GSJ: Volume 9, Issue 7, July 2021, Online: ISSN 2320-9186

www.globalscientificjournal.com

POTENTIAL OF COTTONSEED OIL AS A FEEDSTOCK FOR PRODUCTION OF BIODIESEL

Ezinwa, Sunday Nnaemezie[1]: Department of Science Laboratory Technology, Institute of Management and Technology, Enugu, Nigeria.

Abstract

Potential of cottonseed oil for synthesizing biodiesel was investigated. Biodiesel was produced from crude cottonseed oil by trans-esterification with three different alcohols (methanol, ethanol and butanol) in presence of sodium hydroxide (NaOH). Several sequential and diligently planned experiments were carefully performed to ascertain the optimal process conditions of alcohol/oil molar ratio, catalyst concentration, reaction temperature, reaction time, and rate of mixing alongside biodiesel yield. Based on this endeavor, the validated optimal condition for the production of biodiesel for the respective alcohols were methanol/oil molar ratio 7:1, temperature 55°C, time 45 minutes, catalyst concentration 1%, and rate of mixing 300rpm. Ethanol/oil molar ratio18:1. Temperature, 45°C, time 45 minutes, catalyst concentration 1%, and rate of mixing speed alkyd resin 300rpm. Butanol /oil molar ratio 19:1, temperature, 40°C, time 15minutes, catalyst concentration 0.5%, and mixing speed 300rpm. The conditions were validated with the actual biodiesel yield of 82.5% for methanol, 85% for ethanol and 75% for butanol trans-esterification. Result of the investigation showed that cottonseed oil has high potential as a feedstock for production of biodiesel.

Keywords: *Cottonseed oil, Alcohols, trans-esterification, Fatty acid methyl ester.*

1 Introduction

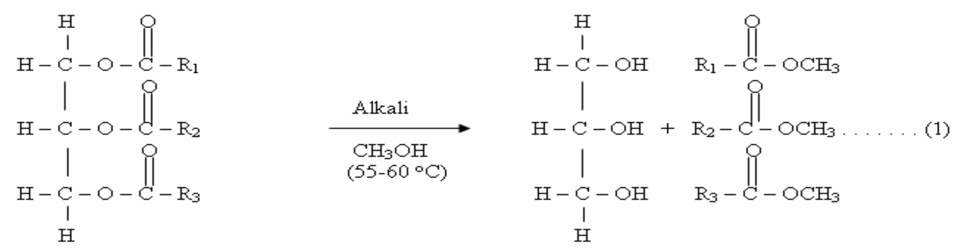
Decisive role of energy in global activities placed energy as an indicator for all forms of development. Currently, a large percentage of the world's total energy output was of fossil derivatives. Fossil reserves are finite and highly concentrated in certain region of the world and those regions without endowment of these resources are often faced with foreign exchange challenges, mainly due to the import of crude petroleum oil.

In another consideration, indiscriminate extraction and consumption of fossil fuels have led to a reduction in fossil fuel reserves hence, the trending opinion that the world current oil and gas reserves would shortly be depleted and consequently, the world faced with multi- challenges of fossil fuel/energy shortage and environmental degradation (Singh and Singh, 2010).

Emissions from the combustion of fossil derived fuel are the greater contributors to global warming, (Muniyappa, et al, 1996). These are causes of concern and have stimulated world-wide research for a cheap, renewable and more eco- friendly alternative energy sources to avert threats of climate change and ensure energy sustainability. Responsively, the need to develop alternative sources of fuels producible from materials available within the locality became obvious. One of the most promising alternatives is biodiesel (Fan, et al, 2011). Biodiesel is the free fatty acid methyl esters, popularly referred to as FAME, derived from fats and vegetable oil sources, (Ude, *et al*, 2019).

Biodiesel maintained the merit primarily due to its outstanding benefits over the conventional petro- diesel. It is renewable, biodegradable, non-toxic, has a high flash point and good reduction in greenhouse emissions (Demirbas, 2009, Kaya, et al, 2009, Ghetsi, et al, 2009, Aderemi, et al, 2010).

Chemical reaction for the manufacturing of biodiesel using vegetable oil is as follows:



Among various processes that have been adopted in production of biodiesel from vegetable oils and animal fats namely; micro-emulsification with alcohols, catalytic cracking, Pyrolysis, trans-esterification and ultrasonic assisted trans-esterification (Kaya, et al, 2009, Aderemi, et al, 2010, Lengl, *et al*,1999 Li, *et al*, 2009, Ramachandran, *et al*, 2013), trans-esterification is the key and foremost important process to produce the cleaner and environmentally safe fuel that can substitute petroleum diesel in diesel engines (Younis , *et al*, 2009, Attanathl, 2004).

In Nigeria, common vegetable oils available for biodiesel production include palm oil, palm kernel oil, groundnut oil, soyabean oil, Jatropha oil, castor oil, neem oil and cotton seed oil. The exploration of cotton seed oil and sesame seed oil for biodiesel production have not been thoroughly investigated (Umaru, et al, 2014). A few numbers of works have been reported on biodiesel production from cottonseed oil in different part of the world hence, a dearth of literature on the effect of various alcohols on the production of biodiesel from crude cottonseed oil.

This study is therefore aimed to investigate the effect of process parameters on the production of biodiesel from crude cottonseed oil with a view to establishing the best process conditions and yield of biodiesel from cottonseed oil using varied alcohols in sodium hydroxide (NaOH) catalyzed process.

2 Materials and Methods

2.0 Materials.

Cottonseeds were purchased from central market, Sabongari Kano, Kano State, Nigeria. Analytical grade of methanol, ethanol, butanol and sodium hydroxide (NaOH) with assay 96% products of Wharefedale Laboratories, Yorkshire, England were obtained from Gerald Chemical Services Ltd, Ogbete Market, Enugu, Enugu state, Nigeria.

2.1 Cottonseed Preparation / Oil Extraction.

Fresh cotton seeds as purchased were sorted of stones pebbles and other undesired materials, washed in water and dried by spreading it under the sun for 24hrs (6hrs per day for four days) .

The sample was weighed and subjected to oven drying at 110^oC during which the sample was weighed at the expiration of every 60mins until the weight remained constant. The sample was milled to sizes below 0.01mm and soaked in N- hexane at a mass ratio of 1:10. The soaked sample was allowed to stand for 48hrs in an air tight enclosure arrangement at 70^oC and cottonseed oil was extracted in a soxhlet apparatus.

The cake was subjected to hot pressing using hydraulic press to collect any oil remnant. The sample was weighed and values obtained were incorporated into the formula given below to estimate the percentage oil yield. Weight of oil obtained and that of the cake were noted.
Yield of oil was calculated thus;

$$\text{Yield (\%)} = \frac{\textbf{Weight of sample before etraction} - \textbf{weight of Cake}}{\textbf{Weight of sample before extration}} \text{ X } 100 \qquad (1)$$

2.2 Characterization of Cottonseed Oil

The physiochemical properties of the oil and the biodiesel were determined according to ASTM D6751-02, (2002) as described by Onukwuli, et al, (2016)

2.3 Treatment of cottonseed oil

2.3.1 Neutralization

The extracted cottonseed oil was heated in a flask to a temperature of 50^oC and 45% solution of sodium hydroxide (2M. Na0H) introduced into the oil to neutralize the free fatty acid (FFA) content. While maintaining the temperature and agitation at constant speed of 300rpm, progress of the neutralization reaction was monitored using phenolphthalein indicator. The neutralization was termed completed when, on introduction of phenolphthalein into withdrawn sample, the color turned to pink. 20% of 1N solution of sodium chloride (1M. NaCl) heated to 90^oC was introduced into the neutralized oil and stirred. The mixture was transferred into a separating funnel and allowed to stand for 3hrs during which the mixture separated into two layers. The milk- colored lower layer was drained out while the upper layer was collected and washed with boiled water. The washing was continued and monitored until the color did not turn to pink on introduction of phenolphthalein indicator.

2.3.2 Dehydration

The neutralized oil was introduced into a beaker, weighed and put into an oven set at 105^oC to evaporate the moisture. Progress of dehydration was monitored by weighing the sample at time intervals of 30minutes until the weight remained constant. Thus weight loss in the process of neutralization and dehydration was estimated.

2.4 Characterization of treated cottonseed oil

The treated oil was re-characterized for same properties using same standard methods as in section (2.2) to re-assess its suitability for trans-esterification.

2.5 Trans-esterification of cottonseed oil

The treated cottonseed oil was quantitatively transferred into a flat bottom flask placed on a hot magnetic stirrer. Specific amount of catalyst (by weight of refined cottonseed oil) dissolved in the required amount of methanol, ethanol and butanol was added. The reaction flask was kept on a hot magnetic stirrer under constant temperature with defined agitation throughout the reaction. At the defined time, sample was withdrawn, cooled, and allowed to stand in separating funnel. The biodiesel (the fatty acid ester- the upper layer) was separated from the by-product (glycerol -

the lower layer) by settlement overnight under ambient conditions. Equal volume of hot distilled water was introduced to wash the product. The mixture was gently stirred and allowed to stand overnight to settle into two phases -water /impurity phase and ester phase. The two phases were separated using separating funnel and the ester obtained was heated to 100^{o}C for 1hr to evaporate any remnant trace of water in the ester. The percentage of biodiesel yield was determined by comparing the mass of biodiesel with the mass of cottonseed oil used. The procedure was repeated by varying the process factors; time, catalyst concentration, temperature, alcohol/oil molar ratio and agitation speed.

$$\text{Yield of biodiesel} = \frac{\text{Weight of fatty acid ester}}{\text{Weight oftreated oil}} \text{x100} \qquad (2)$$

2.6 Physiochemical Properties of Raw Oil, Treated Oil and Biodiesel produced

The physiochemical properties of the oil and the biodiesel were determined according to ASTM D6751-02, (2002) as described by Onukwuli, et al, (2016)

2.6.1. Moisture content

1 g sample of treated oil and each of the biodiesel were weighed out in respective petri dishes of known weight and each samples weighed and placed in an oven set at 105^{o}C to set the samples free of moisture. The weights of the samples were monitored at 30 minute intervals until the weight remained constant. The percentage moisture content of each samples was calculated thus:

$$\text{Percentage moisture content} = \frac{W1\_W2}{W1} \text{ x100} \qquad (3)$$

W_1= original weight of the sample before drying,
W_2 = weight of the sample after drying.

2.6.2 Saponification value

1 g sample of each of the oils and biodiesel samples was dissolved in 25 ml of 0.5 M ethanolic potassium hydroxide solution, using 250 ml quick fit flask. The flask was heated in a steam bath under reflux for 30 minutes. The flasks were swirled once in every 10 minutes to ensure uniform heat distribution. The solution were cooled in water bathe and titrated with 0.5 M HCl using phenolphthalein indicator. A blank determination was carried out under similar conditions. The difference in the titre values gives the number in milli-litres of HC1 acid required to neutralize the alkali after saponification.

The saponification value was calculated as:

$$\text{Saponification value (SV)} = \frac{56.1 \text{ x M x } (B-V)}{W} \qquad (4)$$

M = morality of standard HCl (0.5 M),
B = volume of HCl in ml used in the blank titration,
V = volume of HCl in ml used for oil and biodiesel titration respectively,
56.1 = molar mass of potassium hydroxide, and
W = weight in gram of sample.

2.6.3. Iodine value

1 g of each of the samples was withdrawn and dissolved in 15 ml of carbon tetrachloride. The solution was mixed with 25 ml Wiji’s solution. The flask with the content was stoppered and allowed to stand in the dark for thirty minutes at room temperature, to allow for oxidation to take

place. 100 ml of distilled water and 20 ml of 10% potassium iodide solution were added to the content of the flask and gently stirred to ensure homogenuity. The mixture was titrated with 0.1 M sodium thiosulphate using 10% starch solution. Blank determination was carried out in the same manner under similar conditions. The iodine value was calculated as expressed below

$$\text{Iodine value (IV)} = \frac{12.69 \text{ x M x } (B - V)}{W} \qquad (5)$$

M = morality/ of thiosulphate solution,
B = volume of $Na_2S_20_4$ (ml)used in the blank titration,
V =volume of $Na_2S_20_4$ (ml) used in test titration,
W = weight (*g*m) of the oil sample.

2.6.4. Acid value

1 g sample of each of the samples was dissolved in a 25 ml mixture of equal volume of diethy1 ether and absolute ethanol. The resultant solution was titrated with 0.1 M potassium hydroxide (KOH) using phenolphthalein indicator. The volume at the point the solution turned pink was noted as the titre value. Acid value was calculated thus:

$$\text{Acid value: } = \frac{56.1 \text{ x M x V)}}{W} \qquad (6)$$

M = Morality of standard KOH (0.l M)
V = Titre value (volume (ml) of KOH)
56.1 = Molar mass of potassium hydroxide.
W = Weight in gram of sample.

2.6.5. Free fatty acid

1 g sample each of oil and biodiesel samples was dissolved in a 25 ml neutral mixture (equal volume of diethyl ether and absolute ethanol). The resultant solution was titrated with 0.1 M potassium hydroxide solution using phenolphthalein indicator. Volume of the potassium hydroxide solution titration introduced until the point the solution turned pink permanently. This volume was noted as the titre value. Free fatty acid value in terms of oleic was calculated as below:

$$\text{FFA (\%)} = \frac{V \text{ x } 0.0282}{W} \text{x } 100 \qquad (7)$$

V = Titre value
0.0282 = constant (weight of oleicacid neutralized by 1 mg of KOH.
W = Weight(gm) of the oil/biodiesel sample.

2.6.6 Ester value

Ester value of the oiland biodiesel samples were ca1culated as the difference between the saponification value and the acid value.

$$\text{Ester value} = \text{Saponification value - Acid value} \qquad (8)$$

2.6.7 Calorific value

0.5g of the sample was weighed and introduced into a distillation flask, the flask containing the sample was heated in a hot air oven to vaporize. The vapor was condensed using water circulated glass condenser. Weight of the distillate and weight of residue after condensation were noted for each case of weightings, thus,

$$\text{Calorific value} = (W_s - W_r) * 9 \quad (9)$$

Where; W_s = weight of sample

W_r= weight of residue

9= Conversion factor

2.6.8 Specific gravity, API gravity, Diesel Index, Cetane number.

This experiment was carried out as quickly as possible at the room temperature. An empty and dry 25 ml specific gravity bottle was weighed. The bottle was filled with distilled water and reweighed. The water was drained and the bottle dried for 30mins in an oven set at 100^{o}C. The bottle was filled to mark with the sample and re-weighed. The properties of the oil sample (i.e. cottonseed oil or biodiesel) were calculated respectively from the recorded weights based on the following relations.

$$\text{Specific gravity;(SG)} = \frac{Ws}{Ww} \quad (10)$$

Ws=Weight of sample

Ww=Weight of equal volume of water

$$\text{API gravity} = \frac{141.5}{S.G} -131.5 \quad (11)$$

$$\text{Diesel Index} = \text{Aniline point } (^oF) \times \frac{API\ (°C)}{100} \quad (12)$$

$$\text{Cetane number} = 0.72 \text{ Diesel Index} + 10 \quad (13)$$

where 10 is correction factor

2.6.8 Other vital properties including Peroxide value, viscosity, refractive index, Boiling point , Cloud point and pour point were also determined following same ASTM D6751-02 methods.

3.0 Result and Discussion

3.1 Physico- Chemical Properties of Cottonseed Oil

Characteristics of the cotton seed oil, biodiesel and ASTMD 6751 standards are summarized in the table 1.

Table 1 Characteristics of cotton seed oil, biodiesel from cotton seed oil and ASTM standard.

S/N	Properties	Units	Raw cottonseed oil	Treated cottonseed oil	Biodiesel from cottonseed oil	ASTM D6751 standard
1	Moisture content	% wt	7.85	0.020	0.020	0.050 max
2	Density	Kg/m^2	915	980	867	830-880

3	Acid value	Mg/KOHg	10.20	0.22	0.181	–
4	FFA	%	5.10	0.15	0.11	–
5	Saponification value	Mg/g	191.0	196	165.47	–
6	Ester value	Mg/g		187.72	165.19	–
7	Iodine value	$mgI_2/100$ g	92.67	98.20	125.20	–
8	Peroxide value	Meq/kg		80.00	26.01	–
9	Specific gravity		0.915	0.98	0.87	0.88
10	Kinematic viscosity	mm^2/s		29.22	5.6	1.9–6.0
11	Odour			Agreeable	Agreeable	–
12	Colour		Brqwn	Brown	Light brown	–
13	Viscosity	cP	73.83	43.34		
14	Refractive index	(28 °C)		1.4233	1.344	–
15	Flash point	(°C)		255	180	100–170
16	Cloud point	(°C)		−3.0	7.0	−3–12
17	Pour point	(°C)		−2.3	5.0	−15–10
18	Fire point	(°C)		–	193	_
19	Cetane number				55	48–65
20	Low heating value	MJ/kJ			41.25	
21	High heating value	MJ/kJ			43.3	–

The reddish brown color of the oil is the same with that of petro-diesel and also in conformity with the findings of Orhevba, et al, (2012). Specific gravity of 0.915 is within the range of that for many other vegetable oils such as palm kernel oil, pumkin oil, jathropha oil and others that have been successfully used for the production of bodiesel. Iodine value of 92.67mgKOH/g indicates that the oil is fairly saturated oil and therefore should require well prepared reaction environment for successful trans-esterification.

Free fatty acid value of 5.1 and moisture content of 7.85% are dangerously high considering that base - catalyzed trans-esterification reactions required oil with zero moisture content and free fatty acid value (<1), (Amit, 2012). These properties disqualified the oil for direct use for the proposed base- catalyzed trans-esterification. Consequently the oil was subjected to a pre-treatment process involving neutralization and dehydration.

Results of the property evaluation of the treated (neutralized and dehydrated) also tabulated in table 1 indicated no remarkable change in color as a result of the neutralization and dehydration. The reddish brown color of the oil remained stable. The viscosity dropped from 73.83cP to 43.34cP. This is in trend with the drop in acid value, moisture content and free fatty acid content. These drastically affected the specific gravity which appreciated from 0.91 to 0.98, the iodine value which improved from $92.67gI_2/100g$ oil to $98.20gI_2/100g$ oil and also the saponification value that showed remarkable increase from 191.0 to 196. These are attributable to the molecular condensation of the triglycerides following loss of water molecules during dehydration and also loss of the free fatty acid converted to soap during neutralization. The treatment brought the oil to free fatty acid value of 0.15 and 0.02% moisture content state from their raw oil status of 5.1 and 7.85% respectively, thus qualifying the oil for biodiesel production by base catalytic trans-esterification, (Amit, 2012).

The results show that the free fatty acid (FFA) value of 0.15% for the cottonseed oil is less than 1% while the moisture content of 0.02% is very close to zero. These are acceptable levels for trans-esterification reaction since higher amount of free fatty acids (FFA) (>1% w/w) in the feedstock reduce effectiveness of the catalyst, enables direct reaction with the alkaline catalyst to form soaps which are subject to formation of stable emulsions and prevent separation of the biodiesel from the glycerol fraction and thus decrease the yield of biodiesel (Demirbas, 2003, Demirbas, 2006). The kinematic viscosity, acid value, free fatty acid) are in good agreement with the standard.

The specific gravity of cottonseed oil was reduced from 0.906 to 0.87 after trans-esterification. This value is within the acceptable limit. Drop in saponification, value is 187.95 mg/g of cottonseed oil to 165.47 mg/g of biodiesel implies that the triglycerides of cottonseed oil have higher molecular weight fatty acids (saturated and unsaturated) and a good indication of the extent of trans-esterification. The results obtained compared favorably with the saponification value of palm oil (187–205), olive oil (185–187), and soy oil (187–193). High Iodine value, 98.20 $mgI_{2/g}$ of the cottonseed oil, indicated that cottonseed oil is a good material for biodiesel production because the higher the iodine value, the more the number of double bonds present in molecular structure and less the viscosity of the oil. The peroxide value has direct relation with cetane number and therefore may influence ignition delay time (Mohammed et al, 2012). Peroxide value is directly related to the oxidation stability (Lôbo, et al, 2009,). High peroxide value of 26.01meq/kg found in this work are indeed consistent with reported oxidative stabilities (Fernandes , et al, 2012,) of 3 h 10 min and 2 h 13 min for methyl and ethyl biodiesels from corn, respectively Douglas, et al, (2014) .

3.1 **Effects of Process Parameter on Biodiesel yield.**

3.2.1 Reaction Time.

In this work, the effect of reaction time on the biodiesel yield from methanolysis, ethanolysis and butanolysis were investigated for the time range of 10mins to 90mins. Biodiesel yield increased as the reaction time increased from 10mins to 60mins during methanolysis, 10 to 45min and 10mins to 15mins during ethanolysis and butanolysis respectively. However, decrease in yield of biodiesel was recorded as the reaction prgressed from 60mins to 90mins for methanolysis, 45mins to 90mins for ethanolysis and 15mins to 90mins for butanolysisTherefore optimal reaction time was 60mins and yield of 87.6% for methanolysis, 45mins and yield of 84.3% for ethanolysis and 15mins and yield of 60.24% for butanolysis, (figure 4.1). The drop in the yield after the optimal reaction time is atributable to reversible reaction that may have started after the optimal reaction time.

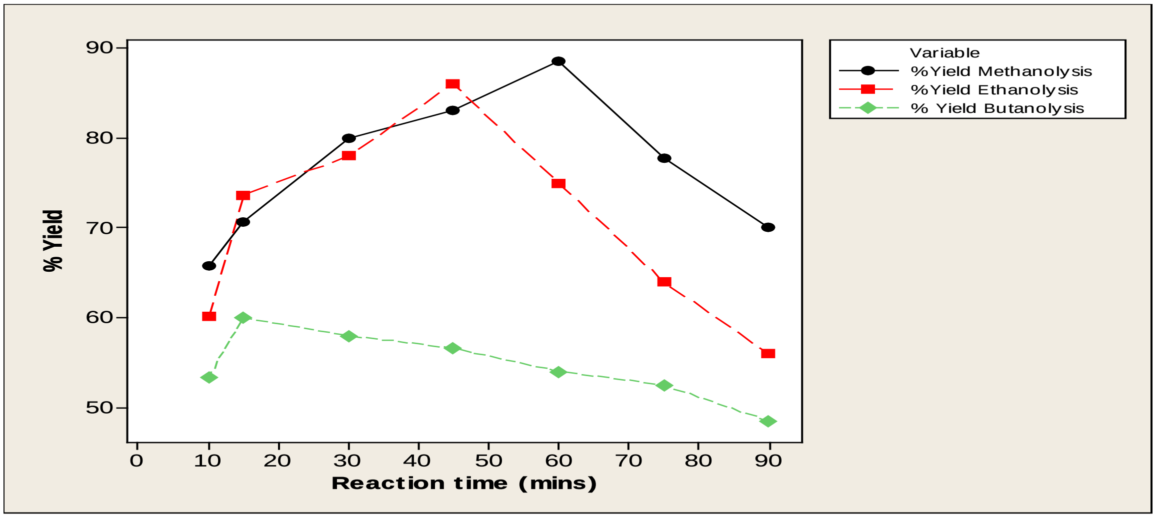


Fig.1 Effect of reaction time on yield of biodiesel.

This result was in agreement with the findings of Moser, (2009), butanolysis reaction is monophasic throughout, which results in a faster initial rate of reaction but may yield lower overall conversion to butyl esters in comparison to methyl or ethyl esters.

3.2.2 Catalyst Concentration

Sodium hydroxide as a catalyst was used at two levels (0.6 and 1.4 wt%) for methanolysis,(0.8 and 1.4wt%) for ethanolysis and (0.2 and 0.8wt%) for butanolysis. In this work, the effect of NaOH concentration expressed as weight percentage (wt%) of the oil on the ester yield was presented in Figure 4.2. The yield of methyl ester increased with increase in catalyst weight percent (wt%) up to 1.0% for methanolysis, 0.8% for ethanolysis and 0.4% for butanolysis and decreased with increase in catalyst concentration beyond 1.0% for methanolysis, 0.8% for ethanolysis and 0.4% for butanolysis.

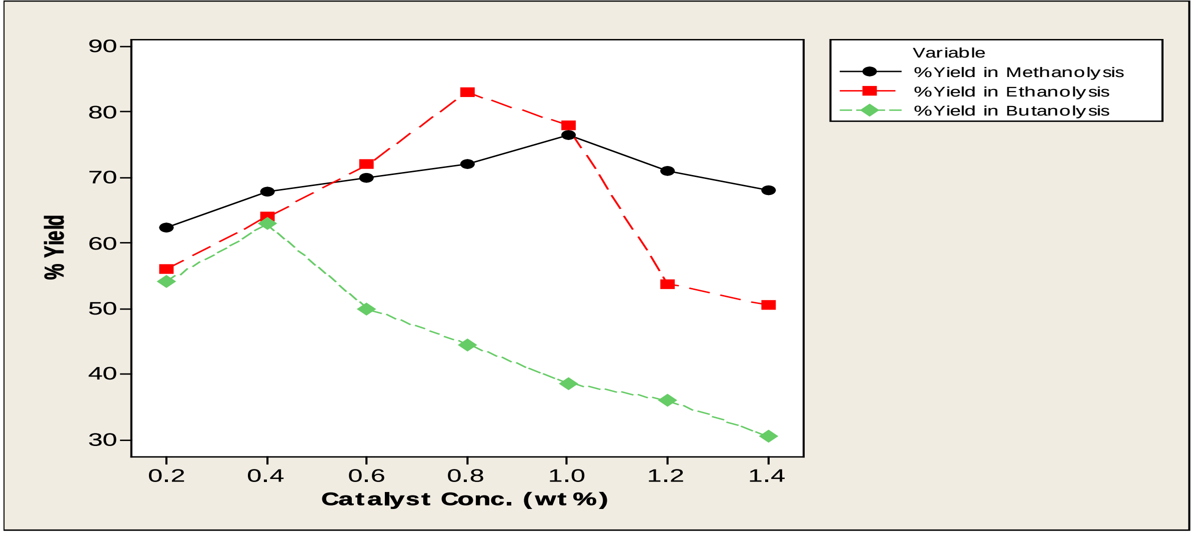


Figure 4.2: Effect of Catalyst Concentration on Biodiesel Yield

This is attributable to the formation of soap by the oil in excess of sodium hydroxide. This is in complete agreement with the findings of Vincente et al, (2007), addition of an excess amount of catalyst beyond the optimum give rise to the formation of an emulsion, increased the viscosity and led to the formation of gels and also hinders the glycerin separation resulting to dilution of ester and the ester yield tend to decrease. However, this result shows quantitative contradiction with the work of Patil, and Deng (2009) that reported an optimum of 0.5wt% for methanolysis trans-esterification of karanja oil but in agreement with the 1 wt% reported for Jatropha oil. This variation could be attributed to the proper pre-treatment given to the oil used in this study.

3.2.3 Alcohol/oil Molar Ratio.

This is due to the increase in the polarity of the reacting system. According to Lalita et al, (2004), increasing molar ratio of methanol to oil above 6:1 (the optimum value) decreased ester yield because higher amount of the alcohol interferes with the separation of glycerin due to increase in solubility and part of the glycerin remained in the biodiesel phase which in turn drive the equilibrium back to a reverse reaction.

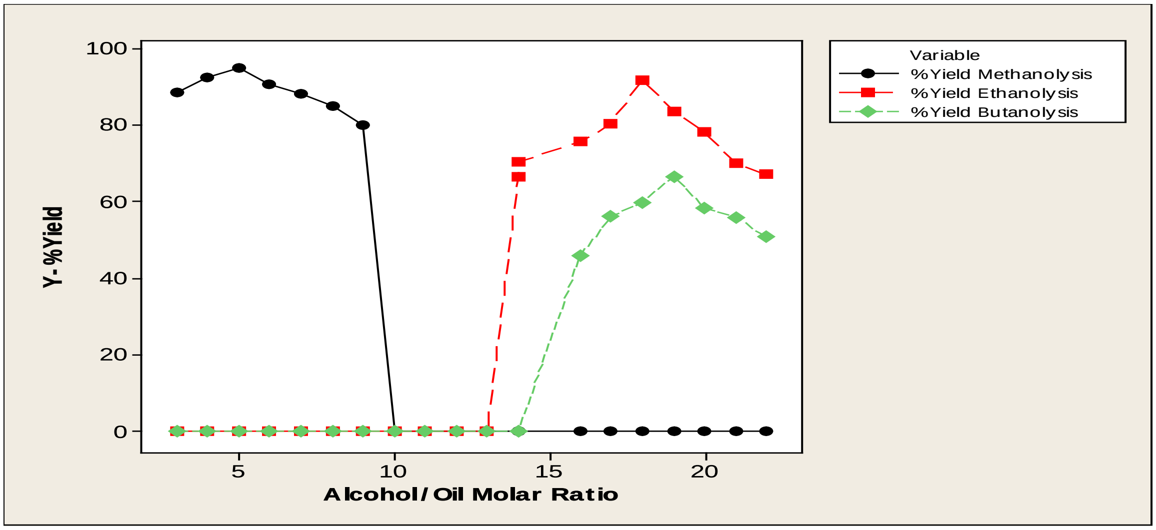


Fig. 4.3: Effect of alcohol/Oil molar ratio on biodiesel yield.

The result of this investigation shows that 6:1 was the most appropriate molar ratio for methanolysis, 18:1 for ethanolysis and 19:1 for butanolysis. This finding show appreciable consistency with the work of Zhang et al, (2003) and Moser, (2009). Therefore, increasing molar ratio of methanol to oil beyond the appropriate value for the respective alcohols (methanol, ethanol and butanol) did not really increase biodiesel yield as well as the ester content but rather complicated the ester recovery process and thereby raising the cost of the end product.

3.2.4 Reaction Temperature

Temperature is one of the important parameter for the production of biodiesel because as an endothermic process, the rate of reaction is strongly influenced by the reaction temperature. Trans-esterification of alcohol can occur at different temperatures depending on the oil used (Ma and Hanna, 1999). The effect of temperature investigated between 35^{o}C and 65^{o}C for methanol, ethanol and butanol respectively showed that the biodiesel yield increased when the temperature was increased from 35^{o}C to 55^{o}C during metanolysis, 35^{o}C to 45^{o}C during ethanolysis and 35^{o}C to 40^{o}C for butanolysi and decreased when the temperature was increased from 55^{o}C to 65^{o}C for methanolysis 45^{o}C to 65^{o}C for ethnolysis and 40^{o}C to 65^{o}C for butanolysis respectively at the respective optimal catalyst concentration and reaction time. This is attributable to the fact that at higher temperature the solubility of the reactants increases leading to difficulties in separation of the ester from the glycerol phase.

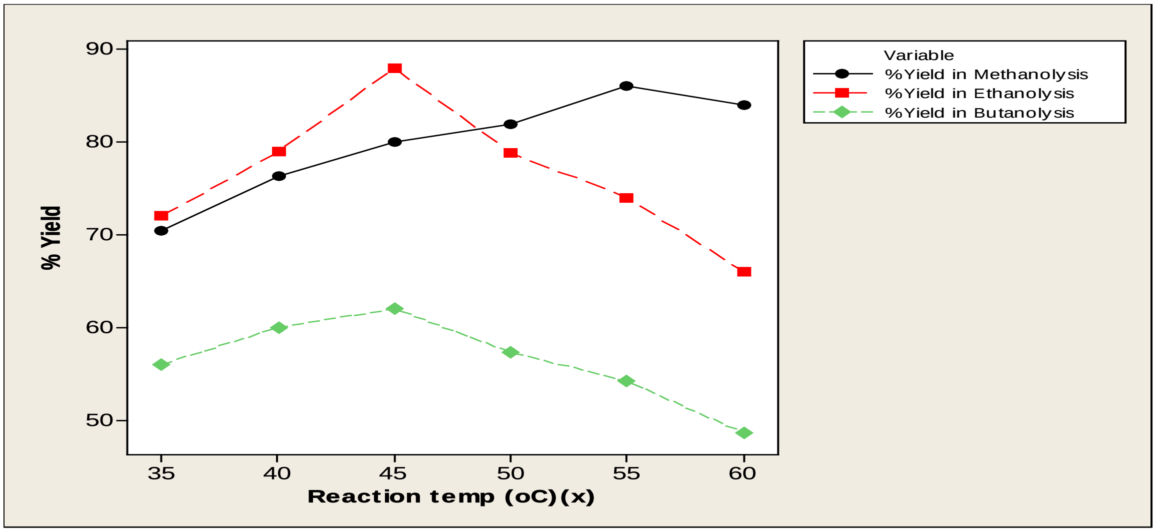


Fig. 4.4: Effect of temperature on biodiesel yield

It is important to note that trans-esterification at higher reaction temperature of 60°C that was closer to the boiling point of the alcohols, the alcohol start to evaporate during the trans-esterification process. Therefore the optimum reaction temperatures were 55°C, 45°C, and 40°C for methanolysis, ethanolysis and butanolysis respectively.

3.2.5 Agitation Speed

Mixing is of particular importance for the trans-esterification process: it ensures homogeneity within the reaction mixture. Mixing enhances interaction between the reacting species and promotes initiation of the reaction. Without mixing, the reaction would occur only at the interface of the two layers and which would be considered too slow to yield feasible result. In this study, methanolysis, ethanolysis and butanolysis were conducted at different rates of mixing, 150, 200, 250, 300 and 350 rotations per minutes (rpm).

The yield of methyl esters at different rate of mixing is as shown in Figures 4.5 were observed for methanolysis, ethanolysis and butanolysis reactions were practically incomplete at 150rpm and only exhibited yields which were too low and difficult to separate. The yield increased with increase in agitation speed between 200 to 300rpm but remained constant as the mixing rate was raised above 300rpm for all the alcohols used. Backward reaction may have been favored when mixing intensity was increased. No effect on the yield was recorded at further increase in agitation speed even though it is expected that further increase in the agitation speed favors soap formation. This implies that variations in the rate of mixing play an important role in the yield of biodiesel up to the optimal speed and further increase does not show any significant effect. On the other hand higher stirring speed favors formation of soap. This is due to the reverse behavior of trans-esterification reaction (Mathiyazhagan et al, 2011).

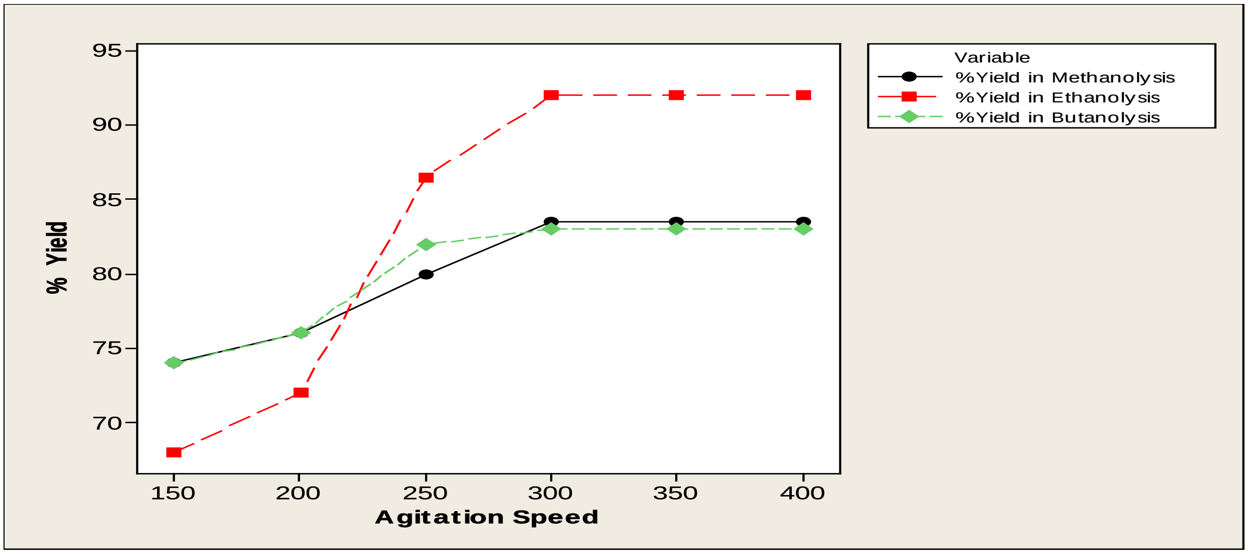


Figure 4.5: Effect of speed on biodiesel yield.

3.3 Physicochemical Properties of the Fuels

Table 1 also gives a summary of all the fuel properties analyzed and the limits that they were compared with ASTM standards).

3.3.1Density

The density was evaluated to be 867kg/m^3 at 30^{o}C which is within the ASTM standard for biodiesel. The biodiesel had a lower density compared to the Cottonseed oil (912.1 kg/m^3). The high density can impact on fuel consumption as fuel introduced into the combustion chamber is determined volumetrically.

3.3.2 Viscosity

The viscosity was 5.6cst.This value falls within the ASTM standard (1.6-6.0 cst) for biodiesel.

Viscosities of pure vegetable oils are many times higher which leads to serious problems in unmodified engines. The increase in viscosity results in poor atomization and incomplete combustion which leads to coking of injector tips. This results in engine power loss. Biodiesel still has higher viscosity than petro-diesel. Viscosity decreases with unsaturation but increases markedly with contamination by mono, di or triglycerides.

3.3.3 Flash point

The flash point of the biodiesel is 180^{o}C. This fell within the ASTM standard and makes it safe for storage. The typical flash point of pure methyl ester is >200^{o}C. Fuels with flash point falls below 130^{o}C are termed flammable and dangerous to handle and store.

3.3.4 Acid value

The product contained 0.181mgKOH/g of total acid. The ASTM value for total acid number (TAN) is 0.5mgKOH/g; this implies that the acid value of the biodiesel is acceptable as it fell within the standard. High fuel acidity is linked with corrosion and engine deposits.

3.3.5 Cetane number

The ester has a cetane number of 55, which is above the lower limit, 47 by ASTM standards. Cetane number serves as a measure of ignition quality. Fuels with low cetane numbers show an increase in emission due to incomplete combustion. Thus, the biodiesel produced is of good quality.

Conclusion

Primary treatment of cottonseed oil left it with low acid value, iodine value and saponification value that enable it undergo direct trans-esterification with methanol, ethanol and butanol respectively to achieve fatty acid methyl ester. Increase in process parameters such as reaction time, catalyst concentration, methanol/oil ratio, reaction temperature and agitation speed increased the yield of methyl ester to a reasonable point before it decreased hence their effects were found to be significant in the process. The optimum values of the parameters were reaction time of 45minutes for both methanol and ethanol and 15minutes for butanol, reaction temperature of 55^{o}C (methanol), 40^{o}C (ethanol and butanol), catalyst concentration of 1% (methanol and ethanol) and 0.5% (butanol), methanol/oil molar ratio 7:1 (methanol), 18:1 (ethanol) and 19:1 (butanol) and agitation speed of 300rpm; under these conditions the amount of methyl ester yields achieved were 82.8% (methanol), 85% (ethanol) and 75% (butanol).The density, viscosity, cetane index and higher heating values of biodiesel produced under optimized protocol in the present work meet the ASTM standard and were within the acceptable limits. Cottonseed oil was thus found to possess high potential for production of biodiesel.

REFERENCES

Aderemi, B.O., Hameed B. H. (2010)., Production of Biodiesel from Palm Oil, *Nigeria Society of Chemical Engineers Proceedings*, **40**: 135-143.

ASTM D6751-02 (1986): American Society of Testing and Materials Standard Methods Annual Book of ASTM for Biodiesel Specification. Philadephia

Amit Sarin., (2012): Biodiesel production and properties. Henry Ling Ltd Dorchester DTI IHD, UK ISBN, 971-1-84973-470-7.

ASTM D6751-02 (2002): American Society of Testing and Materials Standard Methods Annual Book of ASTM for Biodiesel Specification. Philadephia.

Attanatho L., Magmee S., Jenvanitpanjakul P(2004). , Factors Affecting the Synthesis of Biodiesel from Crude Palm Kernel Oil. “Proceedings of the Joint International Conference on Sustainable Energy and Environment (SEE)”, December 1-3, 2004. Hua Hin, Thailand; 359-361.

Demirbas, A. (2003): Biodiesel fuels from vegetable oils via catalytic and non-catalyticsupercritical alcohol transesterifications and other methods: a survey Energy Convers.Manag. 44, 2093– 3662109, 367.

Demirbas, A.(2006).: Global biofuel strategies. Energy Edu. Sci. Technol. 17, 27–63.

Deng, X., Fang, Z., Liu, Y.-H., Yu, C.-L, (2011): Production of biodiesel from jatrophaoil catalyzed by nano solid basic catalyst. Energy, homepage:www.elsevier.com/locate/energy.

Douglas, Q.S.,Ana, P.L., Maíra, M. F., David, M.F., Waldomiro, B.N., José, D. F., (2014):Evaluation and Characterization of Biodiesels Obtained Through Ethylic or Methylic Transesterification of Tryacylglicerides in Corn Oil. *AIMS Energy* 2, (2), 183-192.
Fan X., Wang X., Chen F (2011), Biodiesel Production from Crude Cottonseed Oil; An Optimization Process Using Response Surface Methodology, *The Open Fuels and Energy Science Journal*, **4**:1-8
.

Fernandes DM, Serqueira DS, Portela FM, et al. (2012) Preparation and characterization of methylic and ethylic biodiesel from cottonseed oil and effect of tert-butylhydroquinone on its oxidative stability. *Fuel* 97: 658-661.

Ghetsi G. F., De macedo J. L., Parente V. C. I., Dias J. A., Dias S.C.L,(2009) , Synthesis, Characterisation and Reactivity of Lewis Acid/Surfactant Cerium Frisdodecylsulfate Catalyst for Transesterification and Esterification Reaction, *Appl. Cat. A; Gen,* **355**: 139-147.
Kaya C., Hamamei C., Baysal A., Akba O., Erdogan S., Sayduct A (2009), Methyl Ester of Peanut *(Arachis Hypogeal L.*) Seed Oil as Potential Feedstock for Biodiesel Production, *Renewable Energy,* **34**: 1257-1260.
Leng T.y., Mohamed A. R., Bhatia S. (1999) , Catalytic Conversion of Palm Oil to Fuels and Chemicals, *Canad. J. Chem. Eng.,* **77**: 156.
Li H., Shen B., Jabalu J. C., Nchare M. (2009), Enhancing the Production of Biodiesel from Cottonseed Oil by Fixed-Fluidized Bed Catalytic Cracking, *Renewable Energy*, **34**: 1033-1039.

Lôbo IPF, Ferreira SLC, Cruz, RS. (2009) Biodiesel: Parâmetros de Qualidade e Métodos Analíticos. *Quím Nova* 32: 1596-1608.

Mathiyazhagan, M., & Ganapathi, A. (2011). Factors affecting biodiesel production. *Research in plant Biology*, *1*(2).:01-05, 2011 4

Mohammed, S.J. Atuman, E. Ugwu, A.A. Aboje (2012).Synthesis and characterization of
Moser, B. R. (2009):Biodiesel production, properties and feed stock and feed stocks,in vitro cell Dev. Biol. Plant 45, 229-266.
Muniyappa P.R., Brammer S.C., Noureddini H(1996), Improved Conversion of Plant Oils and Fats into Biodiesel and Co-product, *Bioresour. Technol*., **56**: 19 -26.
Onukwuli , D.O., Emembolu, L.N., Ude, C.N., Aliozor, S.O., Menkiti, M.C., (2017): Optimization of biodiesel production from refined cotton seed oil and its characterization. Egyptian Journal of Petroleum 26; (1), 103–110.

Orhevba, B.A., Efomah, A.N. (2012): Extraction and characterization of cottonseed (Gossypium) oil, nt. J. Basic Appl. Sci. 1(2), 398–402 .

Ramachandran K., Suganya T., Nagendra Gandhi N., Ren(2013)ganathan S. (2013), Recent Developments for Biodiesel Production by Ultrasonic Assist Transesterification Using Different Heterogeneous Catalyst: A Review, *Renewable Sustainable Energy Rev.*, **22**: 410-418.
Ude, C. N.,Onukwuli, O. D.,Ugwu, B. I.,Okey-Onyesolu, C. F., Ezidinma, T. A., Ejikeme, P. M.,(2020), Methanolysis Optimization of Cottonseed Oil to Biodiesel Using Heterogeneous Catalysts, *Iran. J. Chem. Chem. Eng. Research* **39**;(4), 355-370

Umaru, M., Aboje, A.A., Mohammed Ibrahim, A., Aliyu, A.M., Munir, S.M., Aminat Olaibi, O. (2014): The effect of process variables on the transesterification of refined cottonseed oil. Lecture Notes in Systems Biology and Bioengineering: Proceedings of the World Congress on Engineering, WCE, London. (I), pp. 622–624.

Vicente G., Martinez M., Aracil J., (2007): Optimisation of Integrate Biodiesel Production, Part I; A Study of the Biodiesel Purity and Yields, *Bioresour. Technol.*, **98**:1724-1733 Lalita et al, (2004),

Younis M. N., Saeed M. S., Khan S., Furqan M. U., Khan R. U., Saleem M (2009)., Production and Characterization of Biodiesel, from Waste and Vegetable Oils, *Journal of Quality and Technology Management*, **5**(1): 111-121.

Zhang, Y., Dube, M.A., Mclean D.D., Kates, M. (2003): Biodiesel production from waste oil via two-step catalyzed process. Energy convers manage 48, 184-188.