour point	^{0}C	4	-10 min.	D97
Specific gravity		0.87	-	D287
Free fatty acid	%	0.23	-	
Refractive index		1.446		

3.5 Effects of petro-diesel blend on fuel properties of Tiger nut oil biodiesel

The effects of blending of petro-diesel with tiger nut oil biodiesel are as shown in table 5. Here, the tiger nut oil biodiesel was blended with #2 diesel oil on a percentage

volume ratio of biodiesel to diesel, 0, 20, 40, 60, 80 and 100% designated as B0, B20, B40, B60, B80 and B100 respectively. The fuel properties of B0 to B80 were determined using the test method employed for B100 and the properties so determined were compared with those of the B100.The density and viscosity of B100 were obtained as 870Kg/m^3 and 4.6mm^2/s and these are within the ASTM standard for biodiesel. From the table it could be observed that the density and viscosity of tiger nut oil biodiesel decreased with decrease of biodiesel fraction in the blend. This is naturally expected as the density and viscosity of the biodiesel are greater than those of diesel and therefore the blends with higher content of biodiesel possess higher density and viscosity. This conforms with the findings of [37] and [38] who studied density and viscosity relationship with biodiesel fraction. The flash point is a determinant for flammability classification of materials. The typical flash point of pure methyl ester is ≥130^{0}C, classifying them as "non-flammable". However, during production and purification of biodiesel, not all the methanol, may be removed, making the fuel flammable and dangerous to handle and store if the flash point falls below 130^{0}C. The determined flash point of the TNOFAME is 160^{0}C. This falls within the ASTM standard as shown in table 5, indicative of its safety in handling and storage. From the table it could be observed that the flash point decreased with decrease in biodiesel fraction in the blend. This trend results as the flash point of biodiesel exceed that of diesel , therefore the blends exhibit flash point proportional to the biodiesel content.

Cetane number serves as a measure of ignition quality of the fuel. This is the most pronounced change from vegetable oil to the transesterified product. Fuels with low cetane number show an increase in emission due to incomplete combustion. The lower limit for cetane number by ASTM standards is 47. The value obtained for the TNO biodiesel is 61. Thus the obtained results which are within the acceptable ASTM limits indicates that the produced biodiesel possess good ignition response. Observation of the table reveals that the cetane number decreased with decrease in the biodiesel fraction in the blend since biodiesel exhibit higher cetane number than diesel. The water content of B100 is within the ASTM limit and the water content of the blends are constant. The calorific value of B100, 35.4MJ/Kg is slightly lower the ASTM standard and much lower than that of diesels. The value was found to increase with decrease in biodiesel fraction. The cloud point which is the lowest temperature of first appearance of wax-like material on cooling the biodiesel was determined as 7^{0}C for TNOFAME. From the table it could be observed that the cloud and pour point increased with increase in biodiesel fraction in the blend. The pour point which is the lowest temperature at which the fuel will still pour was determined as 4^{0}C. The cloud and pour points are not sufficiently low and might give rise to cold flow problems in cold season especially in the temperate and cold regions. This problem however could be overcome by the addition of suitable cloud and pour point depressants or by blending with diesel oil [36].The properties of the biodiesel produced are within the ASTM limit for biodiesel, as shown in table 5. Compression ignition engine fuel requires a biodiesel of equivalent properties as diesel fuel. It could be observed from the table that B0, B20 and to some extent B40 possess close fuel properties as diesel which makes them suitable for use in diesel engines with little or no modification of the engine.

Table 5: Effect of petro-diesel blend on the fuel properties of tiger nut oil biodiesel

Properties	B0	B20	B40	B60	B80	B100	ASTM standards	Test method
Density (Kg/m^3)	850	852	858	863	867	870	800-900	D93
Kinematic viscosity ((mm^2/s)	3.95	4.25	4.3	4.38	4.45	4.6	1.9-6.0	D445
Flash point (^{0}C)	100	140	146	150	155	160	100-170	D03
Cetane number	40	50	54	56	58	61	47	D613
Water & sediment (%)	0.02	0.03	0.03	0.03	0.03	0.03	0.05	D2729
Acid value (mgKOH/g)	0.32	0.39	0.41	0.45	0.45	0.45	0.50	D664
Calorific value (MJ/Kg)	45.5	43	40	39	37	35.4	42.06	D35
Iodine value (gI_2/100g)	-	55	57	60	63	65.2	42-116	
Cloud point (^{0}C)	-	6	6	6	7	7	-	D2500
Specific gravity	0.85	0.85	0.86	0.86	0.87	0.87	0.85	D287
Free fatty acid (%)	0.25	0.25	0.26	0.27	0.27	0.28	-	
Refractive index	-	1.440	1.440	1.442	1.446	1.446	.-	
Pour point (^{0}C)	-	2	3.5	3.8	4	4	-	D97

IV CONCLUSION

The process conditions for production of tiger nut oil biodiesel, methanol to oil molar ratio, catalyst concentration, reaction temperature, reaction time and agitation speed significantly affected the yield of the biodiesel as their increase resulted to higher yield of TNOFAME but excessive increase resulted to decrease in

biodiesel yield. Blending of the TNOFAME with petro-diesel resulted to imparting of good fuel properties of both fuels on the blends. However at present only a small proportion of biodiesel (≤20%) need to be blend with petro-diesel to give fuel of equivalent property as the diesel for use in compression ignition engine without needing modification of the engine.

REFERENCES

1 H. Fukuda, A. Kondo, & H. Noda, (2001). Biodiesel fuel production by transesterificatio Of oils, *Bioscience Bioengineering Journal*, 92, 405-416.

2 A. Demirbas, (2009). Progress and recent trends in biodiesel fuels. *Energy Conversion and Management* 50, 14-34.

3 D.Y.C. Leung, & Y Guo, (2010). Transesterification of meat and used frying oil: Optimization for biodiesel production. Fuel *Process Technology*, 87. 883-890.

4 H. Lu, Y. Liu, H. Zhou, Y. Yang, M. Chen, & B. Liang, (2009). Production of biodiesess from *Jatropha curcas* L. oil. *Computer and Chemical Engineering* 33(5), 1091-1096.

5 B.O. Aderemi, and B.H. Hamid, (2010). Production of Biodiesel from palm oil. *Nigerian Society of Chemical Engineers Proceedings*, 40, 135-143. Abuja, Nigeria.

6 N.A.N. Younis, S.K. Kamarudin, and Z.Yaakub, (2011). Overview of the current trends in biodiesel production. Energy Conversion and Management, 52(7), 2741-2751.

7 L. Attanatho, S. Magmee, P. Jenvanitpanjakul, (2004).Factors affecting the synthesis obiodiesel from crude palm kernel oil. *The Joint International Conference on Energy and Environment* (SSE), Hua Hin, Thailand, 1-3 December 2004.

8 R.M .Venkata , M.Y. Mallikarjun, & N.R.G. Lakshmi, (2012). Biodiesel production from Palm oil by transesterification method, *International Journal of Current Research*, 4(8), 083-088.

9 M. Gui, K. Lee, & S. Bhatia, (2008). Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. *Energy*, 33(11): 1646-1653.

10 H.J. Berchmans, & S. Hirata, (2008). Biodiesel production from crude *Jatropha curcas* L. Seed oil with a high content of free fatty acids. *Bioresource Technology*, 99(6), 1716-1721.

11 S, Jain , & M. Sharma, (2010). Kinetics of acid base catalyzed transesterification of *Jatrophacurcas* oil. *Bioresource Technology*,101(20), 7701-7706.

12 G.C. Nina, M. Ukeyima, A.F. Ogori, H. Lukas, H. Moroslava G. Alexey, L. Alexey, Anna, D.Pigorev, I., P. Sergey, I.A Mohammad, Investigayion of Physiochemical and Storage conditions on the properties of extracted tiger nut oil from different cultivars,Journal of Microbiology. Biotechnology and Food Sciences, 9(5), pp983-993, 2020.

13 E.L. Bamishaiye, and O.M. Bamishaiye, Tiger nut: As a plant, its derivatives and benefits, AJFAND Scholarly Peer Reviewed, 11(5), September 2011.

14 F.M. Ali Rahab, and A.M. El Anany, Physiochemical Studies on sunflower oil biodiesel with cold pressed tiger nut oil during deep frying process, Grasas Aceites 2012, 63, 665-666.

15 O. Laseckan, S.M. Abdulkarim, Extraction of oil from tiger nut (cyperus esculentus L.) with supercritical carbon dioxide (SC-CO2), LWT-Food Sci. Technology 2012, 47, 287-292.

16 S.O. Yeboah, Y.C. Mitei, J.C.Ngila, I. Wesjohann, J. Schmidt, Compositional and structural studies of the oils from two edible seeds: Tiger nut Cyperus esculentus and asiato , pachira insignis, from Ghana. Food Res.Int. 2012, 47, 259-266.

17 M. Hanumanth, O.D. Hebbal, & M.C. Navindgi, (2012). Extraction of biodiesel from vegetable oil and their comparisons; *International Journal of Advanced Scientific Research and Technology*, 2(2), 2249-9954.

18 K.I. Ogunwa, S. Ofodile, O. Achugasim, Feasibility study of mellon seed oil as a source of biodiesel. Journal of Power and Energy Engineering, 3(8), August 2015.

19 A. Abitogun, A. Omesheyin, O. Oloye, O, Alademeshin, Extraction and characterization of sunflower oil. The International Journal of Nutrition and Wellness, 8(2), 2008

20 F.U. Ozioko, Extraction and characterization of soya bean oil based bio-lubricant. Assumption University Journal of Technology (AUJT), 15(4), 260-264, April 2012.

21 S. Lee, and Y.T. Shah, (2013). Biofuels and Bioenergy: Processes and Technologies. CRC Press, Taylor and Francis Group, 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL. ISBN 978-1-4200-8955-4.

22 J.C. Umeuzuegbu E.E. Ezennajiego, O.D. Onukwuli, Production ,Characterization and Optimization 0f Biodiesel from Gmelina seed oil. *World Journal of Innovative Research (WJIR)*, 8(4) April 2020 pp74-86.

23 N. Muhammad, E. Bamishaiye, O. Bamishaiye, L. Usman, et al, Physiochemical Properties Properties and fatty acid composition of cyperus esculentus (Tiger nut) tuber oil, Biores.Bull.2011,5, 51-54.

24 L.B. Fomuso, C.C. Akoh, Lipase-catalyzed acidolysis of olive oil and caprylic acid in a bench scale packed bed bioresource. Food Res. Int.2002,37,15-21.

25 F. Visioli, C. Galli, The effect of minor constituents ofolive oil on cardiovascular disease:New findings. Nutri. Rev. 1998, 56, 142 147.

26 Y. Zhang, M.A. Dube, D.D. McLean, & Kates, M. (2003). Biodiesel production From waste cooking oil. Process design and technological assessment. *Bioresources Technology*, 89, 1–16.

27 B. Freedman, E.H. Pryde, & T.L. Mounts, (1999). Variables affecting the yields of fatty esters from transesterified vegetable oils, 61, 1638–1643.

28 U. Rashid, and F. Anwar, (2008). Production of Biodiesel through Optimized Alkaline Catalyzed Transesterification of Rapeseed Oil. Fuel, 87, 265 – 273.

29 J.M. Encinar, J.F. Gonzalez, A. Rodriguez-Reinares, (2005). Biodiesel from used frying oil,Variables affecting the yields and characteristics of the biodiesel, *Industrial and Engineering chemistry Research*, 44(15), 5491-5499.

30 S.S. Jagadale, & L.M. Jugulkar, (2012). Review of various reaction parameters and other factors affecting on production of chicken fat based biodiesel, *International Journal on Model Engineering Resource*, 2(2), 407–411.

31 H.O. Ogunsuyi, (2015). Production of biodiesel using African pear (*Dacryodesedulis*) seed oil as feedstock. *Academic Journal Biotechnology* 3(5), 085-092.

32 N. Nakatani, H. Takamori, K. Takeda, & H. Sakugawa, (2009). Transesterification of soybean oil using combusted oyster shell waste as a catalyst. *Bioresource Technology*, 100(3), 1510–1513.

33 M.M.P. Endah, M. Rachimoellah, S. Nidya, & P. Ferdy, (2012). Biodiesel production from kapok seed oil (*Ceiba pentandra*) through the transesterification process by using Cao as catalyst, *International Research Journal*, 12(2),3-7.

34 C.C, Ezekwe, . & V. Ajiwe, (2014). The variations of physiochemical properties of biodiesel blends with the blend ratios. *International Journal of Science Innovations and Discoveries*, 4, 11-14.

35 A.A. Aboje, A.A. Kovo, A.A. Agbo, O.D. Aderemi, Optimal Process Conditions for Enhanced Co-Solvent Based Transesterification of Tiger nut Oil. Nigerian Journal of Engineering and Applied Sciences 6(2), 2019.

36 D.P. Prafulla, G.G. Veera, K.R. Harvind, M. Tapaswy, & d. Shuguang, (2012). Biodiesel production from waste cooking oil using sulfuric acid and microwave irradiation processes. *Journal of Environmental Protection*, 3, 111 -117.

37 J.C. Umeuzuegbu, The effect of Temperature and Blending On The Density and Viscosi of Neem Fatty Acid Methyl Ester. World Journal of Innovative Research, 8(3), March 2020 pp80-86.

38 R.H. Al Naumi, and S.C. Vishweshwara, Temperature-Viscocity Correlation for Biodiesel Blends Derived from Corn, Olive and Palm Oil. International Journal of Multidisciplinary Science and Engineering, 6(11), November 2015.

Umeuzuegbu J.C., Department of Chemical Engineering , Chukwuemeka Odumegwu Ojukwu University, Anambra State, Nigeria.