DEVELOPMENT OF HIERARCHICAL ZEOLITE Y CATALYST FOR BIODIESEL PRODUCTION USING WASTE COOKING OIL AS FEEDSTOCK

BY

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ABSRACT

This study reports development of hierarchical zeolite Y (HZY) catalyst from commercial zeolite Y (CZY) for biodiesel production using waste cooking oil as feedstock. The hierarchical zeolite Y catalyst developed was characterized using X-Ray diffraction (XRD), scanning electron microscopy (SEM) and Brunnauer, Emmett and Teller (BET) analyses. The BET showed that mole concentration of simultaneous desilication and mild dealumination determine the hierarchical factor of the produced hierarchical Y zeolite. Furthermore, this process was optimized by varying both the mole concentration of aqueous solutions of Sodium Hydrides (NaOH) and Ethylenediaminetetraacetic acid (H_4EDTA). The two (2) process variables NaOH and H_4EDTA were found to be statistically significant for high surface area, pore volume and pore size. The values obtained for surface area of samples HZY-1,HZY-2,HZY-3 and HZY-4 were 193.83, 216.03, 212.34 and 218.33 m^2/g while the hierarchy factor were calculated to be 0.0571, 0.1540, 0.1781 and 0.1042 respectively. The highest value of hierarchy factor (0.1781) of hierarchical zeolite Y sample (HZY-3) occur at 0.3 M of NaOH and 0.3 M of H_4EDTA with pore volume of 0.3785 c m^3/g and pore size 8.5512 nm, which represent the most suitable for optimum reactivity compared to the other samples. The X-Ray diffraction (XRD) of hierarchical zeolite Y shows slight decrease in the peak intensity which is associated with partial extraction of Si and Al from zeolite framework during alkaline to acid treatment. Some peaks were also formed which showed that the level of crystallinity had increased. The SEM/EDX determined the crystallite size and the morphology. From the EDX, the hierarchical zeolite Y Si/Al ratio was calculated to be 15.0. HZY gave biodiesel yield of 95 % at 55 °C for 90 min. while CZY gave yield of 62.00% at the same conditions. Reusability test was also carried out and it was observed that at repeated 5th runs, biodiesel yield using the same HZY catalyst dropped to 83 % which was still reasonable enough compared to CZY catalyst which was observed to have dropped to 41 %. This indicates that the hierarchy factor of the HZY catalysts produced influences the activity of the catalysts in biodiesel production.

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ABBREVIATION, GLOSSARIES AND SYMBOLS

WCO - Waste Cooking Oil

HF - Hierarchy Factor

FFA - Free Fatty Acid

FAME - Fatty Acid Methyl

EsterXRD - X-Ray Diffraction

SEM - Scanning Electron Microscopy

EDS - Electron Dispersive

SpectroscopyBET - Brunnauer, Emmeitt and

Teller

GC-MS - Gas Chromatography - Mass

SpectrometryRSM - Response Surface Methodology

DOE - Design of Experiment

CCD - Central Composite Design

ASTM - American Biodiesel Quality

StandardCZY - Commercial Zeolite Y

HZY - Hierarchical Zeolite Y

NaOH - Sodium Hydrides

H_4EDTA - Ethylenediaminetetraacetic Acid

KOH - Potassium Hydroxide

GHG - Green House Gas

SG - Specific Gravity

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

The need for energy is increasing continuously due to increased industrialization activities and population increase, and this is adding to the issue of global warming. Therefore, scientists are encouraged to develop alternative fuels that are renewable and sustainable (Kulkarni and Dalai, 2006; Prafulla *et al*., 2012). Biodiesel is a form of diesel fuel derived from plants or animals and consisting of long-chain fatty acid esters. It is typically made by chemically reacting lipids such as animal fat (tallow), soybean oil or some other cooking oil with an alcohol, producing a methyl ethyl or propyl ester. Chemically, biodiesel can also be defined as the monoalkyl esters of long-chain fatty acids derived from renewable biolipids. Typically, it is produced through the reaction of an oil or animal fat with methanol or ethanol in the presence of a catalyst to yield methyl or ethyl esters (biodiesel) and glycerol. Fatty acid methyl esters or biodiesels from processed organic oil are produced from cooking oil or animal fats, (Demirbas, 2009). Biodiesel is similar to petroleum diesel in many aspects of its chemical and physical properties, (Vashist and Ahmad, 2014). However, the performance of an engine and fuel consumption was favorable making it a better substitute diesel (Bajpai and Tyagi, 2006).

Waste cooking oil (WCO) is generated locally wherever food is cooked or fried in oils. These are derived from cooking oil (i.e. soybean, cottonseed, groundnut, sunflower, rapeseed, sesame, corn, olive, palm, palm kernel, coconut, linseed, castor, and soy among a wide variety of plant sources) and animal fats/oils (butter, lard, tallow, grease and fish oil) (No SY, 2011). WCOs and fats cause disposal problems in many parts of the world. These problems could be changed into both economic and environmental benefits by suitable utilization and management of WCO as a fuel substitute. Many developed countries have set policies that guide the disposal of WCO (Prafulla *et al*., 2012), which can be converted to biodiesel.

There are at least four ways in which oils and fats can be converted to biodiesel namely: pyrolysis (thermal cracking), micro-emulsification, dilution and transesterification (Demirbas, 2009; Singh and Singh, 2010). A comparison of the various biodiesel production techniques showed that emulsion and thermal treatment techniques consumes more energy, produces large amount of unwanted byproducts and require high cost equipment as compared to transesterification. Also, higher yield and purity of biodiesel is obtainable using transesterification (Atabani *et al*., 2012). Therefore, transesterification technique is currently the most and the best technique researchers used for producing higher quality biodiesel (Sharma *et al*., 2013; Talebian-Kiakalaieh *et al*., 2013). Transesterification (also known as alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. Commonly, the reaction rate and yield can be improved by using a catalyst. It consists of a number of uninterrupted, reversible reactions. The triglycerides are converted step wise to triglycerides, monoglycerides and finally glycerol (Singh and Singh, 2010).

The main catalysts used can be classified as homogeneous or heterogeneous catalysts according to their chemical presence in the transesterification reaction (Demirbas, 2009). Homogeneous catalysts act in the same liquid phase as the reaction mixture, whereas heterogeneous catalysts act in a different phase from the reaction mixture, usually as a solid (Borges and Díaz, 2012). Homogeneous alkaline catalysis received wide acceptance because of its fast rate of reaction. Moreover, production and raw material costs are hindering this production technology. Most WCOs or feedstock contain water and FFAs. Hydrolysis of triglycerides into new fatty acids and diglycerides occur due to the presence of water which then leads to the formation of stable emulsions and saponification. Therefore, during separation stage the soaps dissolve into the glycerol phase still to pay to their polarity, this makes the separation and purification becomes difficult and expensive, (Sani, *et al*., 2013). The alkaline catalyzed processes also cause environmental problem due to the waste water generated during washing and the same time cause loss of catalysts which results to small financial issues. Heterogeneous catalysts are non-corrosive, a green process and environmentally friendly. They can be recycled and used several times, thus offering a more economic pathway for biodiesel production. From the process point of view, to recover the catalyst it is not necessary to undertake aqueous treatment and purification steps so giving more simplified and very high yields of methyl esters (Farooq *et al*., 2018).

Generally, researchers have argued that the use of heterogeneous catalysts in the transesterification process of WCOs has good prospects for the future. WCO is a very appropriate feedstock for biodiesel production because it is cheaper and can overcome the problem of environmental disposal. However, many obstacles must be considered, including the absence of a systematic method of collecting WCOs from households, restaurants, hotels and the food industry. Talebian-Kiakalaieh *et al*. (2013) stated that more than 80 % of WCO is produced by households. This is a huge amount in utilizing WCO as a raw material in the production of biodiesel through transesterification. From the technical point of view, a heterogeneous catalyst can be easily separated from the reaction mixture and can be reused several times with consistent activity, so that it can be developed as a good catalyst for industrial biodiesel processes. It presents good catalytic activity in fine particles form, opening the possibility of undertaking a continuous catalytic process for biodiesel production with both slurry and fixed bed configuration reactors, with the capability of using the residue frying oil as inexpensive feedstock, contributing also to the elimination of residue together with the production of biodiesel (Borges and Díaz, 2013). The heterogeneous acid-catalyzed process is an efficient technology in producing biodiesel directly from low cost. However, the research into FAME from WCO using these types of catalyst is limited (Talebian-Kiakalaieh *et al*., 2013). Heterogeneous catalysts have drawbacks, namely their low reaction rates in comparison with the homogeneous process in biodiesel production (Jincheng *et al*., 2011), their unsuitability with very high FFA content feedstock and the production of soaps (Borges and Díaz, 2013). Another obstacle associated with the development of heterogeneous base catalysts is their inability to tolerate the FFA content of feedstock under mild reaction conditions and their reusability. For this reason, researchers have developed catalyst called bifunctional heterogeneous catalysts such as zeolite catalyst that can simultaneously conduct the esterification of FFAs and transesterification of triglycerides for sustainable biodiesel production technology.

Zeolites are microporous aluminosilicate materials with 3-dimensional pore structure that play an important role in many industrial and chemical processes. Zeolite catalysts are of great importance in a number of chemical reactions that associated with the (petro) chemical and oil refining industries, (Vermeiren and Gilson, 2009), and raise substantial interest in new applications, such as the conversion of biomass into valuable chemicals (Taarning *et al*., 2011.) Nevertheless, most especially during the processing of bulky molecules in the liquid phase, a sub-optimal utilization of the active sites present in zeolites is often implied by limited access and slow intra-crystalline diffusion in their micropores (Vermeiren and Gilson, 2009). In order to make it bifunctional catalyst, this can act as an acid and base at the same time. It can be easily modified to introduce the desired physicochemical properties so that the presence of FFAs does not adversely affect the reaction steps during the transesterification process (Farooq *et al*., 2018; Endalew *et* *al*., 2011). In response to the need of improved catalytic processes, hierarchical (mesoporous) zeolites were conceived through which simultaneous disilication and mild dealumintion are carried out. These modified zeolites integrate the native microporosity with an auxiliary level of inter or intra-crystalline mesopores, increasing the external surface area substantially. This brings enhanced accessibility due to the increased number of pore mouths and shortened average diffusion path length in the micropores (Pérez-Ramírez *et al*., 2008). The superior lab-scale performance of hierarchical zeolites compared to conventional counterparts in a wide range of catalyzed reactions is unquestionable. In this study, commercial zeolite Y and hierarchical zeolite Y were investigated. The hierarchical zeolite Y catalyst produced were characterizated using X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Brunnauer, Emmett and Teller (BET) analysis.

1.2 Statement of the Problem

The need for energy is increasing continuously due to increased industrialization activities and population increase and the adverse effects of conventional fossil fuel on climate change cannot be overemphasized. The world is continuously searching for sources of fuel with low carbon content so as to drastically reduce emission of greenhouse gases. Secondly, the issues related to catalyst particularly the use of homogeneous catalyst have a lot of difficulty. It has been noted that homogeneous basic catalysts basically have a better activity compare to their acidic counterpart (Farag *et al*., 2012). However, transesterification with homogeneous basic catalysts have various drawbacks. These include catalyst separation to purify the biodiesel, soap formation and separation of glycerol requires large amount of water which leads to production of wastewater (Intarapong *et al*., 2012). Moreover, homogeneous acid catalysts corrode the reactor and are very difficult to separate from the product. Therefore, it is important to seek an alternative for the homogeneous catalyst to avoid catalyst separation corrosion and pollution issues. Thirdly, this research therefore focuses on the possibility of solving the issue of using conventional zeolite Y catalyst for biodiesel production that has limited access and slow intra-crystalline diffusion in their micropores (Vermeiren and Gilson, 2009). These occur most especially during the processing of bulky molecules in the liquid phase. They are also limited due to inadequate number of pore mouths that result to shorten of average diffusion path length.

1.3 Aim and Objectives

The aim of this study is to produce Hierarchical Zeolite Y as heterogeneous catalyst by method of desilication and mild dealumination for production of biodiesel from waste cooking oil as a feedstock.

The specific objectives are:

i To carry out desilication and mild dealumination of commercial zeolite Y.

ii To study effect of concentration of desilication and dealumination reagents.

iii To carry out protonation and characterization of the hierarchical zeolite Y using X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Brunnauer, Emmeitt and Teller (BET) analyses.

iv Optimization of biodiesel production using commercial zeolite Y catalyst and hierarchical zeolite Y catalyst produced via Response Surface Methodology (RSM).

v Characterization and determination of the physiochemical properties of the biodiesel produced.

1.4 Justification of the Study

The use of waste materials has attracted a great deal of attention in the production of biodiesel whereby feedstock cost plays a critical role in determining the competitiveness of biodiesel. Biofuel has shown to be economically and environmentally friendly and countries all around the world are working to develop alternative means of fuel that is cheap, available and requires no special means of storage or dispensing facilities. Biodiesel is considered an alternative as it meets the aforementioned qualities. In order to produce quality biodiesel and have a safe environment, the method to apply is very important. For this study, heterogeneous catalyst was use due to it suitable eco-friendly alternatives because of their ease of separation from the reaction medium, corrosion reduction and reusability (De Almeida *et al*., 2008). Their improvement could aid process design for the continuous production of biodiesel to minimize purification costs. In this research, hierarchical zeolite Y catalyst was used since the conventional zeoite Y catalyst has a challenge. Over the years, zeolites with hierarchical porosity have been reported to outperform their purely micro porous counterparts in numerous acid catalyzed reactions (Pérez-Ramírez *et al*., 2008). Usually; this behavior is assigned to improved mass transfer due to the introduction of a secondary mesoporous network of inter- or intra-crystalline nature. Indeed, hierarchically porous zeolites offer enhanced accessibility and transport of molecules to and from the active sites (Groen *et. al*., 2006), therefore enhancing catalyst effectiveness.

1.5 Scope of the Study

This work will cover the use of zeolite Y as heterogeneous catalyst in biodiesel production via transesterification process, by investigating interactive effects among process variables (methanol-to-oil molar ratio, catalyst dosage and reaction time). Also the commercial zeolite Y obtained from Zeolyst International (CBV780) with Si/Al of

2.4 and hierarchical zeolite Y catalyst produced were used. Production of hierarchical zeolite Y catalyst was done using different solution of NaOH and H_4EDTA at different concentration (0.1 M, 0.3 M and 0.5 M). Then each concentration was carried out with a reflux heating for 30 min. Then the characterization of protonated hierarchical zeolite Y produced was carried out by Scanning Electron Microscopy (SEM), to show the morphology structure of the element, X-Ray diffraction (XRD) and N_2 adsorption. The hierarchical zeolite Y catalyst obtained through desilication and mild dealumination process and the raw commercial zeoite Y were tested to see the efficacy of it in biodiesel production via transesterification process, using methanol and waste cooking oil (WCO) as feedstock to produce the methyl ester (biodiesel) and glycerol (by product).

1.6 Limitation of the Study.

Every research has one limitation or the other, in this research the effect of water composition of the WCO and economic analysis of the biodiesel production will not be covered. The sustainability, environmental impact assessment of waste cooking oil in biodiesel production and any other factor not stated are beyond the scope of this work.

CHAPTER TWO

2.0 LITERATURE REVIEW

Demand for sustainable production of biodiesel as an alternative energy source is ever increasing. This is because of their environmental friendliness, acceptable quality of exhaust gasses and similarity to petroleum diesel (Biswas *et al*., 2019). These demands arise from the need to minimize the use of fossil fuel by replacement with a suitable alternative energy source that is renewable and sustainable. This effort is being accelerated by depletion of fossil fuel reserve, ever-increasing fuel price and environmental pollution via greenhouse gas (GHG) emission (Ounas *et al*., 2011). Therefore, there arises a need to find fuel processing techniques that could help to obtain quality fuel products. Biodiesel is an essential renewable and sustainable energy source of this repute.

Generally, one can use homogeneous basic or acid catalyst or their heterogeneous counterpart for biodiesel production. However, homogeneous basic is said to be about 4000 times faster than heterogeneous catalysts (Farag *et al*., 2012). This is because they dissolve in the reaction medium to facilitate interaction with the reactants. However, they are not reusable. Likewise, the process is plagued by soap formation, corrosion of reaction medium and production of a large amount of wastewater during glycerol separation. Solid acid catalysts are in principle much more suitable heterogeneous catalyst for biodiesel production (Rinaldi *et al*., 2009). This is because of their ease of separation from the product thereby making it reusable. Furthermore, they do not corrode the reaction medium nor pose any environmental challenge when disposed.

2.1 History of Biodiesel

The history of bio oil is traced back to the development of biodiesel in the 1890s by an inventor Rudolph Diesel, who invented the diesel engine that became the engine of choice for power, reliability, and high fuel economy, worldwide. Modern biodiesel fuel, which is made by converting cooking oils into compounds called unsaturated fat methyl esters (Shalini *et al.*, 2012).

Cooking oil based biodiesel fuel was initially shown at the 1900 world's fair, when the French government custom-assembled the Otto organization to construct a diesel motor to run on shelled nut oil. However, amid the 1920's, because of the lower consistency and accessibility of petrol diesel contrasted with biodiesel, diesel motor makers determined to adjust their motors to match the properties of petrol diesel. Despite the predominant utilization of petrol diesel, a few nations amid World War II, for example, Belgium, France, Portugal, Italy, Brazil, United Kingdom, Germany, Japan, Argentina and China tested and utilized cooking oil as fuels. The transformation of cooking oil for their uses as fuel was proposed by a Belgian Inventor. This technique portrayed the transesterification of cooking oil utilizing ethanol to change over the cooking oil into unsaturated fat mono alkyl ester (FAME). This most likely is the first record of biodiesel creation in biodiesel fuel history. Germany accounts for 50 % of biodiesel comprehensively, thereby making the nation the biggest maker of biodiesel on the planet (Etim, 2012).

The biodiesel business in Europe is upheld by duty motivators (tax incentives), production market, consequently making it the most noteworthy maker and purchaser of biodiesel on the planet. The enthusiasm of Asia in biodiesel creation is to enhance power era, yet Japan specifically is seeking after restrictive positions in unconventional processing methods (Blume and Hearn, 2007). Some nations in Africa because of high petroleum costs, potential for monetary and rural improvement, foreign exchange saving, are considering bio fuels production. Hence since mid-2000s, there has been an enthusiasm toward bio fuel production in Africa. In 1979 in South Africa, transesterified oil was refined to diesel fuel standard and in 1983 the system for assembling engine-tested, fuel-quality biodiesel was finished and made accessible globally.

The ability of the world to create renewable feedstock, for example, cooking oil and fat to keep the expense of biodiesel competitive with petroleum diesel without relocating area fundamental for sustenance of generation will play far to impact the fate of biodiesel. As a result of progress in production technology and the increasing number of oil companies investing in biodiesel, it shows that the biodiesel fuel will account for a larger share of petroleum diesel pool in the future. Therefore, Governments across the world are inclining towards unconventional forms of energy as crude oil prices continue to rise (Blume and Hearn, 2007). Refiners that invest in biodiesel production are not only guaranteed present and future profits, they will also demonstrate to be the most important to the regions they serve because of their adaptability and also their innovation (Blume and Hearn, 2007).

2.2 Biodiesel Production

Biodiesel production is the act of producing biodiesel through transesterification or alcoholysis. The process involves reacting cooking oils or animal fats catalytically with short-chain aliphatic alcohols (typically methanol or ethanol). There are a number of methods used in the production of biodiesel; the three most widely used technologies in this context are pyrolysis, micro emulsification and transesterification (Schwab *et. al,* 1987).

2.2.1 Biodiesel production techniques

The direct use of cooking and animal oil as fuel in diesel engines has been considered both unsatisfactory and impractical majorly due to high kinematic viscosity, low volatility and high fatty acid content of such oils which leads to gum formation due to oxidation, carbon deposit during combustion and polymerization during storage (Sakai *et al*., 2009). As such different techniques have been developed to alter the properties of lipids to approximate that of diesel. Major techniques for biodiesel production are direct use or blending of raw oil, micro-emulsion, thermal cracking, and transesterification (Siddiquee and Rohani, 2011). A comparison of the various biodiesel production techniques showed that emulsion and thermal treatment techniques consumes more energy, produces large amount of unwanted byproducts and require high cost equipment as compared to transesterification. Also, higher yield and purity of biodiesel is obtainable using transesterification (Atabani *et al.*, 2012). Therefore, transesterification technique is currently the most used by researchers (Verma *et al*., 2016).

2.2.2 Mechanism for transesterification

Transesterification is the most widely researched biodiesel technique by the scientific community (Khan *et al*., 2017). The alcohol or acid groups are exchanged when esters are heated with alcohols, acids or other esters in the presence of a catalyst. This process is called transesterification. This reaction is usually accelerated by the presence of small amount of acid or alkali. Transesterification consists of a sequence of three consecutive reversible reactions as represented in Figure 2.1. Initial conversion of triglyceride to diglyceride is followed by conversion of diglyceride to monoglyceride and finally monoglyceride to glycerol with each step yielding one ester molecule from glyceride conversion. There are three types of transesterification reactions namely alcoholysis (exchange of alcohol groups), acidolysis (exchange of acid groups) and esterification (ester exchange). Alcoholysis is commonly referred to as tranesterification and in biodiesel production, alcoholysis and esterification are most commonly used (Lam *et al*., 2010

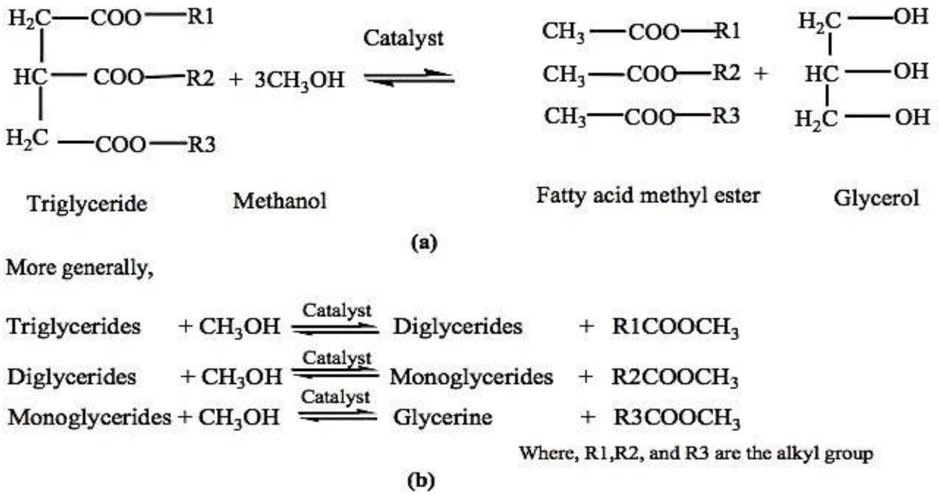

Figure 2.1: Reaction for transesterification of triglycerides (Lam *et al*., 2010).

A lot of work has been done on transesterification by researchers. Using rapeseed oil, transesterification reaction of triglyceride to produce fatty methyl ester was investigated using doped lithium calcium oxide. Biodiesel yield of 97 % was obtained at optimum conditions (Khurshid, 2014). Biodiesel production from rubber seed oil via transesterification reaction was performed by Gimbun *et al*. (2012). Result of the reaction showed efficient conversion of rubber seed oil. FAME yield of up to 96.9 % at reaction temperature of 65 ^{o}C, reaction time of 4 hour and methanol to oil ratio of 5:1 was achieved. Buasri *et al*. (2013) carried out transesterification of palm oil using waste shell as catalyst to produce biodiesel of good quality. In optimizing biodiesel production, the conducted transesterification to produce biodiesel from palm oil using chicken egg shell as catalyst and 92 % yield at optimum conditions was recorded. Biodiesel was synthesized from waste frying oil (WFO) using calcium oxide catalyst by transesterification reaction. A yield of 94.25 % was attained at methanol to oil ratio of

12:1, reaction time of 1 hour and temperature of 65 ^{o}C (Niju *et al*., 2014). Over 97 % of conversion to FAME was achieved for both soapnut and jatropha oil when tranesterification reaction was performed by Chhetri *et al*. (2008). Parametric study of biodiesel production from waste cooking oil (WCO) by transesterification using calcium oxide supported with silica from egg shell mixed with rice husk was performed. At optimum operating condition, biodiesel yield of 90 % was obtained (Lani *et al*., 2017). According to Akaagerger *et al*. (2016) in their research on transesterification of desert date for biodiesel production recorded that FAME yield of 82 % obtained compared very well with international biodiesel standards.

In an attempt to improve the process of transeterification particularly with respect to reaction time and biodiesel quality, techniques like microwave assisted transesterification, transesterification reaction at supercritical conditions, and ultrasonic assisted transesterification was suggested. Liu` (2013) demonstrated the potential for use of transesterification reactions in supercritical methanol to produce biodiesel fuels from microalgae oil. Another study on tranesterification of karabi oil using ultrasonic assisted method resulted in efficient conversion to biodiesel (Yadav *et al*., 2018). Also, Zhang *et al*. (2010) performed an experiment using microwave technique for transesterification of yellow horn oil to produce biodiesel and recorded FAME yield of 97 %. The effect of microwave radiation on transesterification of waste cooking oil in the presence of alkali catalyst in batch process was studied. A comparison of this technique with that of conventional heating process of transesterification showed a significant reduction in reaction time when transesterification was aided by microwave for biodiesel production (AlSuleimani and Dwivedi, 2014).

2.3 Feedstock for Biodiesel Production

There are different feedstock use depending on the availability and economic benefits. The predominant feedstock used in the United States is soybean oil, while rapeseed oil is mainly used in Europe. Other cooking oils, such as corn, cottonseed, flax, sunflower and peanut, also can be used. These seed oils generally are more expensive than soybean oil. Palm oil and palm kernel oils have also been used successfully by Pedavoa (2010). Animal-derived products such as tallow, choice white grease (lard), poultry fat and yellow grease are also triglycerides and are used as a biodiesel feedstock. These products, when compared to plant-derived oils, often offer an economical advantage as a feedstock. There is also some indication that these sources, which are high in saturated fats, produce less nitrous oxide compared to plant oils. The third main source of triglycerides is recycled oil and grease, usually from restaurants and food processing plants. Although more pre-treatment is required for this feedstock compared to virgin cooking oils, economically it can be a very attractive feedstock. The use of a recycled product such as used cooking oil is an environmentally friendly process since it solves a waste disposal problem.

Table 2.1: Lipid-Rich Raw Materials for Biodiesel Production (Rostagno *et al*., 2011)

Edible Oils	**Nonedible Oils**	**Animal Fats**	**Other Resources**
Coconut	Castor	Beef tallow	Algae
Corn	Cottonseed	Chicken fats	Cooking oil
Hemp seed	Desert date	Fish fats	Pomace oil
Mustard seed	Jatropha	Porklard	Soap stocks
Olive	Jojoba	Waste salmon	Tall oil
Palm	Karanja		
Peanut	Linseed		
Pumpkin seed	Mahua		
Rapeseed	Moringa		
Safflower seed	Polonga		
Sesame seed	Rubber seed		
Soybean	Tobacco seed		

2.3.1 Feedstock pretreatment

Before transesterification, the feedstock or oil has to usually undergo a number of treatment stages to get rid of impurities such as phosphatides, free fatty acids, waxes, tocophenols or colorants, which may interfere with the reaction. The process of degumming is usually used to remove phosphatides which make the oil turbid during storage and enhances the accumulation of water in the biodiesel. Degumming could be water or acid based. Soluble phosphatides are removed by adding water to the oil at a temperature of 60˚- 90˚C and centrifuging. The insoluble phosphatides are removed adding acid solutions to decompose the material (Gutsche, 1997). A recent development for effectively getting rid of both soluble and insoluble phosphatides is the use of enzymatic hydrolysis. Deacidification is used in treating edible oils to prevent the rancid flavor in the product. For transesterrification the removal of excess amount of Free Fatty Acids (FFA) is vital. This is because they favour soap formation and impede the separation of glycerol phase due to emulsifying effects of soaps. In extreme cases the oil might gel after the addition of base catalyst when FFA is greater than 5 %. Deacidification is achieved by neutralization with alkali. Solvent extraction and distillation have both proved successful in deacidification. If waste cooking oil (WCO) is used, it is filtered to remove dirt, charred food, and other non-oil material often found. Water is removed because its presence causes the triglycerides to hydrolyze, giving salts of the fatty acids (soaps) instead of undergoing transesterification to give biodiesel.

2.3.2 Animal fats and oil

Animal fats and oils are referred to as lipids materials derived from animals. In most cases the physical appearance of oils is liquid at standard room temperature, while fats are basically solid. Chemically, both fats and oils are composed of triglyceride. Saturated Fatty acids are those without double bonds, that is those with more than one bond are referred to as unsaturated; one double bond are called monounsaturated while many double bonds are called polyunsaturated. Generally, triglyceride is likely to be fat (solid) as chains become longer and/or more saturated, while as chains become shorter and/or more unsaturated is more likely to be an oil. Animal fats are highly viscous and mostly in solid form at ambient temperature because of their high content of saturated fatty acids. The high viscous fuels lead to poor atomization and result in incomplete combustion. The consequences are the increased emissions of pollutants and particulate in the exhaust gas (Kerihuel *et al.,* 2006). Although many animal parts and secretions may yield oil, in commercial practice, oil is extracted primarily from tissue fats obtained from livestock animals like pigs, chickens and cows. Flesh and animal fat have a melting temperature of about 184 °C, a boiling point of around 200 °C and an ignition point of 280 °C where it will burst into flames without spark (Okruszek, 2012). Animal fats are commonly consumed as part of a western diet in their semi-solid form as milk, butter, lard, schmaltz, and dripping or more commonly as filler in factory produced meat, pet food and fast-food products. The main difference between animal fat and cooking oil is their fatty acid composition. Cooking oils have high content of unsaturated fatty acids, mainly oleic and linoleic acid, while animal fat composition has higher proportion of saturated fatty acids.

Table 2.2: Average Fatty Acid Composition of some Cooking Oil and Animal Fat (Rostagno *et al.*, 2011)

Oil or Fat	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:4	≥20
Chicken	1.3	17-20.7	5.4	6-12	42.7	20.7	0.7-1.3	0.1	1.6
Melon	-	12.88	0.74	6.70	13.23	62.35	2.42	-	-
Lard	1-2	23.6-30	2.8	12-18	40-50	7-13	0-1	1.7	1.3
Tallow	3-6	23.3-32	4.4	19-25	37-43	2-3	0.6-0.9	0.2	1.8
Fish	6.1	14.3	10.0	3.0	15.1	1.4	0.7	0.7	56
Butter	7-10	24-26	-	10-13	1-2.5	2-5	-	-	-
Soybean	0.1	6-10.2	-	2-5	20-30	50-60	-	-	-
Rapeseed	0.1	3.9	0.2	1.7	60.0	18.8	9.5	-	4.0
Corn	1-2	8-12	0.1	2-5	19-49	34-62	0.7	-	2.0
Olive	-	9-10	-	2-3	73-84	10-12	Traces	-	-
Cotton	-	20-25	-	1-2	23-35	40-50	Traces	-	-

2.3.3 Cooking oil

Cooking oil is a triglyceride extracted from a plant, the source of cooking oil is plants. Most, but not all cooking oils are extracted from the fruits or seeds of plants, and the oils may be classified by grouping oils from similar plants, such as "nut oils". Cooking oils as renewable raw materials for new industrial products such as lubricants, they have been a great benefit to mankind because of the emphasis on environmental friendly lubricants is large in demand due to the rapid depletion of world fossil fuel reverses and increasing concern for environmental pollution from excessive mineral oil use. Its lubricating properties are high viscosity index, low volatility and good lubricates. However, due to its instability and easily damaged nature, limit its application in the lubricant industries. This includes hydrolytic instability, poor low temperature properties, oxidative properties and poor thermal properties. These short comings can be solved through combining the oil with additives or through chemical modification such as esterification, epoxidation and hydrogenation (Salimon and Asmaa'Ishak, 2012).There are many types of cooking oils: melon seed oil, Cottons seed oil, Poppy seed oil, Rapeseed oil, safflower seed oil, sunflowers seed oil, sesame seed oil, linseed oil, Wheat grain oil, Corn marrow oil, Castor seed oil, Soybean oil, Peanut kernel oil, Hazelnut kernel oil, Walnut kernel oil, Olive kernel oil, Almond kernel oil. These Cooking oils are majorly grouped into two classes, based on their human usage; these are the edible and non-edible oil.

2.3.4. Edible cooking oil

These are group of cooking oil (plant source) that is directly consumed by man as food. The edible oils such as palm, groundnut, melon, sun flower, soybeans and coconut oil are for human consumption as food, cosmetics, and also for the production of biodiesel and bio lubricant. The table below shows the world consumption rate of some edible cooking oil and its application.

Table 2.3: World Consumption Rate of Common Cooking Oils (Rostagno *et al.,* 2011)

Oil source	World consumption (million metric tons)	Uses
Olive	2.84	Used in cooking, cosmetics, soaps and as a fuel for traditional oil lamps.
Soybean	41.28	Accounts for about half of worldwide edible oil production
Palm	41.31	The most widely produced tropical oil, also used to make bio fuel
Coconut	3.48	Used in soaps and cooking
Cottonseed	4.99	A major food oil, often used in industrial food processing
Peanut	4.82	Mild-flavoured cooking oil
Sunflower seed	9.91	A common cooking oil, also used to make biodiesel

2.3.5 Non-Edible oils for biodiesel

It has been found that one way of reducing cost of production for biodiesel is the use of non-edible oils, which tend to be considerably cheaper than edible cooking oils (Srivastava and Prassad, 2000). A number of plant oils contain substances which make them unsuitable for consumption; coaster oil has ricin, a highly toxic lectin. It is also not suitable for consumption due to its laxative effects which is ascribed to its property that about 90% of the oil is ricinoleic acid. Jatropha (physic nut) cannot be used for food purposes because of its content of a toxalbumine called curcine and the presence of various toxic phorbol esters. Other oils such as karanja, crambe, neem and rubber seed oils are all non-edible and can be used as feedstock. In some cases, these toxic substances can be removed by refining. However, in many cases the removal of toxic components from the fatty material has not been accomplished or even attempted yet (Pedavoah, 2010).

2.4 Alcohol for Biodiesel Production

In transesterification, the reactivity is greatly correlated to the alcohol: the longer the alkyl chain of alcohol, the longer the reaction treatment while in alkyl esterification of fatty acids, the conversion does not depend on the alcohol type because they have a similar reactivity. Therefore, the selection of alcohol in biodiesel production should be based on consideration of its performance properties and its economics. Various alcohols such as methanol, ethanol, propyl alcohol and butanol can be used for the process of transesterification, however; in most production, methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters). This is because of its low price and high reactivity as compared to longer-chain alcohols. Alkali catalyzed methanolysis can be conducted at room temperature and gives ester yields of more than 80 % even after as little a reaction time as five minutes (Mittelbach, 1989). Also the separation of alkyl ester and glycerol proceeds fast and completely. Furthermore, methanol is easily in the absolute form (has higher purity), compared to ethanol hence hydrolysis and soap formation due to water contained in the alcohol can be minimized.

2.5 Factors Affecting Biodiesel Production

Dhikrah *et al.* (2018) reported that factors such as the alcohol to oil ratio, reaction temperature, reaction time and catalyst play an important role in biodiesel yield. The optimum molar ratio between methanol and oil depends on the type of catalyst used. From the stoichiometry of transesterification, the reaction requires three moles of alcohol per mole of triglyceride (Mittelbach *et al*., 1983). However, in order to shift the equilibrium to the right, an excess of the alcohol is frequently recommended. A molar ratio of 6:1 was suggested by Freedman *et al*., 1986 for the transesterification of soybean oil for alkali-catalyzed reaction in order to obtain the maximum ester yields. It has been found that higher amounts of alcohol in the reaction mixture are likely to interfere in the separation of the glycerol phase (Srivastava and Prassad, 2000). However, molar ratio 30:1 has been frequently reported for acid catalyzed transesterification (freedman *et al*, 1984). Also, Ismail *et al*. (2020) reported that an increase in the reaction temperature help moves the equilibrium point to the right as such leading to a successful biodiesel production. The author also stated that an increase in the reaction time usually favored the conversion rate leading to more biodiesel yield however a lengthened reaction time would result in no appreciable change in the biodiesel conversion process. Other factors that affect biodiesel yield include the option of the alcohol used, the presence of water and the use of and the type of catalyst used.

2.6 Catalyst

At high temperatures and pressures, transesterification of triglycerides with lower alcohols can proceed in the absence of a catalyst. The advantage of not using a catalyst is that high purity esters and glycerol are produced. The use of supercritical methanol without catalyst has been reported, this is, however, not economical due to the high energy requirements (Kusdiana and Saka, 2001). Thus to achieve satisfactory ester yields under mild reaction conditions, biodiesel production is generally done in the presence of some type of catalyst; alkaline and acid materials as well as transition metal compounds, silicates and lipases. A catalyst is usually used to generate an alternative pathway for a reaction to occur, in transesterification an acid, alkaline or enzyme may be used as a catalyst. Alkaline catalysis is by far the most commonly used reaction type for biodiesel production. This method has the advantage over the acid-catalyzed transesterification due to its high conversion under mild conditions in comparatively short reaction time (Freedman *et. al*, 1986). In this present work, zeolites with hierarchical porosity have been chosen as source of heterogeneous catalyst due to its enhanced catalyst effectiveness. In the past few decades, zeolites with hierarchical porosity have been reported to outperformed their purely microporous counterparts in numerous acid catalysed reactions (Pérez-Ramírez *et al.*, 2009). There are three different types of catalysts that can be employed in the transesterification process of biodiesel: acid catalysts, base catalysts and biocatalyst (Pathak, 2015).

2.6.1 Homogeneous acid and base catalyst

The most used acid catalyst is concentrated sulphuric acid (Conc.H_2SO_4), this is because it is of lower price and hygroscopic, which is necessary for the esterification of FFAs (removing released water from the reaction mixture). The disadvantages are, however, that it is corrosive, has the tendency to attack double bonds in unsaturated fatty acids and may cause darkening of ester product. Unfortunately, though the alcoholates and alkali metals enable high conversion, they are expensive and pose a safety risk, thus, unattractive for commercial biodiesel production. According to Mittelbach *et al*. (1983), alkali hydroxides might be the promising alternative which is cheaper and easier to handle. These also showed that alkali catalyzed hydrolysis and soap formation played an insignificant role in water free alcohols. Also, in methanolysis, the fast separation of the glycerol phase removes most of the catalyst from the reaction mixture, thus the produced esters will hardly come in contact with hydroxides. This is common with KOH than NaOH, as it increases phase separation by increasing the density of the glycerol layer due to its higher molecular weight (Mittelbach, 1989). Ester losses are also reduced due to decrease in the amount of methyl esters dissolved in the glycerol phase. The by product, such as; potassium dihydrogen can be processed into fertilizers, whereas the byproduct of NaOH transesterification processes are faster and NaOH is cheaper than KOH. The major disadvantages of homogenous catalysts are that they cannot be reused and catalyst residues have to be removed by a series of washings, which increases production cost.

2.6.2 Heterogeneous acid and base catalyst

In recent time heterogeneous catalysis has become more prominent for use in biodiesel production because it is insensitive to excess FFA, easily removed from reaction mixture, reusable, and readily available (Talha and Sulaiman, 2016). Heterogeneous catalysts are catalysts that are not in the same phase as the reactant in the reaction process. The extra purification stage incurred by use of homogeneous acid catalyst in the process of its extraction from product has led to higher biodiesel production cost. The introduction of heterogeneous acid catalyst has been observed to address the issue of the need of extra purification step thereby reducing the cost of biodiesel production (Talha and Sulaiman, 2016). Also, heterogeneous acid catalyst is hydrophobic and can tolerate water in feed stock up to 20 % without significant reduction in catalytic activity (Issariyakul and Dalai, 2014). Other advantages of the use of heterogeneous acid catalyst relative to homogeneous acid and base catalyst include its ability to handle simultaneously esterification and transesterification reaction, elimination of extra washing step of biodiesel and reduced corrosiveness. Solid acid catalysts are preferred to liquid acid catalysts because they contain multiple sites with different strength of Lewis or Bronsted acidity which confers on it the ability to perform esterification and transesterification simultaneously.

2.6.3 Enzymatic catalysts

Enzymatic catalysts possess properties of both homogeneous and heterogeneous catalysts. In recent years, enzymatic reactions using lipase have attracted growing attention due to its advantages over chemical catalysts: it has easy product recovery, environmental-friendly properties, high selectivity and a low alcohol-to-oil molar ratio (Vyas *et al*., 2010). Enzyme catalysts tolerate FFA and water content, facilitating easy purification of biodiesel and glycerol. Enzyme catalysts are expensive, though, and biodiesel can be contaminated by residual enzymes. While enzymes can be easily deactivated, a long reaction time is required. These major drawbacks limit industrial application of enzymes in the production of biodiesel (Boey *et al.*, 2009; Endalew *et al*., 2011). In order to minimize some of these limitations, immobilized enzymes are employed. These facilitate multiple uses and consequent cost reduction. However, the build-up of glycerol limits the number of their reusability (Vyas *et al*., 2010).

2.6.4 Zeolites as catalyst from natural sources for industrial and chemical processes

Zeolites are microporous aluminosilicate materials with a three dimensional pore structure that play an important role in many industrial and chemical processes as molecular sieves. Their shape selective properties allow control of product allocation in chemical processes and have made them invaluable as catalysts in the petrochemical industry (Chen and Garwood, 1986). ZSM-5 zeolite has been utilized in many catalytic reactions such as cracking; production of light olefins, olefin oligomerisation, isomerization and alkylation processes (Pan *et al*., 2014). While ZSM-5 is generally synthesized using costly chemicals finding cheaper raw materials for zeolite synthesis could lead to cost effective and sustainable production as a whole. In the recent past researchers have examined the use of natural cheaper minerals such as rice husk ash (Kordatos *et al*., 2008; Panpa and Jinawath, 2009), fly ash, expanded perlite, kanemit, palygorskite (Kovo *et al*., 2009) as starting materials in the synthesis of ZSM-5. These studies have shown that the compel to utilize natural minerals is their significant aluminosilicate contents which is the main ingredient for the synthesis of zeolites, relative abundance, cost effectiveness and innovation of synthetic routes that are more environmentally friendly and reduce overall costs. However, the minerals differ in their chemical and mineralogical compositions which may affect the final product if used as precursors for zeolites. Kaolin has been used as a staring material and was successfully converted to a range of zeolites (Belviso *et al*., 2013; Kovo and Holmes, 2010). Low silica zeolites such as zeolite A and X are easily synthesised from kaolinite due to the similarity in Si/Al ratios (Pan *et al*., 2014). However, synthesis of high silica zeolites such as Y and ZSM-5 require addition of an external silica source or dealumination of kaolinite to obtain a favourable Si/Al ratio (Feng and Shan, 2009; Liu *et al*., 2007). Only a few studies have been performed on raw kaolins with high quartz content such as those by Kovo (2011) using Ahoko Nigerian kaolin to synthesise ZSM-5 and zeolite A respectively. The respective zeolites could be synthesised after using beneficiation techniques (i.e. extensive settling and flocculation) or a modified autoclave to separate impurities from the synthesis gel. However, the ZSM-5 final product still contained quartz and mordenite impurities attributed to unreacted metakaolin and similarities in the synthesis conditions for both ZSM-5 and mordenite. The zeolite A purity was affected by colloidal impurities in the dispersion and the ‘virgin’ kaolins till required some treatment before use. Therefore, beneficiation of kaolinis are necessary pre-treatment in the synthesis of ZSM-5. Furthermore, the difference in chemical reactivity of kaolins from around the world of various geological areas does affect the synthesis conditions of various zeolites and must be optimised for particular kaolins.

2.6.4.1 Activation of zeolite by alkali

Alkali activation adjusts the acidity, surface area, pore size, and volume as well as its adsorption strength. This makes it a suitable precursor for solid basic catalyst (Colina *et al*., 2002; Slaty *et al*., 2013). Activation technique using alkali, deprotonates aluminol and silanol groups from kaolinite. This leads to simultaneous dealumination and desilication of the kaolinite material (Hu and Yang, 2013). However, the extent of dealumination is always low or insignificant (Serrano and Pizarro 2013). Kumar *et al*.

(2013) reported that kaolinite treated with 3 M of NaOH at 110 °C exhibits significant changes. This change includes surface area (23 to 76 m^2/g), pore volume (0.361to 0.591 cm^3/g).

2.6.4.2 Activation of zeolite by acid

Acid activated zeolites are popular in adsorption, ion exchange and silica aluminaphosphate such as SAPO-34 and SAPO-5. Acid activation enhances zeolite acidity, surface area, pore size, and volume as well as its catalytic properties. This makes it a suitable precursor for a solid acid catalyst for petrochemical processes (Lenarda *et al*., 2007). Organic and inorganic acid activate kaolinite chemically (Hussin *et al*., 2011). Acid activation leads to dealumination, removal of mineral impurities, disaggregation of kaolinite particles, and external layer dissolution. This changes the structure and chemical composition of the kaolinite materials (Panda *et al*., 2010). Recently, synthesizing solid acid catalysts from zeolites for petrochemical industries has received great attention from numerous consortia. These interests highlight the importance of acid activated kaolinite for heavy molecule conversions. This is because it is cheaper, and its pore size and structure is more suitable than that of zeolites (Lenarda *et al*., 2007). However, for effective chemical activation, ~ 550 to 950 °C is the calcination temperature range for forming metakaolin from kaolinite. This is because of the presence of strong hydrogen bond between its layers, making it resistance to chemical attack (Dudkin *et al*., 2004). Aside increasing kaolinite porosity, acid activation also enhances acid center and surface area. Further, kaolinite is suitable as an inorganic host for intercalation and exfoliation (Valášková *et al*., 2011). Acid activation protonates the aluminol (AlOH) group using the hydrogen ion from aqueous acid medium and this leads to dealumination and increasing the Si/Al ratio of the synthesis materials (Hu and Yang, 2013). The synthesized material is a mixture of inactivated kaolinite, amorphous and hydrous aluminosilicate as well as some partially protonated silica lamellae (Belver *et al*., 2002). The solubility of kaolinite varies from acid to acid, ratio of kaolinite to acid, operating temperature, leaching period, kaolinite particle size as well as the concentration of the acid. Kaolinite solubility increases with acid concentration and leaching period, but excessive leaching leads to decrease in surface area (Panda *et al*., 2010). Activation with inorganic acids is more effective in generating new surface acid sites. This leads to a collapse of the kaolinite structure because of excessive leaching of the octahedral layer. On the other hand, organic acids do not generate new acid sites as effective as the mineral acids. Meanwhile, they preserve the kaolinite structure because of their low activation power.

2.6.4.3 Zeolite as catalysts for biodiesel production

Zeolite catalysts are of distinguished importance in a number of chemical reactions associated with the (petro) chemical and oil refining industries, (Vermeiren and Gilson, 2009), and raise substantial interest in new applications,such as the conversion of biomass into valuable chemicals (West *et al*., 2010). Nevertheless, especially during the processing of bulky molecules in the liquid phase, a sub-optimal utilization of the active sites present in zeolites is often implied by limited access and slow intra-crystalline diffusion in their micropores (Vermeiren and Gilson, 2009). In response to the need of improved catalytic processes, hierarchical (mesoporous) zeolites were conceived. These modified zeolites integrate the native microporosity with an auxiliary level of inter or intra-crystalline mesopores, increasing the external surface area substantially. This brings enhanced accessibility due to the increased number of pore mouths and shortened average diffusion pathlength in the micropores (Pérez-Ramírez *et al*., 2008).

The superior lab-scale performance of hierarchical zeolites compared to conventional counterparts in a wide range of catalyzed reactions is unquestionable. Currently, a varied assortment of top-down and bottom-up approaches is available to synthesize hierarchically structured zeolites (Tosheva *et al.,* 2005; Roth and Cejka, 2011; Verboekend *et al*., 2011). The synthetic elegance of bottom-up methods is counteracted by a low chance for industrialization, since they commonly necessitate the use of costly and commercially unavailable reactants as mesopore-inducing agents, (Chen *et al*., 2011; Chal *et al*., 2010; Choi *et al*., 2009) and/or lead to products not easily separated from the mother liquor, nanocrystals or nano-sheets (Verboekend and Perez-Ramirez, 2011). On the other hand, top-down approaches such as demetallation are highly effective and scalable at a reasonable cost. As a matter of fact, post-synthetic modifications are largely responsible for the success of zeolites in general, yielding superior catalysts in terms of stability, composition, and acid site speciation (Vermeiren and Gilson, 2009). The ultra-stable derivative (zeolite USY) is widely used in industry for fluid catalytic cracking and hydrocracking, (Vermeiren and Gilson, 2009) and a generalized protocol to synthesize hierarchical analogues would be of prominent value because of the relatively bulky hydrocarbons involved and the need to control selectivity and to increase lifetime.

The dealumination of the framework can, besides increasing (hydro) thermal stability, also lead to the introduction of a secondary network of mesopores in the zeolite crystal. Nevertheless, in the case of steam treatment, the formed mesopores do not significantly affect intra-crystalline diffusion of probe molecules (Kortunov *et al*., 2005) since they are mostly present as cavities. In the last decade, base leaching, known as desilication, has become a widely-applied post synthetic treatment, since it enables to introduce a network of connected intra-crystalline mesopores, while conserving the intrinsic zeolite properties. Desilication has been routinely applied to introduce a secondary network of mesopores in multiple high-silica frameworks in the Si/Al range 10 to infinite (Groen *et* *al*., 2006 and Verboekend *et al*., 2011). However, alkaline treatment on zeolites with high Al content (Si/Al ratio < 10) remains relatively unexplored.

2.6.4.4 Zeolites and hierarchical structures

Zeolites are an important class of inorganic microporous crystalline materials widely used in ion exchange, gas adsorption, and heterogeneous catalysis. Zeolites are among the most important solid catalysts in the chemical industry because of their unique shape selectivity, strong intrinsic acidity, and high stability (Li, *et al*., 2018). Shape selectivity in particular renders zeolites of paramount importance in heterogeneous catalysis. This molecular handle affords screening of reactants and/or products that diffuse into or out of the zeolites according to their molecular sizes (Kaerger and Valiullin, 2013), and only the stable and pertained transition states can be formed under the steric constraints of the pores, cages, and zeolite channels (Csicsery, 1986). The philosophy of shape selectivity in zeolites has been well accepted in the petroleum and petrochemical industries and in fine-chemical catalytic processes.

However, the shortcomings of single-sized zeolite micropores cannot be neglected. On the one hand, the narrow zeolite pore sizes that afford high selectivity to catalytic reactions fail to affect molecules with molecular dimensions greater than that of the characteristic pore size. On the other hand, the small pore sizes and long diffusion path lengths not only reduce transport efficiency but also cause poor catalyst utilization and decreased catalytic rates. Therefore, it is highly desirable to enhance the accessibility of bulky molecules to the active sites located in the zeolite channels and to reduce the impact of diffusional limitations while maintaining high selectivity and catalytic activity. Besides, exploring extra-large pore zeolites and nanosized zeolites (Mintova, *et al.*, 2015), significant effort has been expended towards fabricating hierarchical zeolites to overcome these transport limitations. These hierarchical zeolites feature at least two levels of pore systems integrating intrinsic zeolite micropores with mesopores and/or macropores (Schwieger, *et al.*, 2016). Hierarchical zeolites offer the potential to: (i) reduce steric limitations for converting bulky molecules; (ii) increase the rate of intracrystalline diffusion; (iii) inhibit deactivation due to coking; (iv) maximize catalyst utilization; (v) and modulate selectivity towards target products (Schwieger, *et al.*, 2016). These advantages endow hierarchical zeolites with superior catalytic performance compared with their microporous counterparts, especially in the case of reactions where coke deposits readily or those involving relatively large molecules

2.6.4.5 Hierarchy factor of hierarchical zeolite catalyst

Hierarchy factor is a viable tool for measurement of the degree of structural order of a material. It also helps to correlate and to make quantitative comparison of various zeolite materials produced from different synthesis strategies (Pérez-Ramírez *et al*., 2009; Zheng *et al*., 2011; Zheng *et al*., 2010). Pérez-Ramírez *et al*. (2009) proposed a model as a tool for classification of hierarchical mesoporous zeolites as derived from the conventional N_2 adsorption analysis. From the effect of the micropore volume on the total pore volume and the effect of the mesopore specific surface area on the total specific surface area of the weighed sample, they defined hierarchy factor (HF) of any zeolite as follow;

HF = (2.1)

Where,

V_{Micro} = Micropore volume

S_{Meso} = Mesopore specific surface area

V_{Total} = Total volume

S_{BET} = Total specific surface area

In order to maximize the value of HF, the mesopore surface area needs enhancement without penalizing the micropore volume severely. That is to say, rather than playing a competition role; both porosity levels must complement each other: while the micropores play the active sites, the auxiliary mesopores solved the problem of mass transfer limitation. It is also important to note that two or more different zeolite catalysts prepared through different synthesis strategies but with the same value of hierarchical factor may not necessarily exhibit the same catalytic performance in the same reaction due to varying acid strength and distribution. For instance, the one with the highest number of Brönsted acid sites will surely exhibit the best performance (Zheng *et al*., 2010).

2.6.4.6 Reusability of catalyst

Reusability is of a great importance for industrial application, as this may contribute to the decrease of biodiesel production costs. The reusability of several catalysts has been studied intensively. Many heterogeneous catalysts can be reused several times (three-20 cycles) depending on their chemical properties. Catalyst activity is a function of its surface area, acid strength, base strength, surface morphology, chemical composition and acid site concentration (Achanai *et al*., 2013). The structure texture of a catalyst depends on the preparation method (Achanai *et al*., 2013). Catalysts can be easily separated from reaction mixture by filtration or centrifugation and reused for several runs (Hu and Yang 2013). In studying the deactivation of catalysts, (Liu, 2013) discovered that the SrO catalyst could be reused for 10 cycles before decreasing in activity by 90 %. Likewise, Thanh *et al*. (2012) demonstrated that $MnCO_3/ZnO$ catalyst in subcritical methanol processes with soybean oil could be used for more than 17 cycles. The results indicated that TG conversion and FAME yield kept their values above 92 % and 86 % respectively without a regeneration process.

2.7 Optimization of Biodiesel Production

The optimization study is carried out in order to determine how the various process parameters affect the response. The response surface methodology, central composite design is used to carry out the optimization study.

2.7.1 Response surface methodology

The response surface methodology (RSM) is a statistical method which uses quantitative data from appropriate experimental designs to determine and simultaneously solve multivariate equations. This tool can be used in process optimization studies where it serves three primary purposes of; (1) determining the combination of factors which would yield the optimum response; (2) determining how the response is affected by a given set of factor levels; (3) and describing the interrelationship between the process parameters. Design of Experiment (DOE) is an important aspect of RSM which dictate points at which response is to be evaluated (Cavazzuti, 2013). The response surface experimental designs yield polynomial models which may be first order (linear), second order (quadratic) or third order (cubic). The first order models are described by 2^k factorial designs where k is the level of each factor and second order models are described by 2^k +2K+1.

Optimization of a two stage process for biodiesel production from shea butter (SB) using response surface methodology was carried out. Four operating conditions were investigated to reduce the percentage FFA of SB and increase yield of shea butter biodiesel. The operating conditions were temperature (40 – 60 °C), agitation speed (200-1400 rpm), methanol: oil of 2:1 – 6:1(w/w) for esterification and 4:1 – 8:1(w/w) for transesterification and catalyst loading 1 – 2 % (H2SO4, v/v) for esterification and KOH, (v/v) for transesterification.

2.7.2 Central composite design

A 2*k* full factorial to which the central point and the star points are added is known as Central composite design (CCD). The star points refer to the sample points in which all the parameters but one is set at the mean level (m). The value of the remaining parameter is given in terms of distance from the central point. An advantage of CCD lies in the fact that it provides information on the response of interest for levels below and above the chosen factor levels (Cavazzuti, 2013). In their effort to optimize the reaction conditions of biodiesel production from animal fat, Kumar and Math (2016), used RSM – CCD to investigate the combined effects of catalyst concentration, reaction time and methanol quantity of biodiesel yield. A second order statistical model predicted the maximum animal fat methyl ester yield of 85.93 % volume of oil at optimized parameters of methanol quantity (35 % volume of oil), base catalyst concentration (0.46 % weight of oil) and reaction time (90 minutes). Experimentally, maximum yield of 91 % was obtained at the above parameters while a variation of 5.56 % was observed between predicted maximum and experimental maximum yield.

A five-level-four-factorial Central Composite Design (CCD) using Response Surface Methodology (RSM) was employed to optimize the process variables for minimizing the FFA of Jathropha crude oil (JCO) and maximizing the Jathropha crude biodiesel (JCB) yield. Also, JCB yield of 98.3 % was achieved with methanol/oil molar ratio (11:1) using NaOH as catalyst (1 % w/w) in 110 min time at 55 ^{o}C temperature. Second-order model equations were obtained to predict the FFA content and JCB yield as a function of input parameters. Alhassan *et al*. (2013), used a five-level-three-factor central composite rotatable design model of response surface methodology to study the synergistic and antagonistic effects of catalyst concentration, reaction temperature and time, using base catalyzed transesterification process for production of biodiesel from

Gossypium arboreum seed oil. A predicted yield of 94.93±6.92 % for catalyst concentration of 0.53 % by weight of the oil, 60 °C for 105 min was obtained using the least square reduced cubic model (Sharma *et al.*, 2014). The model reliability tests conducted were found to be impressive and conclusively for the optimization of the oil under stated conditions.

2.8 Quality Specifications of Biodiesel

The assessment of fuel quality of biodiesel is usually determined by the ASTM standards. Quality standards are prerequisites for the commercial use of any fuel product. They serve as guide lines for the production process, guarantee consumers that they are buying high quality fuels, and provide authorities with approved tools for the assessment of safety risks and environmental pollution (Prankl, 2002). Manufacturers of engines and automobiles also rely on fuel standards for releasing warranties for their vehicles to be operated on biodiesel, therefore, Table 2.4 show the American Biodiesel Quality Standard and their units.

Table 2.4: The American Biodiesel Quality Standard (ASTM D6751)

Property	**Method**	**Limits**	**Units**
Flash point, closed cup	D 93	130 min	° C
Water and sediment	D 2709	0.050 max	%volume
Kinematic viscosity, 40 ° C	D 445	1.9 – 6.0	mm^2/s
Sulfated ash	D 874	0.020 max	wt. %
Total Sulfur	D 5453	0.05 max	wt. %
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	-	° C
Carbon residue	D 4530	0.050 max	wt. %
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020	wt. %
Total glycerin	D 6584	0.240	wt. %
Phosphorus	D 4951	0.0010	wt. %
Vacuum distillation end point	D 1160	360 °C max, at T-90	% distilled

2.8.1 Comparison between diesel and biodiesel

Table 2.5 show the comparison between petrol diesel oil and biodiesel oil base on American Society for Testing Material.

Table 2.5: ASTM standards of biodiesel and petroleum diesel (ASTM)

Property	**Test method**	**ASTM D975 (Petro diesel)**	**ASTM D6751 (biodiesel, B100)**
Flash point	D 93	325 K min	403 K
Water and sediment	D 2709	0.05 max %vol	0.05 max %vol
Kinematic viscosity (at 313 K)	D 445	1.3 – 4.1 mm^2/s	1.9 – 6.0 mm^2/s
Sulphated ash	D 874	-	-
Ash	D 482	0.01 max %wt	-
Sulfur	D 5453	0.05 max %wt	-
Cetane number	D 613	40 min	47 min
Aromaticity	D 1319	35 max %vol	-
Carbon residue	D 4530	-	0.05 max %mass

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1. Materials

Waste cooking oil (WCO) was collected from Safara Restaurant Minna, Niger State and pre-treatment processes were carried out to remove impurities. The major pre-treatment processes which were conducted were filtration and dehydration. The zeolites Y that was used in this study were provided by Zeolyst International, that is zeolite Y (CBV780) with Si/Al = 2.4. Table 3.1 provides a summary of chemicals used in the experimental work which are all of analytical grade, while the list of equipment and apparatus are also presented in Table 3.2.

Table 3.1: List of Chemical used

S/N	CHEMICAL	Quality	MANUFACTURER	SOURCE
1	H_4ETDA	99.8	Analar BDH	WAFT
2	MeOH		Analar BDH	Panlac, Minna
3	NaOH	99.8	Analar BDH	Chemical Lab.
4	NH_4Cl_2	99.8	Analar BDH	Chemical Lab.
4	KOH	99.8	Analar BDH	Panlac, Minna
5	Phenolphthalein Indicator	-	-	Panlac, Minna
6	Ether		-	WAFT
7	Potassium iodide		-	Panlac, Minna
9	Acetone		-	Panlac, Minna

Table 3.2: List of Equipment and Apparatus used

S/N	Equipment	Model	Manufacturer	Source
1.	Filter Paper	-	-	WAFT LAB
2.	Weighing Balance	MP300	Citizen	WAFT LAB
3.	Refractometer	-	Gallen Kamp	WAFT LAB
4.	Pycnometer	-	Pyrex England	WAFT LAB
5.	Beaker	-	Pyrex England	WAFT LAB
6.	PH meter	PH 25	REX	WAFT LAB
7.	Measuring Cylinder	Jaytec	Pyrex England	WAFT LAB
8.	Burrete	-	Pyrex England	WAFT LAB
9.	Conical Flask	-	Pyrex England	WAFT LAB
10.	Funnel	-	-	WAFT LAB
11.	Pippette	-	Pyrex England	WAFT LAB
12.	Round Bottom Flask	-	Pyrex England	WAFT LAB
13.	Glass Rod	-	-	WAFT LAB
14.	Thermometer	Deluxe	-	WAFT LAB
15.	Heating Mantle	-	-	WAFT LAB
16.	Aluminum Foil	-	-	WAFT LAB
18.	Electric furnace	-	-	WAFT LAB
19.	Magnetic Stirring			CHEM LAB

3.2 Methods

3.2.1 Desilication and mild dealumination of commercial zeolite Y

The Commercial Zeolites Y (CBV780) were obtained from zeolyst international Netherland with Si/Al = 2.4, which was used in this study as the major starting material for production of hierarchical zeolite Y. Production of hierarchical zeolite Y using aqueous solutions of Ethylenediaminetetraacetic acid (H_4EDTA), Sodium Hydrides (NaOH), and NH_4Cl_2, were performed.

Plate I: Experimental Setup of Desilication and Mild Dealumination of Zeolite Y

In a typical experiment of alkaline treatment of the zeolite sample The desired amount of zeolite Y (5 g) was added to a vigorously stirred solution of the desired solute, molarity (0.1M, 0.3M and 0.5 M), at temperature of 333 K (60 ^{o}C), and was left to react for the required time of (30min) each at reflux. Afterwards, the reaction was quenched and the resulting solid was filtered, washed using distilled water until it has neutral pH and then oven dried overnight at 65 ^{o}C. The three desilicated samples were represented as (AT$_1$, AT$_2$ and AT$_3$) was subdivided into three each to undergone acid treatment that is 0.1 M, 0.3 M, and 0.5 M Ethylenediaminetetraacetic acid (H$_4$EDTA) which were prepared, each of the subdivided desilicated sample were further reacted to 0.1 M, 0.3 M and 0.5 M H$_4$EDTA prepared respectively and then allowed to reacted about 3h at a temperature of 80 ^{0}C each using 5 g desilicated zeolite Y per 100 cm^3 of (H4EDTA) at reflux. The reaction was quenched and the resulting solid was filtered, washed using distilled water until it has neutral pH and then oven dried overnight at 65 ^{0}C.

Table 3.3: Zeolite Y Catalyst Preparation Processes at Different Mole Concentration and their Symbols

Zeolite YSamples	Alkaline Treatment (M)	Acid Treatment (M)
HZY-1	0.1 M NaOH	0.1 M EDTA
HZY-2	0.3 M NaOH	0.5 M EDTA
HZY-3	0.3 M NaOH	0.3 M EDTA
HZY-4	0.5 M NaOH	0.3 M EDTA

3.2.2 Protonation and characterization

Treated zeolites Y samples were brought in to protonic form whereby 0.1 M of NH_4Cl_2 was prepared and then mixed with the desilicated and dealuminated Zeolite Y each. Heat was applied on the mixture under reflux at 90 °C for 2 h, and afterwards filters and dried at 80 °C then calcined in static air at 550 ^{o}C for 3 h. The raw zeolite Y also undergone protonation process and then calcined at 550 ^{o}C for 3 h in order to compare the two catalyst effectiveness biodiesel production. The hierarchical zeolite Y sample obtained was characterized using X-ray diffraction (XRD), Scanning Electronic Microscopy (SEM) and Brunnauer, Emmett and Teller (BET) analyses.

3.2.2.1 X-ray diffraction (XRD)

First, 2 g of hierarchical zeolite Y sample was pressed in stainless steel holder and then identification of the crystalline phase was conducted by X-ray Diffractometer system named (EMPYREAN) using Cu as an anode material whereby Kα radiation operated at 45 kV, 40 mA with 0.026° 2θ step size and then scan speed continuously. High-quality diffraction data of the sample was obtaining via this method.

3.2.2.2 Scanning electron microscope (SEM) analysis

The physical surface morphology of catalyst sample obtained was examined using LEO S-440 Scanning Electron Microscope. Little among of hierarchical zeolite Y catalyst sample was raised on an aluminum holder by a double-sided tape. To avoid poor image resolution and discharge of electrostatics, the catalyst sample was coated with gold (Au) to thickness of 1.5 to 3 nm. The test was conducted at different magnifications and data generated was recorded.

3.2.2.3 Brunnauer, emmeitt and teller (BET) analysis

The BET apparatus analyzed the N_2 adsorption–desorption isotherms at liquid nitrogen temperature. Out gassing at 77.100 K with equilibration interval of 10 second before each measurement ensured accurate results on all the samples. T-plot methods and Brunauer–Emmett–Teller (BET) were used to analyze the specific surface area, microporous area, microporous volume and pore-size distribution.

3.2.2.4 Catalyst reusability test

Reusability test was conducted to study the efficiency of hierarachical zeolite Y catalyst produced. The catalyst that gave the highest biodiesel conversion using the same reaction condition as given by design of experiment was used. After the first reaction was done, the catalyst was separated from the reaction product. The catalyst was then washed with acetone for three times to remove the non-polar compounds attached on the catalyst. The catalyst was dried in oven for 24 hours and further used in the next transesterification reaction. The procedures were repeated until no conversion can be recorded.

3.2.3 Physical and chemical characterization of waste cooking oil (WCO)

Before the production of biodiesel, waste cooking oil was characterized for color, odor, fatty acid and viscosity to be sure of its physical and chemical properties. The physical properties determined for the waste cooking oil include moisture content, density, specific gravity, kinematic viscosity, while the chemical properties tested for include pH value, acid value/free fatty acid (FFA), and ester value.

3.2.3.1 Moisture content

The moisture content of oil was quantitatively determined by oven drying method at 105 ^{0}C for 1 hour. 5g of oil was weighed in a crucible using the electronic mass balance. The weight of the crucible and oil obtained was recorded then together was placed in an oven at 105 degrees for a time period of 1 hour after then, it was kept in the desiccators for 15 minutes and then the weight was taken out and weighed with a new mass for both oil and crucible were obtained. The percentage (%) moisture content was determined using the expression:

$$\% Moisture = \frac{W_m - W_d}{W_m} \times 100 \qquad (3.1)$$

Where:

W_m = weight of moist sample

W_d = weight of dry sample

3.2.3.2 Specific gravity (S.G.)

Specific gravity and density of the waste cooking oil sample was done in accordance to the procedure giving by standard ASTM D5355-95 (2012) using 25 ml pycnometer. Dry empty bottle of 25 ml capacity was weighed to give W_o and then filled with the oil and reweighed to give W_1. The oil was then substituted with water and reweighed after the bottle had been washed and dried which then gave a weight W_2. Specific gravity was then calculated using Equation (3.2):

$$\text{Specificgravity} = \frac{W_1 - W_o}{W_2 - W_o} \qquad (3.2)$$

Where:

W_0 = mass (g) of empty Pycnometer,

W_1= mass (g) of the Pycnometer filled with oil sample and

W_2 = mass (g) of the Pycnometer filled with water

Similarly, the density of the WCO was calculated as:

3.2.3.3 Determination of density

Beaker and pipette were washed with detergent and water; this was followed by drying. 5 ml of the waste cooking oil was measured with the aid of pipette into beaker. The oil was weighed 2 to 3 times and the average weight was determined, the measurements were carried out at room temperature. The density was evaluated by Equation (3.3)

$$\text{Density} = \frac{weightofoil\ (g)}{volumeofoil\ (ml)} \tag{3.3}$$

3.2.3.4 Kinematic viscosity

Kinematic viscosity was measured using the procedure described in ASTM D445 test method for opaque and viscous liquids. A clean dry viscometer with a flow time above 200 seconds for the fluid to be tested was selected. The sample was filtered through a sintered glass (fine mesh screen) to eliminate dust and other solid materials in the liquid sample. The viscosity meter was charged with the sample by inverting the tube's thinner arm into the liquid and applied suction force was used to draw it up to the timing mark of the viscometer. The instrument was then turned into its normal vertical position. The viscometer was placed into a holder and inserted to a constant temperature bath set at 30^{o}C and allowed for approximately 10 minutes, so that the sample may attain that temperature. Suction force was then applied to the thinner arm to draw the sample slightly above the upper timing mark. The afflux time by timing the flow of the sample as it flowed freely from the upper timing mark to the lower timing mark was recorded. The procedure was repeated three (3) times and the average value was taken which was then multiplied with the viscometer calibration to give the kinematic viscosity. The kinematic viscosity was determined using Equation (3.4);

$$v = C \text{ x } t \tag{3.4}$$

Where:

v = kinematic viscosity (mm^2/s);

C = calibration constant of the viscosity [(mm^2/s)/s];

t = mean flow time (s).

3.2.3.5 pH value

In accordance with ASTM E70 – 07 standards to determine the pH value of the sample, in this work the pH meter was used to measure the pH of the oil sample by inserting its probe into the sample to read it for about 2 to 3 minutes so that the readings stabilize. The value was then recorded.

3.2.3.6 Acid value/free fatty acid

0.1N KOH solution was prepared by dissolving 5.61g KOH (pellet) with 1000ml distilled water. Furthermore, a mixture of 99.7% pure ethanol and 98% pure benzene in a ratio of 1:1 by volume was prepared by mixing 50 ml benzene and 50 ml of ethanol. About 1g of the oil was weighed and dissolved in the mixture of ethanol and benzene. The solution was titrated with 0.1N KOH solution in presence of 2 drops of phenolphthalein as indicator until the end point with the appearance of a pale permanent pink. The titre volume of 0.1 N KOH (V) was noted. The total acidity (acid number) in mgKOH/g was calculated using Equation (3.5);

$$\mathrm{AcidValue} = \frac{V_{KOH} x N of KOH x MW_{KOH}}{W} \qquad (3.5)$$

Where:

N = Normality of potassium hydroxide solution (0.1 N).

W = weight of oil sample;

V = volume of potassium hydroxide solution (KOH) used in titration;

MW_{KOH} = molecular weight of potassium hydroxide (56.1g).

$$\% \,\text{FreeFattyAcid(FFA)} = \frac{\text{AV}}{2} \tag{3.6}$$

3.2.4 Production and optimization of biodiesel

3.2.4.1 Heterogeneous catalyzed transesterification

Transesterification reaction with both hierarchical zeolite Y catalyst and the raw zeolite Y catalyst was carried out in a 250 ml three-neck round-bottom flask equipped with a condenser and a magnetic stirrer. For all reactions which took place in a water bath, the reaction mixture consisted of 50 ml of treated waste cooking oil, percentage weight of catalyst, molar ratio of methanol to oil and time according to the design of experiment at a constant desired temperature of 60 °C. Once the reaction was completed, the excess catalyst and other by products like glycerin, methanol, and water were separated from the mixture by allowing the reaction mixture to settle for 24 hours. Biodiesel obtained after separation by decantation from mixture was washed by passing the esters through warm water of temperature of 45 °C to remove impurities. After washing, biodiesel was dried by gradually heating to a temperature of 100 °C to obtain a clean biodiesel. The conversion of biodiesel was calculated (Vafakish & Barari, 2017).

3.2.4.2 Design of experiment

Response surface methodology (RSM) with five-level-four-factor central composite design (CCD) was applied to optimize is to maximize production of biodiesel from waste cooking oil using DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA) software. In this study three factors were considered which are methanol to oil ratio, catalyst loading and reaction time. A total of 20 experiments runs were conducted separately to obtain experimental responses for percentage yield of biodiesel. The independent factors used in this study for transesterification of waste cooking oil are given in Tables 3.4

Table 3.4: Independent Factors used for CCD in Transesterification of Waste Cooking Oil

Variables	**Low**	**High**	**Unit**
Methanol to Oil ratio	6:1	10:1	(v/v)
Catalyst Loading	0.2	0.5	(%vol)
Reaction Time	60	120	(minutes)

Independent Factors for CCD, shows in table 3.4 was used to generate number of runs for transesterification of waste cooking oil, where three (3) variables are considered for the experiment. The lower and the high value are selected based on the preliminary study which was carried out.

3.2.5 Characterization of biodiesel produced

As a way of quality control, biodiesel produced was characterized using American Society for Testing and Materials (ASTM) in order to confirm the biodiesel produced if it meets up with standard.

3.2.5.1 Kinematic viscosity

A viscometer was inserted into a water bath with a set temperature and left for 30 min. The biodiesel sample was added to the viscometer and allowed to remain in the bath as long as it reaches the test thermometer. The sample was allowed to flow freely and the time required for the meniscus to pass from the first to the second timing mark was taken using a stop watch. The procedure was conducted according to ASTM D445 and was repeated a number of times and the average value were taken which was then multiplied with the viscometer calibration to give the kinematic viscosity.

3.2.5.2 Cetane number

Cetane Number is a measure of the fuel's ignition delay. Higher cetane numbers indicate shorter times between the injection of the fuel and its ignition. Higher numbers have been associated with reduced engine roughness and with lower starting temperatures for engines.

3.2.5.3 Flash point

The flash point of biodiesel was tested in accordance to ASTM D93. Sample of biodiesel was heated in a close vessel and ignited. When the sample burns, the temperature was recorded; the pensky-martens cup tester measures the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. The biodiesel was placed in a cup in such quantity as to just touch the prescribed mark on the interior of the cup. The cover was then fitted onto the position on the cup and Bunsen burner was used to supply heat to the apparatus at a rate of about 5 ^{o}C per minute. During heating, the biodiesel was constantly stirred. As the biodiesel approached its flashing, the injector burner was lighted and injected into the oil container at 12 seconds interval until a distinct flash was observed within the container. The temperature at which the flash occurred was recorded. The steps were repeated three times and the average taken.

3.2.5.4 Acid value/free fatty acid

Both values were determined using the procedure reported in ASTM D5555 – 95 (2011) standards. 10 g of biodiesel was poured into a 250 ml conical flask and a few drops of phenolphthalein added. 25 ml of ethanol and 25 ml of diethyl ether were mixed in a separate beaker to which 0.2 ml of phenolphthalein solution was also added and then poured into the conical flask. The mixture was agitated continuously and titrated with the solution of potassium hydroxide until a pink color was noticed which lasted for at least 10 seconds, the titration was stopped.

$$\text{AcidValue} = \frac{V_{KOH} \text{xNofKOHx} \, MW_{KOH}}{W} \qquad (3.7)$$

Where:

N = Normality of potassium hydroxide solution (0.1 N).

W = weight of biodiesel

V = volume of potassium hydroxide solution (KOH) used in titration;

MW_{KOH} = molecular weight of potassium hydroxide (56.1g).

$$\%\ \text{FreeFattyAcid(FFA)} = \frac{\text{AV}}{2} \tag{3.8}$$

3.2.5.5 Sulphur content

ASTM D5453 was used to measure the sulphur content in the biodiesel produced. The sulphur content was determined by the energy dispersive X-ray fluorescence spectroscopy technique. Biodiesel sample was placed in disposable plate covered with male and female cells; the sample was placed in oil in sulphur test equipment and left for 10 minutes. The equipment measured the sulphur content of the biodiesel three consecutive times and the average was recorded as the sulphur content.

3.2.5.6 Pour point

Sample of biodiesel produced was kept in the freezer to a temperature of 50 ^{o}C then placed in a heating mantle to melt. The temperature at the bottom of the test jar was the temperature at which the biodiesel starts to pour and was taken as the pour point.

3.2.5.7 pH value

The pH value of the sample was determined in accordance with ASTM E70 – 07 standards. The pH meter was used to measure the pH of the biodiesel sample by inserting its probe into the sample and for about 3 minutes so that the readings stabilize. The value was then recorded.

3.2.5.8 Cloud point

This was carried out by filling a test-tube to about one third of its capacity with the biodiesel sample. A thermometer was then inserted through the test tubes coke until its bulb was immersed in the biodiesel sample. The setup was kept in a refrigeration unit. The setup was checked at regular intervals until a cloudy mist began to form on the test tubes neck. This marked the cloud point and the temperature was read off.

3.2.5.9 Iodine value

Iodine value (IV) determination in the biodiesel sample was carried out based on the standard accepted procedure by ASTM D5768 - 02(2010). 2g of the oil was weighed and poured into a glass-stopper. 10ml of carbon tetra chloride was added to the biodiesel sample to dissolve it. 20 ml of Wijs solution was added and the mixture was left to stay in the dark for about 30 minutes. 15 ml of potassium iodide solution (10%) and 100 ml of water was then added and the mixture was thoroughly mixed and titrated with 0.1M sodium thiosulphate solution using starch as an indicator. A blank was also carried out using the same procedure. The iodine value was determined using Equation (3.9):

$$IV = \frac{0.1269 \times (B-A) \times N \times 100}{W_{OIL}} \tag{3.9}$$

Where:

B= volume of sodium thiosulphate used in blank titration.

A= volume of sodium thiosulpate used in titration with oil.

N= normality of sodium thiosulphate.

W_{oil} = weight of oil used.

3.2.5.10 Saponification value

Saponification value was determined in accordance with the ATSM 5558–95(2011) standard. 2 g of the biodiesel was weighed into a conical flask, 25 ml of 0.1N ethanolic potassium hydroxide was then added. A reflux condenser was placed over the flask. The setup was then placed over a heating mantle and allowed to boil gently with continuous stirring for 60 minutes. The flask was allowed to cool and few drops of phenolphthalein indicator added. It was then titrated with 0.5M HCl to the end point (i.e. when a pink color appears). A blank test was also carried out.

$$\text{S.V} = \frac{56.1\text{N}(\text{Vo}-V_1)}{\text{M}} \quad (3.10)$$

V_O = ml of HCl used in blank
V_1 = ml of HCl used in titrating sample
M = weight of sample
N = normality of HCl

3.2.5.11 Ester value

This is simply the number of mg of potassium hydroxide required to saponify the esters in 1.0 g of the sample expressed as

$$\text{Ester value} = \text{saponifiction value} - \text{acid value} \quad (3.11)$$

CHAPTER FOUR

4.0 DISCUSSION OF RESULTS

This section presents a comprehensive view of the results obtained from the experimental study. It also contains statistical analysis of the results as well as evaluation of the effect of selected process variables of heterogeneous catalyzed transesterification of the waste cooking oil to produced biodiesel. The discussion of result is also presented here.

4.1 Results of protonated and Characterization of Hierarchical Zeolite Y Catalyst

The hierarchical zeolite Y catalyst and zeolite Y bought from zeolyst international were characterized and evaluated using, X-ray diffraction (XRD), Scanning Electronic Microscopy (SEM/EDX) and (BET) Analysis which are discussed in details.

4.1.1 X-ray diffraction (XRD) analysis of commercial zeolite Y (CZY) sample

Figure 4.1 show the XRD pattern of Commercial Zeolite Y (CZY) Sample to determine the crystalline phase.

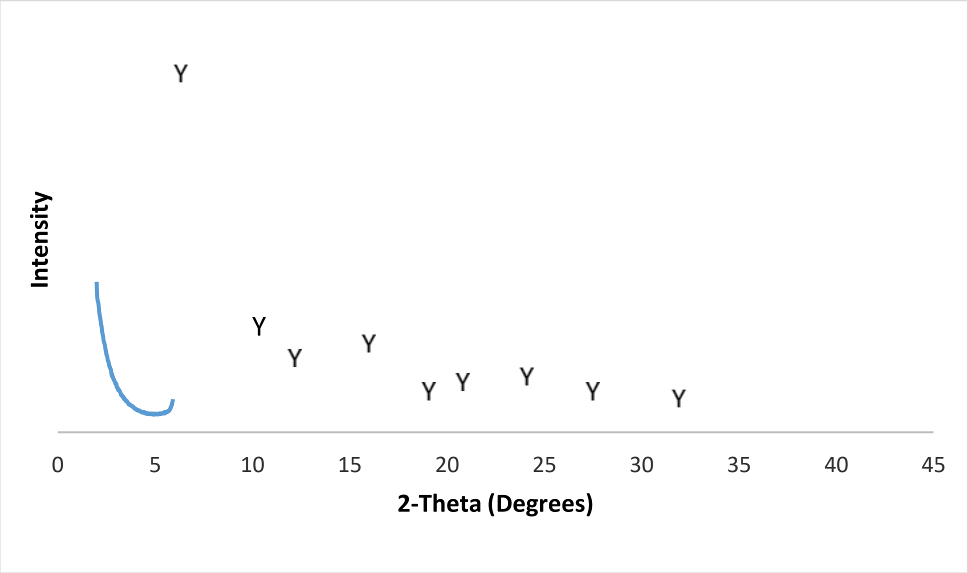

Figure 4.1: XRD Pattern of Commercial Zeolite Y (CZY) Sample

4.1.2 X-ray diffraction (XRD) analysis of hierarchical zeolite y (HZY) sample

Figure 4.1 show the XRD pattern of hierarchical zeolite Y (HZY) sample to determine the crystalline phase.

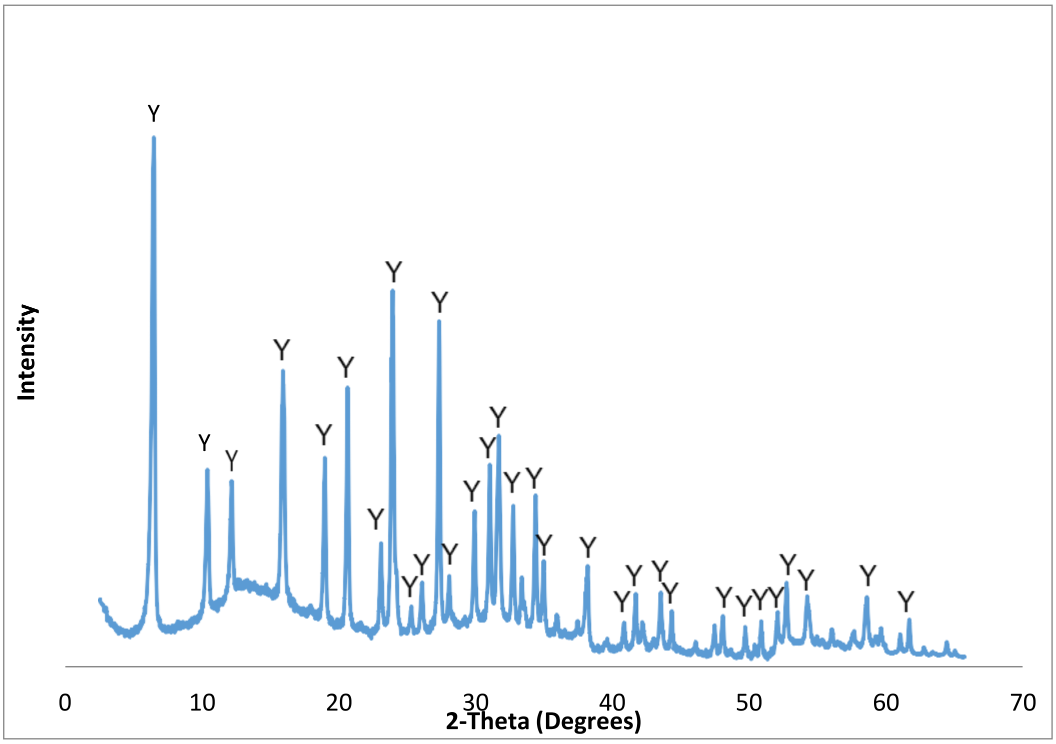

Figure 4.2: XRD Pattern of Hierarchical Zeolite Y sample produced (HZY)

Figure 4.1 and 4.2 represent the X-ray diffraction (XRD) spectrometry of CZY and HZY samples, which showed series of characteristic diffraction peaks assigned to the zeolite Y type. It can be seen that hierarchical zeolites Y produced had strong characteristic peaks of Y zeolites. The peaks occurred at position 2θ of 6°, 10°, 12°, 16°, 19°, 21°, 25° and 30° (Wittayakun *et al.*, 2008). Figure 4.2 showed high crystallinity which is a function of the physical nature of the characteristic peaks. Broad peaks indicate low crystallinity while sharp X-ray peaks indicate high crystallinity of HZY and the background comes up as a result of impurities and other debris. The XRD patterns or peaks of HZY show high crytallinity compared it with CZY and it was also observed that the finger print or characteristics of zeolite Y was not tempered with.

4.1.3 Scanning electron microscopy (SEM) analysis

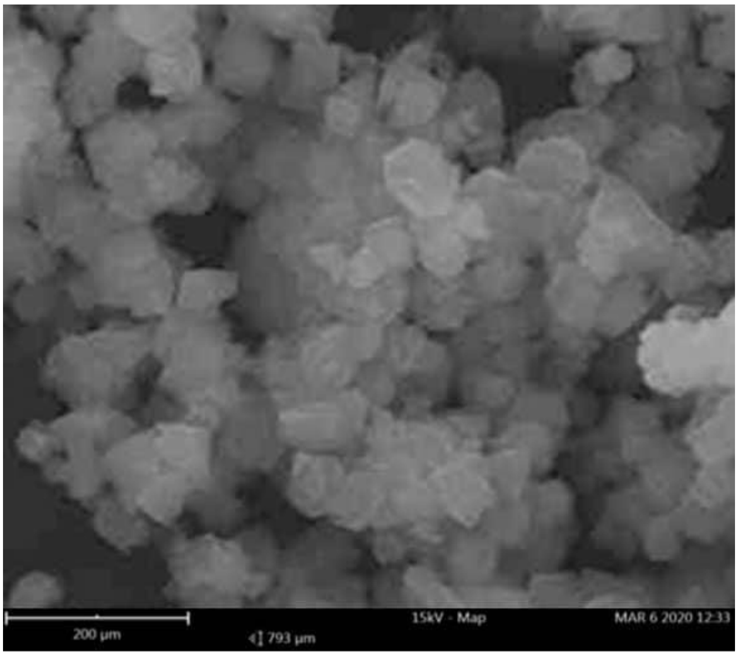

Figure 4.3: SEM micrograph of Hierarchical Zeolite Y catalyst

The SEM images in Figure 4.3: showed the morphology of hierarchical zeolite Y sample. The sample (hierarchical zeolite Y) maintains the same surface structure. The SEM of this sample indicated that this sample is crystalline and it also suggests that the large hysteresis loop in the N_2 isotherm come from crystalline material. It was also observed that the mesopore was high and explaining why the mesopore volume was high, this maybe as a result of some crystalline silica that appeared on the surface of the crystals, the acid treatment of the zeolite sample extracted aluminum atoms from the zeolite framework leading to significant increase in its Si/Al ratio while the base treatment also decreased the Si/Al molar ration because of extraction of silicon atoms from the framework. In this study Si/Al was determined to be 15.00 from Figure 4.5

4.1.3.1 Electron dispersive spectroscopy (EDS)

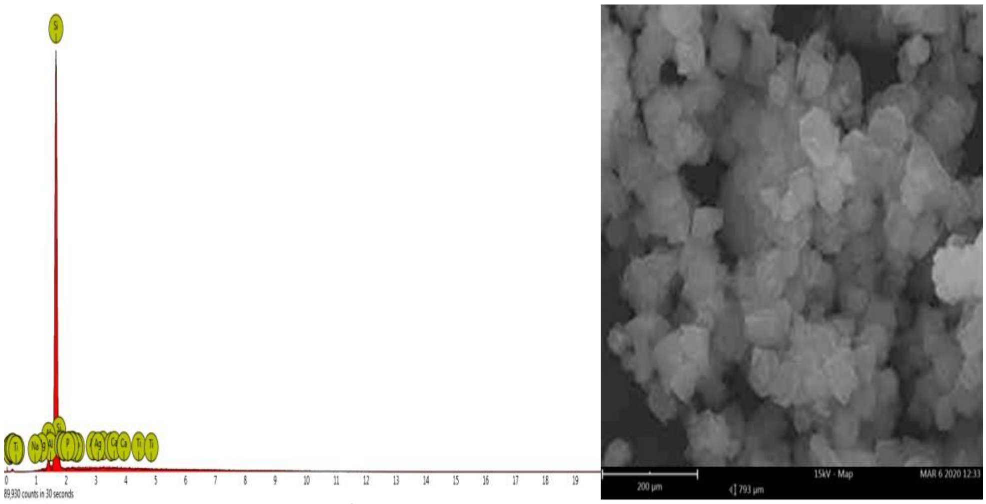

Figure 4.4: EDS spectroscopy of the Hierarchical zeolite Y Produced Catalyst

This is an add-on function of SEM used to identify chemical elements distributed on the surface of the sample. The EDS analysis shows that Silicon was the main element present on the catalyst surface follow by Aluminium. The summary of the elements present in the catalyst are shown in Figure 4.5.

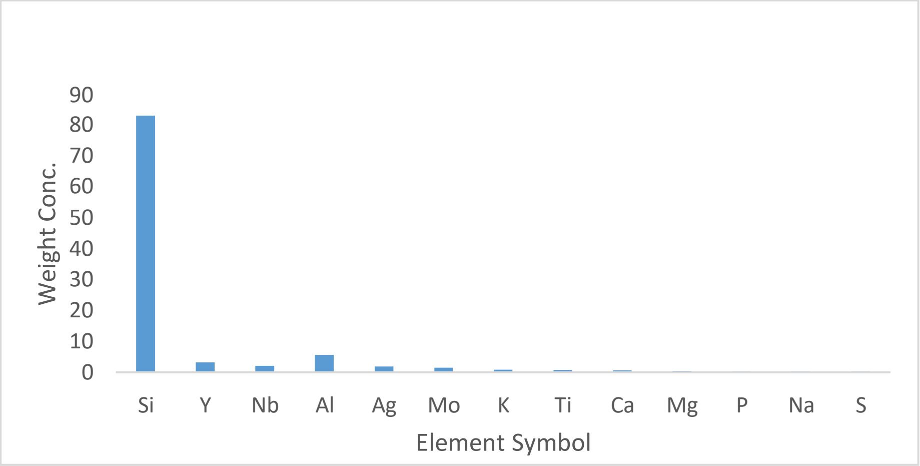

Figure 4.5: Elemental Weight Composition of Hierarchical Zeolite Y Produced Catalyst

Figure 4.5 shows the EDS elemental analysis of hierarchical zeolite Y (HZY) obtained from commercial zeolite Y obtained from the Zeolyst international Netherland. This was carried out to determine the elemental weight composition of the hierarchical zeolite Y sample. Result obtained revealed that hierarchical zeolite Y from zeolyst international Netherland mainly contains Silicon (82.84 %) weight percent as a major component follow by Aluminium of (5.52 %) weight percent. Also present in varying proportions are Yttrium, Niobium, Silver, manganese, magnesium, sodium, phosphorus and titanium.

4.1.4 Brunnauer, emmett and teller (BET) analysis

The BET analysis of zerolite Y samples which was treated at different concentration of NaOH and H_4EDTA shows the surface area, pore volume and pore size of the different samples. The important of this selection was to control the simultaneous desilication and mild dealumination of the zeolite Y whereby the details of the result obtained in table 4.1 and 4.2.

Table 4.1: Notation of the Samples and Treatment Conditions

Zeolite Y Samples	Alkaline Treatment (M)	Acid Treatment (M)
HZY-1	0.1 M of NaOH	0.1 M of EDTA
HZY-2	0.3 M of NaOH	0.5 M of EDTA
HZY-3	0.3 M of NaOH	0.3 M of EDTA
HZY-4	0.5 M of NaOH	0.3 M of EDTA

Table 4.2: Textural Parameters of the Synthesized Hierarchical Zeolites Y

Zeolite Y Sample	S_{BET} m^2/g	S_{micro} m^2/g	S_{meso} m^2/g	V_{total} cm^3/g	V_{micro} cm^3/g	D_{meso} (nm)	HF
HZY-1	193.83	181.85	11.98	0.3860	0.3566	8.7278	0.0571
HZY-2	216.03	180.94	35.09	0.4971	0.4712	10.175	0.1540
HZY-3	212.34	171.71	40.62	0.4065	0.3785	8.5512	0,1781
HZY-4	218.33	193.76	24.56	0.3299	0.3055	6.1673	0.1042

Table 4.2 shows the textural properties of the catalyst samples that has undergone treatment. The simultaneous desilication and mild dealumination of the zeolite Y via NaOH and H_4EDTA leads to drastic increase in the specific surface area (SSA), mesopore volume and pore size. The HF in Table 4.2 were calculated using Equation 2.1 for the different values of V_{Micro}, S_{Meso}, V_{Total} and S_{BET} of the HZY samples. According to table 4.2, it was also observed that the higher the value of mesopore area (S_{meso}), the higher hierarchy factor (HF) which measured the degree of structural order of the material.

Hierarchical zeolite Y (HZY-4) sample has the highest specific surface area of 218.33 m^2/g with hierarchy factor (HF) of 0.1042 while Hierarchical Zeolite Y sample (HZY-3) has a specific surface area of 212.34 m^2/g with hierarchy factor (HF) of 0.178. Therefore, HZY-3 sample was the best and most suitable for optimum reactivity since it has the highest value of hierarchy factor (HF) when compared with others.

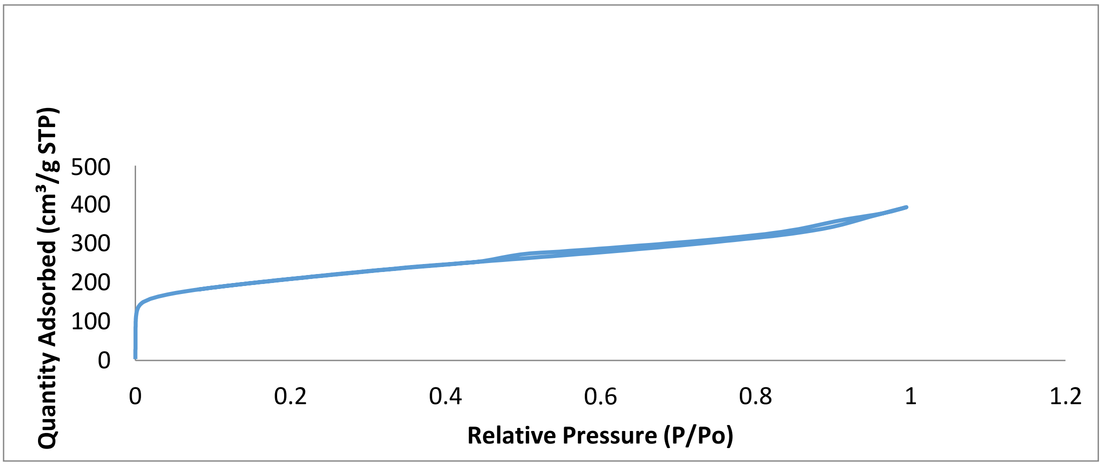

Figure 4.6: N_2 Adsorption (BET) Analysis of Starting Zeolite Y

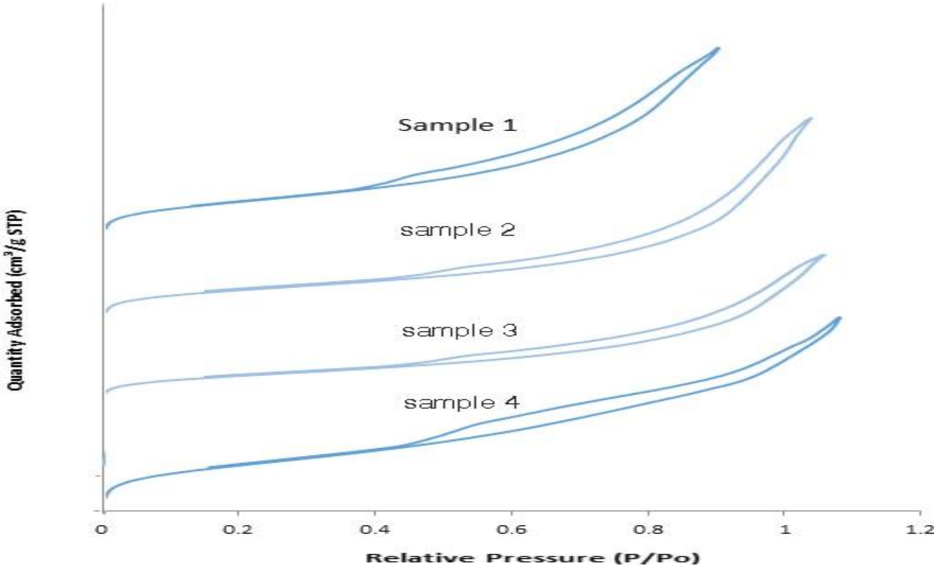

Figure 4.7: Hysteresis Loop of Hierarchical Zeolite Y Samples

The nitrogen adsorption isotherms in Figure 4.6, revealed the enhancement in both surface area and pore size of the hierarchical zeolite Y sample produced where all the sample produced were observe to have been transform to mesopores material. The result showed that simultaneous desilication and mild dealumination of CZY result to the transformation whereby the best treatment ratio or optimum point occur at 0.3 M of NaOH and 0.3 M of H_4EDTAthat considerably increases the mesoporosity of sample HZY-3. The mesopores may have been formed by opening two larg pores as a result of the elimination of aluminum and silicon when comparing raw sample N_2 Adsorptionto the hysteresis loop of the hierarchical zeolite Y sample. It was also observed that change in the hysteresis loop as well as reduction in the adsorbed volume serve as evident of desilication and mild dealumination treatment they have undergone. Therefore, the shapes can be classified as H2 link-bottle pores.

4.2 Feedstock Quality Characterization

The suitability of a feed stock for biodiesel production relies heavily on its properties. The following results were obtained based on the characterization of the feed stock (Waste Cooking Oil).

Table 4.3: Properties of the Waste Cooking Oil

S/N	Property	Unit	Value
1.	% Moisture Content	wt. %	9.2
2.	Density	g/cm^3	0.898
3.	Specific Gravity at 40 ^{o} C	-	0.93
4.	Kinematic Viscosity at 40 ^{o} C	mm^2/s	23.6
5.	pH Value	-	7.32
6.	Saponification Value	mgKOH/g	241.45
7.	Acid Value	mgKOH/g	19.6
8.	Ester value	wt. %	221.85
9.	Iodine Value	mgI/100g	61.7
10.	Peroxide Value	Mmol peroxide/kg sample	5.5
11.	Flash Point	^{o} C	167
12.	Free Fatty Acid (FFA)	wt. %	9.8

During the course of this work, filtration process was applied to remove the solid dirt content in the waste cooking oil using filter paper for 24 hours while dehydration process was also applied to remove traces of water content 9.2 % present in oil by drying it in an air-dry oven at 105°c atmospheric pressure. Also analyses of acid value were conducted on the waste oil to determine the quantity and quality of free fatty acid.

4.3 Optimization of Biodiesel Production from Waste Cooking Oil.

Optimization of the transesterification process from Waste Cooking Oil) was conducted for both hierarchical zeolite Y and commercial zeolite Y using the DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA) software. The parameters considered include methanol to oil ratio (A), reaction time (B) and catalyst dosage (C).

Table 4.4: Optimization of Biodiesel Production from WCO for CZY and HZY Catalyst

Run No.	A (v/v)	B (mins)	C (%wt)	CZY Catalyst Biodiesel yield (%)	HZY Catalyst Biodiesel yield (%)
1	6	60	0.5	56.00	89.72
2	6	90	0.35	55.33	89.95
3	10	120	0.5	62.00	84.10
4	8	120	0.35	56.67	89.95
5	8	90	0.35	62.0	94.80
6	8	90	0.2	56.67	88.80
7	10	60	0.5	60.00	90.00
8	10	90	0.35	47.67	82.00
9	8	90	0.35	57.00	86.67
10	10	60	0.2	51.00	78.00
11	8	90	0.5	52.50	81.00
12	6	120	0.5	60.93	80.00
13	10	120	0.2	48.87	70.00
14	8	90	0.5	58.33	88.60
15	8	120	0.35	56.67	88.90
16	6	120	0.2	56.67	88.40
17	8	60	0.35	55.33	83.33
18	8	90	0.2	57.48	78.00
19	8	90	0.35	56.67	93.85
20	8	120	0.5	67.33	87.67

From the optimization study carried out following the parameters investigated that is, methanol/oil molar ratio, catalyst dosage and reaction time shows that at methanol/oil molar ratio of 8:1, 0.35 wt% catalyst, and 90 minute reaction time at constant temperature 55 °C. HZY catalyst gave the optimum biodiesel yield of 95.00 % while the raw CZY catalyst gave the optimum biodiesel yield of 67.33 % at different condition. Comparing the condition where HZY catalyst obtained it optimum to be 95.00 % yield, it was observed that the CZY catalyst gave 52 % yield which maybe reduction in catalyst dosage or reduction in reaction time. More details of these statistical analyses of transesterification reaction of WCO for both HZY and CZY are discussed below.

4.3.1 Statistical analysis of transesterification reaction of WCO using commercial zeolite Y

The analysis of variance (ANOVA) was carried out using DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA). The experiments were conducted based on the Response Surface Method (RSM) and Central Composite Design (CCD)

4.3.1.1 Analysis of variance for transesterification with commercial zeolite Y (CZY)

The analysis of the variance (ANOVA) for the response surface quadratic model is shown in Table 4.5 the model expression developed that relates the biodiesel yield.

Table 4.5: Analysis of Variance of the transesterification of WCO for CZY

	Sum of Square	**Degree of Freedom**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	385.39	9	42.82	133.21	0.0001
A- Methanol to Oil ratio	99.48	1	99.48	309.47	0.0001
B- Reaction Time	25.86	1	25.86	80.44	0.0001
C- Catalyst dosage	212.24	1	212.24	660.28	0.0001
AB	21.16	1	21.16	65.82	0.0001
AC	0.12	1	0.12	0.38	0.5508
BC	0.85	1	0.85	2.65	0.1347
$A^{\wedge 2}$	14.92	1	14.92	46.43	0.0001
$B^{\wedge 2}$	19.61	1	19.61	61.01	0.0001
$C^{\wedge 2}$	0.020	1	0.020	0.8007	0.0220
Residual	3.21	10	0.32		
Lack of Fit	2.84	5	0.57	7.59	0.3216
Pure Error	0.37	5	0.075		
Cor Total	388.60	19			

The three reaction parameters considered (A, B, C), was suitable because its p-values is less than 0.05 each. The model F-value of 133.21 implies the model is significant. The F-value is the ratio of the model SS / residual SS and shows the relative contribution of the model variance to the residual variance. A large number indicates more of the variance being explained by the model; a small number says the variance may be more due to noise. The significant factors from ANOVA analysis are the methanol to oil ratio and the reaction time with p-values of 0.0001 respectively which is less than 0.05. The other significant factors are the interaction effect of the methanol to oil ratio and reaction time and the interaction effect of methanol to oil and catalyst dosage with p-values of

0.0001 and 0.5508. Similarly, the quadratic effects of the catalyst dosage and the quadratic effect of reaction time are also significant factors with p-values of 0.0001 respectively. The other factors of the model are not statistically significant.

Table 4.6: Fit Statistics

Std. Dev.	Mean	C.V. %	R^2	Adjusted R^2	Predicted R^2	Adeq Precision
0.57	56.26	1.01	0.99175	0.9843	0.9134	46.739

From table 4.6, the model fit is checked with the correlation factor R^2, which equals to 99.17 % indicating that the sample variation of 99.17 % is attributed to independent variables and 0.83 % of the total variation is not explained by the model. The value of the coefficient of variation (CV% = 1.01) gives the precision and reliability of the experiment carried out where a lower value of CV% indicates a better precision and reliability of the experiments carried out. The adjusted R^2 of 0.9843 is in reasonable agreement with predicted R^2 of 0.9134 whereby the difference is equals to 0.0709 which is less than 0.2. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 46.739 indicates an adequate signal. Therefore, this model can be used to navigate the design space.

Table 4.7: Coefficients in Terms of Coded Factors

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	56.47	1	0.19	56.03	56.90	
A-Methanol:Oil r	3.15	1	0.18	2.75	3.55	1.0000
B- Reaction Time	1.61	1	0.18	1.21	2.01	1.0000
C-Catalyst dosage	4.61	1	0.18	4.21	5.01	1.0000
AB	1.63	1	0.20	1.18	2.07	1.0000
AC	0.12	1	0.20	-0.32	0.57	1.0000
BC	-0.33	1	0.20	-0.77	0.12	1.0000
A^2	2.33	1	0.34	1.57	3.09	1.82
B^2	-2.67	1	0.34	-4.34	-1.91	1.82
C^2	-0.085	1	0.34	-0.85	0.68	1.82

From table 4.7, the coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multi-colinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable. The regression analysis produced the following coded equation:

Biodiesel Yield = $56.47+3.15A+1.61B+4.61C+1.63AB+0.12AC-0.33BC+2.33A^2-2.67B^2-0.085C^2$

The linear effect of A, B and C, the interaction effect of AB and AC and the quadratic effect of A^2 are the general determining factors of transesterification of waste cooking oil as they have the larger coefficients.In this statistical analysis the catalyst dosage (factor C) has the highest coefficient among the three independent variables. This implies that the tranesterification of cooking oil relies greatly on this factor.

Figure 4.8 shows the graph of the predicted value vs the actual values obtained in the tranesterification of cooking oil. It was observed that the actual data was in agreement with the predicted data by the model. From Figure 4.8 the minimum predicted value of the biodiesel obtained from the tranesterification of cooking oil was 66.84 % while the actual experimental value is 67.33 %. The optimization solution obtained shows that a biodiesel yield of 66.84 % was obtained at a methanol to oil ratio of 6:1, a catalyst loading of 0.2 g, at constant temperature and time of 55 ^{o} C and 60 minutes respectively.

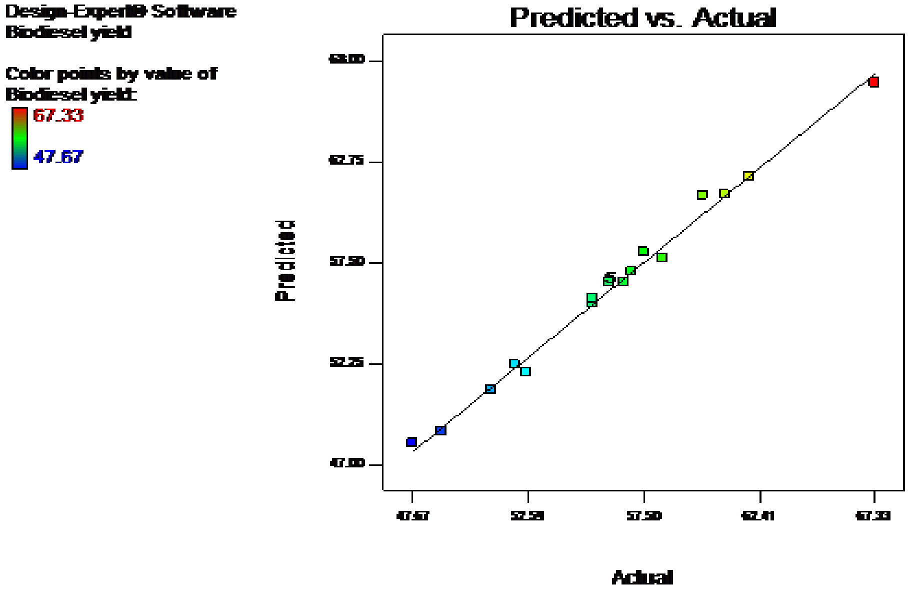

Figure 4.8: Predicted values vs. actual values obtained from the tranesterification of waste cooking oil.

Figure 4.8 the actual values obtained from the study lie close to the regression line as such they correlated with the predicted values generated by design expert. This shows that there is no much disperity between the actual and predicted results and this quadratic model is proper model for this study.

4.3.1.2 Effect of interaction between process parameter

The Three-dimensional response surfaces are plotted on the basis of the generated model equation to examine the interaction among variables and to determine the optimum condition of each factor for maximum biodiesel yield.

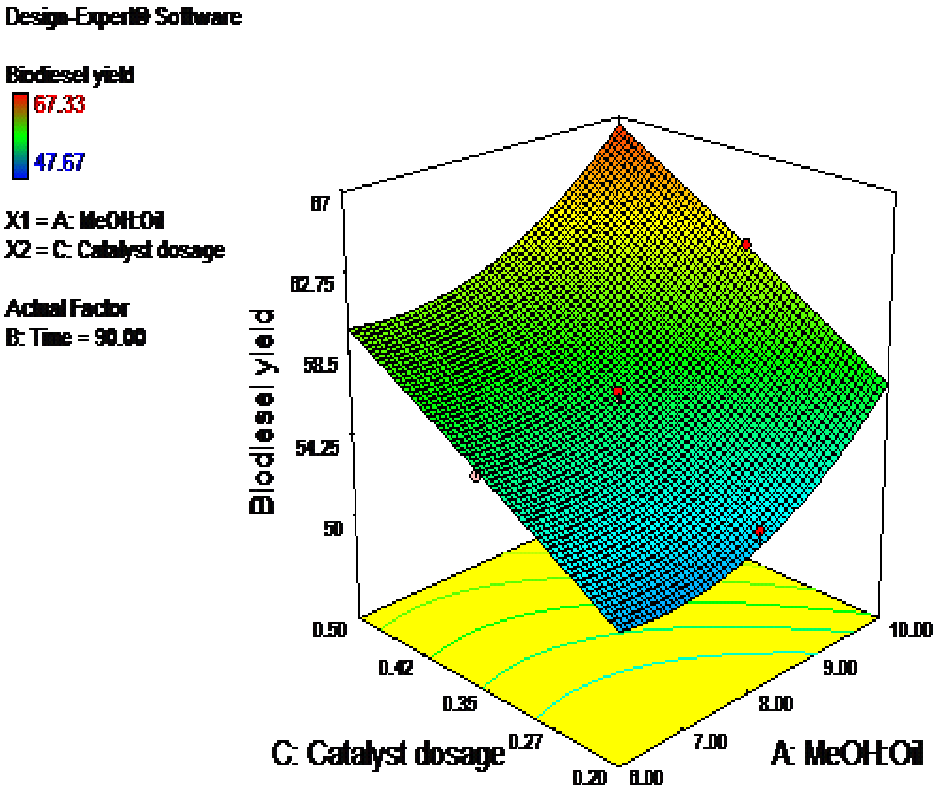

Figure 4.9: Response surface plot of the interaction effect of methanol: oil ratio and catalyst dosage on the biodiesel yield

Figure 4.9 represents the 3D plot of the interaction effect of methanol: oil ratio and catalyst dosage on the biodiesel yield at reaction time of 90 minutes and at a constant temperature of 55^{o} C. From the plot it was observed that the plane was inclined towards both x and z axes indicating a decline in the catalyst loading resulted in an increase in the biodiesel yield similarly as the methanol to oil ratio increased from 6:1 to 10:1 so did the biodiesel yield increase progressively. In terms of the interaction of the methanol to oil ratio and the catalyst dosage on the biodiesel yield, an experimental optimum biodiesel yield of 67.33 % was obtained at a methanol to oil ratio of 10:1 and catalyst dosage of 0.2 g at a constant temperature and time of 55 ^{o}C and 90 minutes respectively.

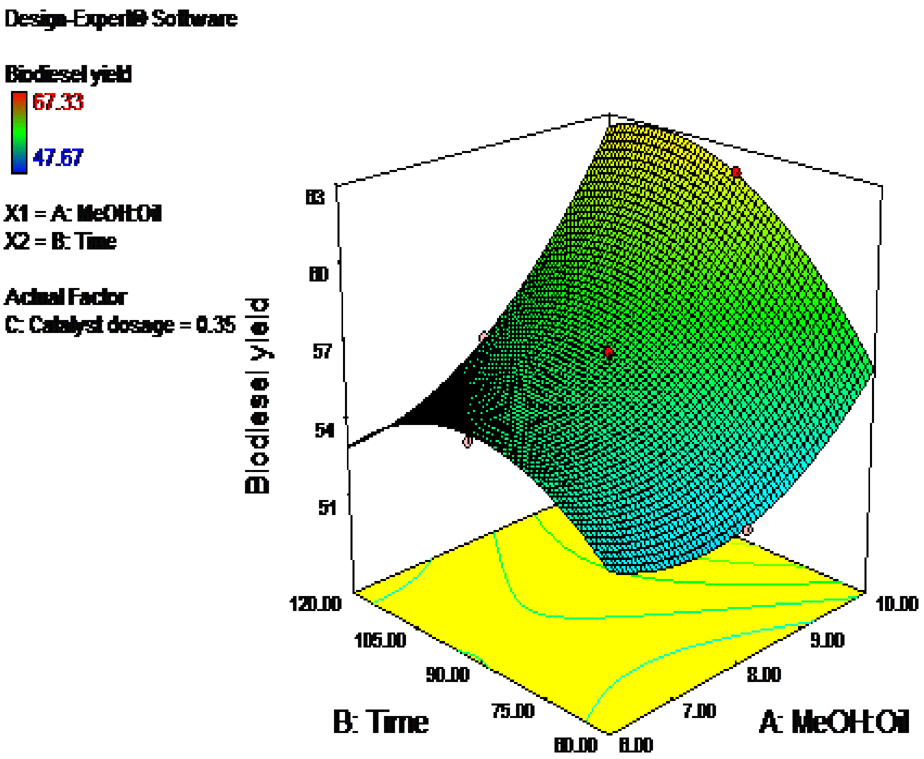

Figure 4.10: Response surface plot of the interaction effect of methanol:oil ratio and reaction time on the biodiesel yield

Figure 4.10 represents the 3D plot of the interaction effect of methanol: oil ratio and reaction time on the biodiesel yield at a reaction temperature of 55 °C and a catalyst dosage 0.35 g. From the plot it was observed that as the methanol to oil ratio increased from 6:1 to 10:1 so did the biodiesel yield increase progressively. Similarly, an increase in the reaction time resulted in an increase in biodiesel yield although this trend panned out at a reaction time of 100 minutes with further increment in the reaction time resulting in a dip in the biodiesel yield. In terms of interaction effect of the methanol: oil ratio and reaction time on the biodiesel yield at a reaction temperature of 55 °C and a catalyst loading 0.35 g an optimum biodiesel yield of 62 % occur at 10:1 methanol to oil ratio and 105 minutes reaction time.

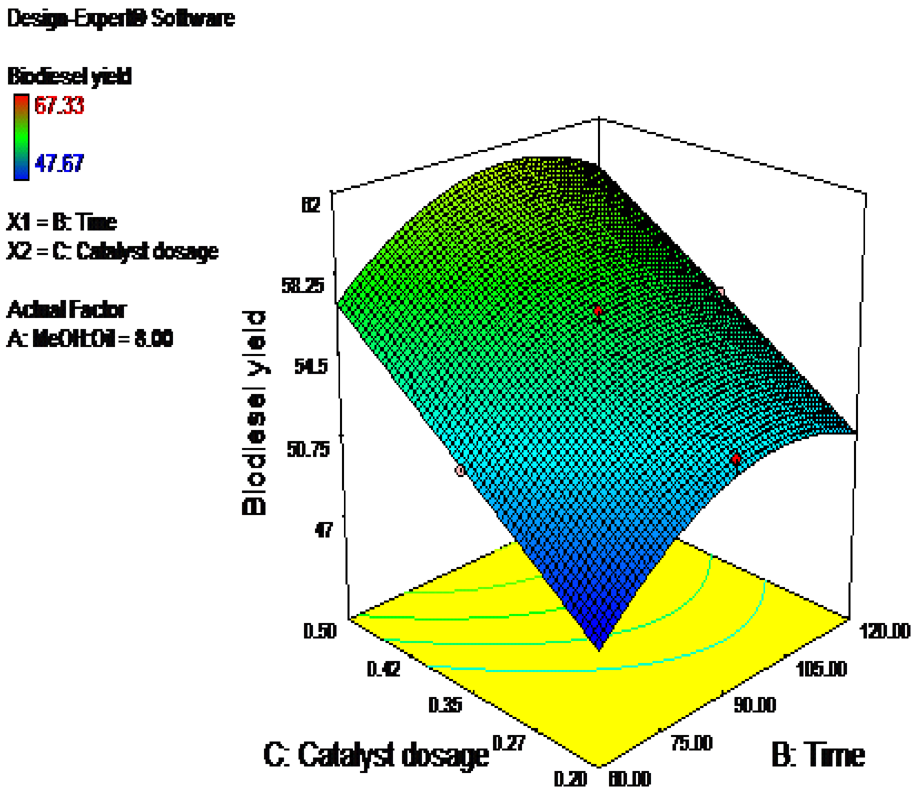

Figure 4.11: Response surface plot of the interaction effect of catalyst dosage and reaction time on the biodiesel yield

From Figure 4.11, the 3D plot is slightly inclined on both x-axis and z-axis. This shows interaction among the three (3) variables; methanol to oil ratio, reaction time and catalyst dosage. Optimum biodiesel yield of 56.67% was observed at temperature of 55 ^{o}C, methanol to oil ratio of 8:1, catalyst concentration of 0.35g and a reaction time of 90 minutes.

4.4 Optimization of Biodiesel Production from Waste Cooking Oil using Hierarchical Zeolite Y Catalyst

Optimization of the transesterification process from Waste Cooking Oil) was conducted for hierarchical zeolite Y (HZY) using the DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA) software. The parameters considered include methanol to oil ratio (A), reaction time (B) and catalyst dosage (C) as in appendix C.

4.4.1 Statistical analysis of transesterification reaction of (WCO) with (HZY)

The analysis of variance (ANOVA) was carried out using DESIGN EXPERT (Version 7.0.0, Stat Ease, Inc., USA). The experiments were conducted based on the Response Surface Method (RSM) Central Composite Design (CCD).

4.4.1.1 Analysis of variance for transesterificationof (WCO) with (HZY)

Table 4.8 shows the analysis of the variance (ANOVA) for the response surface quadratic model.

Table 4.8: Analysis of Variance of the transesterification of (WCO) with (HZY)

Source	**Sum of Square**	**Degree of Freedom**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	631.81	9	70.20	43.46	0.0001
A- Methanol to Oil ratio	0.80	1	0.80	0.5	0.4974
B- Reaction Time	3.98	1	3.8	2.46	0.1475
C- Catalyst dosage	237.56	1	237.56	147.06	0.0001
AB	58.32	1	58.32	36.10	0.0001
AC	16.82	1	16.82	10.41	0.0091
BC	39.34	1	39.34	24.35	0.0006
$A^{\wedge 2}$	103.89	1	103.89	64.31	0.0001
$B^{\wedge 2}$	0.036	1	0.036	0.022	0.8851
$C^{\wedge 2}$	10.58	1	10.58	6.55	0.0284
Residual	16.15	10	1.62		
Lack of Fit	14.48	5	2.90	8.66	0.0167
Pure Error	1.67	5	0.33		
Cor Total	647.96	19			

The model expression developed that relates the biodiesel yield and the three reaction parameters considered (A, B, C), was suitable because its p-values is less than 0.05 each. The model F-value of 70.20 implies the model is significant. The F-value is the ratio of the model SS / residual SS and shows the relative contribution of the model variance to the residual variance. A large number indicates more of the variance being explained by the model; a small number says the variance may be more due to noise. The significant factors from ANOVA analysis of catalyst dosage with p-value of 0.0001 which is less than 0.05 which shown that catalyst dosage is significant parameter when compared with the one with CZY, the three parameter considered are all significant. The other significant factors are the interaction effect of the methanol to oil ratio and reaction time and the interaction effect of methanol to oil and catalyst dosage with p-values of 0.0001 and 0.0091. Similarly, the quadratic effects of methanol to oil and the quadratic effect of catalyst dosage are also significant factors with p-values of 0.0001 and 0,0284 respectively which are less than 0.05. The other factors of the model have no statistically significant effect

Table 4.9: Fit Statistics for HZY

Std. Dev.	**Mean**	**C.V. %**	**R²**	**Adjusted R²**	**Predicted R²**	**Adeq Precision**
1.27	85.46	1.49	0.9751	0.9526	0.8140	25.032

In this table 4.9, the model fit is checked with the correlation factor R^2, which equals to 97.51% indicating that the sample variation of 97.51% is attributed to independent variables and 3.49% of the total variation is not explained by the model. The value of the coefficient of variation (CV% = 1.49) gives the precision and reliability of the experiment carried out where a lower value of CV% indicates a better precision and reliability of the experiments carried out. The predicted R^2 of 0.8140 is in reasonable agreement with the adjusted R^2 of 0.9526 with a difference less than 0.2. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 25.032 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.10: Coefficients in Terms of Coded Factors for HZY

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	89.46	1	0.44	88.4	90.44	
A-Methanol:Oil	-0.28	1	0.40	-1.18	0.61	1.0000
B- Reaction Time	-0.63	1	0.40	-1.53	0.26	1.0000
C-Catalyst dosage	4.87	1	0.40	3.98	5.77	1.0000
AB	2.70	1	0.45	1.70	3.70	1.0000
AC	-1.45	1	0.45	-2.45	-0.45	1.0000
BC	2.22	1	0.45	1.22	3.22	1.0000
A^2	-6.15	1	0.77	-7.85	-4.44	1.82
B^2	0.11	1	0.77	-1.59	1.82	1.82
C^2	-1.96	1	0.77	-3.67	-0.25	1.82

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multi-colinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable. The regression analysis produced the following coded equation:

$$\text{Biodiesel Yield} = 89.46 - 0.28A - 0.63B + 4.87C + 2.70AB - 01.45AC + 2.22BC - 6.15A^2 + 0.11B^2 - 1.96C^2$$

The linear effect of C, the interaction effect of AB and BC and the quadratic effect of B^2 are the general determining factors of transesterification of waste cooking oil as they have the larger coefficients.In this statistical analysis the catalyst dosage (factor C) has the highest coefficient among the three independent variables. This implies that the tranesterification of cooking oil relies greatly on this factor. Comparing the two catalyst (CZY and HZY) in term ofcatalyst dosage (factor C) using their various coded equations, HZY has the highest coefficient to be equals to 4.87 compared to CZY which was equals to 1.61 as tranesterification of cooking oil relies greatly on this factor.

Figure 4.12 shows the graph of the predicted value vs the actual values obtained in the tranesterification of waste cooking oil. It was noted that the actual data was in agreement with the predicted data by the model. From Figure 4.12, the maximum predicted value of the biodiesel obtained from the tranesterification of waste cooking oil was 92.37 % while the actual experimental value is 94.80 %. The optimization solution obtained shows that a biodiesel yield of 92.37 % was obtained at a methanol to oil ratio of 8:1, a catalyst loading of 0.35, at a constant temperature and time of 55^o C and 90 minutes respectively.

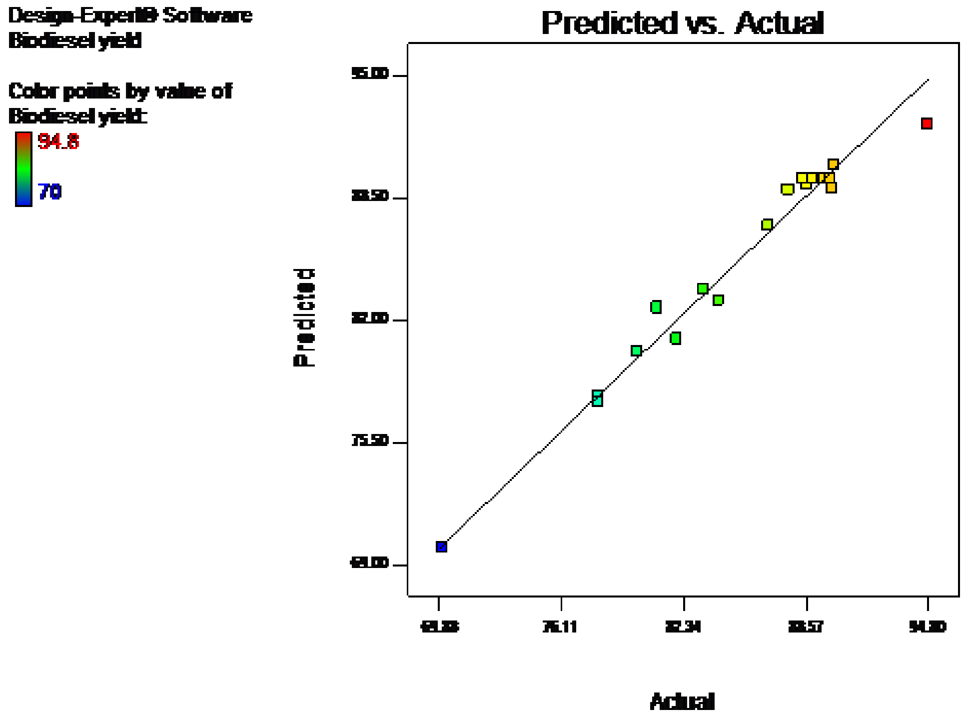

Figure 4.12: Graph of predicted values vs. actual values obtained from the tranesterification of waste cooking oil.

As shown in Figure 4.12, the actual values obtained from the study lie close to the regression line as such they correlated with the predicted values generated by design expert. This shows that there is no much disperity between the actual and predicted results and this quadratic model is appropriate model for this study.

4.4 Effect of Interaction between Process Parameters for HZY Catalyst

The Three-dimensional response surfaces are plotted on the basis of the generated model equation to investigate the interaction among variables and to determine the optimum condition of each factor for maximum biodiesel yield.

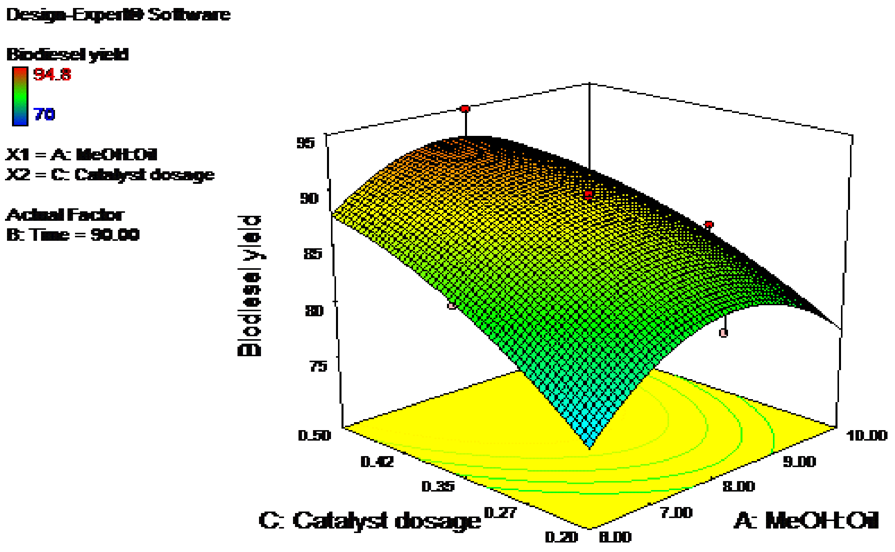

Figure 4.13: Response surface plot of the interaction effect of methanol : oil ratio and catalyst loading on the biodiesel yield

Figure 4.13 shows the 3D plot of the interaction effect of methanol: oil ratio and catalyst loading on the biodiesel yield at reaction time of 90 minutes and at a constant temperature of 55 ^{o}C. From the plot it was observed that the plane was inclined towards on x axes indicating an increase in the catalyst dosage resulted in an increase in the biodiesel yield, similarly as the methanol to oil ratio increased from 6:1 to 8:1 so did the biodiesel yield increase progressively. In terms of the interaction of the methanol to oil ratio and the catalyst dosage on the biodiesel yield, it was observed that an optimum biodiesel yield of 94.33 % was obtained at a methanol to oil ratio of 8:1 and catalyst loading of 0.35 g at a constant reaction temperature and time of 55 ^{o}C and 90 minutes respectively.

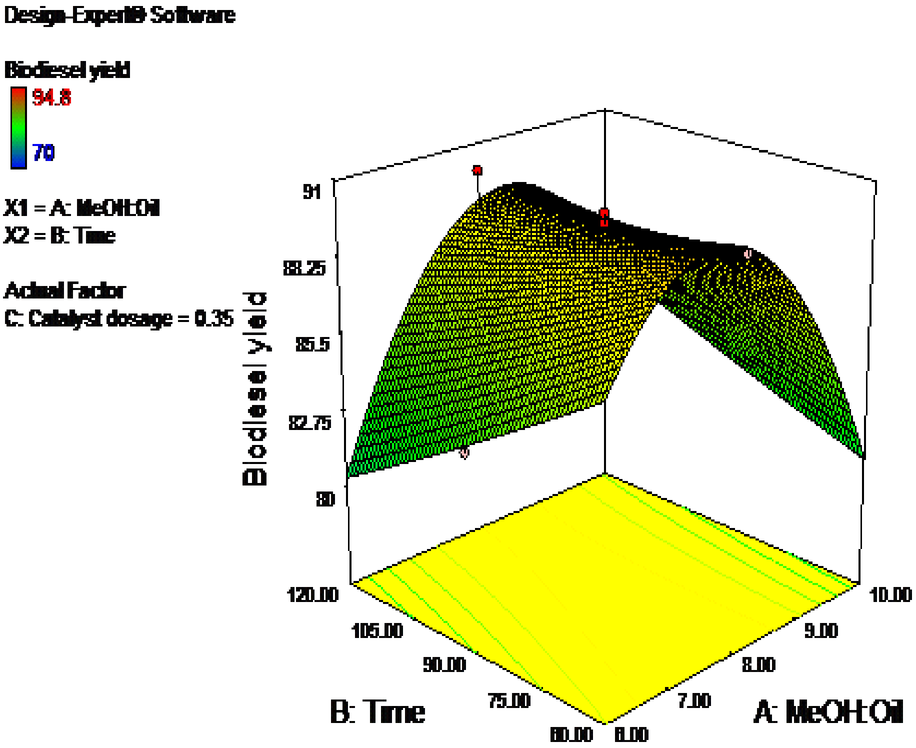

Figure 4.14: Response surface plot of the interaction effect of methanol : oil ratio and reaction time on the biodiesel yield

Figure 4.14 shows the 3D plot of the interaction effect of methanol: oil ratio and reaction time on the biodiesel yield at constant temperature of 55 °C and a catalyst dosage 0.35 g. From the plot it was observed that as the methanol to oil ratio increased from 6:1 to 8:1 so did the biodiesel yield increase progressively. Similarly, an increase in the reaction time resulted in an increase in biodiesel yield although this trend panned out at a reaction time of 90 minutes with further increment in the reaction time resulting in a dip in the biodiesel yield. In terms of interaction effect of the methanol: oil ratio and reaction time on the biodiesel yield at a temperature of 55 °C and a catalyst dosage 0.35 g an optimum biodiesel yield of 90 % at a methanol to oil ratio and reaction time of 8:1 and 90 minutes.

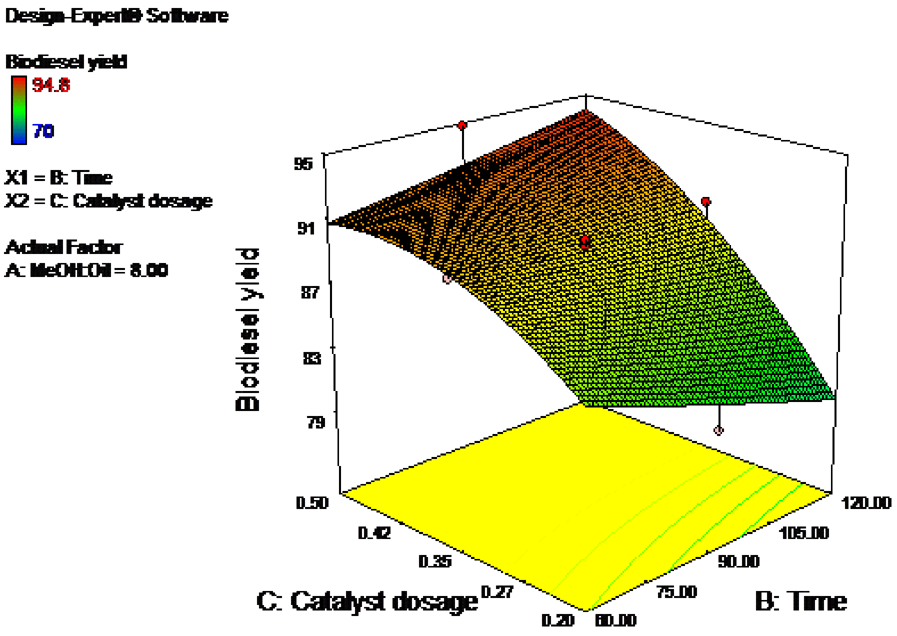

Figure 4.15: Response surface plot of the interaction effect of catalyst loading and reaction time on the biodiesel yield

From Figure 4.15, the 3D plot is slightly inclined on both x-axis and y-axis. This shows interaction between biodiesel yield, reaction time and catalyst dosage. Optimum biodiesel yield of 93.33 % was obtained at constant temperature of 55 °C, methanol to oil ratio of 8:1, catalyst concentration of 0.5 g and a reaction time of 120 minutes.

4.5 Reusability Test

The result of reusability test shows how many times the same catalyst can be used to produce biodiesel. It was observed that at repeated 6th runs, biodiesel yield using the same HZY catalyst dropped to 79 % which was still reasonable enough compare to CZY catalyst which was observed to have dropped below 45 %.

Table 4.11: Effect of Repeated Use of Catalyst on Biodiesel Yield

Times of repeated run	1	2	3	4	5
HZY Biodiesel yield (%)	95	91	90	85	83
CZY Biodiesel yield (%)	66	61	55	48	41

4.6 Biodiesel Quality Determinations

The produced biodiesel was characterized and compared against established biodiesel standards such as the American Standards and Testing Materials. The ASTM D6751 serves as a guideline which provides information on the properties and quality of good Biodiesel.

Table 4.12: Characterization of Produced Biodiesel from WCO

S/N	Property	Unit	Result Obtained	ASTM D6751
1.	Density 40 ^{o} C	g/cm^3	0.928	-
2.	Flash Point	^{o}C	154	130
3.	Kinematic Viscosity at 40 ^{o} C	mm^2/s	5.4	1.9 – 6.0
4.	Cetane Index		56	47
5.	pH Value		7.2	-
6.	Color		Amber Yellow	-
7.	Pour Point	^{o}C	5	18 max
8.	Cloud point	^{o}C	11	-
9.	Iodine Value	mgI/100g	54.4	120 max
10.	Ester Value	wt. %	141.3	96.5
11.	Acid value	mgKOH/g	0.836	0.8 max
12.	FFA	wt %	0.418	-

4.7 GC-MS Analysis of Synthesized Biodiesel

Gas Chromatography - Mass Spectrometry (GC-MS) analysis of the biodiesel produced was done to determine the composition and structure of the fatty esters comprising the biodiesel and the result are presented show in Figure 4.16 and Table 4.12.

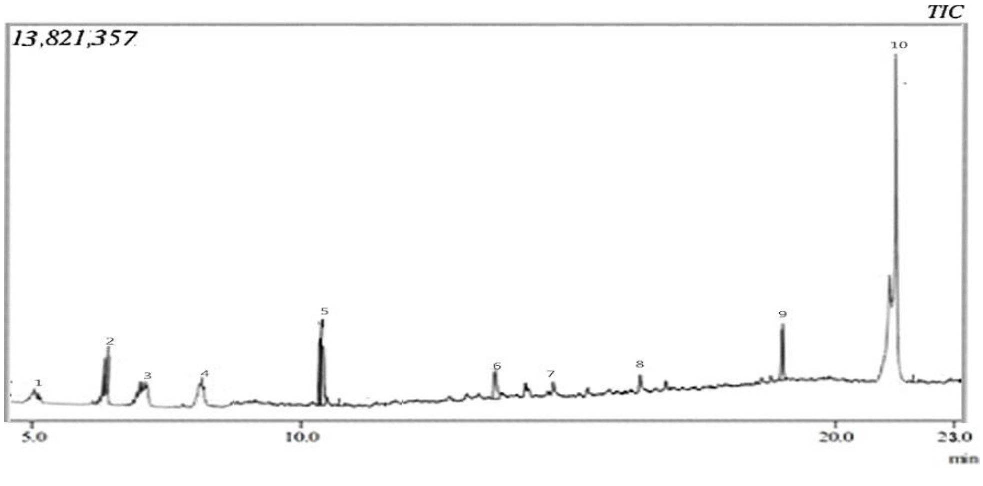

Figure 4.16: GC-MS Analysis of Biodiesel Produced

One of the major principles associated with biodiesel production is the composition and structure of the fatty esters comprising the biodiesel. This investigation was carried out using the GC-MS where the relative peak areas in the GC-MS analysis of the components are relative to the weight proportion of the components. The components present in the biodiesel sample are presented in Table 4.13.

Table 4.13: Chemical Composition of Biodiesel Produced

Peak No.	Retention time (min)	Compound Name	Molecular Formula	Area (%)	Height (%)
1	5.001	Methyl butanoate	$C_5H_{10}O_2$	1.61	1.77
2	6.574	Tetracosanoic acid methyl ester	$C_{25}H_{50}O_2$	0.47	14.98
3	7.262	Docosanoic acid Methyl ester	$C_{23}H_{46}O_2$	16.10	3.12
4	8.322	Beta-sitosterol	$C_{29}H_5OO$	6.25	4.38
5	10.897	Eicosanoic acid methyl ester (Methyl Eicosanoate)	$C_{21}H_{42}O_2$	19.82	14.63
6	13.825	Hexadecanoic acid methyl ester(Methyl Hexadecanoat).	$C_{17}H_{34}O_2$	18.26	16.31
7	14.632	Methyl15-methylhexadecanoate (Methyl Hexadecanoate)	$C_{17}H_{34}O_2$	13.73	4.62
8	16.472	11,14-Eicosadienoic acid methyl ester (Methyl Eicosanoate)	$C_{21}H_{38}O_2$	5.34	14.52
9	19.205	2-Naphthalendol, 1,2-dihydro,acetate	$C_{12}H_{12}O_2$	5.52	7.49
10	21.458	Methyl 11-octadecenoate (Methyl Octadecanoate)	$C_{19}H_{36}O_2$	10.86	17.86

Hydrocarbon grouping is differentiated as <C15, C15 – C20, C20 – C30 and >C30 with respect to the retention time of standard hydrocarbons like octadecane, heptadecane, eicosane, tricosane and molecular carbon chain length, according to Hariram and Bharathwaaj (2016). From the GC-MS analysis available in Table 4.13, it discovered the presence of hexadecanoic acid methyl ester, methyl 11-octadecenoate, eicosanoic acid methyl ester, methyl butanoate, docosanoic acid methyl ester, 11,14-eicosadienoic acid methyl ester, 8-Heptadecene and tetracosanoic acid methyl ester as the methyl esters present in the biodiesel while Beta-sitosterol is considered as an impurity. The major methyl ester is the hexadecanoic acid methyl ester. From the GC-MS analysis the saturated fatty acids include methyl butanoate, tetracosanoic acid methyl ester, docosanoic acid methyl ester, hexadecanoic acid methyl ester and eicosanoic acid methyl ester which account for 79.8 % of the biodiesel makeup. Similarly, 11, 14-eicosadienoic acid methyl ester and methyl 11-octadecenoate (elaidic acid methyl ester) are unsaturated fatty acids and make up 19.92 % of the biodiesel make up while Beta-sitosterol accounts for 0.28 % of the biodiesel makeup. The presence of low level of unsaturated fatty acids is enviable as these unsaturated fatty acids results in reduced oxidative stability of the fuel while a high presence of saturated fatty acids enhances the biodiesel fuel oxidative capacity, Koria and Nithya (2012). Likewise, (Kaisan *et al*., 2016) reported that higher degree of unsaturation in the fatty acid methyl esters limits its suitability for use as a fuel due to high polymerization affinity which is caused by peroxidation. For that reason, since the predominant methyl ester is Methyl Hexadecanoate which is a saturated fatty acid and as such has an affinity for oxygen therefore the tendency for peroxidation to occur in the car engine leading to engine failure would not arise.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In conclusion, good quality biodiesel was produced using waste cooking oil and hierarchical zeolite Y from starting zeolite Y as catalysts via transesterification process.

The prepared catalyst was characterized using X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM) and BET analyses. From the calculated value for the hierarchy factor of each sample via BET analysis showed that higher surface area alone is not enough to determine good quality catalyst.

Response surfaces methodology was successfully applied for transesterification of methanol for both CZY and HZY.

The process parameters considered for the optimization study of the transesterification reaction for CZY resulted in an optimum biodiesel yield of 67.33% at operating conditions of catalyst dosage of 0.5 g, methanol to oil ratio of 6:1 and a reaction time of 60 minutes while that of the transesterification reaction for HZY resulted in an optimum biodiesel yield of 95.0 % at methanol to oil ratio of 8:1, catalyst dosage of 0.35 g and reaction time of 90 minutes. HZY and CZY catalysts were compared at the same condition and CZY catalyst gave 62.00 % while HZY gave 95 % at optimum point. The high regression coefficients showed that the model was well fitted to the experimental data.

Therefore, it can be concluded that hierarchical zeolite Y catalyst produced took advantage of the enhanced surface area, mesopore area, pore size and it hierarchy factor to improve the FAME diffusion.

5.2 Recommendations

This study reported on the primary objectives, focusing on the production of biodiesel using waste cooking oil as feedstock in the presence of hierarchical zeolite Y as catalyst, based on the findings of this study, we recommend the use of kaolin as the starting aluminosilicate material for cheaper synthesis of hierarchical zeolite Y and its derivatives as solid acid/base catalysts. In addition, Future work should explore the economic feasibility for a better understanding and potential for implementation and further process optimization should be carried out to take into consideration of effect of process parameters like agitation speed, pressure of the reacting mixture, the type of alcohol and catalyst used.

5.3 Contribution to Knowledge

1 The effect of concentration on the production of hierarchical zeolite Y catalyst using desilication and mild dealumination was successfully studied and it was observed that at 0.3 M of NaOH and 0.3 M of EDTA, the best hierarchical zeolite Y catalyst was obtained having the highest hierarchy factor of 0.1781.

2 This research was able to solve the problems micro porous catalyst of conventional zeolite Y that gave biodiesel yield of 67.33% while hierarchical zeolite Y with mesoporous network therefore improved mass transfer and enable accessibility and transport of molecules to and from the active sites yield 95%.

3 An optimization study of the transesterification reactions using commercial zeolite Y catalyst and hierarchical zeolite Y catalyst were also carried out, at methanol/oil molar ratio of 8:1, catalyst dosage of 0.35 wt%, and reaction time of 90 mins at constant temperature of 55 °C. The biodiesel yield for commercial zeolite Y catalyst gave 62.00% while that of hierarchical zeolite Y catalyst gave 95 %.

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APPENDICES

APPENDIX A

I. Preparation of the Reagent used

To prepare 0.1 M of NaOH Solution;

Mass Conc. = Molar Conc. × Molar Mass

Molar mass of NaOH ; 23 + 16 + 1 = 40g

Molar Conc = 0.1 M

Mass Conc. = 0.1 × 40 = 4 g/ dm^3

Note: 1 dm^3 = 1000 ml

Therefore 0.1 dm^3 = 100 ml

So 0.4 g was top up to 100 ml.

The same was done for 0.3 M & 0.5 M for NaOH

To prepare for EDTA solution at 0.1 M;

Mass Conc. = Molar Conc. × Molar Mass

Molar mass of H_4EDTA was giving to be 372.24 g/mol

Molar Conc = 0.1 M

Mass Conc. = 0.1 × 372.24 = 37.224 g/ dm^3

Note: 1 dm^3 = 1000 ml

Therefore 0.1 dm^3 = 100 ml

So 37.224 g was top up to 100 ml.

The same was done for 0.3 M & 0.5 M for H_4EDTA

To prepare 0.1 M of NH_4Cl Solution;

Mass Conc. = Molar Conc. × Molar Mass

Molar mass of NH_4Cl was giving to be 53.49 g

Molar Conc = 0.1 M

Mass Conc. = 0.1 × 53.49 = 5.349 g/ dm^3

Note: 1 dm^3 = 1000 ml

Therefore 0.5349 dm^3 = 100 ml

So 0.5349 g was top up to 100 ml.

APPENDIX B

II. Characterization of the Feedstock

Determination of Saponification Value

Using this formula Saponification value $= \frac{(b-s)\times 0.5\times 56.10}{\text{Weight of beef tallow oil sample}}$

S.V $= \frac{(56.1-47.49)\times 0.5\times 56.10}{1} = 241.45\frac{\text{mgKOH}}{\text{g}}$

Determination of Acid Value

Using this formula Acid value $\left(\frac{\text{mgKOH}}{\text{g}}\right) = \frac{56.1\times V\times N}{W}$

Acid Value $= \frac{196\times 1\times 0.1}{1} = 19.6\ \frac{\text{mgKOH}}{\text{g}}$

Determination of Free Fatty Acid

Using this formula Free Fatty Acid(FFA) value $\left(\frac{\text{mgKOH}}{\text{g}}\right) = \frac{\text{Acid value}}{2}$

FFA $= \frac{19.6}{2} = 9.8\ \left(\frac{\text{mgKOH}}{\text{g}}\right)$

Determination of Specific Gravity and Density

Using the formula Specific gravity $= \left(\frac{W_2 - w}{W_1 - w}\right)$

Specific Gravity $= \left(\frac{46.154-22.704}{47.964-22.704}\right) = \frac{23.28}{25.22} = 0.923$

UsingDensity $= \frac{\text{Weight of beef tallow oil}}{\text{Volume of beef tallow oil in Relative density bottle}}$

Density$= \frac{23.49}{25} = 0.898$ g/ml

Determination of Peroxide Value

Using this formula Peroxide value $= \frac{V_2 - V_1\times M\times 1000\frac{\text{meq}}{\text{kg}}}{W\ (g)}$

Peroxide value $= \frac{0.275\times 0.02\times 1000\frac{\text{meq}}{\text{kg}}}{1\ (g)} = 5.5$ mmolO$_2$/kg

Determination of Iodine Value

Using this formula Iodine value $= \frac{(b-a)\times M\times 12.69}{W\ (g)}$

Iodine Value = 61.7 mgI/100g

Determination of Ester Value

Using this formula

$$\text{ESTER VALUE} = \text{SAPONIFICATION VALUE} - \text{ACID VALUE}$$

Ester Value = $241.45 - 19.6 = 221.85$ w%

III. Calculations for Biodiesel Production

Molar mass of Oil = 856.92 g/mol

Density of Oil = 0.898 g/cm^3

$$\text{no of mole (n)} = \frac{\text{Mass (M)}}{\text{Molar mass (m)}}$$

But $\text{Mass (M)} = \text{Density } (\rho) \text{ x Volume (V)}$

Therefore, using 30ml of Oil as basis.

$$\text{no of moles of oil} = \frac{\rho \text{ x V}}{\text{m}} = \frac{0.898 \text{ x } 30}{856.92} = 0.0314 \text{ Moles}$$

Since the optimization between was carried out between a methanol molar ratio of 6:1 and 10:1.

For a methanol ratio of 4:1

$$4 \text{ x } 0.0314 = 0.126 \text{ moles}$$

$$\text{since n} = \frac{\rho \text{ x V}}{\text{m}}$$

$$\text{therefore V} = \frac{\text{m x n}}{\rho}$$

Where the parameters V, m, n and ρ are all for methanol.

Molar mass (m) of methanol = 32

Density (ρ) of methanol = 0.7914

$$\text{V} = \frac{0.126 \text{ x } 32}{0.7194} = 5.6 \text{ ml}$$

For methanol molar ratio of 6:1.

$6 \text{ x } 0.0314 = 0.1884 \text{ moles}$

The Volume of methanol required

$$V = \frac{0.1884 \text{ x } 32}{0.7194} = 8.38 \text{ ml}$$

For methanol molar ratio of 8:1.

$8 \text{ x } 0.0314 = \ 0.2512\text{moles}$

The volume of methanol required

$$V = \ \frac{0.2512 \text{ x } 32}{0.7194} = 11.17 \text{ ml}$$

For methanol ratio of 10:1

$10 \text{ x } 0.0314 = 0.314$

The volume of methanol required

$$V = \ \frac{0.314 \text{ x } 32}{0.7194} = 13.97 \text{ ml}$$

For Catalyst ratio

$\text{Amt of Catalyst} = \text{wt\% x Mass of Oil}$

$\text{Amt of catalyst} = \text{wt\% x } \rho \text{ of oil x volume of oil}$

For catalyst Ratio of 0.2

$\text{amt of catalyst} = 0.2\% \text{ x } 0.898 \text{ x } 30 = 0.054\text{g}$

For catalyst ratio of 0.35

$\text{amt of catalyst} = 035\% \text{ x } 0.898 \text{ x } 30 = 0.094\text{g}$

For a catalyst ratio of 0.5

$\text{amt of catalyst} = 0.5\% \text{ x } 0.898 \text{ x } 30 = 0.135\text{g}$

IV. Characterization of Biodiesel produced from waste cooking oil

Determination of Kinematic Viscosity

K.v = $5.4 \text{ mm}^2/\text{s}$

Determination of Acid Value

Using this formula Acid value $\left(\frac{\text{mgKOH}}{\text{g}}\right) = \frac{56.1 \times \text{V} \times \text{N}}{\text{W}}$

A.v = $\frac{56.1 \times 0.15 \times 0.1}{1} = 0.836\ \frac{\text{mgKOH}}{\text{g}}$

Determination of Free Fatty Acid

Using this formula Free Fatty Acid(FFA) value $\left(\frac{\text{mgKOH}}{\text{g}}\right) = \frac{\text{Acid value}}{2}$

FFA = $\frac{0.836}{2} = 0.418\ \left(\frac{\text{mgKOH}}{\text{g}}\right)$

Determination of Iodine Value

Using this formula Iodine value $= \frac{(\text{b}-\text{a}) \times \text{M} \times 12.69}{\text{W (g)}}$

Iodine Value = 49.8. mgI/100g

Determination of Cetane Number

Using this formula $= 46.3 + \left(\frac{5458}{\text{s.v}}\right) - (0.225\ \times \text{i.v})$

Waste Cooking Oil BD$= 46.3 + \left(\frac{5458}{\text{s.v}}\right) - (0.225\ \times 49.8) = 61$

APPENDIX C

Table C.1: Optimization of Biodiesel production from WCO for CZY

Run No.	A (v/v)	B (mins)	C (%wt)	Actual Value (%)	Predicted Value (%)
1	6	60	0.5	56.00	56.47
2	6	90	0.35	55.33	55.41
3	10	120	0.5	62.00	61.95
4	8	90	0.35	56.67	56.47
5	8	90	0.35	52.00	52.19
6	8	90	0.35	56.67	56.47
7	10	60	0.5	60.00	60.99
8	10	90	0.35	47.67	48.10
9	8	90	0.35	57.00	57.03
10	10	60	0.2	51.00	50.91
11	8	90	0.35	52.50	51.78
12	6	120	0.5	60.93	61.02
13	10	120	0.2	48.87	48.71
14	8	90	0.5	58.33	57.72
15	8	120	0.35	56.67	56.47
16	6	120	0.2	56.67	56.47
17	8	60	0.35	55.33	55.64
18	8	90	0.2	57.48	58.03
19	8	90	0.35	56.67	56.47
20	6	60	0.2	67.33	66.84

Table C.2: Optimization of Biodiesel production from WCO for HZY

Standard Order	**Actual Value**	**Predicted Value**	**Residual**
1	89.72	89.46	0.26
2	89.95	88.94	1.01
3	84.10	83.03	1.07
4	89.50	89.46	0.038
5	90.00	90.21	-0.21
6	88.80	89.46	-0.66
7	94.80	92.37	2.43
8	82.00	80.97	1.03
9	86.67	86.96	-0.29
10	78.00	77.91	0.091
11	81.00	82.63	-1.63
12	80.00	80.32	-0.32
13	70.00	69.88	0.12
14	88.60	89.19	-0.59
15	88.90	89.46	-0.56
16	88.40	89.46	-1.06
17	83.33	83.60	-0.27
18	78.00	77.61	0.39
19	89.85	89.46	0.39
20	87.67	88.89	-1.

Appendix D

Determination of Hierarchical Factorm (HF)

HF = $\frac{\text{Vmicro}\times\text{Smeso}}{\text{VTotal}\times\text{SBET}}$

Therefore,

For Sample 1

HF = $\frac{0.3566\times11.98}{0.3860\times193.83}$ =0.0571

For sample 2

HF = $\frac{0.4712\times35.09}{0.4971\times216.03}$ = 0.1540

For Sample 3

HF = $\frac{0.3785\times24.56}{0.4065\times212.34}$ = 0.1781

For Sample 4

HF = $\frac{0.3055\times24.56}{0.3299\times218.33}$ = 0.1042