

SYNTHESIS OF BIODIESEL USING PALM

FATTY ACID DISTILLATES

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DEPARTMENT OF CHEMISTRY,

SCHOOL OF SCIENCE,

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OWERRI

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A PROJECT REPORT SUBMITTED TO THE

DEPARTMENT OF CHEMISTRY,

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**IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
AWARD OF BACHELOR OF TECHNOLOGY (B-TECH) IN INDUSTRIAL
CHEMISTRY**

SUPERVISOR: ATU A. AYUK, D. Sc

NOVEMBER, 2010.

CERTIFICATION

I hereby certify that this thesis is original and written by me. It is an accurate record of my research work and has not been presented before for the award of any other degree.

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DECLARATION

We declare that this thesis entitled “Synthesis of Biodiesel Using Palm Fatty Acid Distillates” by Meshach Emmanuel Ekeoma with registration number 20051467105 carried out under supervision has been examined and found out to have met the regulations of the Federal university of Technology Owerri for the award of Bachelor of Technology (B-Tech) degree in Chemistry (Industrial Chemistry option).

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DEDICATION

This thesis is dedicated to the family of Mr. Meshach Ekeoma for the parental support and their endeavor to ensure that I move my academic career to this level.

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In special way, I acknowledged the goodwill of God in my life from inception till now. I strongly appreciate the effort of my parents and relations that in one way or the other contributed to the success of this project work.

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Meshach Emmanuel Ekeoma,

Owerri,

November, 2010.

ABSTRACT

This work deals with esterification of palm fatty acid distillates to produce fatty acid methyl esters which is the biodiesel in a batch reactor, using 98 % concentrated tetraoxosulphate (vi) acid catalyst. The optimum requirement of ratio of reactants, catalyst, reaction time, and temperature was studied. The following parameters was used for the efficient and economical production of biodiesel : 68 g of methanol per 50 g of palm fatty acid distillates, 5.50 g of tetraoxosulphate (vi) acid per 50 g of palm fatty acid distillates, retention time of 60 minutes, and reaction temperature of 65 °C. This gave a maximum percentage conversion yield of 98.45 %. The biodiesel produced was purified by neutralization with 3 M sodium hydroxide in water solution at a reaction temperature of 65 °C for 40 minutes. Other parameters obtained include: acid value of 0.1878 mg KOH/g, iodine value of 17.8649, flash point of 205 °C, viscosity (at 40 °C) of 3.975 mm²/s, density (at 20 °C) of 0.8789 g/cm³, water content of 430 mg/kg, ester content of 98.45 %, and soap content (as Na) of 3.20 mg/kg. From the obtained results, the biodiesel produced met with the prescribed standard for biodiesel.

Keywords: Esterification, Palm fatty acid distillates, Fatty acid methyl esters, Biodiesel, Optimum requirements.

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CHAPTER ONE

1.0 INTRODUCTION

One of the hottest issues, in the history of mankind is energy. He needs energy to meet his daily requirements. Energy is also needed to light up houses, to cook food, to heat homes, to run vehicles, to meet with official tasks, and many more. Life seems impossible without energy.

There are several conventional resources which can be exploited to meet the energy requirement but the dilemmas of these sources are not only their limitations but also their side effects. Coal, petroleum, compressed natural gas etc. have simultaneously remained the benefactors and the damagers of mankind, but now they are being exhausted in their respective capacities. Need of the hour is to surge their alternatives- the source that can prove themselves not only long lasting but also environment friendly [1].

The best one can find today is (natural) renewable resources that are compatible to fulfill the increasing need of mankind without causing harm to the natural order of the universe. The task of energy consumption can be achieved by the virtue of solar panels, wind turbines, river dams, geothermal power points, biofuels, etc. These sources will not only replace the ever decreasing conventional modes of

energy but will also help in diluting global warming. The increasing temperatures on earth will one day swallow living beings. The evolution of science and technology has exempted any queries in the placement and utilization of natural sources to create energy.

1.1 GREEN TECHNOLOGY

Earth, the only known life reservoir in this universe, is turning into a heap of garbage covered by polluted air. Human beings have tremendously sorted out ways to comfort their lives but their comfort has disturbed the natural balance of the environment. As human beings are responsible for damaging the planet, it is their duty to device ways to restore the environmental equilibrium on the face of the earth. Although mankind is now planning to save the mother earth but collective effort is required on a massive scale to tackle the emerging monster of increasing pollution [3].

When knowledge is practiced, it is named technology. When environmental science is utilized to conserve the natural resources and environment then it is called Green Technology. The technology is comprised of emerging method for producing energy to non-toxic cleaning products. The significance of Green technology has multiplied due the drastic effects caused by the random human inventions.

Technologies like flue gas treatment deals directly with the energy conservation where emerging technologies decrease the amount of waste produced by a number of human activities. Using alternate sources of energy can also control the amount of the pollution [1, 3].

1.2 ALTERNATIVE FUELS

Alternative fuels are basically non-conventional or advanced fuels or in other words are any substances that possibly could be used as fuels other than conventional fuels. Conventional fuels as we know are the fossil fuels. Organic fuels such as firewood and gas are the largest forms of energy worldwide.

However, because of the scarcity of these resources, their higher prices and their environment destroying factors, the world has started to develop new ways of getting substitute fuels. The alternative fuel types are more environmentally friendly and economical. There are many forms and ways of producing alternative fuels.

For the sake of our planet's health we will eventually have to leave petroleum based fuels behind and look forward to the alternative fuels.

1.3 TYPES OF ALTERNATIVE FUELS

Nuclear energy was earlier given the place of jewel in its discovery as a useful energy fuel. Afterwards it was realized that this energy source is injurious to human health. The research over the nuclear energy sources has made it easier to use, but not suitable for the environment and mankind. This is the most expensive natural source of energy. Handling nuclear fission involves lot of risk and dangerous toxins. However, this source of energy is much practical but some international organizations have restricted its use because of the severe health concerns it can generate.

Hydroelectric power like wind energy, is an extremely old and established form of energy. However as compared to wind power, the expansion of this source is limited. The scarcity of more water reservoirs and its unwanted use has put mankind under immense pressure to look for substitutes.

Hydrogen may also be used as an alternative fuel. However, there is no easily available natural reservoir, and only little can be found in earth's external atmosphere. Therefore, it must first be created utilizing another energy source, making it a means to transferred energy, rather than a source of energy, almost similar to a rechargeable battery which can be recharge at anytime. Hydrogen could be a very environmentally friendly fuel, and it has proved to be a very good

source of fuel energy for vehicles. There are also questions on its energy efficiency, as so far, it takes more energy to manufacture than to produce it.

Biofuels are a wide range of fuels which are derived from biomass. The term covers solid biomass, liquid fuels and various biogases [1]. Biofuels are gaining increase public and scientific attention, driven by factors such as oil price hikes and the need for increased energy security.

1.4 WHAT IS BIODIESEL

Biodiesel is an alternative fuel similar to conventional or fossil diesel which is produced from vegetable oil, and animal oils/fats. The largest possible source of suitable oil comes from oil crops such as rapeseed, soybean or palm etc. Biodiesel is a completely natural, renewable fuel applicable in any situation where conventional petroleum diesel is used. No modifications on engine are needed. Even though “diesel” is part of its name, there is no petroleum or other fossil fuels in biodiesel. Biodiesel is 100% fatty acid based.

This environment-friendly fuel reduces tailpipe emissions, visible smoke and obnoxious odors. Biodiesel can also be used in blends with conventional diesel while still achieving substantial reductions in emissions. Technically, biodiesel is Fatty Acid Methyl Ester (FAME). It is formed by replacing the glycerol from each

triglyceride molecule of vegetable oil with methyl from methanol (that is by the reaction of free fatty acid and methanol).

The FAME is similar to petroleum diesel fuel to a diesel engine. But there is some notable difference. The biodiesel molecules are simple hydrocarbon chains, containing no sulfur, ring molecules, or aromatics that are associated with fossil fuels. Biodiesel is made up of almost 10% oxygen, making it a naturally “oxygenated” fuel [12].

1.5 WHY BIODIESEL

The rising costs of fuel and the impact of petroleum based fuels in the environment are the reasons for the need and discovery of biodiesel. Biodiesel is basically a fuel that is used as an alternative fuel that is made using renewable resources like vegetable oils and animal fats. It may be produced from a variety of natural crops such as rapeseed, soybean, sunflower, hemp, canola and last but the least palm oil [12].

1.6 BIODIESEL FUEL FEATURES

Power: One of the major advantages is the fact that it can be used in existing engines and fuel injection equipment (no modification required) without negative impact to operating performance.

Production/refining: Can be done at home and farms, being the only alternative fuel that can boast of a zero total emissions production facility.

Fuel availability/ economy: Virtually the same mile per gallon (MPG) rating as petro-diesel and the only alternative fuel for heavy-weight vehicles requiring no special dispensing and storage equipment.

Storage: Readily blends and stays blended with petro-diesel so it can be stored and dispensed wherever diesel is stored or sold.

Combustibility/ safety: Biodiesel has a very high flash point making it one of the safest of all alternative fuel.

Lubricity: The only alternative fuel that can actually extend engine life because of its superior lubricating and cleansing properties.

Environmental impact: The only renewable alternative diesel fuel that actually reduces a major green house gas component in the atmosphere. The use of biodiesel will also reduce the following emission

- Carbon monoxide
- Ozone-forming hydrocarbons
- Hazardous diesel particulate

- Acid rain-causing sulfur dioxide
- Life cycle of carbon dioxide[6]

1.7 THE BENEFITS OF BIODIESEL

Biodiesel has many environmentally beneficial properties. The main benefit of biodiesel is that it can be described as “carbon neutral”. This means that the fuel produces no net output of carbon in the form of carbon dioxide (CO₂). This effect occurs because when the oil crops grow they absorb the same amount of carbon dioxide as is released when the fuel is combusted [7].

Biodiesel is rapidly biodegradable and completely non-toxic, meaning spillages represent far less of a risk than fossil diesel spillages.

Biodiesel has a higher flash point than fossil diesel and so is safer in the event of a crash.

Biodiesel production can be completed on a small scale with relatively inexpensive equipment. The process is straightforward and methodical and can produce consistent results. That is to say, in technical terms, the method of producing biodiesel is feasible.

The real cost of biodiesel technology is contained in the oil feedstock [7].

1.8 PROBLEMS WITH AND DISADVANTAGES OF BIODIESEL

While biodiesel has a myriad of advantages and benefits, there is a flip side as well. This section provides inputs on the various perceived disadvantages of biodiesel, as well as problems that have been reported while using biodiesel. Some of the disadvantages of and problems with biodiesel are:

- It is currently more expensive.
- Disadvantages of using biodiesel produced from agricultural crops involve additional land use, as land area is taken up and various agricultural inputs, their environmental effects are inevitable. Switching to biodiesel on a large scale requires considerable use of our arable land. If that could happen all over the world, the impact on global food supply could be a major concern, and could make some countries being net importers of food products, from their current status of net exporters. It could so happen that most lands on the planet are deployed to produce food for diesel engines not people.
- It gives out more nitrogen oxide emissions.
- Transportation and storage of biodiesel requires special management. Some properties of biodiesel make it undesirable for use of high concentrations. For example, pure biodiesel does not flow well at low temperatures, which can cause problems for customers with out door storage tanks in colder

climates. A related disadvantage is that biodiesel, because of its nature, cannot be transported in pipelines. It has to be transported by truck or rail, which increases the cost.

- Biodiesel is less suitable for use in low temperatures than petrol-diesel. The “cloud point” is the temperature at which a sample of the fuel starts to appear cloudy, indicating that wax crystals have begun to form. At even lower temperatures, the fuel becomes a gel that cannot be pumped. The “pour point” is the temperature below which the fuel will not flow. As the cloud points and pour points for biodiesel are higher than those for petroleum diesel, the performance of biodiesel in cold conditions is markedly worse than that of petroleum diesel. At low temperatures, biodiesel fuel forms wax crystals, which can clog fuel lines and filters in a vehicle’s fuel system.
- Another disadvantage of biodiesel is that it tends to reduce fuel economy.
- There have been a few concerns regarding biodiesel’s impact on engine durability.
- Biodiesel has excellent solvent properties. Hence, any deposits in the filters and in the delivery systems may be dissolved by biodiesel and resulting in need for replacement of the filters. Petroleum diesel forms a deposit s in

vehicular fuel systems, and because biodiesel can loosen those deposit, they can migrate and clog fuel lines and filters

- The solvent property of biodiesel could also cause other fuel system problems. Biodiesel may be incompatible with the seals used in the fuel systems of older vehicles and machinery necessitating the replacement of those parts if biodiesel blends are used [9-11].

1.9 AIM OF STUDY

Using palm fatty acid distillate as a starting raw material for the synthesis of biodiesel, with the aim of reducing the cost of diesel fuel.

1.10 OBJECTIVE OF STUDY

- (a) Optimizing the conditions necessary for the economical yield of biodiesel.
- (b) To produce a fuel that will not encourage global warming.
- (c) To produce a fuel that will be biodegradable.

CHAPTER TWO

2.0 LITERATURE REVIEW

In the course of this project topic, “Synthesis of Biodiesel Using Palm Fatty Acid Distillate”, many journals were consulted, which are reviewed here.

According to Adison (2004), a Brazilian scientist Expedito Parente, in 1977 produced biodiesel by transesterifying palm oil for two hours and later separated a layer of fatty acid methyl ester FAME for use as biodiesel[8].

Drewette and Dwyer (2005), in their research titled “Biofuels for Transport”, discovered that there are three basic routes to production of fatty acid methyl esters (FAME): esterification of fatty acid distillates to fatty acid methyl esters, base-catalyzed transesterification of triglyceride oils, and acid catalyzed transesterification.

The work of Alamu O. J., et al., (2007) “Optimal Tranesterification Duration for Biodiesel Production from Nigerian Palm Kernel Oil”, investigated the effect of variation of mixing time on palm kernel oil (PKO) biodiesel yield. Three replicated transesterification experimental runs were carried out for each of the mixing duration 30, 45, 60, 75, 90, 105, and 120 minutes under identical typical tranesterification reaction conditions of 100 g PKO, 60 °C temperature, 1.0 %

potassium hydroxide (KOH) concentration and 20 % ethanol (wt % PKO). His results showed PKO biodiesel fuel properties (viscosity, cloud point, specific gravity, pour point and flash point) to be within international biodiesel standard specifications while average PKO biodiesel yield of 87.4, 90.1, 92.5, 94.2, 96.0 and 96.0 % were obtained for the respective mixing duration. Optimal yield of the PKO biodiesel, within the constraint of the typical transesterification process parameters used, was found to be 90 minutes[9].

Chongkhong S. et al., (2007), in his research work, “Biodiesel Production by Esterification of Palm Fatty Acid Distillate”, used the following procedure. The production was carried out in 250 cm³ screw capped bottle. Preheated palm fatty acid distillate (PFAD) was first measured into the bottle, followed by methanol and tetraoxosulphate (VI) acid as catalyst. Operating parameters for efficient esterification include reaction temperatures in the range of 70-100 °C, molar ratios of methanol to PFAD in the range of 0.4:1- 8:1, quantity of tetraoxosulphate (VI) acid catalyst in the range of 0.0- 3.5 weight percent of PFAD, and reaction times in the range of 15-90 minutes were investigated. The production mixture was poured in a separating funnel and then allowed to settle into two phases. The bottom fatty acid methyl ester (FAME) layer was separated and purified by washing with water before being analyzed. According to his results, the final FAME product met with the Thai biodiesel quality standard, and ASTM D6751-02[14].

Donato et al., (2007) deals with esterification of palm fatty acids to produce biodiesel in a batch reactor in his work “Acid-Catalyzed Homogeneous Esterification Reaction for Biodiesel Production from Palm Fatty Acids”. The reactions were performed in a stainless steel 600 ml batch reactor, maximum pressure of 10,000 psi and equipped with a sample withdrawal, stirring velocity was kept constant (500 rpm). Reaction mixture consisted of 307 g of fatty acid mixture, 149 ml methanol or 215 ml ethanol, providing an alcohol/fatty acid molar ratio (A/FA) of 3. Reactants were introduced together with the appropriated catalyst mass (generally 0.1% w/w) and time of reaction was considered when desired temperature (generally 130 °C) was reached. Sample was withdrawn at 5, 10, 15, 20, 25, 30, 45, and 60 minutes. Reaction conversion was estimated from the free fatty acid (FFA) content of the medium by NaOH titration. They evaluated the effects of alcohol used, presence of water, type and concentration of catalysts. In their results, methanesulfonic and sulfuric acid were the best catalyst. Reaction with methanol showed greater yields. It was shown very clearly that the presence of water in the reaction medium showed a negative effect in the reaction velocity. Kinetic parameters were estimated and molecular modeling was performed [13].

According to the article “Waste Cooking Oil as an Alternate Feedstock for Biodiesel production” by Arjun B. Chhetri et al., (2008), they said alternate fuels should be economically attractive in order to compete with currently used fossil

fuels. In this work, biodiesel (ethyl ester) was prepared from waste cooking oil collected from a local restaurant in Halifax, Nova Scotia, Canada. Ethyl alcohol with sodium hydroxide as a catalyst was used for the transesterification process. The fatty acid composition of the final biodiesel esters was determined by gas chromatography. The biodiesel was characterized by its physical and fuel properties including density, viscosity, acid value, flash point, cloud point, pour point, cetane index, water and sediment content, total and free glycerin content, diglycerides and monoglycerides, phosphorus content and sulfur content according to ASTM standards. The viscosity of the biodiesel ethyl ester was found to be $5.03 \text{ mm}^2/\text{sec}$ at $40 \text{ }^\circ\text{C}$. The viscosity of waste cooking oil measured at room temperature ($21 \text{ }^\circ\text{C}$) was $72 \text{ mm}^2/\text{sec}$. From the tests, the flash point was found to be $164 \text{ }^\circ\text{C}$, the phosphorous content was 2 ppm, those of calcium and magnesium were 1 ppm combined, water and sediment was 0 %, sulfur content was 2 ppm, total acid number was 0.29 mgKOH/g , cetane index was 61, cloud point was 1°C and pour point was $16 \text{ }^\circ\text{C}$. They concluded that the production of biodiesel from waste cooking oils for diesel substitute is particularly important because of the decreasing trend of economical oil reserves, environmental problems caused due to fossil fuel use and the high price of petroleum products in the international market [16].

O. J. Alamu et al., (2008) in their work “Characterization of palm-kernel oil (PKO) biodiesel produced through NaOH-catalyzed transesterification process”, biodiesel was produced from palm kernel oil with ethanol using sodium hydroxide (NaOH) catalyst. The biodiesel was characterized as alternative fuel for diesel engine through ASTM standard fuel tests. The transesterification process using 100 g PKO, 20.0 % ethanol (wt % PKO), 1.0 % NaOH, 60 °C reaction temperature and 90 minutes reaction time yielded average 95.80 % PKO biodiesel for three replications. From their results, fuel tests conducted on the biodiesel showed an 85.06 % reduction of viscosity over its raw PKO at 40 °C. Also higher specific gravity, cloud and pour points were obtained compared to that of petroleum diesel [11].

In the research work, “ Production of Biodiesel from Palm Fatty Acid Distillate”, P. Boonnoun, A. Manesiri, and C. Pattamaprom (2008) produced biodiesel by esterifying PFAD and maintaining it at the reaction temperature in a refluxed batch reactor. The mixture of the methanol and concentrated sulfuric acid were added to the molten PFAD with continuous stirring for 120 minutes. In their study, the variables investigated in the esterification step were the molar ratio of methanol to PFAD (varied from 16:1 to 24:1) and reaction temperatures (60 and 70 °C) by using concentrated sulfuric acid catalyst (1 % v/w of PFAD). From their experimental results, the esterification processes reduce the acid value of the raw

material down from 183 mg/g KOH to less than 0.50 mg/g KOH. The purities of biodiesel were between 80-90 % and viscosities were between 4-6 mm²/s. Transesterification post-treatment after esterification process was also studied. In the transesterification step, the reactions were carried out with 0.6 % of KOH catalysts, methanol to PFAD ratio of 8:1 and reaction time of 40 minutes. After transesterification post-treatment, the acid value of the biodiesel was found to reduce below 0.80 % with the purity of biodiesel higher than 98 % [10].

F. Halek et al., (2009) in their work “Biodiesel as an Alternative Fuel for Diesel Engines” said that diesel engines operated on biodiesel have lower emissions of carbon monoxide, unburnt hydrocarbons, particulate matter, and air toxics than when operated on petroleum-based diesel fuel. Production of fatty acid methyl ester (FAME) from rapeseed (non-edible oil) fatty acid distillate having high free fatty acids (FFA) was investigated in this work. Conditions for esterification process of rapeseed oil were 1.8 % H₂SO₄ as catalyst, methanol/oil of molar ratio 2: 0.1 and reaction temperature 65 °C, for a period of 3 hours. The yield of methyl ester was > 90 % in 1 hour. The amount of FFA was reduced from 93 wt % to less than 2 wt % at the end of the esterification process. The FAME was purified by neutralization with 1 M sodium hydroxide in water solution at a reaction temperature of 62 °C. The final FAME product met with the biodiesel quality standard, and ASTM D 6751[18].

From the work of Hsiao-Ching et al., (2010) which was distributed under the Creative Commons Attribution License, which permits unrestricted use of the article “ Continuous Production of Lipase-Catalyzed Biodiesel in a Packed-Bed Reactor: Optimization and Enzyme Reuse Study”. An optimal continuous production of biodiesel by methanolysis of soybean oil in a packed-bed reactor was developed using immobilized lipase (Novozym 435) as a catalyst in a tert-butanol solvent system. Response surface methodology (RSM) and Box-Behnken design were employed to evaluate the effects of reaction temperature, flow rate, and substrate molar ratio on the molar conversion of biodiesel. The results showed that flow rate and temperature have significant effects on the percentage of molar conversion. On the basis of ridge max analysis, the optimum conditions were as follows: flow rate 0.1 ml/min, temperature 52.10 °C, and substrate molar ratio 1:4. The predicted and experimental values of molar conversion were 83.31 ± 2.07 % and 82.81 ± 0.98 %, respectively. Furthermore, the continuous process over 30 days showed no appreciable decrease in the molar conversion. The paper demonstrated the applicability of using immobilized lipase and a packed-bed reactor for continuous biodiesel synthesis [12].

2.1 BIODIESEL PRODUCTION

As mentioned above, biodiesel can be produced from straight vegetable oil, animal oils/fats, tallow, and waste oils. There are three basic routes to biodiesel production from oils and fats:

- Base catalyzed transesterification of the oil.
- Direct acid catalyzed transesterification of the oil.
- Esterification of fatty acid distillate

2.2 TRANSESTERIFICATION PRODUCTION OVERVIEW

Biodiesel is most commonly made by chemically altering organic oil through the use of a catalyst and an alcohol. The chemical reaction that occurs through this process breaks down the oil molecules and replaces the glycerol portion of the molecule with an alcohol molecule. The glycerol falls to the bottom and is drained off resulting in biodiesel. The oil, catalyst, and alcohol mixture are then mixed for a period of time and then allowed to settle. The top layer will be biodiesel, chemically called an Ester, the next layer may contain soap, and the bottom layer will be glycerol. Once the layering has occurred, the glycerol and soap are drained off. The biodiesel is then washed with distilled water. The washing is done to

remove any additional soap, alcohol, or other impurities in the biodiesel [2, 6, 9, 13].

To avoid the complications of the transesterification method, the oil feedstock is best converted to fatty acid where esterification method of production is then used.

2.3 PRECAUTIONS

- Because what are involved in the production are toxic chemicals, the potential to seriously hurt, injure, and even kill one self and others exist. It is therefore important to apply safety measures.
- Biodiesel should always be made in a well ventilated area away from children and pets with the proper safety equipment utilized.
- Dealing with some strong chemicals, an alcohol called methanol, fair amounts of heat, and the transferring of flammable fluid from one container to another so it is a good idea to have a fire extinguisher around the premises that is capable of putting off an oil base fire.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 MATERIALS

500 ml round bottom flask, 250 ml beakers, clamp, electronic weighing balance (0.001- 300 g), reagent bottles, thermometer, water bath, reflux condenser, separation funnel, hot plate with magnetic stirrer, burette, pipette, and funnel.

3.2 CHEMICALS

Palm fatty acid distillate (PFAD) was obtained from Nifex Vegetable Oil Company Ohanze Umuibe, Abia State Nigeria. Its purity is 92 wt %, moisture content 0.50 %, saponification value 263, colour 11R, unsaponification value 0.6. All chemicals including 99 % methanol (CH_3OH), 98 % tetraoxosulphate (vi) acid (H_2SO_4), sodium hydroxide (NaOH) are commercial grade from BDH Laboratory Chemicals.

3.3 PROCEDURE

(A) Esterification step

The PFAD is being analyzed to know the acid value of the stock palm fatty acid distillate before the reaction for the synthesis of FAME commences.

The esterification step was carried out by melting PFAD and maintaining it at the reaction temperature in a refluxed batch reactor. The mixture of methanol and concentrated sulfuric acid were added to the molten PFAD with continuous stirring for 90 minutes. The reactor was kept at the desired temperature by a thermostatic water bath. In order to prevent alcohol loss by volatility, the water that circulated inside the reflux condenser was cooled by a thermostatic water bath. The starting time of the reaction was the addition of the catalyst (H_2SO_4).

After the reaction, the mixture was settled in a separating funnel. The methyl ester in the lower layer was separated out from the upper layer which is made up of water, excess methanol, and the catalyst.

(B) Washing and Drying (Purification)

The washing process is important for removal of methanol, catalyst, and contaminants. The washing step was carried out by using distilled water, where the

washing circle is repeated twice. After washing, the methyl ester was heated up to 100 °C to remove excess water and methanol.

(C) **Characterization**

The biodiesel produced was characterized for viscosity, acid value, cloud point, flash point. Viscosity of biodiesel was tested using viscometer at 40 °C according to ASTM D445. The cloud point was measured by recording the onset temperature of biodiesel transition from translucent to opaque. The acid value was determined by titration of a known concentration of potassium hydroxide (KOH) against one gram of the sample dissolved in 100 ml of ethanol according to ASTM D664 [5].

When the required reaction time was completed, acid value is analyzed by titration of a known concentration of KOH against one gram of sample dissolved in 100 ml of ethanol. The indicator is phenolphthalen.

The acid value is calculated by using the formula below.

$$\text{Acid value (mg KOH/g)} = \frac{\text{Normality of base} \times \text{titre value} \times 56.1}{\text{Weight of acid taken}}$$

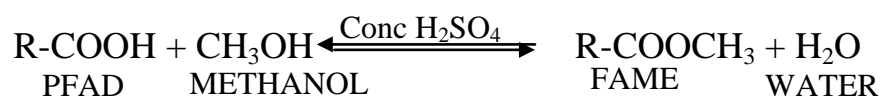
Weight of acid taken

The percentage conversion is calculated to know the extent at which the palm fatty acid distillate (PFAD) is being converted to fatty acid methyl ester (FAME).

It is calculated thus

$$\% \text{ conversion} = \frac{\text{Change in acid value}}{\text{Initial acid value}} \times 100$$

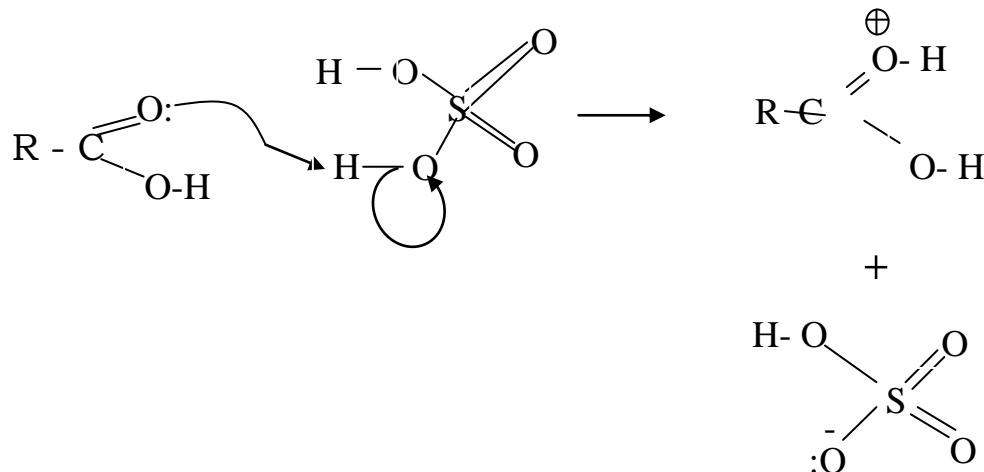
Initial acid value 1



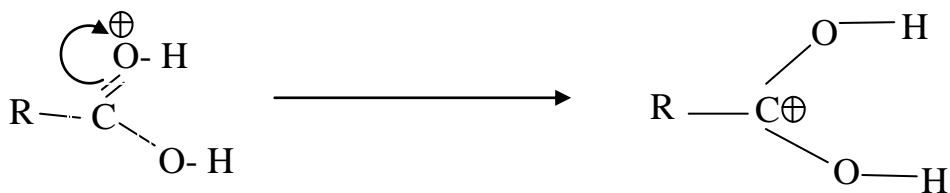
3.4 THE MECHANISMS FOR THE FORMATION OF FAME

Step 1

In the first step, the PFAD takes a proton (a hydrogen atom) from the concentrated sulfuric acid. The proton becomes attached to one of the lone pairs of electrons on the oxygen which is solely bonded to carbon.

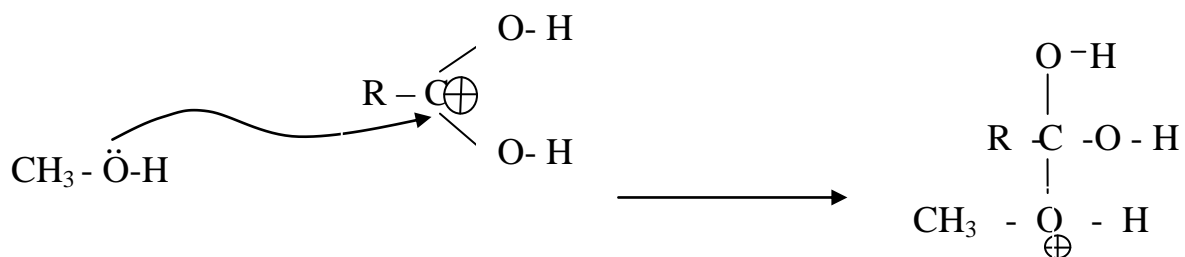


The positive charge is delocalized over the whole of the right handed end of the ion, with a fair amount of positiveness on the carbon atom.



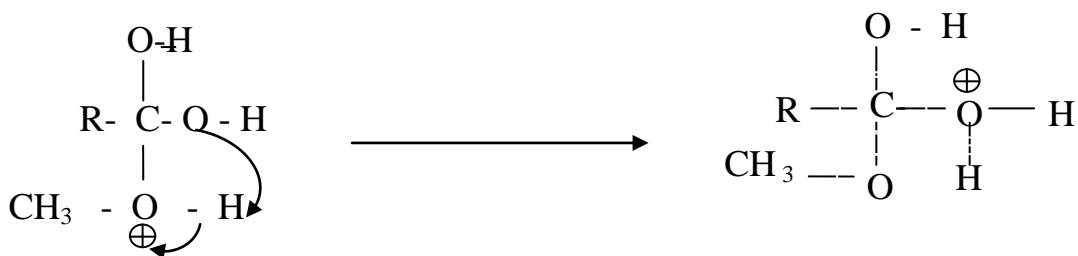
Step 2

The positive charge on the carbon atom is attacked by one of the lone pairs of electrons on the oxygen of the methanol molecule



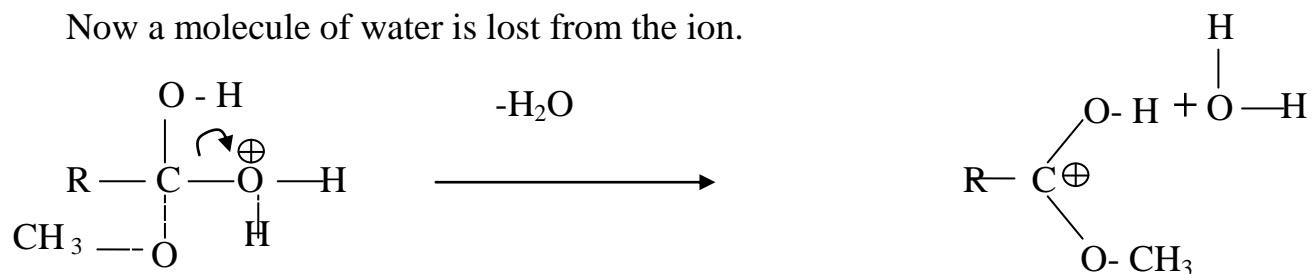
Step 3

What happens next is that a proton (a hydrogen atom) is transferred from the bottom oxygen atom to any of the oxygen in the methanol-fatty acid molecule.



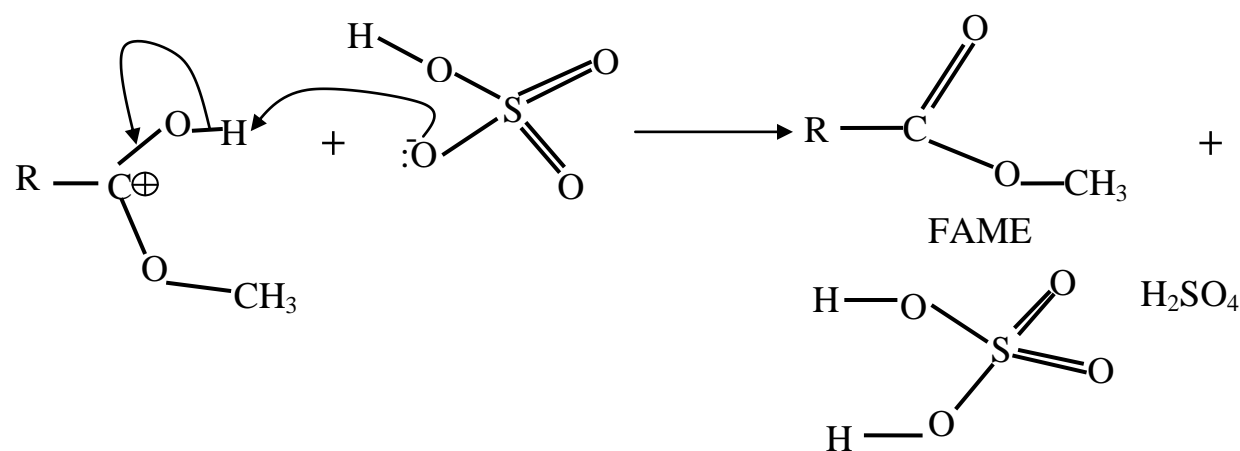
Step 4

Now a molecule of water is lost from the ion.



Step 5

The hydrogen is removed from the oxygen by reaction with the hydrogen sulphate ion which was formed way back in the first step.



3.5 EXPERIMENT ONE

3.6 Determination of the optimum mole ratio of methanol

A clean and dry round bottom flask was weighed and 50 grams of fatty acid distillate was weighed into the flask. Next 20 grams of 99 % methanol was added, also 9.8 grams of 98 % H₂SO₄ was weighed into the flask. The flask with its contents was fixed to a reflux condenser, and heated in a water bath heated by a hot

plate. The reaction was allowed to proceed for 90 minutes at a temperature 70 °C, after which the contents of the flask were poured into a separating funnel and allowed to completely separate into two layers, the fatty acid methyl esters (FAME's) being at the bottom. The bottom layer FAME (contaminated with some methanol and H₂SO₄) was separated and washed with hot water to remove traces of methanol and H₂SO₄. The FAME was later dried for 30 minutes at 100 °C. The purified FAME was analyzed for acid value.

The extent of the reaction is indicated by the reduction of acid value, and is represented in terms of percentage conversion in. The same synthesis was repeated with 24 g, 28 g, 32 g, 36 g, 40 g, 44 g, 48 g, 52 g, 56 g, 60 g, 64 g, 68 g, 72 g, 76 g, and 80 g of methanol respectively.

3.7 EXPERIMENT TWO

3.8 Determination of the optimum mole ratio of catalyst (H₂SO₄)

Using 50 grams of PFAD, and the optimum methanol ratio, the synthesis, separation and purification were repeated using the same procedure at 70 °C for 90 minutes with the following amounts of catalyst: 0.50 g, 1.00 g, 1.50 g, 2.00 g, 2.50 g, 3.00 g, 3.50 g, 4.00 g, 4.50 g, 5.00 g, 5.50 g, 6.00 g, 6.50 g, and 7.00 g of sulfuric acid respectively.

3.9 EXPERIMENT THREE

3.10 Determination of the optimum reaction time

Using 50 grams of PFAD, optimum ratios of methanol and catalyst, the synthesis, separation, and purification were repeated using the same procedure at 70 °C for 10 minutes, 20 minutes, 30 minutes, 40 minutes, 50 minutes, 60 minutes, 70 minutes, 80 minutes, and 90 minutes respectively.

3.11 EXPERIMENT FOUR

3.12 Determination of the optimum reaction temperature

Using 50 grams of PFAD, optimum ratios of methanol and catalyst, the synthesis, separation, and purification were repeated using the same procedure at 50 °C, 55 °C, 60 °C, 65 °C, and 70 °C, for the optimum time each.

Finally, using 50 grams of PFAD, the optimum values of methanol, catalyst, reaction time and temperature, the synthesis, separation, and purification was repeated using the same procedure to characterize the quality of biodiesel (FAME) produced compared with standards.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

Determining the optimum amount of methanol required to esterify 50g of PFAD, the acid value of the PFAD was first calculated thus: by titration of NaOH solution of normality 0.5388N against 1g aliquot of the biodiesel, the acid value was calculated using the formula below.

$$\text{Acid value (mg KOH/g)} = \frac{\text{Normality of NaOH} \times \text{Titre value} \times 56.1}{\text{Weight of acid}}$$

Weight of acid

$$\text{Normality of NaOH} = 0.5388 \text{ N}$$

$$\text{Titre Value} = 5.90 \text{ cm}^3$$

$$\text{Weight of acid taken} = 0.9799 \text{ g}$$

$$\text{Acid value} = \frac{0.5388 \times 5.90 \times 56.1}{0.9799}$$

$$= 181.99 \text{ mg KOH/g}$$

The acid value of the palm fatty acid distillate used for the entire esterification reaction is 181.99 mg KOH/g.

4.1 EXPERIMENT ONE

Now, to determine the optimum ratio of methanol that can esterify 50 g of PFAD, the esterification reaction was started with 20 g of methanol, after which, the weight of methanol was varied with an increase of 4 g of methanol. At the end of each reaction for 90 minutes, the acid value and the percentage conversion was checked with the following formula:

$$\text{Acid value (mg KOH/g)} = \frac{\text{Normality of NaOH} \times \text{Titre value} \times 56.1}{\text{Weight of acid}}$$

Weight of acid

$$\text{Percentage conversion (\%)} = \frac{\text{Initial acid value} - \text{final acid value}}{\text{Initial acid value}} \times 100$$

Initial acid value

1

Table 4.1 Determination of the optimum ratio of methanol in weight to 50g of PFAD

Weight of methanol reacting with 50 g of PFAD (g)	Acid value of the biodiesel at the end of 90 minutes (mg KOH/g)	Percentage Conversion (%)
20	32.05	82.39
24	24.50	85.99
28	17.01	90.65
32	9.70	94.67
36	8.01	95.60
40	6.37	96.50
44	5.24	97.12
48	5.02	97.24
52	3.84	97.89
56	3.42	98.12
60	3.20	98.24
64	3.05	98.32
68	2.93	98.39
72	2.93	98.39
76	2.93	98.39
80	2.93	98.39

From the table 4.1 above, 68 g of methanol gives a conversion yield of 98.39 %, which is the optimum percentage conversion yield in the table. The acid value was found to drop from 181.99 mg KOH/g to 2.93 mg KOH/g. This means that $181.99 - 2.93 = 179.06$ mg KOH/g of PFAD was converted to biodiesel at 70 °C within 90 minutes.

$$\% \text{ conversion} = \frac{179.06}{181.99} \times 100$$

$$= \frac{179.06}{181.99} \times 100 = 98.39 \%$$

Therefore, the optimum weight of methanol to esterify 50 grams of PFAD is 68 grams within 90 minutes at 70 °C in the presence of 9.8 g H₂SO₄ catalyst.

4.2 EXPERIMENT TWO

Esterifying 50 g of PFAD with 68 g of methanol to determine the optimum % w/w of hydrogen tetraoxosulphate (vi) acid catalyst that will give the maximum yield of FAME at 70 °C within 90 minutes. The following results were obtained.

Table 4.2 Determination of the optimum ratio of H₂SO₄ catalyst in weight to 50g PFAD

Weight of catalyst (g)	Acid value of the biodiesel at the end of 90 minutes (mg KOH/g)	Percentage conversion (%)
0.50	33.85	81.40
1.00	29.48	83.80
1.50	27.28	85.01
2.00	24.75	86.40
2.50	23.08	87.32
3.00	13.83	92.40
3.50	7.83	95.70
4.00	5.64	96.90
4.50	3.97	97.82
5.00	3.75	97.93
5.50	2.93	98.39
6.00	2.93	98.39
6.50	2.93	98.39
7.00	2.93	98.39

From the table 4.2 above, 5.50 g of hydrogen tetraoxosulphate (vi) acid catalyst gives the maximum percentage conversion of PFAD to FAME. The acid value of the PFAD was reduced by $181.99 - 2.93 = 179.06$ mg KOH/g

Percentage conversion (%) = $\frac{179.06}{181.99} \times 100$

$$\frac{179.06}{181.99} \times 100 = 98.39 \%$$

Therefore the optimum catalyst required to esterify 50 g of PFAD with 68 g of methanol is 5.50 g of H₂SO₄ at 70 °C within 90 minutes.

4.3 EXPERIMENT THREE

Esterifying 50 g of PFAD with 68 g of methanol in the presence of 5.50 g H₂SO₄ catalyst to determine the optimum reaction time at 70 °C, the following result was obtained.

Table 4.3 Determination of the optimum reaction time for esterifying 50g PFAD

Reaction time in minutes	Acid value of the biodiesel at the end of 90 minutes (mg KOH/g)	Percentage conversion (%)
10	63.33	65.20
20	53.83	70.42
30	38.20	79.01
40	25.11	86.20
50	9.26	94.91
60	2.95	98.38
70	2.95	98.38
80	2.95	98.38
90	2.95	98.38

From the results above, the acid value falls to 2.95 mg KOH/g at 60 minutes. After that time, the acid value remains constant. The acid value was reduced by $181.99 - 2.95 = 179.04$ mg KOH/g

Percentage conversion (%) = $\frac{179.04}{181.99} \times 100$

$$= \frac{179.04}{181.99} \times 100 = 98.38 \%$$

Therefore, the optimum reaction time for the esterification of 50 g PFAD with 68 g of methanol in the presence of 5.50 g H₂SO₄ catalyst is 60 minutes at 70 °C.

4.4 EXPERIMENT FOUR

Esterifying 50 g of PFAD with 68 g of methanol in the presence of 5.50 g of H₂SO₄ to determine the optimum reaction temperature for 60 minutes each of the examined temperatures, the following result was obtained.

Table 4.4 Determination of the optimal reaction temperature to esterify 50g of PFAD

Reaction temperature (°C)	Acid value of the biodiesel at the end of 60 minutes (mg KOH/g)	Percentage conversion (%)
45	38.36	78.92
50	32.83	81.96
55	20.00	89.01
60	10.45	94.26
65	2.93	98.39
70	2.93	98.39

From the results the acid value of the PFAD falls to 2.93 mg KOH/g when the reaction temperature was maintained at 65 °C. The fatty acid that was converted to biodiesel is $181.99 - 2.93 = 179.06$ mg KOH/g.

The percentage conversion (%) = $\frac{179.06}{181.99} \times 100$

$$\frac{179.06}{181.99} \times 100 = 98.39 \%$$

Therefore, the optimum reaction temperature for esterifying 50 g of PFAD with 68 g methanol in the presence of 5.50 g H₂SO₄ catalyst is 65 °C within 60 minutes.

Table 4.5 Optimum conditions for the synthesis of FAME

Reaction conditions	Optimal values
Methanol to PFAD in grams	68:50
H ₂ SO ₄ to PFAD in grams	5.50 :50
Reaction time in minutes	60
Reaction temperature in °C	65

Finally, from the optimal values, the synthesis of FAME was carried out with 50 g PFAD, 68 g H₂SO₄, for 60 minutes at 65 °C. The acid value was reduced by $181.99 - 2.82 = 179.17$ mg KOH/g

The percentage conversion (%) = $\frac{179.17}{181.99} \times 100$

$$\frac{179.17}{181.99} \times 100 = 98.45 \%$$

The percentage conversion of the fatty acid to biodiesel when the optimal values were used for the synthesis is 98.45 %, which is a good yield of biodiesel from fatty acid. The FAME produced was neutralized with 3 M NaOH at 65 °C for 40 minutes, so that the biodiesel will meet the international standard. The acid value of the FAME falls to 0.1878 mg KOH/g after neutralization.

The biodiesel produced from the optimal values was characterized for quality, and the result was compared with standards.

Table 4.6 Qualitative results of the biodiesel compared with standards

Parameters	Results	Standards
Acid value	0.1878 mg KOH/g	≤ 0.50 mg KOH/g
Iodine value	17.8649	≤120
Flash point	205 °C	≥120 °C
Viscosity (at 40°C)	3.975 mm ² /s	3.5-5.5 mm ² /s
Density (at 20°C)	0.8789 g/cm ³	0.86-0.90 g/cm ³
Water content	430 mg/kg	≤500 mg/kg
Ester content	97.45 %	≥96.5 %
Soap content (as Na)	3.20 mg/kg	≤ 5.0 mg/kg

CHAPTER FIVE

RECOMMENDATION AND CONCLUSION

5.0 RECOMMENDATION

Biodiesel producers should be encouraged to make use of the by-product (fatty acid distillates), since there are such vegetable oil refining companies in our country Nigeria.

5.1 CONCLUSION

The qualitative analysis of the purified biodiesel shows that the method of the synthesis was efficient. With an acid value of 0.1878 mg KOH/g, iodine value of 17.8649, flash point of 205 °C, viscosity of 3.975 mm²/s, density of 0.8789 g/cm³, water content of 430mg/kg, ester content of 97.45 %, and soap content of 3.20 mg/kg, the results show that the quality of the synthesized biodiesel agrees with both American and European standards for biodiesel.

Comparing the results in table 4.6 above with the results in the work of Alamu et al., (2007) “Optimal transesterification duration for biodiesel production from Nigerian palm kernel oil”, biodiesel produced through base catalyzed transesterification of fats and oils requires retention time of about 90 minutes, and have optimal percentage yield of 96 %. In contrast, biodiesel produced through

esterification of palm fatty acid distillates requires retention time of only about 60 minutes and have optimal percentage conversion of 98.45 %. Thus the method of biodiesel production used in this work is more economical in terms of production costs.

Reports from foreign agencies according to Andrew B. (2007), have spoken against biofuel production, claiming it will cause a displacement of food crops, leading to possible food scarcity and inflation of food prizes. In line with the argument, palm fatty acid distillates from palm kernel oil refinery and methanol used in this work are not edible, making them better raw materials to be used for biodiesel production to avoid soaring of food prices.

This research has proved that biodiesel should be sourced not only from triglyceride oils, but from fatty acid distillates which is a by-product of vegetable oils refineries.

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