

# Transesterification reaction between locally produced ethanol (Ogogoro wine) and the oil of peanut (Arachis hypogea) catalysed by potassium hydroxide from cassava peels yields an independent fuel that competes favorably with petrodiesel . Makurdi Benue State Nigeria

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## Abstract

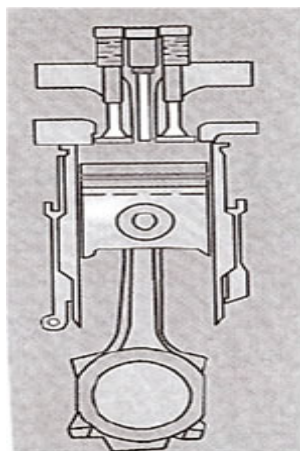
With a starting laboratory temperature condition of about 300c the oil of peanut *Arachis hypogea* which is primarily made up of fatty acids like oleic acid (46.8% as olein), linoleic acid (33.4% as linolein), and palmitic acid (10.0% as palmitin) produced in Makurdi Benue and neighbouring States in Nigeria was reacted with locally produced ethanol (ogogoro) and with potassium hydroxide as catalyst according to ASTM D 6751 method . The new ester was completely insoluble in water , also showed a specific gravity  $g/cm^3$  0.94 compared to petrodiesel 0.859 Latent boiling temperature of 57oc compared to petrodiesel 90 oC , Smoke point 185 oC compared to petrodiesel of 52 oC , Flash Point 190 oC, compared to petrodiesel of 67 oC , an Acid Value of  $Mg/KOH/g$  0.94 compared to 0.281 of petrodiesel and percentage yield was 91 oC compared to petrodiesel of 70 oC . These results show the combustibility condition of the new ester competing favorably with petro diesel which has extra disadvantaged characteristics ( not treated in the scope of this article ) that even reduces its potency.The attainable local materials like peanut oil ,ethanol ( ogogoro) and potassium hydroxide also locally sourced give great hope for encouragement in large scale farming and reduction on emphasis on petro diesel .

**Key words** Combustible , Flash Point ,Glycerol , Petroleum Diesel , Transesterification

## 1 INTRODUCTION

Fuel generates heat and powers engines, may also be used to generate electricity and can be made from organic material produced by living things . Fossil fuels such as coal, petroleum, natural gas come from long-dead plants and microorganisms but the main purpose of fuel is to store energy, which should be in a stable form and that can be easily transported to the place of use . Biofuels are animal fats or vegetable oils and other renewable resources that come from animals like pork and whale , plants such as jatropha, soybean, sunflowers, corn, olive, peanut, palm, coconut, safflower, canola, sesame and cottonseed. Once these fats or oils are filtered from their hydrocarbons and then combined with alcohol like ethanol biodiesel is produced in this chemical reaction. According to *Anyasor et al. (2009)* peanut oil has a high smoke point relative to many other cooking oils, so is commonly used for frying . Heating the oil produces free fatty acids and above the temperature of the smoke point is the flash point, the point at which the vapours from the oil can first ignite when mixed with air. From literature other raw materials can either be mixed with pure diesel to make various proportions, or used alone. Biodiesel will release smaller number of pollutants (carbon monoxide particulates and hydrocarbons) than conventional diesel, because biodiesel burns both cleanly and more efficiently. Even with regular diesel's reduced quantity of sulfur from the ULSD (ultra-low sulfur diesel) invention, biodiesel exceeds those levels because it is sulfur-free. Ayhan Demirbas (2008). Methanol and ethanol fuel are primary sources of energy; they are convenient fuels for storing and transporting energy. These alcohols can be used in internal combustion engines as alternative fuels. Butanol has another advantage: it is the only alcohol-based motor fuel that can be transported readily by existing petroleum-product pipeline networks, instead of only by tanker trucks and railroad cars According to "The UK oil industry over the past 100 years" ( March 2007. p. 5.) diesel fuel originated from experiments conducted by German scientist and inventor Rudolf Diesel for his compression-ignition engine he invented in 1892. Diesel originally designed his engine to use coal dust as fuel, and experimented with other fuels including vegetable oils such as peanut oil, which was used to power the engines which he exhibited at the 1900 Paris Exposition and the 1911 World's Fair in Paris. Diesel fuel produces power in an engine when it is atomized and mixed with air in the combustion chamber. Pressure caused by the piston rising in the cylinder causes a rapid temperature increase. When fuel is injected, the fuel/air mixture ignites and

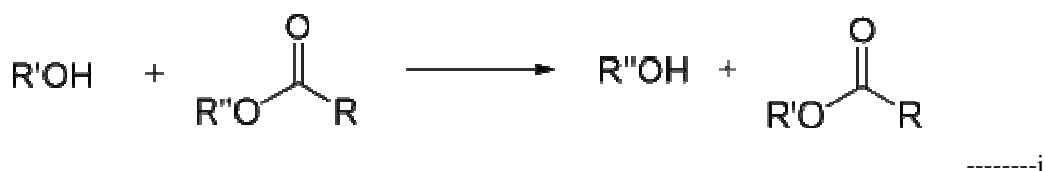
the energy of the diesel fuel is released forcing the piston downwards and turning the crankshaft as indicated in the Diagram below.



\*Courtesy of Chevron Corporation

## 2.1 Transesterification

Transesterification is the process of exchanging the organic group R'' of an ester with the organic group R' of an alcohol. These reactions are often catalyzed by the addition of an acid or base catalyst.



Transesterification: alcohol + ester → different alcohol + different ester

Bases catalyse the reaction by removing a proton from the alcohol, thus making it more nucleophilic. Esters with larger alkoxy groups can be made from methyl or ethyl esters in high purity by heating the mixture of ester, acid/base, and large alcohol and evaporating the small alcohol to drive equilibrium.

## 2.2 Base catalyzed trans esterification mechanism.

The transesterification reaction is base catalyzed. Any strong base capable of deprotonating the alcohol will do (NaOH and KOH) and are chosen for their low cost.

In the trans esterification mechanism, the carbonyl carbon of the starting ester (RCOOR<sup>1</sup>) undergoes nucleophilic attack by the incoming alkoxide (R<sup>2</sup>O<sup>-</sup>) to give a tetrahedral intermediate which either reverts to the starting material, or proceeds to the trans esterified products (RCOOR<sup>2</sup>). The various species exists in equilibrium, and the product distribution depends on the relative energies of the reactant and product.

### **2.3 Similarities Between Biodiesel and Petroleum Diesel.**

They are all mixture of hydrocarbons carbon chains with hydrogens bonded to the carbons. They are all liquids, flammable, lighter than water, and have negative health effects on humans. Combustion of any of them releases about 19,000 BTUS per pound of fuel and about 3 pounds of carbon dioxide (a greenhouse gas) per pound of fuel burned. (Fernado et al, 2007).

### **2.4 Melt or Pour Point**

This refers to the temperature at which the oil in solid form starts to melt or pour. In cases where the temperatures fall below the melt point, the entire fuel system including all fuel lines and fuel tank will need to be heated.

### **2.5 Cloud point**

The temperature at which an oil starts to solidify is known as the cloud point (Engineers, 2015) an engine at temperatures below an oil's cloud point, heating will be necessary in order to avoid waxing of the fuel.

### **2.6 Flash point**

The flash point temperature of diesel fuel is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source. (ILPI, 2015) flash point varies inversely with the fuel's volatility. Minimum flash point temperatures are required for proper safety and handling of diesel fuel.

### **2.7 Iodine Value**

This is the amount of iodine, measured in grams, absorbed by 100 grams of a given oil. Iodine value is commonly used as a measure of the chemical stability properties of different biodiesel fuels against such oxidation as described above.

Iodine value is determined by measuring the number of double bond positions. Thus a higher IV number indicates a higher quantity of double bonds in the sample, greater potential to polymerize and hence lesser stability.

### **2.8 Viscosity**

Refers to the thickness of the oil, and is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified size. Viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Diesel fuels with high viscosity tend to form larger droplets on injection which can cause poor combustion, increased exhaust smoke and emissions.

### **2.9 Cetane number**

This is a relative measure of the interval between the beginning of injection and auto ignition of the fuel. The higher the cetane number, the shorter the delay interval and the greater its combustibility. Fuels with low cetane numbers will result in difficult starting, noise and exhaust smoke. In general, diesel engines will operate better on fuels with cetane numbers above 50.

## 2.10 Density

Is the weight per unit volume. Oils that are denser contain more energy. E.g petrol and diesel fuels give comparable energy by weight, but diesel is denser and hence gives more energy per litre.

## 2.11 Ash percentage

Ash content is a measure of the amount of metals contained in the fuels. High concentrations of these materials can cause injector tip plugging, combustion deposits and injection system wear. The ash content is important for the heating values, as heating value decreases with increasing ash content.

Ash content for biofuels is typically lower than for most coals, and sulphur content is much lower than for many fossil fuels. Unlike coal ash, which may contain toxic metals and other trace contaminants, biomass ash may be used as a soil amendment to help replenish nutrient removed by harvest.

## 2.12 Smoke Point

The smoke point of an oil or fat is the temperature at which under defined conditions, enough volatile compounds emerge when a bluish smoke becomes clearly visible from the oil. At this temperature, volatile compounds such as free fatty acids, and short-chain degradation products of oxidation come up from the oil. These volatile compounds degrade in air to give soot. The smoke point indicates the temperature limit up to which that oil can be used.

## 3.0 METHODOLOGY

### 3.1 EXTRACTION OF PEANUT OIL FROM PEANUT

Having succeeded in getting the peanut and clearing out and picking out the dirt in order for the taste and colour not to be affected, also the purity. A pre-blanching process was carried out under low heat in order to rupture the oil cells and also to make it easy to remove the husk. Next the winning process was carried out. This was achieved by robing within the palms in order to remove the back coat. The coat was then winnowed from the seed. The seed was taken to the mill for grinding. A paste was gotten after grinding. A little hot water was added to the paste and squeezed continuously until a reasonable amount of oil was gotten. The remaining oil from the cake was extracted by frying.

### 3.2 POTASSIUM HYDROXIDE (KOH) PRODUCED FROM CASSAVA PEELS

Dry cassava peels were burned in open air using a match stick and the ashes collected. Plastic bucket was used and elevated so that underneath, a leaching hole was made small enough and lined by a thick layer of charcoal for the ashes not to go through in order to collect the lye water. Boiled water half of the capacity of the bucket was poured gently over the ashes. As soon as the water made contact with the ash it started hissing and bubbling. To test the strength of the alkali, a chicken feather was placed in it. The feather did not dissolve, the lye was not strong enough. It had to be re-boiled until the chicken feather dissolved in it.

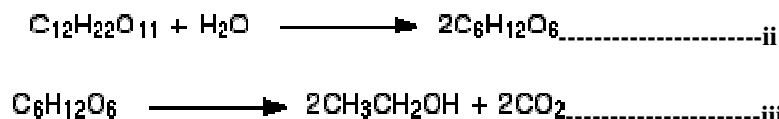
### 3.3 Cassava starch used to produce alcohol

The starting material for the process was cassava starch and the first step was to break the cassava starch into a simpler carbohydrate called maltose,  $C_{12}H_{22}O_{11}$ .

Maltose has the same molecular formula as sucrose but contains two glucose units joined together, whereas sucrose contains one glucose and one fructose unit.

Yeast was then added and the mixture kept warm at 35°C for 3 days until fermentation was complete. Air was kept out of the mixture to prevent oxidation of the ethanol produced to ethanoic acid (vinegar).

Enzymes in the yeast first converted the carbohydrates maltose and sucrose into simpler ones ( glucose and fructose) both C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, and then convert these in turn into ethanol and carbon dioxide..



The ethanol was separated from the mixture by fractional distillation to give 96% pure ethanol .

### 3.4 PRODUCTION OF BIODIESEL

Peanut oil was transesterified with ethanol catalized by 1.0% potassium hydroxide. 1 litre of oil was transferred to the reaction flask and preheated at 65C for an hour, 1% potassium hydroxide was dissolved in 6litres ethanol.

The solution of KOH and ethanol was also preheated to 65C. The two were mixed and placed on the hotplate with constant stirring speed maintained. After reaction, the reaction mixtures was poured into separatory funnel and allowed to settle overnight. After settlement, the top layer, ethyl ester was first washed with water and heated on the hotplate till it turned clear. Conversion to biodiesel was obtained.

### 3.5 DETERMINATION OF FLASHPOINT USING CLEVELAND OPEN-CUP METHOD

The cup of the apparatus was filled with 3g of biodiesel. Then temperature was increased rapidly and then at a slow constant rate as it approaches the theoretical flashpoint. The increase in temperature caused the chemical to begin to produce flammable vapour in increasing quantities and density.

The lowest temperature at which a small test flame passed over the surface of the liquid which caused the vapour to ignite is the flashpoint. Same procedure was repeated for petroleum diesel.

### 3.6 DETERMINATION OF THE CONCENTRATION OF KOH IN THE SOLUTION

The KOH in the solution was gotten by adding water to the burnt cassava peels. To find the concentration of the KOH in the solution, the solution was titrated with 25ml standard HCL solution using a burette and a few drops of phenolphthalein indicator was poured in. 25cm of KOH solution was completely neutralized by 14.5cm of HCL solution. The pink indicator became colourless.

The standard solution of HCL WAS 0.1

The concentration of KOH was calculated using the formula

$$\begin{aligned} & \frac{C_A V_A}{C_B V_B} \text{-----iv} \\ & C_A = 25\text{ml (concentration of HCL)} \\ & V_A = 14\text{cm}^3 \text{ (volume of HCL)} \end{aligned}$$

$$C_B = ? \text{ (concentration of KOH)}$$

$$V_B = 25\text{cm}^3 \text{ ( the volume of KOH)}$$

$$C_B = \frac{14.5 \times 14 \times 1}{25 \times 1}$$

$$C_B = \frac{203}{14}$$

$$C_B = 14.5\text{mol/dm}^3$$

### 3.7 PERCENTAGE YIELD

This was determined by the fomula

$$\frac{\text{Actual yield}}{\text{theoretical yield}} \times 100 \text{-----v}$$

Actual yield = How much product was actually synthesized in the experiment.

Theoretical yield = How much product will be synthesized.

### 3.8 DETERMINATION OF ACID VALUE

1g of peanut oil was weighed into a 25ml conical flask. 50ml of a mixture of 50% petroleum ester was added containing 6ml of phenolphthalein indicator. This was titrated against 0.1m potassium hydroxide shaking constantly with a pink colour, which persisted for 15 seconds was obtained. The same procedure was repeated for biodiesel and petrodiesel.

The acid value was determined by the formula

$$\text{Acid value} = \frac{V \times N \times 56.1}{\text{weight of sample}} \text{-----vi}$$

### 3.9 DETERMINATION OF SPECIFIC GRAVITY BY DENSITY BOTTLE METHOD.

The mass of the density bottle including the stopper was taken as  $M_1$

The mass of the density bottle + stopper + sample was taken as  $M_2$

The mass of density bottle including stopper + distilled water was taken as  $M_3$

Specific gravity was given by the formula

$$\text{Specific gravity} = \frac{M_3 - M_1}{M_2 - M_1} \text{-----vii}$$

The procedure was repeated for two times and the average specific gravities were taken. The specific gravity of peanut was also determined.

### 4.0 RESULTS

PARAMETERS	UNITS	PEANUTOIL	BIODIESEL	PETRODIESEL
ACID VALUE	Mg/KOH/g		0.32	0.281
SPECIFIC GRAVITY	g/cm <sup>3</sup>		0.94	0.859
PERCENTAGE YIELD	% by vol		91	70
FLASHPOINT	°C		190	67
COLOUR		YELLOW	LIGHT YELLOW	LIGHT BROWN
SMOKE POINT	°C		185	52
REACTION TIME	( MINS)		33	20

## 5.1 DISCUSSION

From the analysis carried out on the biodiesel, petrodiesel and peanut oil, their characteristics are shown in the above table. The acid value of the biodiesel and petrodiesel obtained under the same conditions are 0.32mg/KOH/g and 0.28mg/KOH/g respectively. These values fall within the accepted value given by ASTM specification for biodiesel B100 which is 0.50max. (Astm.org, 2016). This makes the ethyl ester good for the engine because the presence of free fatty acids in biodiesel more than the amount can lead to corrosion of engine parts. (biodiesel analytical method NRELCO68-72www.Astm.org). The specific gravities for biodiesel and petrodiesel determined were 0.942 and 0.859 respectively. The values also fall in agreement with the specification for biodiesel and petrodiesel. The biodiesel is denser than the conventional petrodiesel which means that the biodiesel has good combustion characteristics. Because of the greater density of the diesel fuel, the greater is its heat of combustion per unit volume and therefore, greater is its power of fuel economy. (Kirk and Othman). The flashpoint of biodiesel is higher than that of petrodiesel so it is safer in the event of a crash. The use of locally home grown materials even makes the work easier, accessible and requires encouragement.

## 6.0 CONCLUSION

Transesterification mechanism described above is entirely a laboratory program with little assistance of equipments. Biodiesel and petroleum diesel are useful in propelling of engines to the extent that the biodiesel seem to have an upper hand. The obvious difficulty in acquisition of materials for biodiesel production in commercial quantities is a challenge of our times but considerable quantities can easily be cultivated in Africa and beyond.

According to Alfred Philip Chalkley, Rudolf Diesel (1913). A German scientist Rudolf Diesel an inventor of compression-ignition engine in 1892. himself later conducted related tests and appeared supportive of the biodiesel idea. In a 1912 speech he said "the use of vegetable oil for engine fuels may seem insignificant today but such oils may become, in the course of time, as important as petroleum and the coal tar product of the present time." Despite the widespread use of petroleum derived diesel fuels, interest in vegetable oils as fuel of internal combustion engines was reported in several countries during the 1920 and 1930 and later during world war II. Belgium, France, Italy, The United Kingdom, Portugal, Germany, Brasil, Argentina, Japan and China were reported to have tested and used vegetable oil as diesel fuels during this time, some operational problems were reported due to the high viscosity of vegetable oils compared to petroleum diesel fuel, which results in poor atomization of the fuel in the fuel spray and often leads to deposits and coking of the injectors, combustion chamber and valves. Attempts to overcome these problems include heating of the vegetable oil, blending it with petroleum derived diesel fuel.

More research should be focused on the production and utilization of biodiesel to prevent over dependence on petrodiesel. Large scale production of biodiesel should be encouraged since it is a source of employment to farmers, reduce environmental wastes and it is useful in the sense that it reduces the emission of carbon monoxide, ozone forming hydrocarbons and acid rain causing sulphur dioxide

## 7 ACKNOWLEDGMENT

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