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Production of Biodiesel from Waste Ube Fruit Oil Using Acid-Base Catalysis

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ABSTRACT

A two step process consisting of esterification and transesterification was developed to produce biodiesel from crude waste ube fruit oil. The oil was extracted from the waste ube pulp using solvent extraction process. The free fatty acids (FFA) in the oil were converted to methyl esters in the pre-esterification step using sulphuric acid as catalyst. The FFA was reduced from 77.84% to below 1% in 2hours under 10wt% of methanol, 1wt% Sulphuric acid in oil at 60^{0}C. The yield of biodiesel by transesterification was 95.5% in 60minutes at methanol/oil ratio of 6:1 at temperature of 60^{0}C, KOH catalyst ratio of 1% and reaction time of 60minutes.

Keywords: Ube, Biodiesel, Dacryodes Eduli, Esterification, Transesterification, Acid-base Catalysis.

1.0 INTRODUCTION

The need for increased use of renewable energies has led to the investigation of non-ediblel oil producing crops, most of which have been discovered in the tropical regions of Africa that have potential for use as biofuel feed stocks. Oil seeds such as Jatropha, cotton, soy beans, palm kernel and rice bran has been proposed as potential sources of oil for biodiesel production. The high cost of edible seeds as well as the pressure on food availability made the use of palm kernel, soy beans and cotton seeds less attractive as potential raw materials for biodiesel. A promising example of a potential oil fruit that is yet to be exploited commercially is the Dacryodes edulis fruit (Ube fruit). The ube tree is predominantly found in West Africa and it is commonly known as Ube in the South Eastern part of Nigeria where it is grown in much abandon and primarily cultivated as a food source usually consumed with roasted or boiled corn.

Ube was selected for research and domestication by the World Ago Forestry Centre (ICRAF) in the early 1990s [1]. Since that time research has been initiated to characterize the fruit's chemical, nutritional and market potential as well as the tree's agro-forestry potential. The fruit oil content in particular, has drawn significant attention. The fruit crop from Dacryodes edulis is estimated to yield more oil than commercialized oil crops like coconut and oil palm [2].

The loss of the fruit crop en route the market have been estimated as high as 50% due to harvest, post-harvest handling, and the fruit's inherently short shelf life in tropical climates makes it difficult to be commercialized [3]. Its lipid content and possible annual production rate have general serious consideration by members of the food cosmetics and fuel industries [4]. The present yield capacity of trees Ube can produce as much oil as the cultivated oil palm which has enjoyed a century of selective breeding (National Research Council, 2008). This amounts to 4-6 tons/ha. However, it has been reported that some tree strains have the potential to produce 10-15 t/ha, assuming organized cultivation and ideal growing conditions. This is more than twice the volume of which the cultivated oil palm is capable. Unlike the oil palm, where pulp and kernel have significantly different oil, the oil present in the pulp and kernel of the Ube fruit is very similar. This characteristic has the potential to make harvesting the oil simpler and consequently more economical [5].

The fruit's food potential has been extensively investigated and the oil's lipid characteristics have identified it as a potential raw material for cosmetics, but little has been done as regards its use as a source of raw materials for biodiesel. Ube which is largely considered as a food crop in South Eastern part of Nigeria has a large post-harvest loss rate (40-50%). This reinforces the need to explore the potential recuperation of the loss by processing an otherwise spoilt food product into two marketable products, oil and press cake. Though these products might not be good for human consumption, the oil may be used for cosmetics and fuel while the cake used as feed for livestock. The conversion of the oil to fuel can however cushion the heavy loss incurred by the farmers as a result of the damages and as well as increase food security in the South Eastern part of Nigeria where Ube is prolific. While there is potential for the recovery of post-harvest losses through oil extraction and fuel production, such a path is contingent on basic issues of biofuel viability regarding energy balance and fuel characteristics.

The purpose of this research is to investigate the viability of Ube as a biodiesel feedstock in terms of its fuel characteristics. The extracted oil's characteristics shall be examined to determine its suitability for use as a biodiesel feedstock as well as the fuel's pre-combustion and combustion characteristics such as cloud point, gel/pour point, lubricity, viscosity and flash point help to define the fuel.

2.0 EXPERIMENTAL PROCEDURE

2.1 Materials

The waste ube fruit was picked from the ube plantation in Uga in Aguata Local Government Area of Anambra State South East Nigeria. The partly spoilt fruit was further allowed to detoriorate for ten days while stored in a sack. The waste fruits was screened and sun dried for five days after which it was grinded using the traditional corona grinding machine. The grounded particles was screened using 100µ mesh and then dried using the microwave. The oil was extracted using solvent extraction method with n-hexane as the solvent. The FFA content of the crude oil was analysed after the phospholids was removed through degumming with Phosphoric acid and water. The chemical reagents used were of analytical grade without further purification.

2.2 Esterification Process

Esterification was conducted in a 250ml two neck flask. The flask was equiped with a reflux condenser and heated with magnetic stirrer to control its temperature and speed of agitation. The flask loaded with obe oil and speed of agitation. The flask loaded with ube oil sample was firstly heated to 60^0C after which the methanol and sulphuric acid mixture was added. The reaction was continously agitated at 300rpm for two hours. The products were separated using a separating funnel to obtain the upper layer which was then washed with water several times until the pH of 7 was obtained. The resultant esterified oil was dried using anhydrous magnesium silicate.

2.3. **Transesterification Process**

Transesterification experiments were carried out under atmospheric pressure using 1wt% KOH as the catalyst, methanol/oil ratio of 6:1 at temperature of 50^0C and time of 60 minutes. The reactor and the process were similar to those at esterification. The products were fatty acid methyl ester (FAME) and glycerol was washed with water to remove soap and catalyst before drying

2.4 **Analytical Method**

The composition of the reaction mixture samples were determined by a thin layer chromatography equipped with flame ionization detector (TLC-FID) using an itronscan mk-6s with chromarods type S-111 quartz rod (mitsubishi kayaku). The free fatty acid content was determined by neutralization using 0.1mole NAOH, while the fuel characteristics of the biodiesel was obtained using ASTM standards. The influence of temperature, molar ratio catalyst concentration and reaction time were analyzed using 2^4 factorial design of the Response Surface Methodology.

3.0 EXPERIMENTAL RESULT

The stirring speed was kept constant at 250rpm throughout the experiments. The reaction temperature was varied from 55^0C to 60^oC . the molar ratio of methanol varied from 3:1 to 6:1 the catalyst amount was varied from 0.5% to 1.5%(W_c/W_{oil}) and the process time was varied from 45 minutes to 60 minutes.

Sets of 16 experiments were performed with different combination of molar ratio and catalyst concentration reaction time and temperature. The effect of molar ratio and catalyst on methyl ester yield was evaluated during these experiments. After the exhaustive experiments, combination of optimum values of molar ratio and catalyst concentration of optimum molar ratio and catalyst concentration was evaluated on the basis of maximum percentage yield. Subsequently, transesterification reaction was carried out using optimum value of molar ratio and catalyst concentration keeping temperature constant at 55^0C and reaction time, till the reaction was completed at 60 minutes. Thereafter, four transesterification reactions were carried out using optimum values of molar ratio, catalyst concentration and reaction time at different temperatures ranging from 45^0C to 60^0C with an increment of 5^0C. The results obtained from the experiments are as tabulated below.

Table 1 Experimental Result

Std	Run	Factor1 (A) Molar Ratio	Factor2 (B) Catalyst %	Factor3 (C) Temp (^{0}C)	Factor4 (D) Time (min)	Response 1 Yield (%)
1	2	3:1	0.5	50	50	87.65
2	12	6:1	0.5	50	50	96.86
3	6	3:1	1.5	50	50	90.76
4	15	6:1	1.5	50	50	95.12
5	8	3:1	0.5	60	50	85.87
6	1	6:1	0.5	60	50	91.24
7	11	3:1	1.5	60	50	90.67
8.	7	6:1	1.5	60	50	93.05
9.	4	3:1	0.5	50	60	93.23
10	13	6:1	0.5	50	60	96.45
11	3	3:1	1.5	50	60	92.45
12	9	6:1	1.5	50	60	95.86
13	10	3:1	0.5	60	60	89.54
14	5	6:1	0.5	60	60	94.08
15	14	3:1	1.5	60	60	91.23
16	16	6:1	1.5	60	60	92.54

3.1 Esterification Reaction

The aim of the esterification reaction was to reduce the high concentration of the free fatty acid from 77.84% to less than 1% in the presence of acid catalyst. FFAs react with methanol to form fatty acid methyl ester (FAME) and can be represented as:

FFA + Methanol = FAME + Water (1)

The rate of conversion of triglycerides was much slower compared to that of FFAs in the presence of methanol. The conversion of FFA was measured by comparison of the acid values before and after the reaction. The Free fatty acid profile of the crude ube oil was analyzed prior to the esterification reaction and result as shown in table1 below. The amount of catalyst used was 1.9g H_2SO_4 per 100g oil. The result as obtained from the analysis revealed that the FFA was reduced to less than 0.5% in 2hours. The esterification process was enhanced by the addition of more methanol to favour the forward reaction since the process is reversible.

The essence of esterification reaction was to reduce the very high FFAof the oil (higher than 14.1% reported by Omoti and Okiy (1987). This was as a result of the rancidity of the oil caused by the degree of biodegradation occassioned by the degree of wastage. The high FFA of the oil makes it impossible for transesterification of the oil to take place directly.

Table 2. Free Fatty Acid Profile ofUbe Oil

Properties	Value
Free fatty acid (%)	77.84
Peroxide value (mg/kg)	30
Methyl Stearate C18	7.2186
Linoleic Acid C18:2	1.3837
Magaric Acid C17	0.5727
Lauric Acid C12	40.964
Palmitoleate C16:2	19.211
Palmitic Acid C16	3.2436

Myristste C14	25.216
Behenic Acid C20	2.1885
Monoglyceride	21.628
Diglyceride	10.599
Triglyceride	15.727

3.1 Transesterification Process

The esterification process assisted in converting the FFA to methyl ester but the reaction is very slow and may take days to go into completion since the triglyceride conversion is very slowly under acid catalysis. Therefore, in order to speed up the rate of conversion of the triglycerides, transesterification was introduced using KOH as catalyst. The transesterification process is represented as

Triglyceride(oil) + Methanol = FAME + Glycerol (2)

The yield of FAME was influenced by a number of factors ranging from methanol/oil ratio, temperature, catalyst concentration and reaction time, their influence is discussed as follows:

3.1.1 Influence of the methanol:ube oil molar ratio

The methanol/ube oil molar ratio has a positive influence on the biodiesel yield response. The plot of the interaction between molar ratio and temperature as shown in figs 1,and 2 revealed that at Catalyst concentration of 1%, the yield is highest (95%) at the temperature of 50^{o}C and molar ratio of 6:1. For this reason, an increase in this variable modify the response significantly.

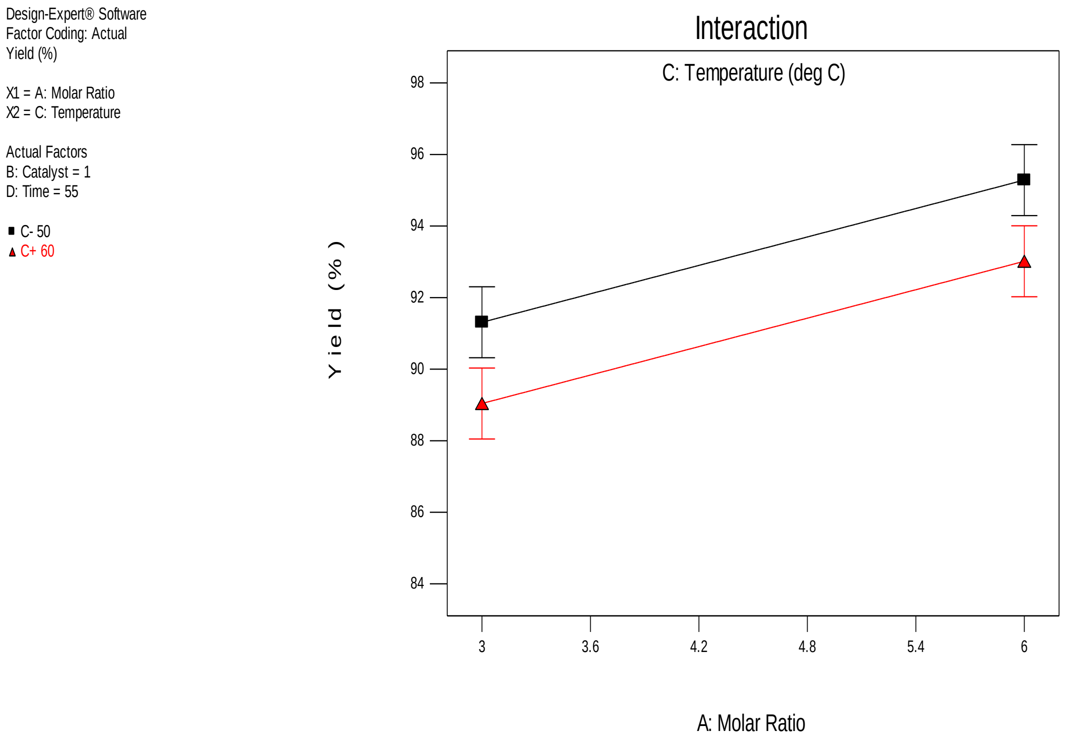

Fig. 1: Interaction of Molar Ratio (Methanol to Oil) and Temperature on Yield.

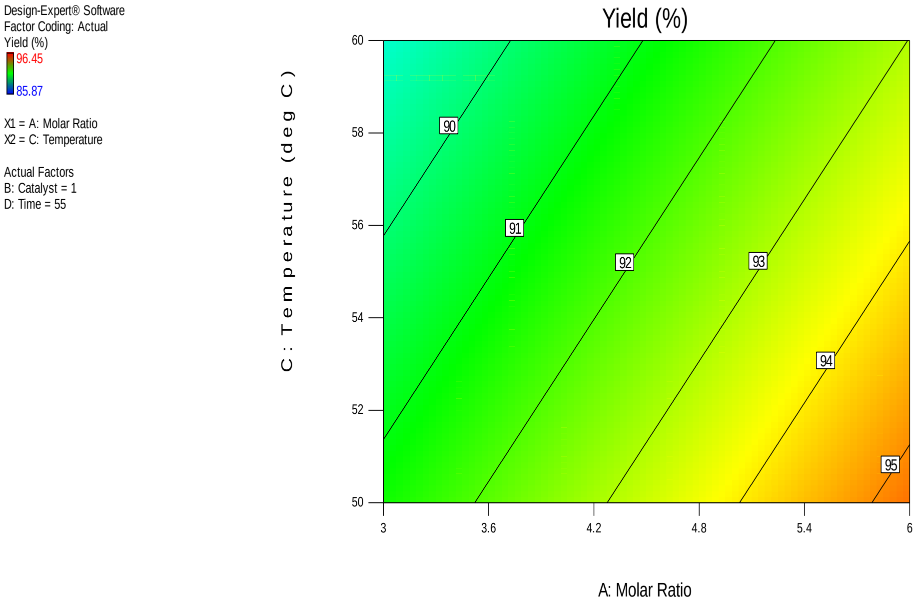

Fig. 2: Contour Plot of Interaction between Molar Ratio and Temperature on Yield.

3.1.2 Influence of temperature

The second factor of importance is the temperature, having a negative influence on the biodiesel yield. The effect of temperature on the material balance responses is the same as for the catalyst concentration in the sense that they both decreases yield as they are increased. The biodiesel molar yield also decreases with the temperature due to the increase of triglyceride saponification and the subsequent dissolution of methyl ester into glycerol. In the same way, both yield losses follow a similar tendency since the increase in triglyceride saponification means an increase in the methyl ester solubility in glycerol. From figs 3, and 4 it could be seen that the yield is highest at the temperature of 50^{o}C (96%) with catalyst concentration of 1% and molar ratio of 6:1.

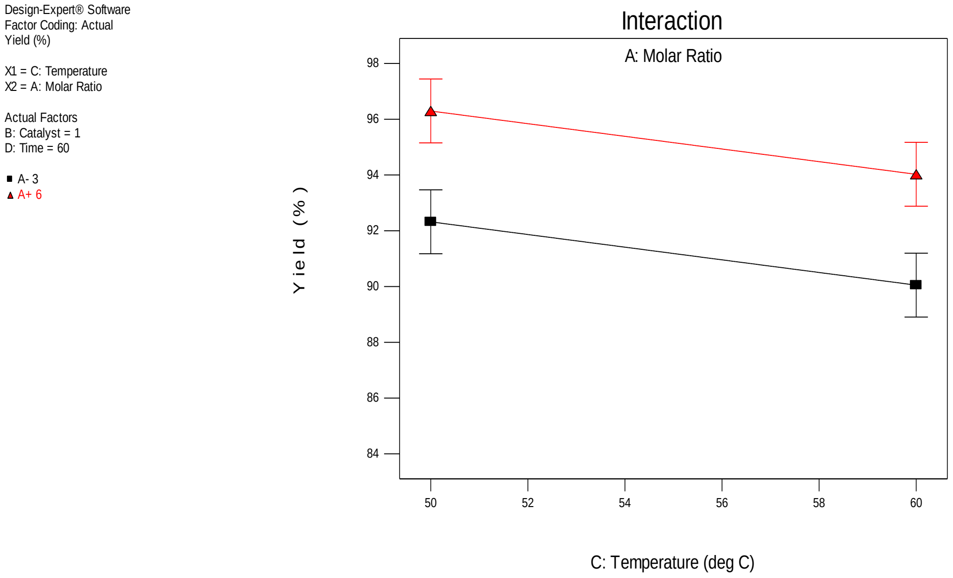

Fig. 3: Plot of interaction between Temperature and Molar Ratio on Yield.

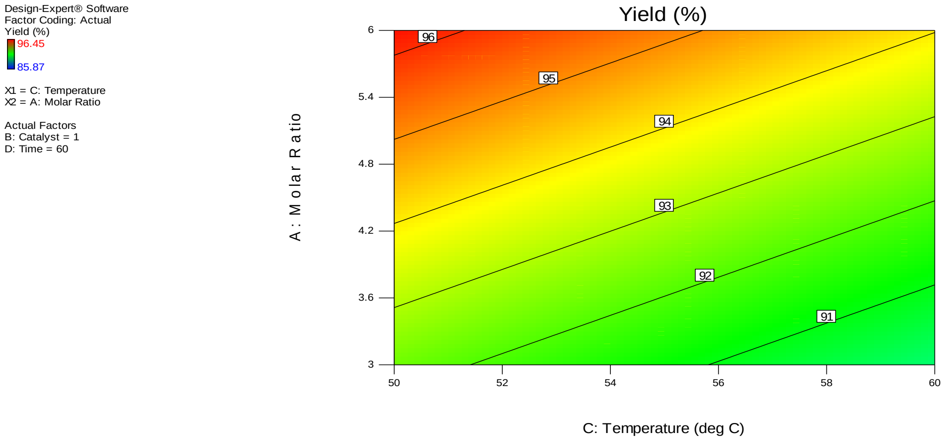

Fig 4: Contour Plot of Interaction between Temperature and Molar Ratio on Yield.

3.1.3 Influence of Time (Ti)

The third factor of importance is the time, having a positive influence on the biodiesel yield. The effect of time on the material balance responses is the same as for the molar ratio since both of factors increases yield as they are increased. The biodiesel molar yield also increases with the time. From figs 5 and 6 it could be seen that the yield is highest at the time of 60 (94%) with catalyst concentration of 1%, temperature of 55^{0}C and molar ratio of 6:1.

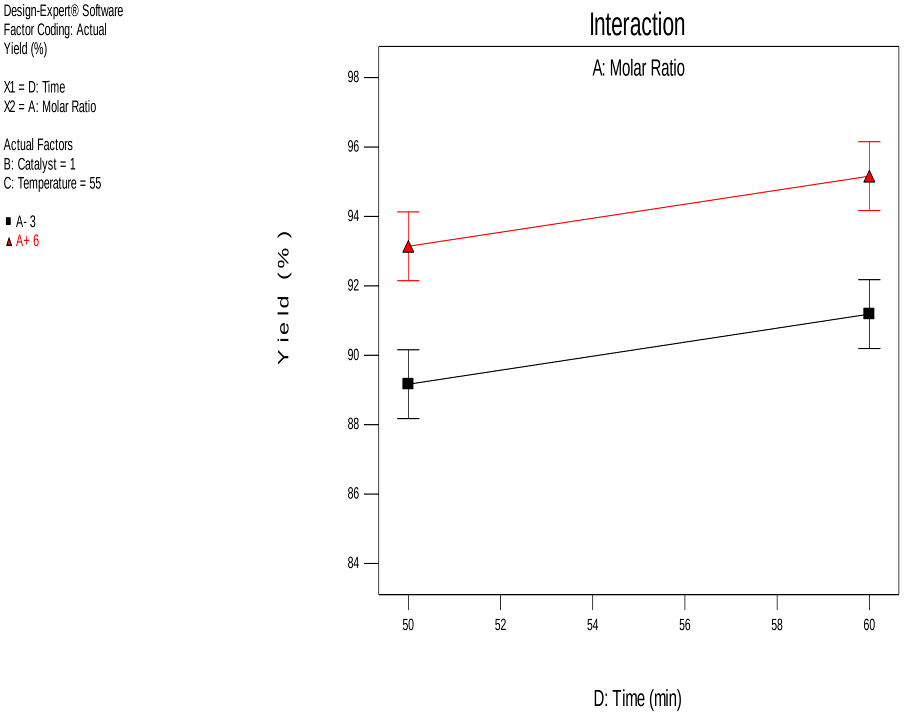

Fig. 5: Plot of Interaction between Molar Ratio and Time on Yield.

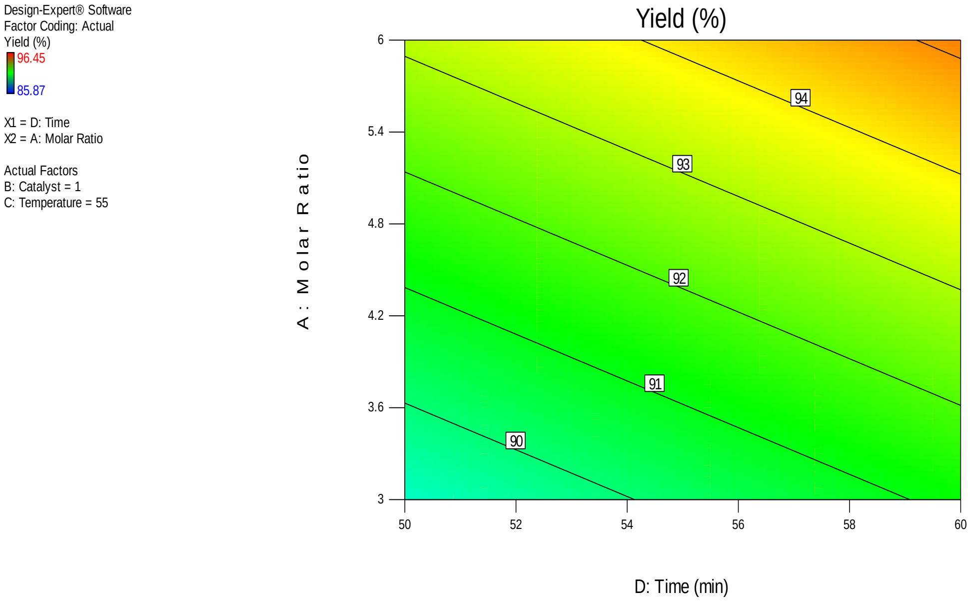

Fig 6: Contour plot of the Effect of Time and Molar ratio on Yield.

3.1.4 Influence of Catalyst Concentration

The statistical models show that for the experimental range, catalyst concentration is the least significant factor in the biodiesel process using esterification and transesterification process, Infact it is not in the model . This could be explained because the very high FFA concentration of the oil (77.86%) has been reduced to less than 0.5% with the esterification reaction. The catalyst did not partake in the reaction to form soap through saponification so as to have influence on the yield losses due to triglyceride saponification and methyl ester dissolution in glycerol. Both yield losses follow a similar negative tendency if only transesterification reaction was done. The contour plot (fig 11) reveals that 95% yield will be achieved at catalyst concntration of 1% molar ratio of 5.8:1 and temperature 0f 55^{o}C. The combination of esterification and transesterification seems to be very effective in the sense that it reduced the yield loss to saponification due to high FFA which would have been reduced by neutralization of the oil.

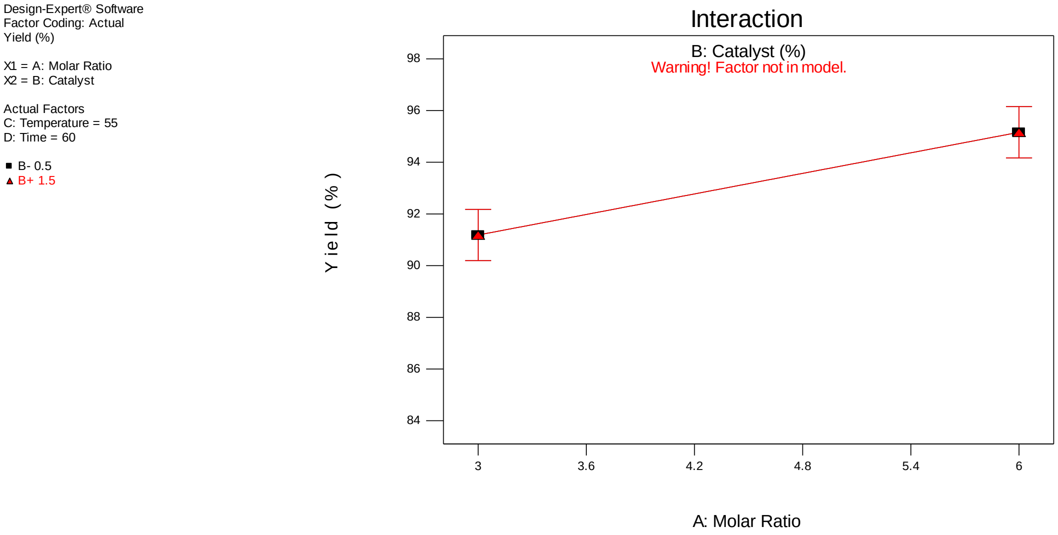

Fig 7: Plot of Interaction between Catalyst Concentration and Molar Ratio on Yield.

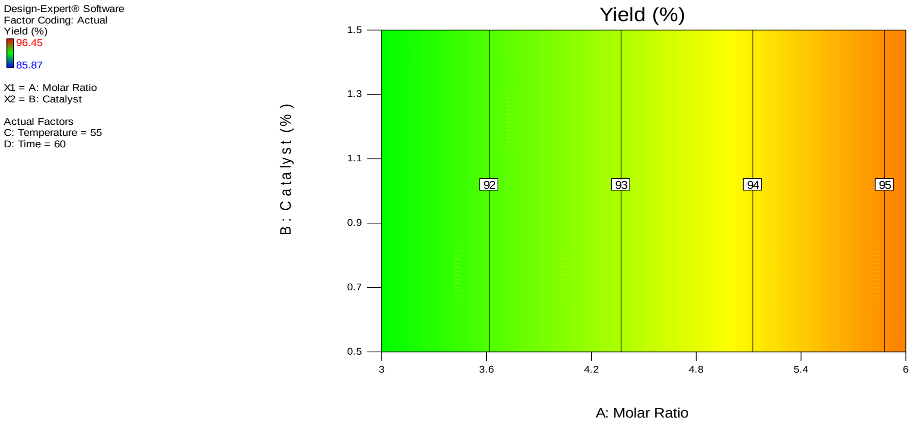

Fig 8: Contour plot of Interaction between Molar Ratio and Catalyst Conc. on Yield.

3.1.5 Analysis of responses

The shapes of the three-dimensional surfaces and contour plots are shown in Figs. 1-8. These graphs represent the material balance responses – the biodiesel yield - versus temperature and molar ratio at 1% catalyst concentration and time 0f 60 minutes. The graphs in Figs. 1, 2, 5 and 6 have the same shape, since yield followed the same tendency. However, the graphs in Figs. 3, 4 and 7 have just the opposite shape to graphs 1,2,5 and 6 because the biodiesel yield followed the opposite trend to the yield losses. The maximum biodiesel yield is obtained at low temperatures, catalyst concentrations of 1% and molar ratio of 6:1.

4.0 PURITY OF BIODIESEL

The biodiesel obtained was analysed using Gas Chromatography to determine the percentage purity of the FAME produced. The purity of FAME means the total fatty acid methyl ester concentration (%wt) in the FAME phase. Fatty acid methyl esters were identified by Gas Chromatography (GC). This method also allows for the identification of monoglyceride, diglyceride, triglyceride and free fatty acids. The software UN-SCAN IT gel 6.1 (Silk Scientific, Inc., USA) was used to quantify all these compounds. The purity of FAME was obtained to be 65%.

4.1 OPTIMIZATION OF THE PROCESS

The process was optimized using the numerical optimization system provided by the Design Expert 9 software by simulating up to 100 process parameters of mole ratio, temperature, time and concentration to generate the optimum conditions as shown in the fig 9. the optimum conditions that gave the highest yield of 96.25% is molar ratio of 6:1, catalyst concentration of 1%, temperature of 55ºC and time of 60 minutes.

The optimum conditions were confirmed by runing four experiments using the optimum parameters at confidence level of 95% to obtain a data mean of 95.51% which confirms the optimum conditions that was predicted in the fig 9.

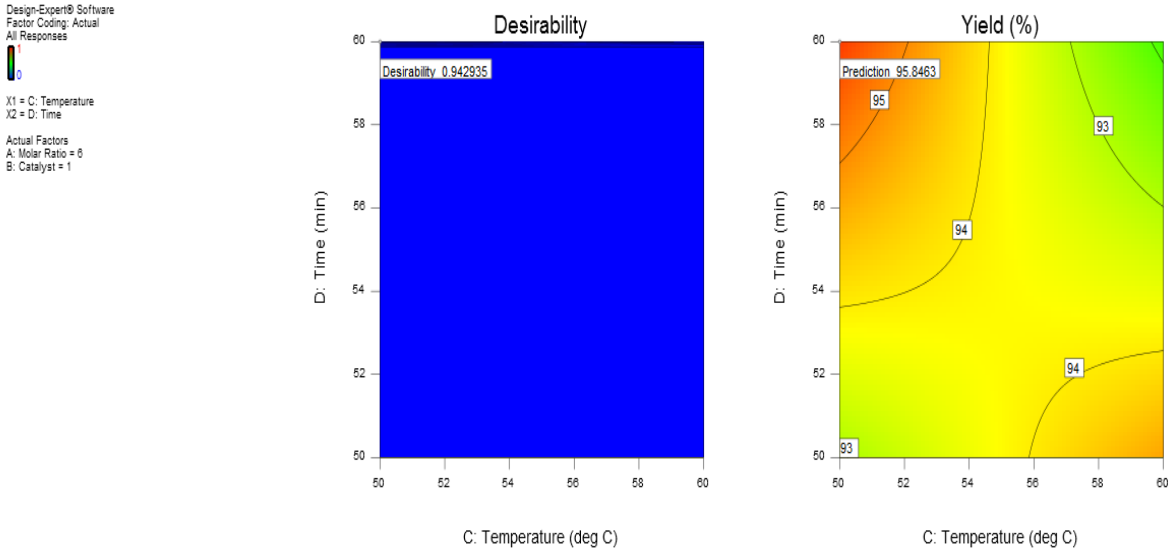

Fig. 9 Contour plot of the optimum Conditions

4.2 BIODIESEL CHARACTERIZATION AND COMPARISON WITH PETROLEUM DIESEL.

The physico-chemical properties of the ube Oil Methyl Ester and the petroleum diesel were determined as per standard test procedures is as shown in Table 2. The properties were evaluated at Energy Resource Laboratory University of Nigeria Nsukka and Springboard Laboratory Awka. Cetane Number is a very important characteristic of a biodiesel, Standard gasoline uses a rating system of octane numbers to measure its efficiency. In a similar manner, diesel uses cetane numbers as a measurement of how well it combusts. However, there is a significant difference in what exactly these two ratings measure. For gasoline, the octane number measures how well the substance will resist spontaneously combusting at average temperatures without a helper ignition source. This is known as *auto-ignition*. Comparatively, the cetane number (or CN for short) tests how long the diesel delays its ignition time after the fuel enters the combustion chamber.

Since diesel works with compression instead of a flame or spark, it is most effective when it ignites as quickly as possible. If it has a high cetane number, this means that the delay period is relatively short. In this case, the short delay period allows the diesel to burn more completely. In turn, it helps the vehicle's engine to run more smoothly and powerfully while producing less emissions. Diesel that takes a longer time to ignite does not work as efficiently. Keep in mind that the cetane number is mostly used for lighter diesel fuels. The efficiency of heavier diesel is measured using a couple of other ratings called the CII and CCAI. The cetane Number of FAME for this experiment was evaluated using the properties of density, fire point and kinematic Viscosity and Higher Heating Value with the formular as obtained from the literature [6] (K.Sivaramakrishnan and P. RaviKumar 2012). The Cetane number obtained was 76.94 which is higher than the minimum standard for biodiesel which is 55 for B100 blend. This result obtained reveals that the FAME is of good quality and will combust completely.

Calorific value is an important property measuring the energy content of the fuel suggest it's suitability as an alternative to petroleum diesel. The calorific value of FAME was measured using parr 6100 calorimeter and was found to be 42.06MJ/Kg as against 44.34MJ/Kg which is 94.86% of the calorific value of diesel. The lower calorific value of FAME is attributed to the presence of oxygen in the ester. The flash point and fire point were determined with the help of a closed cup Pensky Marten's apparatus. The flash point represents the tendency of a fuel to form flammable mixtures when exposed to air. This parameter is essential in the handling storage and safety of the fuels. The high flash points in the case of FAME make it safer to handle. Specific gravity was measured with Anton Paar DMA 4500 density meter was comparable to petroleum diesel. Kinematic viscosity was also determined using petro diesel viscobath. It can be seen from physic-chemical characterization that FAME is very close to petroleum diesel in properties.

Table 2: Fuel Properties Ube Oil, FAME & Diesel.

Properties	Fossil diesel	Ube Oil	FAME	Biodiesel standard
Flash point	70^{0C}	318	180^{0C}	170^{0C}
Fire point	78^{0C}	334	187^{0C}	197^{0C}
Pour point	-6^{0C}	2^{0C}	-3^{0C}	-2
Viscosity	5^{CCT}	103.2	2.9^{cst}	7.78^{cst}
Specific gravity	0.841	0.922	0.945	0.875
Refractive index	1.32	1.423	1.4394	1.38
Calorific value	44.34	38.61	34.03	42.06
Cetane Number	48		76.94	>47

From the table above it can be seen that ube oil methyl ester (FAME) is slightly higher in values than the fossil diesel. The table also revealed that the specific gravity reduced after transesterification reaction viscosity also reduced drastically with calorific value increasing and very close to the fossil fuel. The characterization of the ube oil placed side by side with the biodiesel (Jathropa oil) value obtained from the literature revealed that ube oil biodiesel has properties with ranges close to the Standard biodiesel parameters as obtained from the literature and is closer to the fossil fuel than that of the Jathropa oil. Flash point and fire point are important temperature specified for safety during transport storage and handling. The flash point and fire point of FAME was found to have decreased after transesterification when compared to original vegetable oils, which shows that its volatility had improved and it is also easy to handle.

CONCLUSION

A two step process was developed to produce biodiesel from waste ube oil. The FFA in the crude ube oil were converted to methyl esters in the esterification catalyzed by H_2SO_4 before transesterification catalyzed by KOH. The FFA content was lowered from 77.84% to less than 1% in 2hours at 60^0C at catalyst concentration of 10% by weight of methanol. The yield of biodiesel by transesterification was higher than 95% in 60 minutes of reaction time using 1% KOH as catalyst and a molar ratio of methanol to oil of 6:1 at 55^0C. The characterization of the biodiesel produced revealed that production of biodiesel from waste ube oil is feasible.

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